Sudhakar Srivastava *Editor*

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Preface

The contamination of metalloid arsenic (As) is of global concern. It has been well recognized that intake of arsenic by humans leads to carcinogenesis. In nature, arsenic is present in various inorganic and organic forms. Trivalent arsenite (AsIII) and pentavalent arsenate (AsV) are the two major inorganic arsenic species. Out of these, AsIII is more toxic than AsV. Under oxidized conditions, AsV has a high affinity for iron oxyhydroxides and manganese oxides, which makes it relatively immobile in soil. The AsIII has a lower affinity for these solid phases, making it more mobile. The major route of As contamination for humans is either through drinking water or via food, mainly rice, contaminated with arsenic. Arsenic contamination issue is most severe in Southeast Asian countries, including Bangladesh, India, China, Vietnam, the Philippines, etc., and the major factor recognized in these countries is natural biogeochemical processes. In other regions of the world, arsenic contamination is mainly attributable to historical uses as pesticides, herbicides, and other industrial applications. More than 100 million people living in 23 countries are exposed to arsenic toxicity. Furthermore, arsenic is affecting people from other regions through rice, rice-based products, fishes, etc.

Rice is the most affected crop with arsenic contamination owing to its cultivation in major arsenic-contaminated areas of the world. Furthermore, rice is a crop which is grown anaerobically (i.e., under flooded condition). In these growing conditions, reducing environment prevails that increases the mobility of AsIII present mostly as free H3AsO3. Besides, rice roots assimilate AsIII through silicic acid transporters, which are significantly expressed in rice plants and are responsible for its very high silica accumulation ability. In July 2014, the WHO set worldwide guidelines for safe As levels in rice, i.e., 0.2 mg kg-1 for white rice and 0.4 mg kg-1 for brown rice. As per the Chinese Food Safety Standard, the permissible limit of inorganic arsenic content in rice is 0.15 mg kg-1.

Considering the importance of the issue, the book *Arsenic in Drinking Water and Food* is a timely edition discussing the present global scenario of the problem and prospective solutions available in hand or to be utilized in the future. This book presents situation of arsenic contamination in different continents. The book discusses arsenic contamination of rice, rice-based products, vegetables, fishes, mushrooms, and other foods through which people get exposed to arsenic. The book also addresses human health issues associated to arsenic exposure and possible preventive and curative measures available. In addition, the book discusses the rice-arsenic interactions specifically to provide an update on mechanisms arsenic uptake and translocation and distribution in plants and grains and to shed light on prospective agronomic and transgenic solutions to deal with the problem.

Varanasi, Uttar Pradesh, India Sudhakar Srivastava

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Editor

Sudhakar Srivastava is presently working as an Assistant Professor at the Institute of Environment and Sustainable Development (IESD), Banaras Hindu University (BHU). He completed his M.Sc. and Ph.D. in Botany at the University of Lucknow. He also served as a Scientific Officer at Bhabha Atomic Research Centre (BARC), Mumbai, from 2009 to 2014. He has more than 16 years of research experience in the field of plant-metal interactions, with a major focus on arsenic stress responses in plants. He has published 66 research articles and 21 review and letter articles in high-impact international and national journals. He has also received several awards for his contributions, including a Young Scientist Award from the National Academy of Sciences, India (NASI), Allahabad, in 2011, Young Scientist Award from Uttar Pradesh Council of Science and Technology (UPCST) in 2013–2014, and Young Scientist Award from the Science and Engineering Research Board (SERB) in 2015. Dr. Srivastava is also an Associate of the National Academy of Agricultural Sciences (NAAS) and a Life Member of several societies as well as nongovernmental organizations and serves as an Associate Editor for two respected international journals: *Acta Physiologiae Plantarum* and *Frontiers in Ecology and Evolution*.

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The Status of Arsenic Contamination in India

Anurakti Shukla, Surabhi Awasthi, Reshu Chauhan, and Sudhakar Srivastava

Abstract The presence of arsenic (As) in the groundwater threatens human health throughout the world. The problem is severe in southeastern parts of Asia especially India, Bangladesh, China, etc. because the population density is very high in comparison to the other western countries. Groundwater, which is the main source of drinking water in these areas, has been found to have As as high as 300 ppb. Out of 29 states in India, reports of As contamination have emerged from 17 states. The number of As-affected districts and the number of people affected have grown ever since the initial reports of As contamination came to knowledge in the 1980s. The present situation of As contamination in India is of great concern. This chapter focuses on presenting the As contamination status of India and also elaborates the possible reasons for groundwater As contamination in the Indo-Gangetic region.

Keywords Arsenic · Assam · Bihar · West Bengal · Uttar Pradesh · Manipur

1 Introduction

The growing population of the world creates a shortage of almost all natural resources (de Sherbinin et al. 2007). The problem is of grave concern for developing countries like India and Bangladesh, where a large percentage of the total world population lives in a relatively small area of the world (Bavel 2013). One of the most crucial natural resources is drinking water (Ledder et al. 2002). The two major sources of drinking water include surface water and groundwater. The surface water, which is mainly available in the form of rivers, ponds, and lakes, has become increasingly loaded with tons of toxic chemical compounds and pathogens and is thus unfit for consumption (Mishra and Dubey 2015). Hence, in many urban and

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rural areas, people have switched to and continue to switch over to groundwater. But since the past few decades, the groundwater resources are also facing the problem of natural and anthropogenic pollution (Tiwari et al. 2019).

Arsenic contamination of groundwater has emerged as a huge problem. Arsenic is a toxic element and has been placed in the group I class of carcinogens by IARC (IARC Monograph 2004). Arsenic groundwater contamination is estimated to affect more than 150 million people across the world. The major regions affected are deltas and river basins, for example, Paraiba do Sul delta (Brazil), Bengal Delta (India and Bangladesh), Mekong Delta (Cambodia), Danube River Basin (Hungary), Hetao River Basin (Mongolia), Duero Cenozoic Basin (Spain), Zenne River Basin (Belgium), etc. (Shankar et al. 2014). In India, As groundwater contamination in West Bengal was first noticed in the year 1978 (Mandal and Suzuki 2002). The first case of As poisoning came under the light in the year in 1983 (Rahman et al. 2005). Since then, As contamination has been detected in many states of India including West Bengal, Uttar Pradesh, Jharkhand, Bihar, Haryana, Punjab, Andhra Pradesh, Chhattisgarh, Assam, Karnataka, Rajasthan, Gujarat, etc. (Chaurasia et al. 2012). Bangladesh has eight divisions, namely, Barisal, Chittagong, Dhaka, Khulna, Rajshahi, Rangpur, Sylhet, and Mymensingh. Among these, the most affected areas are Dhaka, Khulna, Rajshahi, Sylhet, Mymensingh, and Chittagong with the recorded concentration of As being more than 50 ppb (Hossain 2006).

The main source of As contamination in the Gangetic river basin and delta sediments is believed to be Himalayan mountains and Shillong Plateau. Apart from this, there are other geological sources like the Gondwana coal region in Rajmahal basin in eastern India, Bihar mica belt in eastern India, the pyrite-bearing region in Vindhya Range in central India, Son River Valley gold belt in the eastern area, and sulfides regions of eastern Himalayas, which have been considered as probable sources of As (Acharyya et al. 2000; Bhattacharya et al. 2015). According to the BGS (2000) reports, the natural sources of As contamination are sulfide and oxide mineral. Pyrite oxidation and sediments transportation have been attributed to the release of As and sulfates in this region. While sulfates were quickly lost in the form of salts in the sea, As was adsorbed by iron oxides, which accumulated over time in the delta region. The worst affected aquifers are the alluvial deposits beneath the floodplains of four major rivers, namely, Ganga, Brahmaputra, Meghna, and Tista (Hossain 2006; Ahmad et al. 2004). There are several industrial processes also, which result in the release of As to the environment, for example, metal mining, iron and steel production, coal combustion, etc. (Pandey et al. 2015), cement production, pharmaceutical industries, and manufacturing of paints and varnishes (Hossain 2006). Further, fertilizers, herbicides, pesticides, insecticides, and fungicides play a crucial role in contaminating agriculture land (Bhattacharya et al. 2011).

Different countries have different permissible limits of As content in drinking water. The World Health Organization (WHO) guideline for drinking water is 10 ppb (10 μg/L) (WHO 1993). Initially, WHO had set 200 ppb as As standard for drinking water in the year 1958. This was later reduced to 50 ppb in 1963 and to 10 ppb in the year 1993 with knowledge and case reports about the adverse health impacts of As that included cancer also (WHO 1958, 1963, 1993, 2011). In the year 2001, USEPA also revised As limit from 50 ppb to 10 ppb as the maximum contaminant level keeping in mind the cost, benefits, and ability of the public water system to detect and remove contaminants (USEPA 2013). In India and Bangladesh, the permissible limit of As in drinking water is 50 ppb (Pal et al. 2009).

2 Arsenic Mobilization and Transportation in Groundwater

There are four main hypotheses for the mobilization and transportation of As in groundwater (Bhattacharya et al. 2015): oxidation of pyrite, competitive ion exchange, reductive dissolution of iron oxyhydroxides, and reduction and re-oxidation. Pyrite oxidation has been considered to play an important role in alluvial sediments of India and Bangladesh where excessive use of groundwater for irrigation has created oxidizing conditions in the aquifers (Chakraborty et al. 2015). The theory of competitive ion exchange suggests the competition between As oxyanions and phosphate ions to be the cause of As release in aquifers (Fakhreddine et al. 2015). However, this is not considered a major factor of As contamination of India and Bangladesh. The most widely accepted theory for India and Bangladesh scenario is the reductive dissolution of iron oxyhydroxides. This theory suggests the release of As through reductive dissolution of metal oxides and Fe hydroxides. In general, most of the As-contaminated water throughout the world has found to have very low redox potential which is an indicator of reducing conditions. This can also be explained by a good relationship between As and bicarbonates present in water. Even the redox potential of such water has been found in the range of Fe^{3+} and As^{5+}. Another hypothesis which also explains As menace is reduction and re-oxidation theory. The first step is the mobilization of As via reduction of Fe oxyhydroxides followed by re-oxidation of pyrite. The reduction and re-oxidation process helps in sequestration of As, but due to reducing environment, complete immobilization of As is not possible, thus making As bioavailable (Bhattacharya et al. 2015).

3 Areas Affected by Arsenic in India

A total of 17states in India along with one union territory have been reported to have As content beyond BIS maximum permissible limit (BIS 2012) of 50 ppb (Fig. 1). Around 19% of Indian population is at risk of As poisoning, i.e., almost 25.46 lakh people. In recent Lok Sabha reports, it has been revealed that around 65% of Assam population, 60% of Bihar population, and 44% of West Bengal population are under sever risk of As poisoning (Jadhav 2017). The occurrence of As in groundwater in India can be broadly classified into two categories: the alluvial terrains of West Bengal, Uttar Pradesh, Bihar, Jharkhand, Assam, Manipur, Punjab, and Haryana and the hard-rock terrain of Karnataka and Chhattisgarh. Other parts, where As contamination is reported in recent years, are Rajasthan, Andhra Pradesh, Telangana, Tamil Nadu, and Gujarat (Bhattarcharya and Lodh 2018).

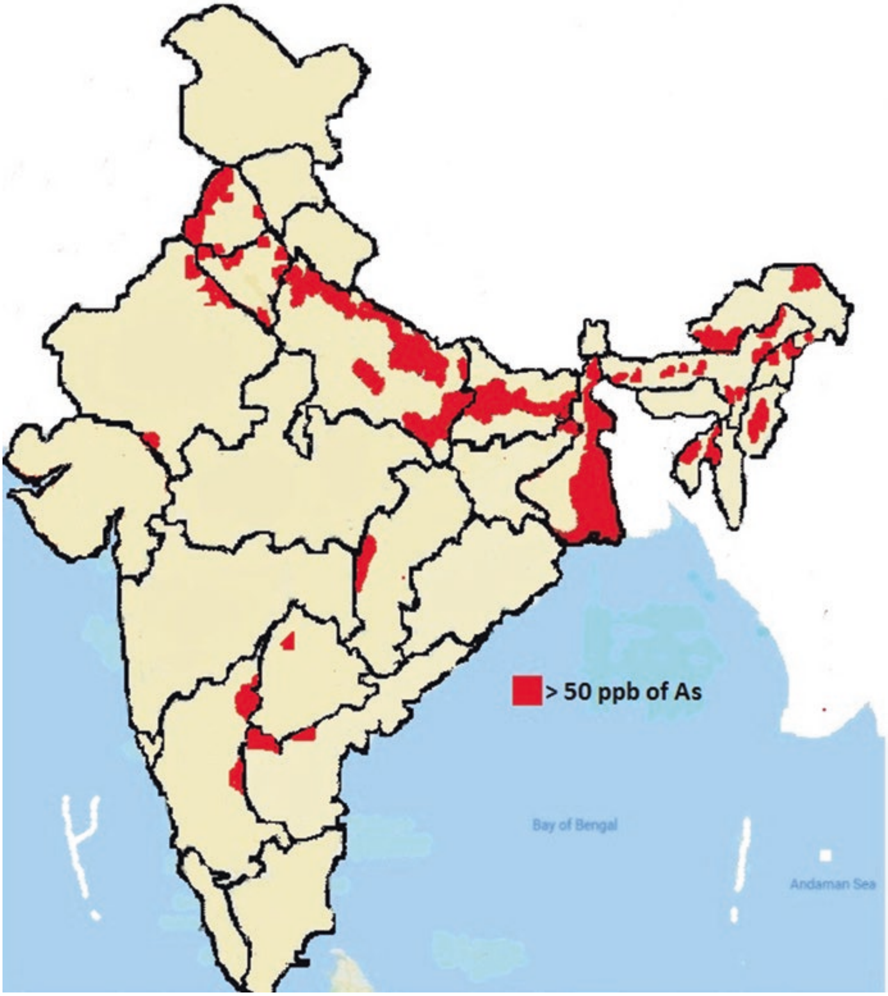

Fig. 1 Indian states that have groundwater or surface water affected with As contamination above than 50 µg/L. In total there are 16 states that are showed here having As level above than BIS permissible limit. (1) Punjab, (2) Haryana, (3) Rajasthan, (4) Uttar Pradesh, (5) Chhattisgarh, (6) Telangana, (7) Karnataka, (8) Andhra Pradesh, (9) Bihar, (10) Jharkhand, (11) West Bengal, (12) Assam, (13) Arunachal Pradesh, (14) Nagaland, (15) Manipur, (16) Tripura

3.1 West Bengal

According to NIH (National Institute of Hydrology, India) and Central Ground Water Board reports (CGWB, West Bengal), there were a total of 9 districts out of 23 in West Bengal in the year 2008, which were reported to have As-contaminated groundwater. The severely affected districts are Murshidabad, North 24 Parganas, South 24 Parganas, Nadia, and Kolkata to the east and Howrah, Purba Bardhaman, and Hugli to the west of Bhagirathi/Hugli and Malda to the north of the Ganges

(CGWB, West Bengal). The concentration of As in these districts was found to be even more than 300 ppb in some places. The severity of this problem in this state has been classified into three subcategories: (i) severely affected areas having more than 300 ppb As, (ii) mildly affected area with As concentration in range of 10–50 ppb (six districts: Darjeeling, Jalpaiguri, Koch Bihar, Dinajpur North, Dinajpur South, and Paschim Bardhaman), and (iii) unaffected area with less than 10 ppb (eight districts: Alipurduar, Kalimpong, Birbhum, Bankura, Purulia, Jhargram, Purba Medinipur, and Paschim Medinipur). There are no reports of As contamination documented till now from As safe districts (Rahman and Sinha 2012; Dey et al. 2014). The alarming fact is that with every new and advanced survey, the number of contaminated villages are increasing resulting in more number of people exposed to As. The severity of the problem has been found to be more on the left side of the Bhagirathi River along the direction groundwater flow. The area has thick alluvial deposition of Quaternary age. In total, about 20% of West Bengal population living in nine severely affected districts (around 19 million people) is affected due to As contamination (Santra 2017).

3.2 Bihar

The presence of elevated As concentration in groundwater was first reported in 2002 from two villages Semaria Ojha Patti and Barisban in Bhojpur district (CGWB, MER, Patna (2013)). The location of this region comes under the flood prone belt of the Sone-Ganga interfluvial region. The As concentration detected was as high as 178 ppb (Bhattacharya and Lodh 2018). Out of 38 districts, 17 districts, namely, Buxar, Bhojpur, Patna, Saran, Darbhanga, Vaishali, Samastipur, Begusarai, Khagaria, Katihar, Munger, Bhagalpur, Lakhisarai, Kishanganj, Supaul, Siwan, and Muzaffarpur, were found to be affected by As concentration of more than 50 ppb (Singh et al. 2014). Simri village (As concentration-1929 ppb) and Tilak Rai Ka Hatta village (As concentration-1908 ppb) were the two most affected villages of Buxar district, and, therefore, it is known to be the most affected district of Bihar by As contamination (Kumar et al. 2016; Singh et al. 2014). It is estimated that more than five million people are drinking water having As concentration of more than 10 ppb (Abhinav et al. 2016). Most of the contaminated districts are located along the course of river Ganga in Bihar. Quaternary alluvium having multi-aquifer system representing medium to fine sands is the primarily geological formation of this region (Bhujal News, CGWB 2010).

3.3 Uttar Pradesh

In Uttar Pradesh, the first report of As contamination of groundwater surfaced in the year 2003 from the survey of nearly 25 villages in Ballia districts (Mukherjee et al. 2006; Bhattacharya and Lodh 2018). Then in the year 2008, two more districts, Ghazipur and Varanasi, were detected with As groundwater contamination (Mukherjee et al. 2006). Currently, 31 districts have higher than 10 ppb As, and in 18 districts, more than 50 ppb As levels are reported by UP Jal Nigam and UNICEF combined report (Pandey et al. 2015). Pandey et al. (2015) reported Bahraich, Ballia, and Lakhimpur Kheri to be the highly contaminated districts with As level of more than 50 ppb. Further, districts like Ambedkar Nagar, Bareli, Basti, Bijnaor, Chaudauli, Faizabad, Ghazipur, Gorakhpur, Meerut, Sant Ravidas Nagar, Shahjahanpur, Siddharth Nagar, Sitapur, Unnao, and Kanpur are also having As level above 10 ppb. The reasons for such a scenario are the same as that of Bihar with almost all the As-affected districts falling along the course of river Ganga and its tributaries and having the same kind of geological formation as that of Bihar (Bhujal News, CGWB 2010).

3.4 Jharkhand and Chhattisgarh

In the year 2003–2004, groundwater As contamination above 50 ppb was reported in Sahebganj district of Jharkhand (Chakraborti et al. 2004). Three blocks that are most affected in this region are Sahibganj, Rajmahal, and Udhawa (Nickson et al. 2007; Nayak et al. 2008; Chaurasia et al. 2012). Till date, only this district is reported for As contamination, and the reason is its geographical location as the river Ganga enters West Bengal from Bihar via Sahibganj district (Nayak et al. 2008). In Chhattisgarh, the only As-affected district reported by CGWB is Rajnandgaon. The As level in this area is more than 50 ppb with the most affected block being Ambagarh Chowki (CGWB, Chhattisgarh 2019; Ghosh et al. 2010). A number of people were detected with arsenical skin lesions and keratosis. The water-bearing formation in the state is weathered and fractured rocks of Proterozoic age, semi-consolidated Gondwana formation with weathered limestone and sandstone having the huge number of aquifers, and unconsolidated sediments including alluvium and laterite. Such geographical formation allows all possible mechanisms of As mobilization and transportation to occur (CGWB, Chhattisgarh 2019).

3.5 Punjab and Haryana

In the year 2004, CGWB surveyed Punjab state and reported that five districts, namely, Amritsar, Gurdaspur, Hoshiarpur, Kapurthala, and Ropar, have As level more than 10 ppb. In many places, the As content in alluvial aquifers was found to be in the range from 3.5 to 688 ppb. The status of As has been therefore classified into various subcategories: (i) low (<10 ppb), (ii) moderate (10–25 ppb), (iii) high (25–50 ppb), and (iv) very high (>50 ppb) (Thakur et al. 2016). In 2012, Government of Punjab also reported As level of more than 50 ppb in five densely populated districts: Amritsar (99 ppb), Rupnagar (91 ppb), Tarn Taran (83 ppb), Gurdaspur

(58 ppb), and Firozpur (55 ppb). Out of 22 districts, 13 districts of Punjab are affected with As in groundwater. Some districts like Amritsar, Fazilka, Tarn Taran, Kapurthala, Mansa, and Rupnagar have As level above the permissible limit (50 ppb) set by BIS, India. The range of As level reported in some areas of these districts is from 10 to 390 ppb (Thakur et al. 2016). The geographical location of this state is in the alluvial region of Indo-Gangetic Plains, which is the home for the sediment forming aquifers. Agricultural, industrial, and even domestic needs of water are fulfilled by using groundwater, and thus, As is released in the environment during the process of heavy abstraction of groundwater (Singh et al. 2015).

In Haryana, Chandigarh was the first district where As concentration of more than 50 ppb was reported (Datta and Kaul 1976). However, to date, there are no reports of arsenical skin lesions and keratosis from any part of Haryana. The districts like Yamunanagar, Karnal, and Sonipat which are reported to have As contamination are located along the course of Yamuna river and its tributaries (Bhattacharya and Lodh 2018). Other districts which are reported with 50 ppb and above As concentration in groundwater are Ambala, Nuh, Mewat, and Fatehabad (Kapur 2015).

3.6 *Karnataka, Andhra Pradesh, and Telangana*

In Karnataka, As in groundwater initially got reported from two districts, Raichur and Yadgir, famous for gold mining and other related activities. The occurrence of As was reported in the Mangaluru greenstone belt, Hutti gold mines (Lingasugur Taluk) of Raichur district, and Shorapur Taluk of Yadgir district. The maximum As load was recorded as 303 ppb in Hutti gold mine area (Chakraborti et al. 2013). The first ever case of arsenicosis and As-related cancer in Karnataka was identified in Kiradalli Tanda village in July 2009 (Sivanandan 2009a, b; Chakraborti et al. 2013). Arsenic is released from arsenopyrite, which is a chemical waste produced during the extraction of gold. This waste chemical compound produces mobile As when it reacts with the rainwater. The As released percolates down in groundwater or flows to the nearest surface water bodies. In the year 2016, another district, Chitradurga, was reported with alarming As concentration of about 103–235 ppb. The occurrence of such high concentration was reported in the copper and gold mines area of Ingaldhal located in Belliguda Hill (Hebbar and Janardhan 2016).

Arsenic problem in Andhra Pradesh and Telangana region is growing rapidly. The leading district is Medak (Telangana), and the area which is highly affected is the industrial belt region of Patancheru. The recorded As level was found to be in range from 140 to 7350 μg/L ppb (IARC Monograph 2004). Other districts with higher than 10 ppb As level recorded are Kurnool and Guntur (CGWB, Andhra Pradesh 2015–2016). The main source of As contamination in Patancheru region is anthropogenic activities. The major contribution comes from industries like Park Trade Center and Gaddapotharam Bulk Drug factories, which manufacture veterinary drugs based on arsonic acid (Kishan 2001; IARC Monograph 2004; Mukherjee et al. 2006).

3.7 Gujarat, Daman and Diu, and Rajasthan

Though the As problem in Gujarat is not that severe, still there are many districts where As level of more than 10 ppb has been recorded. However, none of them was found to have As above 30 ppb (CGWB, Gujarat and Daman and Diu 2015–2016). The districts having more than 10 ppb As are Amreli, Anand, Bharuch, Bhavnagar, Dohad, Patan, Rajkot, and Vadodara. These regions are geographically located on the central part of Kutch and Saurashtra plateau, which are soft rocks and unconsolidated formations holding a large amount of groundwater. The excessive withdrawal of groundwater is giving rise to high As levels (CGWB, Gujarat and Daman and Diu 2015–2016).

Arsenic contamination is reported in 6 out of 33 districts of Rajasthan that include Churu, Hanumangarh, and Sri Ganganagar (Duggal et al. 2012). The land formation of Hanumangarh and Sri Ganganagar comprises of alluvium and wind-blown sand as these are situated along the river Ghaggar. The active aquifers beneath the surface release As in groundwater. Churu was found to have severe As problem because of the stone and marble mining. Other districts with high As content are Jhunjhunu and Udaipur. These areas are the copper mining area (Khetri and Zawar mines) in Rajasthan, and the mining waste (tails/dumps) produced during extraction and mineralization process is the main source of As contamination (Bhattacharya et al. 2015).

3.8 Assam, Manipur, and Other Northeastern States (Arunachal Pradesh, Tripura, and Nagaland)

In Assam, As was first reported in the year 2004 in three districts, Karimganj, Dhemaji, and Dhubri, with a concentration above 50 ppb (IMGAM 2015). Out of 23 districts, 18 districts have As content beyond 10 ppb with around 2571 habitations being severely affected (Devi et al. 2009; Bhattacharya and Lodh 2018). The districts having more than 50 ppb As are Nagaon (48.1–112 ppb), Jorhat (195–657 ppb), Lakhimpur (50–550 ppb), Nalbari (100–422 ppb), Golaghat (100–200 ppb), Dhubri (100–200 ppb), Darrang (200 ppb), Barpeta (100–200 ppb), Dhemaji (100–200 ppb), Cachar (50–350 ppb), and Karimganj (293 ppb) (Shah 2012; Bhattacharya et al. 2015). The possible reason for the contamination of south Assam is that it is located in the low-lying areas of Barak valley, which is composed of Holocene sediments. The aquifers in this region along with the tertiary Barail hill range are the main reason for groundwater contamination (Shah 2012). Other parts of Assam lie along the Brahmaputra basin, which contains active aquifers of Holocene sediments. The reductive dissolution of Fe hydroxides present in these aquifers releases the adsorbed As. Another major reason for As contamination is extensive use of groundwater for agriculture and domestic use (Chetia et al. 2011).

In Manipur, out of 16 districts, 5 have been found to have As-contaminated groundwater with the maximum As detected in Thoubal district (maximum As level, 881 ppb) (Bhattacharya et al. 2015). Other districts which showed As concentration above 50 ppb are Kakching, Imphal East, Imphal West, and Bishnupur (Ghosh et al. 2010). Imphal East had As content >500 ppb followed by other districts with 150–200 ppb of As in groundwater (Chakraborti et al. 2008). The districts, which are reported in Arunachal Pradesh with As content above 50 ppb, are Papum Pare (74 ppb), West Kameng (127 ppb), East Kameng (58 ppb), Lower Subansiri (63–159 ppb), Dibang Valley (618 ppb), and Tirap (90 ppb) (Bhattacharya et al. 2015). Out of eight districts in Tripura, three are reported with high As level in groundwater above 50 ppb (Bhattacharya et al. 2015). Among them, Dhalai was found to have the maximum As contamination in groundwater (65–444 ppb) followed by North Tripura (122–283 ppb) and West Tripura (191 ppb). In Nagaland, Mon and Mokokchung were reported with high As load in groundwater with As concentrations of 67–159 ppb and 50–278 ppb, respectively (Bhattacharya et al. 2015).

4 Conclusions

Arsenic contamination in groundwater is a huge menace for both the countries impacting millions of lives altogether. Each year thousands of people die due to cancer caused by As exposure. The situation is alarming; therefore, together with the help of our governments, we need to find some appropriate solutions to combat this situation. The wells and tube wells found to have higher As concentration should be immediately closed and covered with sand and soil. The municipality of that particular area should provide safe drinking water by processing the surface or groundwater. Follow-up monitoring and educational programs should be done regularly in these areas. The government should promote research which has the potential to find out the affordable solutions on a large scale. Tap water that is supplied by municipality should meet at least drinking water standards for carcinogens and other dangerous compounds. Further, WHO and other international agencies should give sufficient funds to these nations and should even make the problem of As contamination as important as polio, hepatitis, etc. so that the increasing number of cancer patients in these countries could be controlled and reduced with time.

References

Abhinav A, Navin S, Kumar A, Kumar R, Ali M, Verma SK, Ghosh AK (2016) Prevalence of high arsenic concentration in Darbhanga district of Bihar: health assessment. J Environ Anal Toxicol 6:410

Acharyya SK, Lahiri S, Raymahashay BC, Bhowmik A (2000) Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary strartigraphy and Holocene sea-level fluctuation. Environ Geol 39:1127–1137

Ahmad KM, Bhattacharya P, Hasan MA, Akhter SH, Alam SMM, Bhuyian MAH, Imam MB, Khan AA, Sracek O (2004) Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Appl Geochem 19:181–200

Bavel JV (2013) The world population explosion: causes, backgrounds and projection for the future. Facts Views Vis Obgyn 5:281–291

Bhattacharya AK, Lodh R (2018) Arsenic contamination in the groundwater of India with a special focus on the stabilization of arsenic laden sludge from arsenic filters. Electron J Geotech Eng 23:575–600

Bhattacharya P, Mukherjee A, Mukherjee AB (2011) Arsenic contaminated groundwater in India. In: Nriagu J (ed) Encyclopedia of environmental health. Elsevier B.V, Amsterdam, pp 150–164

Bhattacharya P, Mukherjee A, Mukherjee AB (2015) Groundwater arsenic in India: sources, distribution, effects and alternate safe drinking water sources. In: Reference module in earth systems and environmental sciences. Elsevier B.V. The Netherlands, p 19

British Geological Survey (BGS) (2000) Executive summary of the main report of phase I, groundwater studies of as contamination in Bangladesh, by British Geological Survey and Mott MacDonald (UK) for the Government of Bangladesh, Ministry of Local Government, Rural Development and Cooperatives DPHE and DFID (UK), http://www.dainichi-consul.co.jp/english/article/DFID-sum.html. Accessed 22 Jan 2019

Bureau of Indian Standards (BIS) (2012) Drinking water- specification (second revision). IS-10500:2012. p 11

Central Ground Water Board (2010) Special issue on transboundary aquifer system. 25:1–25 http://cgwb.gov.in/Documents/Bhujalnews-25-01-02.pdf. Accessed 27 Mar 2019

Central Ground Water Board (2013) Groundwater information booklet, Bhojpur district, Bihar state, India. http://cgwb.gov.in/District_Profile/Bihar/Bhojpur.pdf. Accessed 27 Mar 2019

Central Ground Water Board, Ministry of Water Resources, River Development & Ganga Rejuvenation Govt. of India ground water year book Andhra Pradesh. Madhnure P, Sudhakar P, Reddy MB, Prasad BKM, Satya Kumar BY, Reddy GRC, Renuka S, Madhusudhan BJ (2015–2016). In: Rao AD. Southern Region, Hyderabad. http://cgwb.gov.in/Regions/GW-year-Books/GWYB-2015-16/GWYB%20SR%20(AP)%202015-16.pdf. Accessed 22 Jan 2019

Central Ground Water Board, Ministry of Water Resources, River Development & Ganga Rejuvenation Govt. of India ground water year book Gujarat state and UT of Daman Diu (2015–2016). http://cgwb.gov.in/Regions/GW-year-Books/GWYB-2015-16/GWYB%20WCR%202015-16.pdf. Accessed 12 Jan 2019

Central Ground Water Board. West Bengal, India. State profile: groundwater scenario of West Bengal. http://cgwb.gov.in/gw_profiles/st_westbengal.htm. Accessed 26 Mar 2019

Central Ground Water Board. Groundwater scenario of Chhattisgarh: state profile. http://cgwb.gov.in/gw_profiles/st_Chhatishgarh.htm. Accessed 12 Jan 2019

Chakraborti D, Sengupta MK, Rahman MM, Ahamed S, Chawdhury UK, Hossain MA, Mukherjee SC (2004) Groundwater arsenic contamination and its health effects in the Ganga-Meghna-Brahmaputra plain. J Environ Monit 6:75–83

Chakraborti D, Singh EJ, Das B, Shah BA, Hossain MA, Nayak B, Ahamed S, Singh NR (2008) Groundwater arsenic contamination in Manipur, one of the seven North-Eastern Hill states of India: a future danger. Environ Geol 56:381–390

Chakraborti D, Rahman MM, Murrill M, Das R, Siddayya PSG, Sarkar A, Dedapeer HJ, Yendigeri S, Ahmed R, Das KK (2013) Environmental arsenic contamination and its health effects in a historic gold mining area of the Mangalur greenstone belt of Northeastern Karnataka, India. J Hazard Mater 262:1048–1055

Chakraborty M, Mukherjee A, Ahmed KM (2015) A review of groundwater arsenic in the Bengal basin, Bangladesh and India: from source to sink. Curr Pollut Rep 1:220–247

Chaurasia N, Mishra A, Pandey SK (2012) Finger print of arsenic contaminated water in India – a review. J Forensic Res 3:3–10

Chetia M, Chatterjee S, Banerjee S, Nath MJ, Singh L, Srivastava RB, · Sarma HP (2011) Groundwater arsenic contamination in Brahmaputra river basin: a water quality assessment in Golaghat (Assam), India. Environ Monit Assess 173: 371–385

Datta DV, Kaul MK (1976) Arsenic content of drinking water in villages in northern India: a concept of arsenicosis. Assoc Physicians India 9:599–604

de Sherbinin A, Carr D, Cassels S, Jiang L (2007) Population and environment. Annu Rev Environ Resour 32:345–373

Devi NL, Yadav IC, Qi S (2009) Recent status of arsenic contamination in groundwater of northeastern India – a review. Recent Opin 9:22–32. https://www.researchgate.net/publication/255627394_Recent_Status_of_Arsenic_Contamination_in_Groundwater_of_Northeastern_India_-_A_Review. Accessed 15 Feb 2019

Dey TK, Banerjee P, Bakshi M, Kar A, Ghosh S (2014) Groundwater arsenic contamination in West Bengal: current scenario, effects and probable ways of mitigation. Int Lett Nat Sci 13:45–58

Duggal V, Rani A, Mehra R (2012) Assessment of arsenic content in groundwater samples collected from four districts of Northern Rajasthan. India Chem Sin 3:1500–1504

Fakhreddine S, Dittmar J, Phipps D, Dadakis J, Fendorf S (2015) Geochemical triggers of arsenic mobilization during managed aquifer recharge. Environ Sci Technol 49:7802–7809

Ghosh NC, Saha D, Sinharay SP, Srivastava SK (2010) Sources and causes of groundwater arsenic contamination in Ganga-Brahmaputra plains. In: Ghosh NC (ed) Mitigation and remedy of ground water arsenic menace in India: a vision document. National Institute of Hydrology, MOWR, Jal Vigyan Bhawan, Roorkee, pp 61–75

Hebbar A, Janardhan MR (2016) Arsenic contamination in groundwater of the areas surrounding Ingaldhal, Chitradurga district, Karnataka state. Int J Geol Agric Environ Sci 6:1–7

Hossain MF (2006) Arsenic contamination in Bangladesh—an overview. Agric Ecosyst Environ 113:1–16

IARC (International Agency for Research on Cancer) (2004) Monographs on the evaluation of carcinogenic risks to humans. Some drinking-water disinfectants and contaminants, including arsenic. monographs.iarc.fr/ENG/Monographs/vol84/mono84.pdf. Accessed 2 Jan 2019

Inter-Ministerial Group for Arsenic Mitigation (2015) A report by Ministry of Water Resources, River Development and Ganga Rejuvenation. http://www.arsenicnetwork.in/wp-content/uploads/2017/11/Arsenic%20Inter%20Ministerial%20Group%20Report.pdf. Accessed 26 Mar 2019

Jadhav R (2017) 19% of Indians drink water with lethal levels of arsenic. TOI (TNN) https://timesofindia.indiatimes.com/india/19-of-indians-drink-water-with-lethal-levels-of-arsenic/articleshow/62226542.cms. Accessed 29 Mar 2019

Kapur A (2015) High arsenic levels found in 12 Punjab, Haryana districts. The Tribune India (March 26 2015). https://www.tribuneindia.com/news/nation/high-arsenic-levels-found-in-12-punjab-haryana-districts/59094.html. Accessed 24 Dec 2018

Kishan RA (2001) Patancheru: a hell on earth. AVRR Memorial Charitable Trust, Patancheru, p 26

Kumar A, Kumar R, Rahman M, Iqubal M, Ali M, Niraj PK, Anand G, Shankar P, Abhinav GAK (2016) Ground water arsenic contamination: a local survey in India. Int J Prev Med 7:100

Leder K, Sinclair MI, McNeil JJ (2002) Water and the environment: a natural resource or a limited luxury? Med J Aust 177:609–613

Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. Talanta 58:201–235

Mishra RK, Dubey SC (2015) Fresh water availability and its global challenge. Int J Eng Sci Invent Res Dev 2:351

Mukherjee A, Sengupta MK, Hossain MA, Ahamed S, Das B, Nayak B, Lodh D, Rahman MM, Chakraborti D (2006) Arsenic contamination in groundwater: a global perspective with emphasis on the Asian scenario. J Health Popul Nutr 24:142–163

Nayak B, Das B, Mukherjee SC, Pal A, Sad A, Hossain MA, Maity P, Dutta RN, Dutta S, Chakraborti D (2008) Groundwater arsenic contamination in the Sahibganj district of Jharkhand state, India in the middle Ganga plain and adverse health effects. Toxicol Environ Chem 90:673–694

Nickson R, Sengupta C, Mita P, Dave SN, Banerjee AK, Bhattacharya A, Basu S, Kakoti N, Moorthy NS, Wasuja M, Kumar M, Mishra DS, Ghosh A, Vaish DP, Srivastava AK, Tripathi RM, Singh SN, Prasad R, Bhattacharya S, Deverill P (2007) Current knowledge on the distribution of arsenic in groundwater in five states of India. J Environ Sci Health A Tox Hazard Subst Environ Eng 42:1707–1718

Pal P, Sen M, Manna A, Pal J, Pal P, Roy S, Roy P (2009) Contamination of groundwater by arsenic: a review of occurrence, causes, impacts, remedies and membrane-based purification. J Integr Environ Sci 6:295–316

Pandey N, Lehri A, Mehrotra S, Srivastava JB (2015) Arsenic pollution scenario in eastern UP. India: a review. Int Res J Environ Sci 4:83–86

Rahman S, Sinha AC (2012) Water regimes: an approach of mitigation arsenic in summer rice (*Oryza sativa* L.) under different topo sequences on arsenic contaminated soil of Bengal delta. Paddy Water Environ 11:397–410

Rahman MM, Sengupta MK, Ahamed S, Lodh D, Das B, Hossain MA, Nayak B, Mukherjee A, Mukherjee SC, Pati S, Saha KC, Palit SK, Kaies I, Barua K, Asad KA (2005) Murshidabad – one of the nine groundwater arsenic affected districts of West Bengal, India, part I: magnitude of contamination and population at risk. Clin Toxicol 43:823–834

Santra BK (2017) Groundwater arsenic contamination and its health effects in the Ganga-Meghna-Brahmaputra plain. IJASE 5:43–46

Shah BA (2012) Role of quaternary stratigraphy on arsenic contaminated groundwater from parts of Barak Valley, Assam, North–East India. Environ Earth Sci 66:2491–2501

Shankar S, Shankar U, Shikha (2014) Arsenic contamination of groundwater: a review of sources, prevalence, health risks, and strategies for mitigation. Sci World J 2014:304524

Singh SK, Ghosh AK, Kumar A, Kislay K, Kumar C, Tiwari RR, Parwez R, Kumar N, Imam MD (2014) Groundwater arsenic contamination and associated health risks in Bihar. India Int J Environ Res 8:49–60

Singh KP, Kishore N, Tuli N, Loyal RS, Sharma M, Dhanda D, Kaur M, Taak JK (2015) Observations on occurrence of arsenic in groundwater especially in parts of South-West Punjab. In: Workshop: Arsenic Contamination in Groundwater, CGWB (Chandigarh), Ministry of Water Resources, River Development and Ganga Rejuvenation, Govt. of India, pp 45–52

Sivanandan TV (2009a). Rare skin cancer breaks out in hamlet due to arsenic poisoning. The Hindu; June 13 2009. http://www.thehindu.com/2009/06/13/stories/2009061358580100.htm. Accessed 12 Jan 2019

Sivanandan TV (2009b). Analysis shows arsenic high in water at Kiradalli Tanda. The Hindu; Jun 14 2009. http://www.thehindu.com/2009/06/14/stories/2009061450040100.htm. Accessed 2 Jan 2019

Thakur T, Rishi MS, Herojeet RK, Renu L, Konchok D (2016) Arsenic contamination in groundwater of Punjab state: an overview. Environ Tradit Sci Res 1:1–7

Tiwari AK, Pisciotta A, Maio M de (2019) Evaluation of groundwater salinization and pollution level on Favignana Island, Italy. Environ Pollut. In Press (accepted manuscript)

USEPA (2013) Arsenic in drinking water. http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/index.cfm. Accessed 16 Dec 2018

WHO (1958) International standards for drinking water. WHO, Geneva

WHO (1963) International standards for drinking water, vol 3, 2nd edn. WHO, Geneva

WHO (1993) Guidelines for drinking water quality, vol 1, 2nd edn. WHO, Geneva

WHO (World Health Organization) (2011) Guidelines for drinking-water quality, vol 4. World Health Organisation, Geneva, pp 315–318

Arsenic Environmental Contamination Status in South Asia

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Abstract Arsenic (As) is a well-known potentially toxic metalloid, which naturally occurs in soils, sediments, and aquatic environments. Arsenic has no essential role for living organisms. Its exposure to living organisms including humans causes severe health issues. Arsenic contamination of groundwater is a global issue especially in the flood plain regions of Asia. Environmental contamination in soil plant systems with As poses severe human and environmental health risk, thereby affecting globally thousands of people with As toxicosis. During the last two to three decades, several studies have reported high levels of this metalloid in the groundwater and soil at the global scale, especially in Asian countries. Pakistan, Bangladesh, and India are among the most As-affected countries of the world. In this book chapter, we have discussed the current environmental contamination status of As in

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South Asia, especially focusing on Pakistan, China, Cambodia, Vietnam, Iran, and Nepal. This chapter highlights groundwater contamination status of As in South Asian countries. Moreover, soil contamination due to irrigation with As-contaminated water as well as its soil-plant transfer has been highlighted using the latest available data. At the end, this chapter discusses the possible health risk associated with the use of As-contaminated groundwater or food (vegetables and crops). Data regarding concentration of As in groundwater and soil of South Asian countries are not fully elucidated in the literature. Based on the current data, it is proposed that the actual status of groundwater contamination by As in many parts of South Asia is still unclear. Therefore, further studies are required to fully illustrate the As level in groundwater and its soil-plant transfer across the Asian countries.

Keywords Arsenic · South Asia · Groundwater · Soil-plant transfer · Health risks

1 Arsenic: A Global Pollutant of High Concern

Arsenic (As) is a naturally occurring toxic metalloid in sediments, soils, and aquatic environments. Environmental contamination by As is a global agricultural and health concern because of its highly toxic and persistent nature (Govil and Krishna 2018; Shahid et al. 2018; Yañez et al. 2018a). In the Earth's crust, As is ranked the 53rd most abundant element with the level of 1.5 mg/L (National Research Council 1977; Sarkar et al. 2011).

Arsenic is a carcinogenic metalloid and is classified as the most toxic element by numerous organizations (USEPA 2014). Subsequently, significant research has been focused worldwide on the distribution of As in different environmental sections (Hughes 2002; Tabassum et al. 2018; Xie et al. 2017). Contamination of groundwater and soils by As has been reported in more than 105 countries worldwide (Naujokas et al. 2013). High levels of this metalloid in the environment are due to its high levels in >200 minerals. Weathering and erosion of As-bearing minerals and rocks are considered the major and most widespread sources of As in water and soil (Abbas et al. 2018). As a result, a great amount of As is released from the contaminated aquifers to different components of the Earth's crust (Govil and Krishna 2018; Khalid et al. 2017; Neidhardt et al. 2012). Probably, the use of As-rich groundwater is the major contributor of As in soil and plants (Arco-Lázaro et al. 2018; Aysha et al. 2017).

The main organic species of As in the Earth's crust include monomethylarsonite, monomethylarsonate, dimethylarsenite, dimethylarsinate, arsenobetaine, arsenosugars, arsenocholine, and trimethylarsine oxide (Abbas et al. 2018). The two inorganic species of As, arsenite As(III) and arsenate As(V), greatly vary regarding their adsorption on soil constituents under different soil physicochemical properties (Khalid et al. 2017; Shakoor et al. 2018b), as well as their potential toxicity to living organisms. Nowadays, it is well-known that the speciation of metals in soil better correlates with their geochemical fate and behavior than total contents in soil

(Natasha et al. 2018a; Shahid et al. 2014b). Hence, As speciation is more imperative than its total contents in soil regarding its phytoavailability and phytotoxicity (Niazi et al. 2011; Shahid et al. 2014a, 2015). Moreover, soil properties greatly affect the As speciation, availability, and mobility in soil and also the uptake by the plants (Abbas et al. 2018; Khalid et al. 2017; Niazi et al. 2018a, b; Rafiq et al. 2018; Tabassum et al. 2018).

High levels of As in the atmosphere, water, soil, or plant are alarming for the environmental health due to daily exposure. Arsenic is not essential for living organisms; however, its exposure causes severe health concerns due to its substantial toxicity even at lower concentrations (Abbas et al. 2018). Excessive As level in growth medium is also a threat for the plants due to various morphological, physiological, and biochemical disorders (Khalid et al. 2017; Rafiq et al. 2017a, b). The accumulation of As in plants is one of the main possible pathways of As transfer to humans. The major route of As to humans is the use of As-rich drinking water (Shahid et al. 2017b; Tabassum et al. 2018).

Besides water and soil, researchers are now focusing on the atmospheric contamination of As bound to particulate matter (PM). High concentrations of As in the atmosphere have been reported globally (Fernández-Olmo et al. 2016; Hassanvand et al. 2015; Mafuyai et al. 2014; Oucher et al. 2015; Vijayanand et al. 2008). Arsenic is washed out of the atmosphere through wet or dry deposition and accumulates in the soil, surface water bodies, and living beings upon exposure (Fig. 1).

Acute As injury occurs due to ingesting a large quantity of As in a short time period. On the other hand, chronic poisoning results from ingestion of As-contaminated food with long time exposure (Herath et al. 2018; Su et al. 2018). High dose of As with less exposure time has less hazardous effects on human health (Gong et al. 2018) as compared to low doses with continuous exposure. Acute expo-

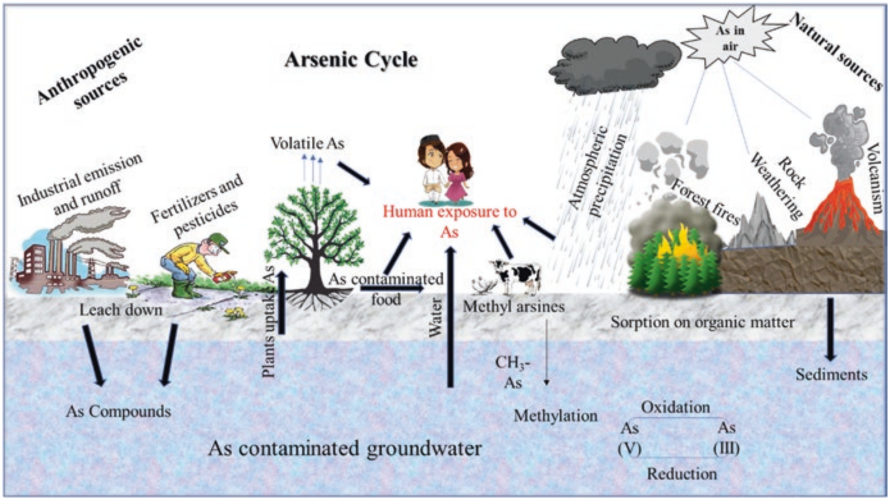

Fig. 1 Arsenic cycle and possible human exposure to As in the environment

sure to As causes numerous human diseases (Shahid et al. 2018). Chronic intoxication causes lung, bladder, liver, kidney, skin, and colon cancer; neurological, vascular, and hematological lesions; cardiovascular diseases; abdominal cramps; weight loss; decline in peripheral nerve conduction velocities; hyperkeratosis; warts; and melanosis (WHO 2000a). Moreover, at the cellular level, heavy metals can overproduce reactive oxygen species (ROS) inside the human body, thus leading to oxidative stress and toxicity to various micro- and macromolecules. Hence, As toxicity is of great concern to sustain the ecosystem viability. Therefore, it is of great importance to monitor As levels in the environment for its possible exposure to humans and associated health hazards. The goal of this chapter is to trace a brief picture of As contamination in the aquifers of South Asia and to know the possible health risks and acute As poisoning.

2 Groundwater Arsenic Contamination: Asian Perspectives

In the recent past, high concentrations of As have been reported in the groundwater samples of various areas worldwide. The problem is intensifying day by day, and more and more areas have been reported with groundwater As contamination. It is anticipated that the groundwater As level varies from <0.5 to >5000 μg/L in more than 70 countries around the globe (Ravenscroft et al. 2009). It is projected that 150 million habitants worldwide consume water from highly As-contaminated aquifers. Owing to high As levels in groundwater, more than 700,000 people have been suffering from As-borne diseases (Rahman et al. 2009; Sikdar 2018; Winkel et al. 2008). The dilemma has spread in recent past in various parts of South Asia (Fendorf et al. 2010; Shakoor et al. 2019). Almost 110 million people using As-rich water live in Asian countries (Table 1). The countries greatly affected by As groundwater contamination in this region include India, Pakistan, Bangladesh, China, Cambodia, Vietnam, numerous states of Nepal, Myanmar, etc. Most of the studied areas in these countries showed the As level greater than the WHO-recommended As limit value in drinking water (10 μg/L) (Table 1).

Table 1 Population at risk: selected countries in South Asia

Country	Population at risk (million)	References
Bangladesh	75	Safiuddin et al. (2011)
Pakistan	50–60	Podgorski et al. (2017)
China	19.6	Rodríguez-Lado et al. (2013)
India	50	Bhattacharya and Mukherjee (2015)
Nepal	2.29	Thakur et al. (2011)
Vietnam	5	Winkel et al. (2011)
Taiwan	0.01	World-Bank (2005)
Myanmar	2.5	Myint and Hla (2017)
Cambodia	2.4	Murphy et al. (2018)

Today, more than 3 million out of 11 million wells in Bangladesh contain >10 μg/L As level, and approximately 20 million habitants in Bangladesh are exposed to water with As level >50 μg/L (Raessler 2018). In India, the As level in the groundwater has been found up to 4730 μg/L (Chakraborti et al. 2018). Despite considerable research, the groundwater level of As in many areas of South Asia is still unclear and needs special attention to save future generations.

In the recent past, Pakistan has gained the attention of researchers due to high As contamination of the groundwater resources (Ahmad and Bhattacharya 2018; Niazi et al. 2017, 2018a; Shahid et al. 2017b; Shakoor et al. 2015, 2016). There are a couple of studies accessing the As level in groundwater in various parts of Pakistan (Rahman et al. 2009; Shakoor et al. 2018; Tabassum et al. 2018). Recently, Shahid et al. (2018) have reported the latest status of groundwater As contamination in Pakistan. Significant data is present on As contamination of the aquifers in Pakistan. About 50–60 million habitants of Pakistan are drinking As-rich water and are at serious risk (Podgorski et al. 2017). Fatima et al. (2018) assessed the influence of the Sutlej River on As contamination of the groundwater resources. The multivariate statistical analysis showed that the As level in 50% of the groundwater samples exceeded 10 μg/L and 17% exceeded 50 μg/L. The high As level might be attributed to oxidative desorption with a rise in evaporative concentration process with other physicochemical parameters. The recent data published on the As level in ground- and surface waters shows As ranging from 0 to 125 and 0–35 μg/L, respectively, in Sindh province of Pakistan (Shahab et al. 2018). According to the international standard, about 26% (30% urban and 23.5% rural) of the population in Pakistan have access to safe drinking water (Ali et al. 2018). The level of As in groundwater of different areas of Asia has been presented in Table 2.

China has the major reserves of As and is one of the top producers of white As in the world. About 87% reserves of As are present in the sulfide ores (Ribeiro et al. 2016). Moreover, the composition of rocks, soil, and sediments contains high As concentrations naturally (Adriano 2001; He and Charlet 2013; Liu et al. 2002; Rodríguez-Lado et al. 2013; Sun 2004; Zheng et al. 1999). Considerable research has been conducted in China due to high As level of the groundwater (Wang et al. 2018; Xie et al. 2018; Zhou et al. 2017). It was estimated that 19 provinces in China have As level >50 μg/L in groundwater (He and Charlet 2013) and 19.6 million habitants are at a serious risk of As poisoning due to drinking As-rich water (Rodríguez-Lado et al. 2013). Duan et al. (2017) reported several times higher As level than 10 μg/L in the groundwater in Jianghan Plain of Central China. The As level ranges from 10 to 400 μg/L in 729 groundwater samples. Some samples showed an As level up to 2620 μg/L, and its concentration increased with increasing depth of the well (Duan et al. 2017). Recently, Wang et al. (2018) studied the As level in groundwater from 100 to 300 m depth. The study showed that the As level raised from 9.9 to 377 μg/L with increasing the depth (Guo et al. 2012). The groundwater level of As in different parts of China is summarized in Table 2.

Like other Asian countries, the Cambodian population especially depends on groundwater sources for drinking, bathing, cleaning, and other daily use activities (Kim et al. 2011). The groundwater of Cambodia is naturally polluted with As (Lear

Table 2 Arsenic concentration (μg/L) in groundwater and the possible cancer risk (CR) in Asian countries

Country/region	As concentration (μg/L)	Source	CR	References
Floodplain, Vietnam	481	Boreholes	0.021	Sø et al. (2018)
Hanoi, Vietnam	52	Tube-well	0.002	Berg et al. (2001)
An Giang, Vietnam	110	Well	0.005	Hoang et al. (2010)
Dong Thap, Vietnam	132	Well	0.006	Merola et al. (2015)
Vinh Tru, Vietnam	348	Tube-well	0.015	Nguyen et al. (2009)
Ly Nhan, Vietnam	420	Tube-well	0.018	Agusa et al. (2014)
Ha Nam, Vietnam	160	Tube-well	0.007	Pham et al. (2017)
Ha Nam, Vietnam	637	–	0.027	Chang et al. (2018)
Giang, Vietnam	550	Well	0.024	Phan and Nguyen (2018)
Kandal, Cambodia	153	Tube-well	0.007	Gault et al. (2008)
Kandal, Cambodia	470	Tube-well	0.020	Luu et al. (2009)
Kandal, Cambodia	209	Well nests	0.009	Lawson et al. (2016)
Prey Veng, Cambodia	21	Tube-well	0.001	O'Neill et al. (2013)
Kratie, Cambodia	17.6	Tube-well	0.001	Phan et al. (2010)
Svay Chrum, Cambodia	118	Tube-well	0.005	Phan et al. (2014)
Preak Russey, Cambodia	959	–	0.041	Murphy et al. (2018)
Rahim Yar Khan, Pakistan	23	Hand pump	0.001	Mahar et al. (2015)
Multan, Pakistan	85	Pumping wells	0.004	Murtaza et al. (2017)
Badarpur, Pakistan	1515	Hand pump/dug wells	0.065	Rasheed et al. (2017)
Tando M. Khan, Pakistan	148	Shallow wells	0.006	Khan et al. (2017)
Vehari, Pakistan	41	Tube-well/pumps	0.002	Shahid et al. (2017b)
Mailsi, Pakistan	42	Tube-well/pumps	0.002	Shahid et al. (2017b)
Hasilpur, Pakistan	16.8	Tube-well	0.001	Tabassum (2017)
Kalalanwala, Pakistan	60	Hand pump	0.003	Farooqi et al. (2007a)
Punjab, Pakistan	123	Deep well	0.005	Farooqi et al. (2007b)
Sindh, Pakistan	46.8	Tube-wells/boreholes	0.002	Shahab et al. (2018)
Vehari, Pakistan	59.9	Tube-well/pumps	0.003	Fatima et al. (2018)
Punjab, Pakistan	49	Hand pump/electric pump	0.002	Shakoor et al. (2018a)
Pakistan	23	Motor pump	0.001	Podgorski et al. (2017)
R. Y. Khan, Pakistan	13.8	Wells	0.001	Qurat-ul-Ain et al. (2017)

(continued)

Table 2 (continued)

Country/region	As concentration (μg/L)	Source	CR	References
Matiari, Pakistan	250	Hand pump/motor pump	0.011	Uqaili et al. (2012)
D.G. Khan, Pakistan	29.3	Hand pump	0.001	Malana and Khosa (2011)
Nagarparkar, Pakistan	683	Surface water	0.029	Brahman et al. (2014)
Tharparkar, Pakistan	2580	Well	0.111	Brahman et al. (2013a)
Tharparkar, Pakistan	3830	Well	0.164	Brahman et al. (2013b)
Gambat, Pakistan	15.4	Tube-well	0.001	Baig et al. (2011)
Sindh, Pakistan	60.2	–	0.003	Kazi et al. (2009)
Rupandehi, Nepal	2620	Tube-well	0.112	Shrestha et al. (2003)
Nawalparasi, Nepal	740	Pumps	0.032	Gurung et al. (2005)
Terai, Nepal	226.9	Tube-well/pumps	0.010	Mueller (2018)
Nawalparasi, Nepal	595	Tube-well	0.026	Yadav et al. (2014)
Nawalparasi, Nepal	448.7	Tube-well	0.019	Yadav et al. (2015a)
Nawalparasi, Nepal	285.6	Tube-well	0.012	Mueller and Hug (2018)
Terai, Nepal	516.5	Tube-well	0.022	Yadav et al. (2015b)
Khorasan, Iran	606	–	0.026	Taheri et al. (2016)
Baba Gurgur, Iran	1233	Well	0.053	Karimi and Alavi (2016)
Kurdistan, Iran	36.8	Well	0.002	Sharifi and Akbar (2017)
Azerbaijan, Iran	12.7	Well	0.001	Mosaferi et al. (2015)
Tabriz, Iran	122.5	Well	0.005	Barzegar et al. (2015)
Qazvin, Iran	950	Surface water	0.041	Yazdi et al. (2015)
Kurdistan, Iran	138	Well/pump	0.006	Mosaferi et al. (2008)
Takab, Iran	986.9	Tube-well	0.042	Keshavarzi et al. (2011)
Mongolia	555	–	0.024	Guo et al. (2013)
Kuitun, China	104.3	Well	0.004	Chen et al. (2018a)
Datong, China	25.5	Well	0.001	Cao et al. (2018)
Jianghan, China	730	Well	0.031	Duan et al. (2015)
Shanyin, China	1090	Tube-well	0.047	Fan et al. (2008)
Jianghan, China	109	Well/pump	0.005	Gan et al. (2014)
Hetao Basin, China	130	–	0.006	Guo et al. (2017)
Shanxi, China	50.1	Tube-well	0.002	Huq et al. (2018)
Shahu, China	121.5	Well	0.005	Li et al. (2018)
Guangdong, China	43.8	Well	0.002	Liu et al. (2010)
Hetao Basin, China	279	Well	0.012	Shen et al. (2018)
Guide Basin, China	109	Well	0.005	Wang et al. (2018)

(continued)

Table 2 (continued)

Country/region	As concentration (μg/L)	Source	CR	References
Hunan, China	1694.8	Surface water	0.073	Wen et al. (2018)
Xinjiang, China	11	Well	0.000	Zeng et al. (2018)
Datong Basin, China	285.6	Well	0.012	Zhang et al. (2017)
Noakhali, Bangladesh	4730	Tube-well	0.203	Chakraborti et al. (2010)
Satyabandi, Bangladesh	225	Deep well	0.010	Aziz et al. (2017)
Chandpur, Bangladesh	347	Tube-well	0.015	Bibi et al. (2008)
Chandpur, Bangladesh	355	Tube-well	0.015	von Brömssen et al. (2007)
Bangladesh	4730	Tube-well	0.203	Chakraborti et al. (2015)
Bangladesh	185	Well	0.008	Van Geen et al. (2006)
Ganges, Bangladesh	1350	Tube-well	0.058	Halim et al. (2009a)
Sherajdikhan, Bangladesh	106	Well	0.005	Halim et al. (2009b)
Comilla, Bangladesh	677	Tube-well	0.029	Hasan et al. (2009)
Jangaal, Sanmandi, Bangladesh	857	Well	0.037	Bhattacharya et al. (2009)
Baylakandi, Bangladesh	500	Well	0.021	Whaley-Martin et al. (2017)
Darikandi, Bangladesh	1200	Tube-well	0.051	Seddique et al. (2008)
Pabna, Bangladesh	49.9	Well	0.002	Uddin et al. (2018)
Sonargaon, Bangladesh	700	Tube-well	0.030	Nakaya et al. (2011)
Baruipur, Bangladesh	349	Tube-well	0.015	Rahman et al. (2015)
Satkhira, Bangladesh	167.9	Tube-well	0.007	Rahman and Hashem (2018)
Rajarampur, Bangladesh	62.4	Well	0.003	Reza et al. (2010b)
Jorgachi, Bangladesh	462	Boreholes	0.020	Reza et al. (2010a)
Bangladesh	366	Tube-well	0.016	Saha and Ali (2007)
Bangladesh	500	Tube-well	0.021	Smith et al. (2000)
Munshiganj, Bangladesh	397	Tube-well	0.017	Dittmar et al. (2007)
Patna, India	90	Tube-well	0.004	Chakraborti et al. (2016a)
Shahpur, India	173	Tube-well	0.007	Chakraborti et al. (2016b)
Ramnagar, India	3700	Tube-well	0.159	Das et al. (2009)
Dehari, India	110	Tube-well	0.005	Alam et al. (2016)

(continued)

Table 2 (continued)

Country/region	As concentration (μg/L)	Source	CR	References
Nadia, India	450	Tube-well	0.019	Bhattacharya (2017)
West Bengal, India	1654	Tube-well	0.071	Chakraborti et al. (2003)
Manipur, India	628	Tube-well	0.027	Chakraborti et al. (2008)
West Bengal, India	5338	Tube-well	0.229	Chakraborti et al. (2009)
Madanpur, India	700	Tube-well	0.030	Chakraborti et al. (2017)
Parganas, India	737	Tube-well	0.032	Das et al. (1996)
Barpeta District	31	Tube-well	0.001	Jain et al. (2018)
Samastipur, India	32	Hand pump/ tube-well	0.001	Kumar et al. (2016)
Ganges, Bangladesh	160	Hand pump/ tube-well	0.007	Mukherjee et al. (2018)
Rajnandgaon, India	506	Tube-well	0.022	Patel et al. (2017)
Gonda, India	510	Tube-well	0.022	Shah (2017)
Dibang, India	618	Bore/open wells	0.026	Singh (2004)
Bhagalpur, India	49.8	Tube-well	0.002	Singh et al. (2014)
Rajnandgaon, India	107	Borewell	0.005	Singhal et al. (2018)

et al. 2007). The primary source of As in groundwater in the area is the weathering of As-bearing rocks (Lawson et al. 2016; Phan et al. 2010; Polya et al. 2010). The unsafe levels of As in water in Cambodia were reported by JICA (1999). The As level up to 943 μg/L in drinking water was observed in the Kandal province, Cambodia (Gault et al. 2008). In the very next year, Luu et al. (2009) reported almost doubled concentration of As (up to 1543 μg/L) in the groundwater of Kandal province. The high As level in water is due to the anoxic condition created by the anaerobic process stimulating the arsenate respiration, thereby promoting As mobilization by the dissolution of As-containing iron oxide minerals (Ying et al. 2015).

Arsenic levels ranged from 1 to 1610 μg/L (mean 217 μg/L) in Southern Vietnam (Berg et al. 2007). Hoang et al. (2010) investigated the As level in the groundwater in four provinces of Vietnam. Their results revealed that the As level in 26% samples was greater than the threshold values with the maximum As level of 1351 μg/L. Around 18 million habitants living in Red River Delta, North Vietnam, are at a serious risk of As poisoning due to the intake of As-rich groundwater with the As concertation up to 632 μg/L (Agusa et al. 2014). Moreover, Merola et al. (2015) reported the high As level (329 μg/L) in the southern part of Vietnam. Nguyen et al. (2009) elaborated that about 40% of the inhabitants of Ha Nam Province, Vietnam, drinking As-rich groundwater are at a serious chronic risk of As poisoning. Recently, Postma et al. (2017) fully explained the mechanism of As entering the groundwater, in Vietnam, under oxidative and reductive environments.

3 Soil-Plant Contamination of As

In South Asia, drinking and irrigation waters are taken from aquifers. Generally, the irrigation waters are drawn deeper by the installation of tube-wells. Moreover, due to lack of resources, the use of wastewater for agricultural practices is quite widespread and is positively correlated with poverty. The contamination of groundwater consequently led to the contamination of wastewater and then soil-plant system (Fig. 2) (Fatta-Kassinos et al. 2011).

It is well explained in the previous section that groundwater in Asian countries is highly contaminated with As (Fendorf et al. 2010; Li et al. 2018; Nga et al. 2018). Water comes in contact with soil and may lead to nearby soil contamination. Most of the heavy metals spilled out from water accumulate in the soil over time (Rashed 2010; Rattan et al. 2005). These metals bound with the organic matter (Grybos et al. 2007; Sauve et al. 2000; Tessier et al. 1979; Zhou et al. 2018a) are not usually found in groundwater, contaminate the soil, and ultimately adversely affect the plants (Gatta et al. 2018; Lai et al. 2018; Rizwan et al. 2018). In either case, we may end up drinking water with toxic amounts of As or consuming food grown in As-contaminated soil.

In Asian countries, the use of As-rich groundwater for crop irrigation is a major cause of As buildup in soil and plants. On a large scale, high amount of As-rich groundwater is applied in the agricultural sector of many regions of South Asia. It can result in food chain contamination and dietary intake of As by the use of As-rich groundwater for crop irrigation. Many As-polluted sites have been reported in China with the As level up to 1217 mg/kg (Wang et al. 2017). Recently, the As level of 15076.8 mg/kg was observed in soil samples of Guangxi China (Chen et al. 2018b). The world background concentration of As is 5 mg/kg in soil (Khalid et al. 2017).

From the recent decades, researchers have investigated the soil As levels in China especially in agricultural and farmland soil. Overexploitation of minerals, ore extraction, mining activities, and smelting processes have resulted in the discharge

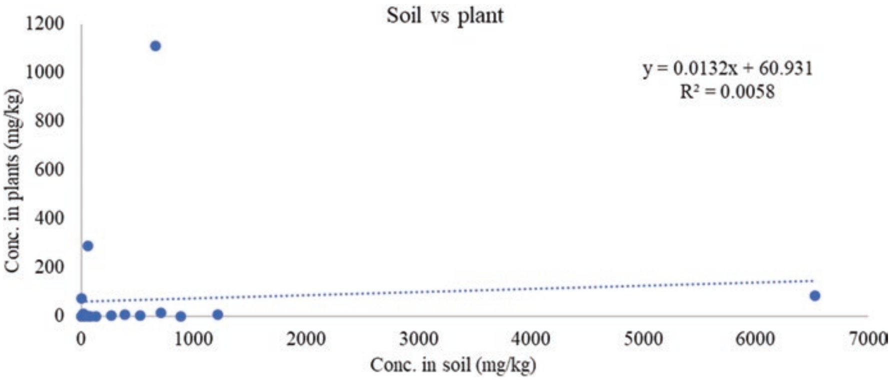

Fig. 2 Scatter plot analysis (correlation) of As contents in soil vs plants in Asia

of As in agricultural/farmland soil which greatly affects the local Chinese soil. Zhou et al. (2018b), recently, published data about As contamination of soil across China. They reported the As level from 2011 to 2016 with a mean of 10.1 and 12.2 mg/kg, respectively. The As level was reported higher in the northern and southern areas of China. In Southwestern China, the As level was reported to be 71.7 mg/kg (Li et al. 2015). Moreover, high As level (83–2224 mg/kg) in the soil was observed in Hunan Province, China (Yang et al. 2018a). Arsenic from soil to plants is a key step of As entering the food chain. Previously, Liu et al. (2005) determined As transfer from soil to vegetables. The As level in soil was 709 mg/kg, and its accumulation in vegetables with a level of 40.7 mg/kg was found with a high health risk. The wheat plants, when grown on contaminated soil (As level 28.7–97.8 mg/kg), accumulated significant concentration of As in all the parts with 0.41 mg/kg in edible grains. A wide range of data is presented on the rice As accumulation in China, as rice is a staple food for about two-thirds of the Chinese population. The buildup of As in plants cultivated on As-polluted soil is presented in Table 3.

The studies focusing on water As contamination also illustrate the potential threat of soil As contamination due to irrigation practices. In Pakistan, in spite of irrigation with groundwater/surface water, the agricultural practices with wastewater irrigation have also been a matter of concern. However, as reported previously, the quality of groundwater used in the municipal sector may not be of high standard in some areas of Pakistan (Niazi et al. 2018a; Shahid et al. 2018; Shakoor et al. 2018a). The occurrence of As in groundwater can be a source of its presence in wastewater produced from the municipal sector and can result in As buildup in the soil-plant-human systems (Simpson et al. 2005). Recently, Rasool et al. (2016) investigated the As levels in tube-well water of Mailsi, Punjab, Pakistan. The average As level in tube-well water was 130 and 139 μg/L, respectively, higher than the irrigation water standard 100 μg/L by FAO (1992) and WWF-Pakistan (2007). Crop cultivation using As-rich water poses an emerging health issue in Pakistan. The As level in soil samples was 46.2 mg/kg (Arain et al. 2009) and 35 mg/kg in soil samples of different areas of Punjab (Farooqi et al. 2009). Moreover, the As content in irrigation water was in the range of 360–683 μg/L and in irrigated soil was 110–266 mg/kg (Brahman et al. 2014). Under high soil As contamination, plants accumulate high quantity of As in edible portions of the plant (Khalid et al. 2018; Rafiq et al. 2017a, b). A wide range of data is present indicating the water-soil-plant contamination of As in different regions of Pakistan. Rehman et al. (2016) quantified the As level in soil and plants of five districts of Khyber Pakhtunkhwa, Pakistan. The mean As level in soil and vegetables was several folds higher than the threshold values (0.1 mg/kg).

Plants can uptake As through the roots and leaves, while uptake from the soil through the roots is a predominant process (Shahid et al. 2017a). A few studies also focused on the foliar absorption of As from the atmosphere (Bondada et al. 2004; Natasha et al. 2018b), but the data remain limited in Asian countries. Majority of the studies focus on the vegetables/crops cultivated on naturally/anthropogenically polluted soils or soil irrigated with untreated wastewater. The local soil contamination

Table 3 Arsenic transfer from soil to plants and its cancer risk (CR) assessment

Country/region	Soil As (mg/kg)	Crop/vegetable	As contents (mg/kg)	CR	References
Pakistan	3.81	*Momordica charantia*	1.38	0.000252	Rehman et al. (2016)
Pakistan	18.4	*Mentha piperita*	1.2	0.000219	Arain et al. (2009)
Pakistan	266	*Phaseolus vulgaris*	4.7	0.000859	Brahman et al. (2014)
China	889.3	*Amaranthus tricolor*	1.42	0.000260	Li et al. (2017)
China	56	*Beta vulgaris*	288	0.052667	Yañez et al. (2018b)
China	20	*Lactuca sativa*	0.06	0.000011	Chang et al. (2014)
China	129	*Oryza sativa*	0.56	0.000102	Liu et al. (2010)
China	522	*Brassica rapa*	1.85	0.000338	Yu et al. (2006)
China	390	*Panax notoginseng*	8.5	0.001554	Yang et al. (2018c)
China	10.2	*Oryza sativa*	0.3	0.000055	Lu et al. (2010)
China	57.2	*Triticum aestivum*	0.42	0.000077	Zhang et al. (2018)
China	709	*Capsicum annuum*	14.7	0.002688	Liu et al. (2005)
China	1217	*Oryza sativa*	7.5	0.001372	Liao et al. (2005)
China	660	*Pteris vittata*	1110	0.202987	Chen et al. (2002)
China	84.6	*Oryza sativa*	0.5	0.000091	Yang et al. (2018b)
China	6.04	*Apium graveolens*	72.1	0.013185	Huang et al. (2006)
Vietnam	39.3	*Oxalis corniculata*	2.9	0.000530	Bui et al. (2016)
Vietnam	16.7	*Allium cepa*	1.02	0.000187	Dahal et al. (2008b)
Cambodia	12.8	*Cucumis sativus*	0.13	0.000024	Phan et al. (2013)
Cambodia	18	*Oryza sativa*	0.2	0.000037	Seyfferth et al. (2014)
Taiwan	15.2	*Raphanus sativus*	5.89	0.001077	Chou et al. (2016)
Iran	6525	*Nonea persica*	84	0.015361	Karimi et al. (2009)
Iran	2.4	*Allium ampeloprasum L.*	0.174	0.000032	Ghasemidehkordi et al. (2018)
Nepal	16.7	*Oryza sativa*	9.3	0.001701	Dahal et al. (2008b)

in specific areas of agricultural importance could pose high ecological and human health-related risks with long-term impacts.

Cambodia is an agricultural country, and most of the people living in rural areas completely rely on agricultural activities for their source of revenue. The farmers use groundwater from deep boreholes or in some cases use shallow groundwater for irrigation. The As contamination of ground- and shallow water tends to accumulate As in the surface soil leading to a potential threat to crop cultivation (Dahal et al. 2008b; Das et al. 2004). For the production of rice in dry seasons, groundwater is widely used throughout Mekong Delta (Shamsudduha et al. 2009) (Cambodia, Myanmar and Vietnam). In Vietnam, Red River Delta is a critical region for the economy of the country and supplies vegetable/crops to 7.5 million inhabitants of the country (Tran and Nguyen 2018). The aquifers in the region are greatly polluted with As. The irrigation will continuously add As in the soil in large quantity over time. The recent identification of As in soil samples from Vietnam was 693 mg/kg (Tran and Nguyen 2018).

In Nepal, soil contamination with As due to highly polluted irrigation water, its buildup, and consequences to plants have been described (Mueller and Hug 2018; Yadav et al. 2015b). According to an estimate, As in water samples of wells (Nawalparasi District) of Nepal showed that about 36% of the wells have As-rich water exceeding the FAO limit values (Dahal et al. 2008a). Thinh et al. (2018) showed the total As level in mangrove forest and paddy field was 26.3 and 13.8 mg/kg, respectively, in the estuarine ecosystem of North Vietnam. The bioavailable concentration of As remained low as compared to the total As content in soil but was in toxic range for the plants. Many studies have focused on the As contamination of soil in India and Bangladesh where As-rich groundwater is often used for irrigation (Ahmed and Kurosawa 2017; Ahmed et al. 2018; Alam et al. 2003; Aysha et al. 2017; Mondal et al. 2018; Rahman et al. 2018; Upadhyay et al. 2018).

4 Health Risk Assessment

Currently, food security and risk assessment are highly noteworthy worldwide due to increased awareness of environmental toxicology and associated health hazards among the local community (Li et al. 2018; Mandal et al. 2019). Moreover, the health and environmental organizations and regularity authorities at local, regional, and global levels have become more concerned about environmental toxicology, food and water security, and health risks. In this study, we calculated cancer risk to trace out possible water and plant-human transfer of As and to predict possible health hazards in the habitants of South Asia.

The high concentration of As in the groundwater of Asian countries showed high carcinogenic risk. The concentration of As in groundwater presented in Table 2 was used for the cancer risk estimation. The cancer risk assessment from the intake of As via food or water has been widely documented in literature (Anawar et al. 2002; Bhowmick et al. 2018; Jomova et al. 2011; Kapaj et al. 2006; Li et al. 2011; Phan et al. 2010; Rahman et al. 2018; Shahid et al. 2018; Sharma et al. 2018; Smith et al. 2000; Tabassum et al. 2018; Wongsasuluk et al. 2014). The cancer risk (CR) assessment in this study indicated that the groundwater As contamination can severely impact the local inhabitants of the area. The carcinogenic assessment showed the value higher than the threshold value.

In this study, the estimated CR values from the consumption of As-contaminated food crops (Table 3) were significantly higher than the threshold value ($CR > 10^{-4}$). This shows that there can be a high cancer risk due to consumption of vegetables/crops cultivated on As-contaminated soil. However, this risk greatly varies with the vegetable/crop type as well as according to actual ingestion rates in individuals. The consumption of As-rich water/food can cause lung, bladder, liver, kidney, skin, and colon cancer; neurological, vascular, and hematological lesions; cardiovascular diseases; abdominal cramps; weight loss; decrease in peripheral nerve conduction rate; hyperkeratosis; warts; and melanosis (WHO 2000b).

5 Conclusions and Future Perspectives

Arsenic naturally occurs in soils, sediments, and aquatic environments as a toxic metalloid. Arsenic is not essential for living organisms; however, its exposure causes severe health concerns even at lower concentrations. In the recent past, high levels of As have been perceived in the groundwater and soil in many areas around the globe, especially in Asian countries.

The problem of environmental contamination by As is worsening day by day. Arsenic levels in groundwater samples range from <0.5 to >5000 μg/L in more than 70 countries around the world. The situation is even worse in Asia. In Asian countries, application of As-rich groundwater for crop cultivation is a major source of As buildup in soil leading to food chain contamination. It adds significant amounts of As in dietary intake and poses a serious threat. The high concentration of As in the groundwater and edible plants showed high carcinogenic risk.

Groundwater concentration of As in many parts of South Asia is still unclear. In the future, there is a need of a thorough assessment of As in groundwater and its contribution in food chain contamination, accumulation in soil and crops across the Asian countries, and As health risk assessment. It is also important to use various environment-friendly strategies to remediate the As-contaminated water, soil, and other environmental compartments.

References

Abbas G, Murtaza B, Bibi I, Shahid M, Niazi NK, Khan MI, Amjad M, Hussain M, Natasha (2018) Arsenic uptake, toxicity, detoxification, and speciation in plants: physiological, biochemical, and molecular aspects. Int J Environ Res Public Health 15:59

Adriano DC (2001) Arsenic. In: Trace elements in terrestrial environments. Springer, New York, pp 219–261

Agusa T, Trang PTK, Lan VM, Anh DH, Tanabe S, Viet PH, Berg M (2014) Human exposure to arsenic from drinking water in Vietnam. Sci Total Environ 488:562–569

Ahmad A, Bhattacharya P (2018) Arsenic contamination of groundwater in Indus River Basin of Pakistan. In: Mukherjee A (ed) Groundwater of South Asia. Springer, Singapore, pp 393–403

Ahmed M, Kurosawa K (2017) Arsenic contamination of water-soil-crop system in an industrial area of Bangladesh. Int J Environ 6:76–86

Ahmed M, Matsumoto M, Kurosawa K (2018) Heavy metal contamination of irrigation water, soil, and vegetables in a multi-industry district of Bangladesh. Int J Environ Res 12:531–542

Alam M, Snow E, Tanaka A (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. Sci Total Environ 308:83–96

Alam MO, Shaikh WA, Chakraborty S, Avishek K, Bhattacharya T (2016) Groundwater arsenic contamination and potential health risk assessment of Gangetic Plains of Jharkhand, India. Expo Health 8:125–142

Ali W, Rasool A, Junaid M, Zhang H (2018) A comprehensive review on current status, mechanism, and possible sources of arsenic contamination in groundwater: a global perspective with prominence of Pakistan scenario. Environ Geochem Health. https://doi.org/10.1007/s10653-018-0169-x

Anawar H, Akai J, Mostofa K, Safiullah S, Tareq S (2002) Arsenic poisoning in groundwater: health risk and geochemical sources in Bangladesh. Environ Int 27:597–604

Arain M, Kazi T, Baig J, Jamali M, Afridi H, Shah A, Jalbani N, Sarfraz R (2009) Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: estimation of daily dietary intake. Food Chem Toxicol 47:242–248

Arco-Lázaro E, Pardo T, Clemente R, Bernal MP (2018) Arsenic adsorption and plant availability in an agricultural soil irrigated with As-rich water: effects of Fe-rich amendments and organic and inorganic fertilisers. J Environ Manag 209:262–272

Aysha M, Zakir H, Haque R, Quadir Q, Choudhury TR, Quraishi S, Mollah M (2017) Health risk assessment for population via consumption of vegetables grown in soils artificially contaminated with arsenic. Arch Curr Res Int 10:1–12

Aziz Z, Bostick B, Zheng Y, Huq M, Rahman M, Ahmed K, Van Geen A (2017) Evidence of decoupling between arsenic and phosphate in shallow groundwater of Bangladesh and potential implications. Appl Geochem 77:167–177

Baig JA, Kazi TG, Shah AQ, Afridi HI, Kandhro GA, Khan S, Kolachi NF, Wadhwa SK, Shah F, Arain MB (2011) Evaluation of arsenic levels in grain crops samples, irrigated by tube well and canal water. Food Chem Toxicol 49:265–270

Barzegar R, Asghari Moghaddam A, Kazemian N (2015) Assessment of heavy metals concentrations with emphasis on arsenic in the Tabriz plain aquifers, Iran. Environ Earth Sci 74:297–313. https://doi.org/10.1007/s12665-015-4123-2

Berg M, Tran HC, Nguyen TC, Pham HV, Schertenleib R, Giger W (2001) Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. Environ Sci Technol 35:2621–2626

Berg M, Stengel C, Trang PTK, Viet PH, Sampson ML, Leng M, Samreth S, Fredericks D (2007) Magnitude of arsenic pollution in the Mekong and Red River Deltas—Cambodia and Vietnam. Sci Total Environ 372:413–425

hattacharya P (2017) Assessment of arsenic accumulation by different varieties of rice (Oryza sativa L.) irrigated with arsenic-contaminated groundwater in West Bengal (India). Environ Pollut Protect 2:92–99

Bhattacharya P, Mukherjee A (2015) Groundwater arsenic in India: source, distribution, effects and alternate safe drinking water sources

Bhattacharya P, Hasan MA, Sracek O, Smith E, Ahmed KM, von Brömssen M, Huq SMI, Naidu R (2009) Groundwater chemistry and arsenic mobilization in the Holocene flood plains in south-central Bangladesh. Environ Geochem Health 31:23–43. https://doi.org/10.1007/s10653-008-9230-5

Bhowmick S, Pramanik S, Singh P, Mondal P, Chatterjee D, Nriagu J (2018) Arsenic in groundwater of West Bengal, India: a review of human health risks and assessment of possible intervention options. Sci Total Environ 612:148–169

Bibi M, Ahmed F, Ishiga H (2008) Geochemical study of arsenic concentrations in groundwater of the Meghna River Delta, Bangladesh. J Geochem Explor 97:43–58

Bondada BR, Tu S, Ma LQ (2004) Absorption of foliar-applied arsenic by the arsenic hyperaccumulating fern (Pteris vittata L.). Sci Total Environ 332:61–70

Brahman KD, Kazi TG, Afridi HI, Naseem S, Arain SS, Ullah N (2013a) Evaluation of high levels of fluoride, arsenic species and other physicochemical parameters in underground water of two sub districts of Tharparkar, Pakistan: a multivariate study. Water Res 47:1005–1020

Brahman KD, Kazi TG, Afridi HI, Naseem S, Arain SS, Wadhwa SK, Shah F (2013b) Simultaneously evaluate the toxic levels of fluoride and arsenic species in underground water of Tharparkar and possible contaminant sources: a multivariate study. Ecotoxicol Environ Saf 89:95–107

Brahman KD, Kazi TG, Baig JA, Afridi HI, Khan A, Arain SS, Arain MB (2014) Fluoride and arsenic exposure through water and grain crops in Nagarparkar, Pakistan. Chemosphere 100:182–189

Bui ATK, Nguyen HTH, Nguyen MN, Tran T-HT, Vu TV, Nguyen CH, Reynolds HL (2016) Accumulation and potential health risks of cadmium, lead and arsenic in vegetables grown near mining sites in Northern Vietnam. Environ Monit Assess 188:525. https://doi.org/10.1007/s10661-016-5535-5

Cao H, Xie X, Wang Y, Pi K, Li J, Zhan H, Liu P (2018) Predicting the risk of groundwater arsenic contamination in drinking water wells. J Hydrol 560:318–325. https://doi.org/10.1016/j.jhydrol.2018.03.007

Chakraborti D, Mukherjee SC, Pati S, Sengupta MK, Rahman MM, Chowdhury UK, Lodh D, Chanda CR, Chakraborti AK, Basu GK (2003) Arsenic groundwater contamination in Middle Ganga Plain, Bihar, India: a future danger? Environ Health Perspect 111:1194

Chakraborti D, Singh EJ, Das B, Shah BA, Hossain MA, Nayak B, Ahamed S, Singh NR (2008) Groundwater arsenic contamination in Manipur, one of the seven North-Eastern Hill states of India: a future danger. Environ Geol 56:381–390

Chakraborti D, Das B, Rahman MM, Chowdhury UK, Biswas B, Goswami A, Nayak B, Pal A, Sengupta MK, Ahamed S (2009) Status of groundwater arsenic contamination in the state of West Bengal, India: a 20-year study report. Mol Nutr Food Res 53:542–551

Chakraborti D, Rahman MM, Das B, Murrill M, Dey S, Mukherjee SC, Dhar RK, Biswas BK, Chowdhury UK, Roy S (2010) Status of groundwater arsenic contamination in Bangladesh: a 14-year study report. Water Res 44:5789–5802

Chakraborti D, Rahman MM, Mukherjee A, Alauddin M, Hassan M, Dutta RN, Pati S, Mukherjee SC, Roy S, Quamruzzman Q (2015) Groundwater arsenic contamination in Bangladesh—21 Years of research. J Trace Elem Med Biol 31:237–248

Chakraborti D, Rahman MM, Ahamed S, Dutta RN, Pati S, Mukherjee SC (2016a) Arsenic groundwater contamination and its health effects in Patna district (capital of Bihar) in the middle Ganga plain, India. Chemosphere 152:520–529

Chakraborti D, Rahman MM, Ahamed S, Dutta RN, Pati S, Mukherjee SC (2016b) Arsenic contamination of groundwater and its induced health effects in Shahpur block, Bhojpur district, Bihar state, India: risk evaluation. Environ Sci Pollut Res 23:9492–9504. https://doi.org/10.1007/s11356-016-6149-8

Chakraborti D, Rahman MM, Das B, Chatterjee A, Das D, Nayak B, Pal A, Chowdhury UK, Ahmed S, Biswas BK, Sengupta MK, Hossain MA, Samanta G, Roy MM, Dutta RN, Saha KC, Mukherjee SC, Pati S, Kar PB, Mukherjee A, Kumar M (2017) Groundwater arsenic contamination and its health effects in India. Hydrogeol J 25:1165–1181. https://doi.org/10.1007/s10040-017-1556-6

Chakraborti D, Singh S, Rahman M, Dutta R, Mukherjee S, Pati S, Kar P (2018) Groundwater arsenic contamination in the Ganga River Basin: a future health danger. Int J Environ Res Public Health 15:180

Chang CY, Yu HY, Chen JJ, Li FB, Zhang HH, Liu CP (2014) Accumulation of heavy metals in leaf vegetables from agricultural soils and associated potential health risks in the Pearl River Delta, South China. Environ Monit Assess 186:1547–1560. https://doi.org/10.1007/s10661-013-3472-0

Chang J-S, Yoon I-H, Kim K-W (2018) Arsenic biotransformation potential of microbial arsH responses in the biogeochemical cycling of arsenic-contaminated groundwater. Chemosphere 191:729–737. https://doi.org/10.1016/j.chemosphere.2017.10.044

Chen T, Wei C, Huang Z, Huang Q, Lu Q, Fan Z (2002) Arsenic hyperaccumulator Pteris vittata L. and its arsenic accumulation. Chin Sci Bull 47:902–905

Chen T, Su Y, Yuan X (2018a) Influences of the petroleum-recovering activity on the arsenic level in groundwater of Kuitun, Xinjiang, China. Hum Ecol Risk Assess: Int J 24:1–14

Chen Y, Xu J, Lv Z, Huang L, Jiang J (2018b) Impacts of biochar and oyster shells waste on the immobilization of arsenic in highly contaminated soils. J Environ Manag 217:646–653

Chou M-L, Jean J-S, Yang C-M, Hseu Z-Y, Chen Y-H, Wang H-L, Das S, Chou L-S (2016) Inhibition of ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe) and calcium peroxide (CaO2) on arsenic uptake by vegetables in arsenic-rich agricultural soil. J Geochem Explor 163:19–27. https://doi.org/10.1016/j.gexplo.2016.01.004

Dahal BM, Fuerhacker M, Mentler A, Shrestha RR, Blum WE (2008a) Screening of arsenic in irrigation water used for vegetable production in Nepal. Arch Agron Soil Sci 54:41–51

Dahal BM, Fuerhacker M, Mentler A, Karki KB, Shrestha RR, Blum WE (2008b) Arsenic contamination of soils and agricultural plants through irrigation water in Nepal. Environ Pollut 155:157–163. https://doi.org/10.1016/j.envpol.2007.10.024

Das D, Samanta G, Mandal BK, Chowdhury TR, Chanda CR, Chowdhury PP, Basu GK, Chakraborti D (1996) Arsenic in groundwater in six districts of West Bengal, India. Environ Geochem Health 18:5–15

Das H, Mitra AK, Sengupta P, Hossain A, Islam F, Rabbani G (2004) Arsenic concentrations in rice, vegetables, and fish in Bangladesh: a preliminary study. Environ Int 30:383–387

Das B, Rahman MM, Nayak B, Pal A, Chowdhury UK, Mukherjee SC, Saha KC, Pati S, Quamruzzaman Q, Chakraborti D (2009) Groundwater arsenic contamination, its health effects and approach for mitigation in West Bengal, India and Bangladesh. Water Qual Expo Health 1:5–21

Dittmar J, Voegelin A, Roberts LC, Hug SJ, Saha GC, Ali MA, Badruzzaman ABM, Kretzschmar R (2007) Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. 2. Paddy soil. Environ Sci Technol 41:5967–5972. https://doi.org/10.1021/es0702972

Duan Y, Gan Y, Wang Y, Deng Y, Guo X, Dong C (2015) Temporal variation of groundwater level and arsenic concentration at Jianghan Plain, central China. J Geochem Explor 149:106–119

Duan Y, Gan Y, Wang Y, Liu C, Yu K, Deng Y, Zhao K, Dong C (2017) Arsenic speciation in aquifer sediment under varying groundwater regime and redox conditions at Jianghan Plain of Central China. Sci Total Environ 607:992–1000

Fan H, Su C, Wang Y, Yao J, Zhao K, Wang Y, Wang G (2008) Sedimentary arsenite-oxidizing and arsenate-reducing bacteria associated with high arsenic groundwater from Shanyin, Northwestern China. J Appl Microbiol 105:529–539

FAO (1992) Wastewater treatment and use in agriculture – FAO irrigation and drainage. Food and Agriculture Organization of the United Nations, Rome

Farooqi A, Masuda H, Firdous N (2007a) Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. Environ Pollut 145:839–849

Farooqi A, Masuda H, Kusakabe M, Naseem M, Firdous N (2007b) Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle. Geochem J 41:213–234

Farooqi A, Masuda H, Siddiqui R, Naseem M (2009) Sources of arsenic and fluoride in highly contaminated soils causing groundwater contamination in Punjab, Pakistan. Arch Environ Contam Toxicol 56:693–706

Fatima S, Hussain I, Rasool A, Xiao T, Farooqi A (2018) Comparison of two alluvial aquifers shows the probable role of river sediments on the release of arsenic in the groundwater of district Vehari, Punjab, Pakistan. Environ Earth Sci 77:382. https://doi.org/10.1007/s12665-018-7542-z

Fatta-Kassinos D, Kalavrouziotis I, Koukoulakis P, Vasquez M (2011) The risks associated with wastewater reuse and xenobiotics in the agroecological environment. Sci Total Environ 409:3555–3563

Fendorf S, Michael HA, van Geen A (2010) Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. Science 328:1123–1127

Fernández-Olmo I, Andecochea C, Ruiz S, Fernández-Ferreras JA, Irabien A (2016) Local source identification of trace metals in urban/industrial mixed land-use areas with daily PM10 limit value exceedances. Atmos Res 171:92–106

Gan Y, Wang Y, Duan Y, Deng Y, Guo X, Ding X (2014) Hydrogeochemistry and arsenic contamination of groundwater in the Jianghan Plain, central China. J Geochem Explor 138:81–93

Gatta G, Gagliardi A, Disciglio G, Lonigro A, Francavilla M, Tarantino E, Giuliani MM (2018) Irrigation with treated municipal wastewater on artichoke crop: assessment of soil and yield heavy metal content and human risk. Water 10:255

Gault AG, Rowland HA, Charnock JM, Wogelius RA, Gomez-Morilla I, Vong S, Leng M, Samreth S, Sampson ML, Polya DA (2008) Arsenic in hair and nails of individuals exposed to arsenic-rich groundwaters in Kandal province, Cambodia. Sci Total Environ 393:168–176

Ghasemidehkordi B, Malekirad AA, Nazem H, Fazilati M, Salavati H, Rezaei M (2018) Arsenic and boron levels in irrigation water, soil, and green leafy vegetables. Int J Veg Sci 24:115–121

Gong C, Wang Z, Dong F, Xing Y, Sun Y (2018) Human health risk assessment from arsenic dietary exposures in Yantai. J Food Saf Qual 9:3650–3655

Govil PK, Krishna AK (2018) Soil and water contamination by potentially hazardous elements: a case history from India. In: Environmental geochemistry (2nd edn). Elsevier, pp 567–597

Grybos M, Davranche M, Gruau G, Petitjean P (2007) Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? J Colloid Interface Sci 314:490–501

Guo H, Zhang Y, Xing L, Jia Y (2012) Spatial variation in arsenic and fluoride concentrations of shallow groundwater from the town of Shahai in the Hetao basin, Inner Mongolia. Appl Geochem 27:2187–2196

Guo H, Zhang Y, Jia Y, Zhao K, Kim K (2013) Spatial and temporal evolutions of groundwater arsenic approximately along the flow path in the Hetao basin, Inner Mongolia. Chin Sci Bull 58:3070–3079

Guo H, Zhang D, Ni P, Cao Y, Li F (2017) Hydrogeological and geochemical comparison of high arsenic groundwaters in inland basins, PR China. Proc Earth Planet Sci 17:416–419

Gurung JK, Ishiga H, Khadka MS (2005) Geological and geochemical examination of arsenic contamination in groundwater in the Holocene Terai Basin, Nepal. Environ Geol 49:98–113. https://doi.org/10.1007/s00254-005-0063-6

Halim M, Majumder R, Nessa S, Hiroshiro Y, Uddin M, Shimada J, Jinno K (2009a) Hydrogeochemistry and arsenic contamination of groundwater in the Ganges Delta Plain, Bangladesh. J Hazard Mater 164:1335–1345

Halim MA, Majumder RK, Nessa SA, Oda K, Hiroshiro Y, Saha BB, Hassain SM, Latif SA, Islam MA, Jinno K (2009b) Groundwater contamination with arsenic in Sherajdikhan, Bangladesh: geochemical and hydrological implications. Environ Geol 58:73–84. https://doi.org/10.1007/s00254-008-1493-8

Hasan MA, Bhattacharya P, Sracek O, Ahmed KM, von Brömssen M, Jacks G (2009) Geological controls on groundwater chemistry and arsenic mobilization: hydrogeochemical study along an E–W transect in the Meghna basin, Bangladesh. J Hydrol 378:105–118

Hassanvand MS, Naddafi K, Faridi S, Nabizadeh R, Sowlat MH, Momeniha F, Gholampour A, Arhami M, Kashani H, Zare A (2015) Characterization of PAHs and metals in indoor/outdoor PM 10/PM 2.5/PM 1 in a retirement home and a school dormitory. Sci Total Environ 527:100–110

He J, Charlet L (2013) A review of arsenic presence in China drinking water. J Hydrol 492:79–88

Herath S, Ayala H, Kawakami T, Nagasawa S, Serikawa Y, Motoyama A, Chaminda G, Weragoda S, Yatigammana S, Amarasooriya A (2018) Arsenic, cadmium, lead, and chromium in well water, rice, and human urine in Sri Lanka in relation to chronic kidney disease of unknown etiology. J Water Health 16:212–222

Hoang TH, Bang S, Kim K-W, Nguyen MH, Dang DM (2010) Arsenic in groundwater and sediment in the Mekong River delta, Vietnam. Environ Pollut 158:2648–2658

Huang R-Q, Gao S-F, Wang W-L, Staunton S, Wang G (2006) Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China. Sci Total Environ 368:531–541

Hughes MF (2002) Arsenic toxicity and potential mechanisms of action. Toxicol Lett 133:1–16

Huq ME, Su C, Fahad S, Li J, Sarven MS, Liu R (2018) Distribution and hydrogeochemical behavior of arsenic enriched groundwater in the sedimentary aquifer comparison between Datong Basin (China) and Kushtia District (Bangladesh). Environ Sci Pollut Res 25:15830–15843

Jain C, Sharma S, Singh S (2018) Physico-chemical characteristics and hydrogeological mechanisms in groundwater with special reference to arsenic contamination in Barpeta District, Assam (India). Environ Monit Assess 190:417

JICA (1999) Japanese International Cooperation Agency. The study of groundwater development in Southern Cambodia. Unpublished Draft Report by Kokusai Kogyo Co Ltd to Ministry of Rural Development, Phnom Penh, Cambodia

Jomova K, Jenisova Z, Feszterova M, Baros S, Liska J, Hudecova D, Rhodes C, Valko M (2011) Arsenic: toxicity, oxidative stress and human disease. J Appl Toxicol 31:95–107

Kapaj S, Peterson H, Liber K, Bhattacharya P (2006) Human health effects from chronic arsenic poisoning – a review. J Environ Sci Health A 41:2399–2428

Karimi N, Alavi M (2016) Arsenic contamination and accumulation in soil, groundwater and wild plant species from Qorveh County, Iran. Biharean Biol 10:69–73

Karimi N, Ghaderian SM, Maroofi H, Schat H (2009) Analysis of arsenic in soil and vegetation of a contaminated area in Zarshuran, Iran. Int J Phytoremediation 12:159–173

Kazi TG, Arain MB, Baig JA, Jamali MK, Afridi HI, Jalbani N, Sarfraz RA, Shah AQ, Niaz A (2009) The correlation of arsenic levels in drinking water with the biological samples of skin disorders. Sci Total Environ 407:1019–1026

Keshavarzi B, Moore F, Mosaferi M, Rahmani F (2011) The source of natural arsenic contamination in groundwater, west of Iran. Water Qual Expo Health 3:135–147

Khalid S, Shahid M, Niazi NK, Rafiq M, Bakhat HF, Imran M, Abbas T, Bibi I, Dumat C (2017) Arsenic behaviour in soil-plant system: biogeochemical reactions and chemical speciation influences. In: Enhancing cleanup of environmental pollutants. Springer, Cham, pp 97–140

Khalid S, Shahid M, Natasha, Bibi I, Sarwar T, Shah A, Niazi N (2018) A review of environmental contamination and health risk assessment of wastewater use for crop irrigation with a focus on low and high-income countries. Int J Environ Res Public Health 15:895

Khan A, Husain V, Bakhtiari AE, Khan H, Arsalan M (2017) Groundwater arsenic contamination in semi-urban areas of Tando Muhammad Khan District: a case study from deltaic flood plain of Sindh, Pakistan. Sustain Environ 2:171

Kim K-W, Chanpiwat P, Hanh HT, Phan K, Sthiannopkao S (2011) Arsenic geochemistry of groundwater in Southeast Asia. Front Med 5:420–433

Kumar M, Rahman MM, Ramanathan A, Naidu R (2016) Arsenic and other elements in drinking water and dietary components from the middle Gangetic plain of Bihar, India: health risk index. Sci Total Environ 539:125–134

Lai H-Y, Lee C-H, Chen Z-S (2018) Taiwan's experiences on soil amendments, phytoremediation, and soil water managements for the cadmium-and arsenic-contaminated soils. In: Twenty years of research and development on soil pollution and remediation in China. Springer, Singapore, pp 441–451

Lawson M, Polya DA, Boyce AJ, Bryant C, Ballentine CJ (2016) Tracing organic matter composition and distribution and its role on arsenic release in shallow Cambodian groundwaters. Geochim Cosmochim Acta 178:160–177

Lear G, Song B, Gault A, Polya D, Lloyd J (2007) Molecular analysis of arsenate-reducing bacteria within Cambodian sediments following amendment with acetate. Appl Environ Microbiol 73:1041–1048

Li G, Sun G-X, Williams PN, Nunes L, Zhu Y-G (2011) Inorganic arsenic in Chinese food and its cancer risk. Environ Int 37:1219–1225

Li K, Liang T, Wang L, Yang Z (2015) Contamination and health risk assessment of heavy metals in road dust in Bayan Obo Mining Region in Inner Mongolia, North China. J Geogr Sci 25:1439–1451

Li L, Hang Z, Yang W-T, Gu J-F, Liao B-H (2017) Arsenic in vegetables poses a health risk in the vicinity of a mining area in the southern Hunan Province, China. Hum Ecol Risk Assess Int J 23:1315–1329

Li R, Kuo Y-M, Liu W-w, Jang C-S, Zhao E, Yao L (2018) Potential health risk assessment through ingestion and dermal contact arsenic-contaminated groundwater in Jianghan Plain, China. Environ Geochem Health 40:1585–1599

Liao X-Y, Chen T-B, Xie H, Liu Y-R (2005) Soil As contamination and its risk assessment in areas near the industrial districts of Chenzhou City, Southern China. Environ Int 31:791–798

Liu J, Zheng B, Aposhian HV, Zhou Y, Chen M-L, Zhang A, Waalkes MP (2002) Chronic arsenic poisoning from burning high-arsenic-containing coal in Guizhou, China. J Peripher Nerv Syst 7:208–208

Liu H, Probst A, Liao B (2005) Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Sci Total Environ 339:153–166

Liu C-P, Luo C-L, Gao Y, Li F-B, Lin L-W, Wu C-A, Li X-D (2010) Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. Environ Pollut 158:820–826. https://doi.org/10.1016/j.envpol.2009.09.029

Lu Y, Dong F, Deacon C, Chen H-j, Raab A, Meharg AA (2010) Arsenic accumulation and phosphorus status in two rice (Oryza sativa L.) cultivars surveyed from fields in South China. Environ Pollut 158:1536–1541

Luu TTG, Sthiannopkao S, Kim K-W (2009) Arsenic and other trace elements contamination in groundwater and a risk assessment study for the residents in the Kandal Province of Cambodia. Environ Int 35:455–460

Mafuyai GM, Eneji IS, Sha'Ato R (2014) Concentration of heavy metals in respirable dust in Jos metropolitan area, Nigeria. Open J Air Pollut 3:10

Mahar MT, Khuhawar MY, Jahangir TM, Baloch MA (2015) Determination of arsenic contents in groundwater of district Rahim Yar Khan southern Punjab, Pakistan. Arab J Geosci 8:10983–10994

Malana MA, Khosa MA (2011) Groundwater pollution with special focus on arsenic, Dera Ghazi Khan-Pakistan. J Saudi Chem Soc 15:39–47

Mandal U, Singh P, Kundu AK, Chatterjee D, Nriagu J, Bhowmick S (2019) Arsenic retention in cooked rice: effects of rice type, cooking water, and indigenous cooking methods in West Bengal, India. Sci Total Environ 648:720–727. https://doi.org/10.1016/j.scitotenv.2018.08.172

Merola R, Hien T, Quyen D, Vengosh A (2015) Arsenic exposure to drinking water in the Mekong Delta. Sci Total Environ 511:544–552

Mondal S, Bandopadhyay P, Dutta P (2018) Arsenic contamination in cropping systems under varying irrigation sources in the deltaic plain of India. Arch Agron Soil Sci 64:1759–1767

Mosaferi M, Yunesian M, Dastgiri S, Mesdaghinia A, Esmailnasab N (2008) Prevalence of skin lesions and exposure to arsenic in drinking water in Iran. Sci Total Environ 390:69–76

Mosaferi M, Mahmoudi M, Pourakbar M, Sheykholeslami S (2015) Groundwater quality assessment in a volcanic region, Iran. In: Proceedings of the 14th International Conference on Environmental Science and Technology, Rhodes

Mueller B (2018) Preliminary trace element analysis of arsenic in Nepalese groundwater may pinpoint its origin. Environ Earth Sci 77:35. https://doi.org/10.1007/s12665-017-7154-z

Mueller B, Hug SJ (2018) Climatic variations and de-coupling between arsenic and iron in arsenic contaminated ground water in the lowlands of Nepal. Chemosphere 210:347–358. https://doi.org/10.1016/j.chemosphere.2018.07.024

Mukherjee A, Fryar AE, Eastridge EM, Nally RS, Chakraborty M, Scanlon BR (2018) Controls on high and low groundwater arsenic on the opposite banks of the lower reaches of River Ganges, Bengal basin, India. Sci Total Environ 645:1371–1387

Murphy T, Phan K, Yumvihoze E, Irvine K, Wilson K, Lean D, Ty B, Poulain A, Laird B, Chan LHM (2018) Groundwater irrigation and arsenic speciation in rice in Cambodia. J Health Pollut 8:180911

Murtaza G, Habib R, Shan A, Sardar K, Rasool F, Javeed T (2017) Municipal solid waste and its relation with groundwater contamination in Multan. Pakistan IJAR 3:434–441

Myint O, Hla NH (2017) Effectiveness of health education on knowledge of groundwater-dependent rural residents regarding arsenic-contaminated water at Kyonpyaw township. Myanmar Health Sci Res J 29:44–50

Nakaya S, Natsume H, Masuda H, Mitamura M, Biswas DK, Seddique AA (2011) Effect of groundwater flow on forming arsenic contaminated groundwater in Sonargaon, Bangladesh. J Hydrol 409:724–736

Natasha, Shahid M, Niazi NK, Khalid S, Murtaza B, Bibi I, Rashid MI (2018a) A critical review of selenium biogeochemical behavior in soil-plant system with an inference to human health. Environ Pollut 234:915–934. https://doi.org/10.1016/j.envpol.2017.12.019

Natasha, Shahid M, Dumat C, Khalid S, Rabbani F, Farooq ABU, Amjad M, Abbas G, Niazi NK (2018b) Foliar uptake of arsenic nanoparticles by spinach: an assessment of physiological and human health risk implications. Environ Sci Pollut Res Int. https://doi.org/10.1007/s11356-018-3867-0

National Research Council (1977) Arsenic: medical and biologic effects of environmental pollutants. The National Academies Press, Washington, DC

Naujokas M, Anderson B, Ahsan H, Vasken A, Graziano J, C T, WA S (2013) The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem. Environ Health Perspect 121:295–302

Neidhardt H, Norra S, Tang X, Guo H, Stüben D (2012) Impact of irrigation with high arsenic burdened groundwater on the soil-plant system: results from a case study in the Inner Mongolia, China. Environ Pollut 163:8–13

Nga DV, Trang PTK, Duyen VT, Mai TT, Lan VTM, Viet PH, Postma D, Jakobsen R (2018) Spatial variations of arsenic in groundwater from a transect in the Northwestern Hanoi. Vietnam J Earth Sci 40:70–77

Nguyen VA, Bang S, Viet PH, Kim K-W (2009) Contamination of groundwater and risk assessment for arsenic exposure in Ha Nam province, Vietnam. Environ Int 35:466–472

Niazi NK, Singh B, Shah P (2011) Arsenic speciation and phytoavailability in contaminated soils using a sequential extraction procedure and XANES spectroscopy. Environ Sci Technol 45:7135–7142

Niazi NK, Bibi I, Shahid M, Ok YS, Shaheen SM, Rinklebe J, Wang H, Murtaza B, Islam E, Farrakh Nawaz M, Lüttge A (2017) Arsenic removal by Japanese oak wood biochar in aqueous solutions and well water: investigating arsenic fate using integrated spectroscopic and microscopic techniques. Sci Total Environ. https://doi.org/10.1016/j.scitotenv.2017.10.063

Niazi NK, Bibi I, Shahid M, Ok YS, Burton ED, Wang H, Shaheen SM, Rinklebe J, Lüttge A (2018a) Arsenic removal by perilla leaf biochar in aqueous solutions and groundwater: an integrated spectroscopic and microscopic examination. Environ Pollut 232:31–41

Niazi NK, Bibi I, Shahid M, Ok YS, Shaheen SM, Rinklebe J, Wang H, Murtaza B, Islam E, Nawaz MF (2018b) Arsenic removal by Japanese oak wood biochar in aqueous solutions and well water: investigating arsenic fate using integrated spectroscopic and microscopic techniques. Sci Total Environ 621:1642–1651

O'Neill A, Phillips D, Kok S, Chea E, Seng B, Gupta BS (2013) Arsenic in groundwater and its influence on exposure risks through traditionally cooked rice in Prey Veng Province, Cambodia. J Hazard Mater 262:1072–1079

Oucher N, Kerbachi R, Ghezloun A, Merabet H (2015) Magnitude of air pollution by heavy metals associated with aerosols particles in algiers. Energy Procedia 74:51–58

Patel KS, Sahu BL, Dahariya NS, Bhatia A, Patel RK, Matini L, Sracek O, Bhattacharya P (2017) Groundwater arsenic and fluoride in Rajnandgaon District, Chhattisgarh, northeastern India. Appl Water Sci 7:1817–1826

Pham LH, Nguyen HT, Van Tran C, Nguyen HM, Nguyen TH, Tu MB (2017) Arsenic and other trace elements in groundwater and human urine in Ha Nam province, the Northern Vietnam:

contamination characteristics and risk assessment. Environ Geochem Health 39:517–529. https://doi.org/10.1007/s10653-016-9831-3

Phan KA, Nguyen TG (2018) Groundwater quality and human health risk assessment related to groundwater consumption in An Giang province. Viet Nam J Vietnam Environ 10:85–91

Phan K, Sthiannopkao S, Kim K-W, Wong MH, Sao V, Hashim JH, Yasin MSM, Aljunid SM (2010) Health risk assessment of inorganic arsenic intake of Cambodia residents through groundwater drinking pathway. Water Res 44:5777–5788

Phan K, Sthiannopkao S, Heng S, Phan S, Huoy L, Wong MH, Kim K-W (2013) Arsenic contamination in the food chain and its risk assessment of populations residing in the Mekong River basin of Cambodia. J Hazard Mater 262:1064–1071

Phan K, Phan S, Heng S, Huoy L, Kim K-W (2014) Assessing arsenic intake from groundwater and rice by residents in Prey Veng province, Cambodia. Environ Pollut 185:84–89

Podgorski JE, Eqani SAMAS, Khanam T, Ullah R, Shen H, Berg M (2017) Extensive arsenic contamination in high-pH unconfined aquifers in the Indus Valley. Sci Adv 3:e1700935. https://doi.org/10.1126/sciadv.1700935

Polya DA, Polizzotto ML, Fendorf S, Lado LR, Hegan A, Lawson M, Rowland HA, Giri AK, Mondal D, Sovann C (2010) Arsenic in groundwaters of Cambodia. In: Water resources and development in Southeast Asia. Southeast Asia Center, New York, pp 31–56

Postma D, Trang PTK, Sø HU, Lan VM, Jakobsen R (2017) Reactive transport modeling of arsenic mobilization in groundwater of the Red River floodplain, Vietnam. Proc Earth Planet Sci 17:85–87

Qurat-ul-Ain, Farooqi A, Sultana J, Masood N (2017) Arsenic and fluoride co-contamination in shallow aquifers from agricultural suburbs and an industrial area of Punjab, Pakistan: spatial trends, sources and human health implications. Toxicol Ind Health 33:655–672

Raessler M (2018) The arsenic contamination of drinking and groundwaters in Bangladesh: featuring biogeochemical aspects and implications on public health. Arch Environ Contam Toxicol 75:1–7. https://doi.org/10.1007/s00244-018-0511-4

Rafiq M, Shahid M, Abbas G, Shamshad S, Khalid S, Niazi NK, Dumat C (2017a) Comparative effect of calcium and EDTA on arsenic uptake and physiological attributes of *Pisum sativum*. Int J Phytoremediation 19:662–669

Rafiq M, Shahid M, Shamshad S, Khalid S, Niazi NK, Abbas G, Saeed MF, Ali M, Murtaza B (2017b) A comparative study to evaluate efficiency of EDTA and calcium in alleviating arsenic toxicity to germinating and young *Vicia faba* L. seedlings. J Soils Sediments. https://doi.org/10.1007/s11368-017-1693-5

Rafiq M, Shahid M, Shamshad S, Khalid S, Niazi NK, Abbas G, Saeed MF, Ali M, Murtaza B (2018) A comparative study to evaluate efficiency of EDTA and calcium in alleviating arsenic toxicity to germinating and young *Vicia faba* L. seedlings. J Soils Sediments 18:2271–2281

Rahman MA, Hashem MA (2018) Arsenic, iron and chloride in drinking water at primary school, Satkhira, Bangladesh. Phys Chem Earth, Parts A/B/C 109:49–58

Rahman MM, Naidu R, Bhattacharya P (2009) Arsenic contamination in groundwater in the Southeast Asia region. Environ Geochem Health 31:9–21

Rahman MM, Dong Z, Naidu R (2015) Concentrations of arsenic and other elements in groundwater of Bangladesh and West Bengal, India: potential cancer risk. Chemosphere 139:54–64

Rahman MA, Rahman A, Khan MZK, Renzaho AM (2018) Human health risks and socioeconomic perspectives of arsenic exposure in bangladesh: a scoping review. Ecotoxicol Environ Saf 150:335–343

Rashed M (2010) Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. J Hazard Mater 178:739–746

Rasheed H, Kay P, Slack R, Gong YY, Carter A (2017) Human exposure assessment of different arsenic species in household water sources in a high risk arsenic area. Sci Total Environ 584:631–641. https://doi.org/10.1016/j.scitotenv.2017.01.089

Rasool A, Xiao T, Farooqi A, Shafeeque M, Masood S, Ali S, Fahad S, Nasim W (2016) Arsenic and heavy metal contaminations in the tube well water of Punjab, Pakistan and risk assessment: a case study. Ecol Eng 95:90–100

Rattan RK, Datta SP, Chhonkar PK, Suribabu K, Singh AK (2005) Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. Agric Ecosyst Environ 109:310–322. https://doi.org/10.1016/j.agee.2005.02.025

Ravenscroft P, Brammer H, Richards K (2009) Arsenic pollution: a global synthesis. Wiley, New York

Rehman ZU, Khan S, Qin K, Brusseau ML, Shah MT, Din I (2016) Quantification of inorganic arsenic exposure and cancer risk via consumption of vegetables in southern selected districts of Pakistan. Sci Total Environ 550:321–329

Reza AS, Jean J-S, Yang H-J, Lee M-K, Woodall B, Liu C-C, Lee J-F, Luo S-D (2010a) Occurrence of arsenic in core sediments and groundwater in the Chapai-Nawabganj District, northwestern Bangladesh. Water Res 44:2021–2037

Reza AS, Jean J-S, Lee M-K, Liu C-C, Bundschuh J, Yang H-J, Lee J-F, Lee Y-C (2010b) Implications of organic matter on arsenic mobilization into groundwater: evidence from northwestern (Chapai-Nawabganj), central (Manikganj) and southeastern (Chandpur) Bangladesh. Water Res 44:5556–5574

Ribeiro AB, Mateus EP, Couto N (2016) Electrokinetics across disciplines and continents. Springer, Cham

Rizwan M, Ali S, Abbas T, Adrees M, Zia-ur-Rehman M, Ibrahim M, Abbas F, Qayyum MF, Nawaz R (2018) Residual effects of biochar on growth, photosynthesis and cadmium uptake in rice (Oryza sativa L.) under Cd stress with different water conditions. J Environ Manag 206:676–683

Rodríguez-Lado L, Sun G, Berg M, Zhang Q, Xue H, Zheng Q, Johnson CA (2013) Groundwater Arsenic Contamination Throughout China. Science 341:866–868. https://doi.org/10.1126/science.1237484

Safiuddin M, Shirazi S, Yusoff S (2011) Arsenic contamination of groundwater in Bangladesh: a review. Int J Phys Sci 6:6791–6800

Saha GC, Ali MA (2007) Dynamics of arsenic in agricultural soils irrigated with arsenic contaminated groundwater in Bangladesh. Sci Total Environ 379:180–189

Sarkar D, Datta R, Hannigan R (2011) Concepts and applications in environmental geochemistry. Elsevier, Amsterdam

Sauve S, Hendershot W, Allen HE (2000) Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. Environ Sci Technol 34:1125–1131

Seddique AA, Masuda H, Mitamura M, Shinoda K, Yamanaka T, Itai T, Maruoka T, Uesugi K, Ahmed KM, Biswas DK (2008) Arsenic release from biotite into a Holocene groundwater aquifer in Bangladesh. Appl Geochem 23:2236–2248

Seyfferth AL, McCurdy S, Schaefer MV, Fendorf S (2014) Arsenic concentrations in paddy soil and rice and health implications for major rice-growing regions of Cambodia. Environ Sci Technol 48:4699–4706

Shah BA (2017) Groundwater arsenic contamination from parts of the Ghaghara Basin, India: influence of fluvial geomorphology and Quaternary morphostratigraphy. Appl Water Sci 7:2587–2595

Shahab A, Qi S, Zaheer M (2018) Arsenic contamination, subsequent water toxicity, and associated public health risks in the lower Indus plain, Sindh province, Pakistan. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-018-2320-8

Shahid M, Dumat C, Pourrut B, Silvestre J, Laplanche C, Pinelli E (2014a) Influence of EDTA and citric acid on lead-induced oxidative stress to *Vicia faba* roots. J Soils Sediments 14:835–843

Shahid M, Austruy A, Echevarria G, Arshad M, Sanaullah M, Aslam M, Nadeem M, Nasim W, Dumat C (2014b) EDTA-enhanced phytoremediation of heavy metals: a review. Soil Sediment Contam Int J 23:389–416

Shahid M, Dumat C, Pourrut B, Abbas G, Shahid N, Pinelli E (2015) Role of metal speciation in lead-induced oxidative stress to *Vicia faba* roots. Russ J Plant Physiol 62:448–454

Shahid M, Dumat C, Khalid S, Schreck E, Xiong T, Niazi NK (2017a) Foliar heavy metal uptake, toxicity and detoxification in plants: a comparison of foliar and root metal uptake. J Hazard Mater 325:36–58. https://doi.org/10.1016/j.jhazmat.2016.11.063

Shahid M, Khalid M, Dumat C, Khalid S, Niazi NK, Imran M, Bibi I, Ahmad I, Hammad HM, Tabassum RA (2017b) Arsenic level and risk assessment of groundwater in Vehari, Punjab Province, Pakistan. Expo Health 10:229–239. https://doi.org/10.1007/s12403-017-0257-7

Shahid M, Niazi NK, Dumat C, Naidu R, Khalid S, Rahman MM, Bibi I (2018) A meta-analysis of the distribution, sources and health risks of arsenic-contaminated groundwater in Pakistan. Environ Pollut 242:307–319

Shakoor MB, Niazi NK, Bibi I, Rahman MM, Naidu R, Dong Z, Shahid M, Arshad M (2015) Unraveling health risk and speciation of arsenic from groundwater in rural areas of Punjab, Pakistan. Int J Environ Res Public Health 12:12371–12390

Shakoor MB, Niazi NK, Bibi I, Murtaza G, Kunhikrishnan A, Seshadri B, Shahid M, Ali S, Bolan NS, Ok YS (2016) Remediation of arsenic-contaminated water using agricultural wastes as biosorbents. Crit Rev Environ Sci Technol 46:467–499

Shakoor MB, Bibi I, Niazi NK, Shahid M, Nawaz MF, Farooqi A, Naidu R, Rahman MM, Murtaza G, Lüttge A (2018a) The evaluation of arsenic contamination potential, speciation and hydrogeochemical behaviour in aquifers of Punjab, Pakistan. Chemosphere 199:737–746

Shakoor MB, Niazi NK, Bibi I, Shahid M, Sharif F, Bashir S, Shaheen SM, Wang H, Tsang DC, Ok YS (2018b) Arsenic removal by natural and chemically modified water melon rind in aqueous solutions and groundwater. Sci Total Environ 645:1444–1455

Shakoor MB, Niazi NK, Bibi I, Shahid M, Saqib ZA, Nawaz MF, Shaheen SM, Wang H, Tsang DC, Bundschuh J (2019) Exploring the arsenic removal potential of various biosorbents from water. Environ Int 123:567–579

Shamsudduha M, Chandler R, Taylor R, Ahmed K (2009) Recent trends in groundwater levels in a highly seasonal hydrological system: the Ganges-Brahmaputra-Meghna Delta. Hydrol Earth Syst Sci 13:2373–2385

Sharifi Z, Akbar A (2017) Assessment of arsenic, nitrate and phosphorus pollutions in shallow groundwater of the rural area in Kurdistan Province (Iran). Curr World Environ 7:233–241

Sharma S, Kaur I, Nagpal AK (2018) Estimation of arsenic, manganese and iron in mustard seeds, maize grains, groundwater and associated human health risks in Ropar wetland, Punjab, India, and its adjoining areas. Environ Monit Assess 190:385

Shen M, Guo H, Jia Y, Cao Y, Zhang D (2018) Partitioning and reactivity of iron oxide minerals in aquifer sediments hosting high arsenic groundwater from the Hetao basin, PR China. Appl Geochem 89:190–201

Shrestha RR, Shrestha MP, Upadhyay NP, Pradhan R, Khadka R, Maskey A, Maharjan M, Tuladhar S, Dahal BM, Shrestha K (2003) Groundwater arsenic contamination, its health impact and mitigation program in Nepal. J Environ Sci Health A 38:185–200

Sikdar PK (2018) Groundwater development and management: issues and challenges in South Asia. Springer, Singapore

Simpson SL, Batley GE, Chariton AA, Stauber JL, King CK, Chapman JC, Hyne RV, Gale SA, Roach AC, Maher WA (2005) Handbook for sediment quality assessment. Centre for Environmental Contaminants Research Bangor, Bangor

Singh A (2004) Arsenic contamination in groundwater of North Eastern India. In: Proceedings of 11th national symposium on hydrology with focal theme on water quality, National Institute of Hydrology, Roorkee, pp 255–262

Singh S, Ghosh A, Kumar A, Kislay K, Kumar C, Tiwari R, Parwez R, Kumar N, Imam M (2014) Groundwater arsenic contamination and associated health risks in Bihar. India Int J Environ Res 8:49–60

Singhal VK, Anurag G, Kumar T (2018) Arsenic concentration in drinking and irrigation water of Ambagarh Chowki Block, Rajnandgaon (Chhattisgarh). Int J Chem Stud 6:733–739

Smith AH, Lingas EO, Rahman M (2000) Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull World Health Organ 78:1093–1103

Sø HU, Postma D, Vi ML, Pham TKT, Kazmierczak J, Dao VN, Pi K, Koch CB, Pham HV, Jakobsen R (2018) Arsenic in Holocene aquifers of the Red River floodplain, Vietnam: effects of sediment-water interactions, sediment burial age and groundwater residence time. Geochim Cosmochim Acta 225:192–209. https://doi.org/10.1016/j.gca.2018.01.010

Su Z, Huang W, Cai WH, Fan J, Huang H, Hu S (2018) Advances in analysis of inorganic arsenic in food. J Food Saf Qual 9:3580–3589

Sun G (2004) Arsenic contamination and arsenicosis in China. Toxicol Appl Pharmacol 198:268–271

Tabassum RA (2017) Arsenic assessment and removal from drinking water of tehsil Hasilpur using agricultural byproducts. Department of Environmental Sciences, Vol. MS. COMSATS Institute of Information Technology, Vehari, pp 1–81

Tabassum RA, Shahid M, Dumat C, Niazi NK, Khalid S, Shah NS, Imran M, Khalid S (2018) Health risk assessment of drinking arsenic-containing groundwater in Hasilpur, Pakistan: effect of sampling area, depth, and source. Environ Sci Pollut Res Int:1–12. https://doi.org/10.1007/s11356-018-1276-z

Tabassum RA, Shahid M, Niazi N, Dumat C, Zhang Y, Imran M, Bakhat H, Hussain I, Khalid S (2019) Arsenic removal from aqueous solutions and groundwater using agricultural biowastes-derived biosorbents and biochar: a column-scale investigation. Int J Phytoremediation 21:509–518

Taheri M, Mehrzad J, Mahmudy Gharaie MH, Afshari R, Dadsetan A, Hami S (2016) High soil and groundwater arsenic levels induce high body arsenic loads, health risk and potential anemia for inhabitants of northeastern Iran. Environ Geochem Health 38:469–482. https://doi.org/10.1007/s10653-015-9733-9

Tessier A, Campbell PG, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851

Thakur JK, Thakur RK, Ramanathan A, Kumar M, Singh SK (2011) Arsenic contamination of groundwater in Nepal—an overview. Water 3:1

Thinh NV, Osanai Y, Adachi T, Thai PK, Nakano N, Ozaki A, Kuwahara Y, Kato R, Makio M, Kurosawa K (2018) Chemical speciation and bioavailability concentration of arsenic and heavy metals in sediment and soil cores in estuarine ecosystem, Vietnam. Microchem J 139:268–277. https://doi.org/10.1016/j.microc.2018.03.005

Tran THM, Nguyen KG (2018) Metal and metalloid concentrations in soil, surface water, and vegetables and the potential ecological and human health risks in the northeastern area of Hanoi, Vietnam. Environ Monit Assess 190:624. https://doi.org/10.1007/s10661-018-6994-7

Uddin MG, Moniruzzaman M, Quader MA, Hasan MA (2018) Spatial variability in the distribution of trace metals in groundwater around the Rooppur nuclear power plant in Ishwardi, Bangladesh. Groundw Sustain Dev 7:220–231

Upadhyay MK, Shukla A, Yadav P, Srivastava S (2018) A review of arsenic in crops, vegetables, animals and food products. Food Chem 276:608–618

Uqaili A, Mughal A, Maheshwari B (2012) Arsenic contamination in ground water sources of district Matiari, Sindh. Int J Chem Environ Eng 3

USEPA (2014) United States Environmental Protection Agency. Toxic and priority pollutants under the clean water act

Van Geen A, Zheng Y, Cheng Z, He Y, Dhar R, Garnier J, Rose J, Seddique A, Hoque M, Ahmed K (2006) Impact of irrigating rice paddies with groundwater containing arsenic in Bangladesh. Sci Total Environ 367:769–777

Vijayanand C, Rajaguru P, Kalaiselvi K, Selvam KP, Palanivel M (2008) Assessment of heavy metal contents in the ambient air of the Coimbatore city, Tamilnadu, India. J Hazard Mater 160:548–553. https://doi.org/10.1016/j.jhazmat.2008.03.071

von Brömssen M, Jakariya M, Bhattacharya P, Ahmed KM, Hasan MA, Sracek O, Jonsson L, Lundell L, Jacks G (2007) Targeting low-arsenic aquifers in Matlab Upazila, southeastern Bangladesh. Sci Total Environ 379:121–132

Wang Y, Ma F, Zhang Q, Peng C, Wu B, Li F, Gu Q (2017) An evaluation of different soil washing solutions for remediating arsenic-contaminated soils. Chemosphere 173:368–372

Wang Z, Guo H, Xiu W, Wang J, Shen M (2018) High arsenic groundwater in the Guide basin, northwestern China: distribution and genesis mechanisms. Sci Total Environ 640:194–206

Wen B, Zhou A, Zhou J, Liu C, Huang Y, Li L (2018) Coupled S and Sr isotope evidences for elevated arsenic concentrations in groundwater from the world's largest antimony mine, Central China. J Hydrol 557:211–221

Whaley-Martin K, Mailloux B, van Geen A, Bostick B, Ahmed K, Choudhury I, Slater G (2017) Human and livestock waste as a reduced carbon source contributing to the release of arsenic to shallow Bangladesh groundwater. Sci Total Environ 595:63–71

WHO (2000a) World Health Organization Air quality guidelines for Europe. WHO Regional Office for Europe, Copenhagen

WHO (2000b) Air quality guidelines for Europe. WHO Regional Office for Europe, Copenhagen

Winkel L, Berg M, Amini M, Hug SJ, Johnson CA (2008) Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. Nat Geosci 1:ngeo254

Winkel LHE, Trang PTK, Lan VM, Stengel C, Amini M, Ha NT, Viet PH, Berg M (2011) Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century. Proc Natl Acad Sci 108:1246–1251. https://doi.org/10.1073/pnas.1011915108

Wongsasuluk P, Chotpantarat S, Siriwong W, Robson M (2014) Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand. Environ Geochem Health 36:169–182

World-Bank (2005) Towards a more effective operational response – arsenic contamination of groundwater in South and East Asian Countries (2): Technical Report (English). World Bank, Washington, DC. http://documents.worldbank.org/curated/en/421381468781203094/Technical-Report

WWF-Pakistan (2007) Irrigation water quality guidelines for Pakistan. National Surface Water Classification Criteria

Xie J-J, Hu X, Shen Y-W, Yuan C-G, Zhang K-G, Zhao X (2017) Bioavailability and speciation of arsenic in urban street dusts from Baoding city, China. Chem Spec Bioavailab 29:135–142

Xie Z, Wang J, Wei X, Li F, Chen M, Wang J, Gao B (2018) Interactions between arsenic adsorption/desorption and indigenous bacterial activity in shallow high arsenic aquifer sediments from the Jianghan Plain, Central China. Sci Total Environ 644:382–388

Yadav IC, Devi NL, Mohan D, Shihua Q, Singh S (2014) Assessment of groundwater quality with special reference to arsenic in Nawalparasi district, Nepal using multivariate statistical techniques. Environ Earth Sci 72:259–273. https://doi.org/10.1007/s12665-013-2952-4

Yadav IC, Devi NL, Singh S (2015a) Spatial and temporal variation in arsenic in the groundwater of upstream of Ganges River Basin, Nepal. Environ Earth Sci 73:1265–1279. https://doi.org/10.1007/s12665-014-3480-6

Yadav IC, Devi NL, Singh S (2015b) Reductive dissolution of iron-oxyhydroxides directs groundwater arsenic mobilization in the upstream of Ganges River basin, Nepal. J Geochem Explor 148:150–160

Yañez L, Alfaro J, Mitre GB (2018a) Absorption of arsenic from soil and water by two chard (Beta vulgaris L.) varieties: a potential risk to human health. J Environ Manag 218:23–30

Yañez LM, Alfaro JA, Bovi Mitre G (2018b) Absorption of arsenic from soil and water by two chard (Beta vulgaris L.) varieties: a potential risk to human health. J Environ Manag 218:23–30. https://doi.org/10.1016/j.jenvman.2018.04.048

Yang F, Xie S, Wei C, Liu J, Zhang H, Chen T, Zhang J (2018a) Arsenic characteristics in the terrestrial environment in the vicinity of the Shimen realgar mine, China. Sci Total Environ 626:77–86

Yang Y-P, Zhang H-M, Yuan H-Y, Duan G-L, Jin D-C, Zhao F-J, Zhu Y-G (2018b) Microbe mediated arsenic release from iron minerals and arsenic methylation in rhizosphere controls arsenic fate in soil-rice system after straw incorporation. Environ Pollut 236:598–608

Yang Y, Zhang A, Chen Y, Liu J, Cao H (2018c) Impacts of silicon addition on arsenic fractionation in soils and arsenic speciation in Panax notoginseng planted in soils contaminated with high levels of arsenic. Ecotoxicol Environ Saf 162:400–407

Yazdi M, Taheri M, Navi P (2015) Environmental geochemistry and sources of natural arsenic in the Kharaqan hot springs, Qazvin, Iran. Environ Earth Sci 73:5395–5404. https://doi.org/10.1007/s12665-014-3794-4

Ying S, Damashek J, Fendorf S, Francis C (2015) Indigenous arsenic (V)-reducing microbial communities in redox-fluctuating near-surface sediments of the M ekong D elta. Geobiology 13:581–587

Yu L, Wang Y-b, Xin G, SU Y-b, Gang W (2006) Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China. J Environ Sci 18:1124–1134

Zeng Y, Zhou Y, Zhou J, Jia R, Wu J (2018) Distribution and enrichment factors of high-arsenic groundwater in Inland Arid area of PR China: a case study of the Shihezi area, Xinjiang. Expo Health 10:1–13

Zhang J, Ma T, Feng L, Yan Y, Abass OK, Wang Z, Cai H (2017) Arsenic behavior in different biogeochemical zonations approximately along the groundwater flow path in Datong Basin, northern China. Sci Total Environ 584:458–468

Zhang Q, Wang S, Nan Z, Li Y, Zang F (2018) Accumulation, fractionation, and risk assessment of mercury and arsenic in the soil-wheat system from the wastewater-irrigated soil in Baiyin, northwest China. Environ Sci Pollut Res 25:14856–14867

Zheng B, Ding Z, Huang R, Zhu J, Yu X, Wang A, Zhou D, Mao D, Su H (1999) Issues of health and disease relating to coal use in southwestern China. Int J Coal Geol 40:119–132

Zhou Y, Zeng Y, Zhou J, Guo H, Li Q, Jia R, Chen Y, Zhao J (2017) Distribution of groundwater arsenic in Xinjiang, P.R. China. Appl Geochem 77:116–125. https://doi.org/10.1016/j.apgeochem.2016.09.005

Zhou T, Wu L, Luo Y, Christie P (2018a) Effects of organic matter fraction and compositional changes on distribution of cadmium and zinc in long-term polluted paddy soils. Environ Pollut 232:514–522

Zhou Y, Niu L, Liu K, Yin S, Liu W (2018b) Arsenic in agricultural soils across China: distribution pattern, accumulation trend, influencing factors, and risk assessment. Sci Total Environ 616:156–163

Arsenic Contamination Status in North America

Milica M. Janković

Abstract Arsenic (As) is a toxic and ubiquitously present element. It is present in some places of the world in excessively high concentrations in water and soil that threaten public health. North America constitutes one of the hotspots of As contamination. In Canada and the USA, a number of reports show the contamination of As in a number of food items including rice, rice-based products, fruits, beverages, animal food items, etc. Further, As contamination of water sources is also known to occur in different states of both Canada and the USA. Thus, the problem of As contamination is widespread and needs attention. This chapter provides an overview of As contamination of water and food sources of North America.

Keywords Arsenic · Canada · Food · Rice · USA

1 Introduction

1.1 *Chemical and Physical Properties of Arsenic*

Arsenic (As) appears in Group 5 (V) of the periodic table, below nitrogen and phosphorus (World Health Organization 2001). Arsenic is classified chemically as a metalloid, having both properties of a metal and a nonmetal; however, it is frequently referred to as a metal (Chou and Harper 2007). Elemental arsenic, which is also referred to as metallic arsenic, [As(0)], normally occurs as the α-crystalline metallic form, which is a steel gray and brittle solid (World Health Organization 2001). However, arsenic is usually found in the environment combined with other elements such as oxygen, chlorine, and sulfur. Arsenic combined with these elements is called inorganic arsenic. Arsenic combined with carbon and hydrogen is referred to as organic arsenic (Chou and Harper 2007).

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Average concentration of arsenic, widely distributed in the earth's crust, is 2 mg/kg. It occurs in trace quantities in all rock, soil, water, and air. Arsenic can exist in four valence states: −3, 0, +3, and +5. Under reducing conditions, arsenite [As(III)] is the dominant form; arsenate [As(V)] is generally the stable form in oxygenated environments (Fawell and Mascarenhas 2003). Elemental arsenic is not soluble in water. Arsenic salts exhibit a wide range of solubility depending on pH and the ionic environment (World Health Organization 2001).

Arsenic occurs naturally in soil and minerals, and it therefore may enter the air, water, and land from wind-blown dust and may get into water from runoff and leaching. Volcanic eruptions are another source of arsenic. Arsenic is associated with ores containing metals, such as copper and lead. Arsenic may enter the environment during the mining and smelting of these ores. Small amounts of arsenic may also be released into the atmosphere from coal-fired power plants and incinerators because coal and waste products often contain some arsenic (Fawell and Mascarenhas 2003).

Observed from two different perspectives (biological and toxicological), arsenic compounds are divided into three groups:

- Inorganic arsenic compounds
- Organic arsenic compounds
- Arsine gas (Fawell and Mascarenhas 2003)

Inorganic arsenic compounds do not have an arsenic-carbon bond, while organic arsenic compounds have an arsenic-carbon bond. Most inorganic and organic arsenic compounds are white or colorless powders that do not evaporate. They have no smell, and most have no special taste. Thus, it is not usually possible to tell if arsenic is present in food, water, or air (Chou and Harper 2007). Of the inorganic arsenic compounds, arsenic trioxide, sodium arsenite, and arsenic trichloride are the most common trivalent compounds, and arsenic pentoxide, arsenic acid, and arsenates (e.g., lead arsenate and calcium arsenate) are the most common pentavalent arsenic compounds. Common organic arsenic compounds include arsanilic acid, methylarsonic acid, dimethyl-arsinic acid (cacodylic acid), and arsenobetaine (Fawell and Mascarenhas 2003). Inorganic arsenic is generally considered more toxic than organic (US Department of Health and Human Services Food and Drug Administration Center for Food Safety and Applied Nutrition 2016).

1.2 Uses of the Arsenic Compounds

Arsenic is mainly obtained as a by-product of the smelting of copper, lead, cobalt, and gold ores. Arsenic trioxide is the primary form in which arsenic is marketed and consumed (Chou and Harper 2007). Arsenic and arsenic compounds have been produced and used commercially for centuries. Current and historical uses of arsenic include pharmaceuticals, wood preservatives, agricultural chemicals, and applications in the metallurgical, glass-making, and semiconductor industries (Fawell and Mascarenhas 2003).

Arsenic was used in some medicinal applications until the 1970s. Inorganic arsenic was used in the treatment of leukemia, psoriasis, and chronic bronchial asthma, and organic arsenic was used in antibiotics for the treatment of spirochetal and protozoal diseases (Fawell and Mascarenhas 2003). About 90% of all arsenic produced is used as a preservative for wood to make it resistant to rotting and decay. In 2003, US manufacturers of wood preservatives began a voluntary transition to preservatives that do not contain arsenic (Chou and Harper 2007). In the past, inorganic arsenic compounds were predominantly used as pesticides. Inorganic arsenic compounds can no longer be used in agriculture. On the other hand, organic compounds (cacodylic acid, disodium methylarsenate, and monosodium methylarsenate) are still used as pesticides in agriculture or as additives in animal feed (Chou and Harper 2007).

1.3 Arsenic in Water

Arsenic is an element that belongs to the group of heavy metals with pronounced toxicity and carcinogenicity, known to cause bladder, kidney, lung, and skin cancer, classified as group 1 carcinogens by the International Agency for Research on Cancer (IARC Working Group WHO (2004)). Together with Hg and Pb, Cd belongs to the group of the most significant, i.e., classical inorganic, contaminants considered to be the oldest toxins known to mankind.

As one of the most common poisons found in the environment, arsenic represents a major global health risk through its widespread presence in groundwater (Canadian Food Inspection Agency 2013b).

2 Canada

Food is generally considered the major source of arsenic exposure except in situations where a population is living near a point source (natural geological source or site of contamination). However, it is difficult to compare the intake of arsenic from food with that from drinking water, as the form (organic vs inorganic), valence, and biological availability of arsenic in these two sources vary.

Arsenic levels in food are usually low; however, the levels are typically higher in aquatic organisms (such as seaweed, fish, and seafood). Under the 2011–2013 Arsenic Speciation in Selected Foods Targeted Survey, 2015 samples were collected at the Canadian retail level and analyzed for arsenic. Seaweed and rice/rice products had the highest occurrence of arsenic, with 100% of samples containing a detectable level of one or more arsenic species. Grain products, fruit products, and beverages had lower occurrences with 96%, 72%, and 68% of products, respectively, containing a detectable level of one or more arsenic species. Overall 87% of samples tested contained a detectable level of one or more arsenic species. The concentrations of total arsenic (calculated as the sum of the arsenic species investigated) quantified in

Table 1 Average total arsenic and inorganic arsenic levels detected in food samples

Commodity type	Number of samples	Samples with detectable arsenic	Samples with no detectable arsenic	Average total arsenic[a](ppb)	Average inorganic arsenic[a] (ppb)
Beverages	575	392	183	3.97	3.84
Fruit products	232	167	65	10.68	6.53
Seaweed products	145	145	0	271.53	37.19
Grain products	454	434	20	69.44	48.37
Rice and rice products	609	609	0	116.17	94.19

[a] Average of the positive results only

individual samples ranged from 0.08 parts per billion (ppb) in infant cereal to 1815.3 ppb in dried seaweed. Overall, beverages had the lowest maximum and average concentrations of total arsenic detected, while seaweed products had the highest maximum and average total arsenic concentrations. It should be noted that the average concentrations were calculated using only those samples for which one or more species of arsenic were detected (i.e., average of the positive results only). When considering only the inorganic arsenic species, rice and rice products had the highest average inorganic arsenic concentrations, while beverages had the lowest average concentrations of inorganic arsenic (Canadian Food Inspection Agency 2013a).

The data in Table 1 illustrates that the majority of the arsenic species measured in this study in seaweed are organic in nature. The remaining product types contained between 79% and 93% inorganic species (Canadian Food Inspection Agency 2013a).

Beverages A total of 575 beverages were sampled and analyzed for arsenic content in the targeted survey. Beverage types included bottled water, flavored beverages, juice/nectars (including apple, orange, pineapple, blends of fruits, grape, cranberry, blackcurrant, blueberry, carrot, cherry, coconut, grapefruit, guava, lemon/lime juice, lemonade, mango, peach, pear, pomegranate, prune, quince, and raspberry), and apple cider. Thirty-two percent of beverage samples analyzed did not contain a detectable level of any arsenic species. Of the remaining 392 samples with a detectable level of one or more arsenic species, non-mineral/spring waters had the lowest levels of both total arsenic and inorganic arsenic. Cranberry juice (which may have included cranberry cocktails) had the highest maximum concentrations of both total arsenic and inorganic arsenic species observed, whereas grape juices had the highest average concentrations of both total and inorganic arsenic. A variety of beverages have been examined in a previous FSAP targeted survey. In 2009–2010, 34 samples of pear juice and nectar were analyzed for the same six arsenic species examined in the current survey. Twenty-three samples (68%) had a detectable level of one or more arsenic species. The concentrations of inorganic arsenic species ranged from 4.15 to 9.01 ppb. It should be noted that the 2010–2011 survey specifically targeted pear-based beverage, 16 products. Of the beverage samples analyzed, 168 of the beverage samples (73%) contained a detectable level of one or more of the arsenic species examined. Concentrations of inorganic arsenic in beverages from the various surveys undertaken by the CFIA were consistent throughout the years (Canadian Food Inspection Agency 2013a).

Fruit Products Two hundred and thirty-two fruit products were sampled for the current survey. Samples were categorized as fruit purées (such as apple sauce, cranberry sauce, fruit sauce, etc.), dried fruit (e.g., apples, apricots, cranberries, dates, mangoes, pineapple, plantain, prune, raisins, and strawberries), fruit snacks (such as fruit leathers, fruit chews, and other fruit-based treats), or canned fruit products (which consisted of fruit in a cup or a can packaged with water or syrup). Of the 232 fruit products analyzed, 65 (28%) did not contain a detectable level of any of the arsenic species analyzed. Of the remaining 167 samples with one or more arsenic species present, canned fruit products contained the lowest levels of both total and inorganic arsenic, while fruit snacks contained the highest levels of both total and inorganic arsenic (Canadian Food Inspection Agency 2013a).

In the 2009–2010 arsenic speciation targeted survey, pear-based baby foods (purées) and pear-based fruit snacks were examined. Similar to the results of the current survey, fruit snacks contained higher concentrations of inorganic arsenic than purées.

The average levels of inorganic arsenic in fruit purées were 1.73 ppb in the 2009–2010 survey. These samples were solely pear-based baby foods. The average inorganic arsenic concentrations were 3.21 ppb and 3.337 ppb in the 2010–2011 and 2011–2013 surveys, respectively. Samples from these survey years encompassed a larger number and wider range of fruit-based purées, which may account for the differences in average concentration. Canned pear products were sampled in the 2010–2011 survey year and showed that there was a low prevalence of inorganic arsenic; only 1 of 19 samples analyzed contained a detectable level of inorganic arsenic (1.49 ppb). In the current survey year, six canned/fruit in a cup-type products were analyzed and exhibited a higher prevalence of inorganic arsenic but showed a similarly low average level of inorganic arsenic detected (1.04 ppb) (Canadian Food Inspection Agency 2013a).

Grain Products Four hundred and fifty-four grain products were analyzed in the current targeted survey. Grain product samples consisted of breakfast cereals targeted at adults, children, and infants, as well as wheat bran. Only 20 samples (4%) did not have detectable levels of one or more arsenic species. Wheat bran had the lowest levels of total and inorganic arsenic detected. Average levels of total arsenic and inorganic arsenic were very similar between product form and showed similar trends in arsenic concentrations in relation to primary grain ingredient. Rice-based and multigrain cereals generally exhibited the highest concentrations of arsenic. Health Canada determined that the inorganic arsenic concentrations in grain products are not expected to pose a safety concern (Canadian Food Inspection Agency 2013a).

Rice and Rice Products Six hundred and nine samples of rice and rice products were collected for the current targeted survey. Sample types included rice-based beverages, rice flour, rice grains, rice bran, and processed rice products (i.e., noodles/pasta, paper/wrappers, crackers/cakes/ crisps, vinegar, pudding, and crumbs). All of the samples analyzed contained detectable levels of at least one arsenic species. Rice beverage samples contained the lowest concentrations of both total and inorganic arsenic, while rice bran contained the highest levels of both total and inorganic arsenic. There appears to be little difference between the ranges of total and inorganic arsenic concentrations for each product type, indicating that the majority of the arsenic in rice and rice products is inorganic in nature (Canadian Food Inspection Agency 2013a).

Rice bran has been shown to accumulate higher levels of arsenic than the other portions of the rice grain, and as brown rice is unmilled (i.e., still contains the germ and bran), it would follow that brown rice would have higher levels of arsenic as well. The average total and inorganic arsenic concentrations in samples labeled as brown rice were approximately 1.7 times higher than concentrations in rice grains of other varieties; however, inorganic arsenic concentrations detected in rice or rice products would not be expected to pose a safety concern (Canadian Food Inspection Agency 2013a).

The average inorganic arsenic concentration for rice and rice products is also presented in Table 2 (Canadian Food Inspection Agency 2013a).

Table 2 Summary of minimum, maximum, and average inorganic arsenic conc. in rice and rice products

Commodity	Survey year	Number of samples	Minimum (ppb)	Maximum (ppb)	Average inorganic arsenic conc. (ppb)
Rice grains	2009–2010	90	18.83	209.67	108.88
	2010–2011	72	2.33	212.1	79.85
	2011–2013	324	2.59	342.8	83.59
Rice flour	2010–2011	25	23.1	182.9	75.00
	2011–2013	84	9.69	166.46	80.74
Processed rice products	2010–2011	90	1.47	199.3	38.75
	2011–2013	154	0.73	220.1	62.25
Rice beverages	2009–2010	40	1.16	22.16	9.65
	2010–2011	72	1.22	19.25	6.22
	2011–2013	19	6.14	23.7	11.98

Seaweed Products One hundred and forty-five seaweed products were analyzed in the current targeted survey. Seaweed samples consisted of dried nori sheets (commonly used for making sushi), dulse, laver, wakame, kombu, and other varieties of dried seaweed. All of the samples analyzed contained a detectable level of one or more arsenic species. Seaweed products contained the highest average and maximum levels of total arsenic observed in this survey (296 ppb and 1815 ppb, respectively) (Canadian Food Inspection Agency 2013a).

In 2007, the Canadian government launched a 5-year initiative in response to a growing number of product recalls and concerns about food safety. This initiative, called the Food and Consumer Safety Action Plan (FCSAP), aims to modernize and strengthen Canada's safety system for food, health, and consumer products. The Canadian Food Inspection Agency's (CFIA's) Food Safety Action Plan (FCAP) is one element of the government's broader FCSAP initiative. The CFIA regularly monitors a variety of metals in federally regulated commodities under the National Chemical Residue Monitoring Program (NCRMP) and the Children's Food Project (CFP) (Canadian Food Inspection Agency 2013b).

There are a variety of food products on the Canadian market which are intended for use as a complete substitute for one or more daily meals or to act as a supplemental source of nutrients for the purpose of increased nutrition. A total of 291 samples were collected from retail stores in 11 Canadian cities between April 2012 and March 2013. The products collected included 87 domestic products, 192 imported products, and 12 products of "unspecified origin," meaning the country of origin could not be confirmed based on the available information on the packaging. The samples collected included 96 dairy-based infant formulas, 48 soy-based infant formulas, 46 meal replacements, and 101 nutritional supplements. Table 3 summarizes survey data of FSAP and CFP data on arsenic levels in infant formula, meal replacements, and nutritional supplements (Canadian Food Inspection Agency 2013b).

In several Canadian provinces were monitored levels of arsenic in water supplies. What is important is that the increased concentration in water is present in areas with natural sources (in wells).

2.1 Prince Edward Island

Levels of inorganic arsenic are generally higher in groundwater sources than in surface water. Where arsenic is found in surface water, some organic forms may be present (NRC 1999). Monitoring data for water supplies have been submitted by several Canadian provinces. Arsenic levels ranged from 0.1 to 26.0 μg/L in groundwater supplies in Prince Edward Island between 1986 and 2002; levels in greater than 99% of samples were below 10 μg/L, the average being approximately 1.5 μg/L (Government of Canada 2003).

Table 3 The level of arsenic in infant formula, meal replacements and nutritional supplements

Author	Year	Number of samples	Number (%) of samples with detectable levels	Minimum (ppm)	Maximum (ppm)	Average[a] (ppm)
Infant formula – dairy						
FSAP	2012–2013	96	10 (10)	0.004	0.023	0.013
	2011–2012	116	27 (23)	0.005	0.063	0.021
CFP	2008–2009	26	26 (100)	0.015	0.085	0.060
Infant formula – soy						
FSAP	2012–2013	48	15 (31)	0.008	0.022	0.014
	2011–2012	41	10 (24)	0.031	0.068	0.041
CFP	2008–2009	9	9 (100)	0.016	0.096	0.065
Meal replacement						
FSAP	2012–2013	46	11 (24)	0.006	0.044	0.021
	2011–2012	66	43 (65)	0.006	0.085	0.025
Nutritional supplements						
FSAP	2012–2013	101	58 (57)	0.006	0.141	0.040
	2011–2012	82	36 (44)	0.007	0.130	0.047

[a] Average of positive results only

2.2 *Quebec*

In Quebec, arsenic levels ranged from 1.0 to 25.0 μg/L in municipal-treated surface water in 523 communities for 1990–2002; levels in more than 99% of samples were less than 10 μg/L, the annual average being 1.6 μg/L. Levels ranged from 1.0 to 60 μg/L in municipal-treated groundwater in 562 communities for the same period; approximately 98% of samples contained levels less than 10 μg/L, the annual average being 2.0 μg/L (Government of Canada 2003).

2.3 *Ontario*

In Ontario, arsenic levels ranged from 0.1 to 18 μg/L in treated groundwater and surface water in 726 communities for 1997–2002. Levels in more than 99% of samples were less than 10 μg/L, the annual average being less than or equal to

0.7 µg/L. Ontario monitoring data submitted by private laboratories indicated that arsenic levels in treated and raw drinking water ranged from less than 2.5–68 µg/L for the period 1999–2002, the average value being less than 2.5 µg/L. The higher values came predominantly from wells (Government of Canada 2003).

2.4 Alberta

In 573 communities arsenic levels ranged from 0.1 to 1000 µg/L in treated groundwater and surface water for 1980–2002 (Government of Canada 2003).

In this area approximately 99% of samples contained less than 10 µg/L of arsenic (Government of Canada 2003).

2.5 Saskatchewan

Arsenic levels ranged from 0.5 to 105.0 µg/L in municipal-treated water supplies in 539 communities between 1976 and 2002; concentrations in 97% of samples were less than or equal to 10 µg/L (Government of Canada 2003).

In Saskatchewan the number of private wells is 66,000, and they are used by 7.7% of the population. Evidence of As exceedance over the stated guideline (10 µg/L) was found in 16% of 1108 wells tested (Chappells et al. 2014).

2.6 Nova Scotia

Arsenic is a naturally occurring toxic metalloid that is widespread throughout Nova Scotia (Dummer et al. 2014). The highest concentrations are most frequently located in southern mainland Nova Scotia, associated with the geologic area known as the Meguma Terrane (Goodwin et al. 2010), consisting of two arsenic-rich geological units, the Halifax Group and the Goldenville Group. In 2008 a scientist found that soil at 56% of the sampling sites evaluated had arsenic levels exceeding the Canadian soil quality guideline of 12 µg g^{-1} (Goodwin et al. 2009).

Between 1991 and 1997, 9% of samples tested for arsenic exceeded 25 µg/L (Nova Scotia Department of the Environment 1998). In 1984, reported levels of arsenic exceeded 50 µg/L in 33–93% of wells in each of seven communities in Nova Scotia; concentrations were greater than 500 µg/L in 10% of the wells sampled (n = 94) (Mèranger et al. 1984). Newfoundland, in public water supplies (54 wells) in 2002, has maximum arsenic levels ranged from 6 to 288 µg/L. Public schools (n = 16) with their own water supplies had levels ranging from 1 to 368 µg/L; approximately 19% of school wells had maximum levels above 10 µg/L (Government of Canada 2003).

The estimated number of private wells was 150,000 used by 40% of the population of this region, and 9% of samples tested in Environmental Chemistry Laboratory (Halifax) between 1991 and 1997 had concentrations of As above 25 μg/L (Chappells et al. 2014).

2.7 British Columbia

Maximum arsenic concentration of 580 μg/L was reported in groundwater samples taken on Bowen Island (Boyle et al. 1998).

The estimated number of private wells in British Columbia is 63,000 and the population that uses them on 8%. In 2007 BC Ministry of Environment tested 2100 wells, and 4.2% of samples have concentrations of As above 10 μg/L. In Surrey-Langley area in 2008, 43% of the 98 wells tested have 10 μg/L. In Sunshine Coast 23% of 258 wells tested have above 25 μg/L of As (Chappells et al. 2014).

2.8 New Brunswick

The number of private wells is 100,000 (22% of population uses). Groundwater samples were tested, and 5.9% of 10,563 samples have concentrations of As above 10 μg/L (Chappells et al. 2014).

3 United States of America

As a major source of inorganic arsenic, according to numerous studies, rice and fish have been shown. In support of this, a study confirms that the level of arsenic in the blood of Asian people compared to other national groups in America is significantly higher because their diet is based on rice and fish. In this study, daily food consumption was estimated and dietary intake of arsenic by combining 24-h dietary intake recall data from the 2011 to 2012 National Health and Nutrition Examination Survey (NHANES) with data from the USDA Food Composition Intake Database and Food and Drug Administration (FDA) Total Dietary Study (Awata et al. 2012).

Estimated food consumption and arsenic intake levels were compared between Asians and other racial/ethnic groups (white, black, Mexican American, and other Hispanics) and with three Asian subgroups (Chinese, Indian Asian, and other Asians). The results showed significant associations ($p < 0.05$) were found between biomarker levels and estimated dietary metal intake for total and inorganic arsenic and mercury among Asians. Asians had the highest daily fish and rice consumption across the racial/ethnic groups. Fish was the major contributor to dietary mercury and total arsenic intake, whereas rice was the major contributor to inorganic arsenic dietary intake. Fish consumption across the Asian subgroups varied, with Asian Indians having lower fish consumption than the other Asian subgroups. Rice consumption was similar across the Asian subgroups. All this confirmed that the estimated dietary intake of arsenic (total and inorganic) is significantly associated with their corresponding biomarkers in US Asians, using nationally representative data (Awata et al. 2012).

Because it is in the environment, inorganic arsenic is found in some foods. Rice and rice-based products have higher levels of inorganic arsenic than other foods tested by the FDA and, given their widespread consumption, are a major food source of inorganic arsenic. Rice tends to have higher arsenic consumption than other cereals crops (such as wheat and barley), because of its ability to take up arsenic from soil and water and because it is typically grown under flooded conditions, which increases the potential for arsenic uptake (US Department of Health and Human Services Food and Drug Administration Center for Food Safety and Applied Nutrition 2016). Since rice is the main source of inorganic arsenic by food, numerous tests have been carried out on its content. The content of inorganic arsenic in rice depends on its shape and the type shown by the results of the study that was conducted in 2013, in different countries of the USA (Food and Drug Administration 2013).

The average content of the inorganic arsenic in different types of rice in the USA is shown in Table 4 (Food and Drug Administration 2013).

The world's major concern is the level of arsenic in baby food, as many are based on rice. As already confirmed by many studies, the main source of arsenic through food is rice, and the first solid food for babies is often a variety of porridges that are precisely based on rice.

In North America, as in the rest of the world, the amount of inorganic arsenic in different baby foods based on rice, but also those that do not contain rice, is tested; the results downloaded from the FDA are shown in Table 5 (Food and Drug Administration, 2013).

The US Food and Drug Administration is taking steps to reduce inorganic arsenic in infant rice cereal, a leading source of arsenic exposure in infants. Relative to body weight, rice intake for infants, primarily through infant rice cereal, is about three times greater than for adults. Moreover, national intake data show that people consume the most rice (relative to their weight) at approximately 8 months of age (US Department of Health and Human Services Food and Drug Administration Center for Food Safety and Applied Nutrition 2016).

Through a draft guidance to industry, the FDA is proposing a limit or "action level" of 100 parts per billion (ppb) for inorganic arsenic in infant rice cereal. This is parallel to the level set by the European Commission (EC) for rice intended for the production of food for infants and young children. (The EC standard concerns the rice itself; the FDA's proposed guidance sets a draft level for inorganic arsenic in infant rice cereal.) FDA testing found that the majority of infant rice cereal currently on the market either meets or is close to the proposed action level (US Department of Health and Human Services Food and Drug Administration Center for Food Safety and Applied Nutrition 2016).

Table 4 The average content of the inorganic arsenic in different types of rice in USA

Product category	Product subcategory	Average inorganic arsenic mcg/serving	Range of inorganic arsenic mcg/serving[a]	Number of samples
Rice	Basmati	3.5	0.9–9.0	53
Rice	Brown	7.2	1.5–11	99
Rice	Instant	2.6	1.4–6.0	14
Rice	Jasmine	3.9	1.5–6.8	13
Rice	Other (incl wild rice[b] Fawell and Mascarenhas (2003), carnaroli, mixed types)	5.6	4.0–7.2	6
Rice	Parboiled	5.1	3.2–8.6	39
Rice	White, long grain	4.6	1.0–8.8	149
Rice	White, medium grain	3.6	1.8–7.8	91
Rice	White, short grain	3.5	2.3–4.6	23

[a] Serving size based on Reference Amounts Customarily Consumed (RACC) per 21CRF 101.12 for each product category

[b] "Wild rice" is not actual rice. Wild rice comes from an aquatic annual grass (*Zizania aquatica*) bearing edible grain

Table 5 The average content of the inorganic arsenic in different types of baby foods

Product category	Average inorganic arsenic[a] (μg/kg)	Range of inorganic arsenic[a] (μg/kg)	Number of samples
Cereal – infant/toddler (rice)	103	20.8–176	76
Cereal – infant/toddler (multigrain)	30.0	22.2–49.6	6
Cereal – infant/toddler (non-rice)	13.9	3.5–68.3	30
Apples	3.0	3.0	10
Cereal – oat ring	17.2	4.4–59.6	30
Grapes	4.5	3.0–15.2	10
Juice – apricot	1.1	0.05–3.0	29
Juice – grape	12.4	0.6–49.6	61
Juice – peach	2.6	0.3–15.2	29
Juice – pear	4.3	1.0–9.7	30
Juice boxes and pouches	5.5	0.9–32.1	40
Peanut butter	3.4	3.0–5.9	29
Quinoa	7.9	0.3–49.0	30
Raisins	8.1	3.0–22.6	23
Stage 2 toddler foods	8.1	0.3–21.3	35
Teething biscuits	44.4	17.0–71.5	27
Toddler puffs	53.9	16.4–145	31

[a] As (III) and As (V) are the most common oxidation states for inorganic arsenic. Most, if not all, of the inorganic arsenic will be present as either As (III) or As (V). Therefore, adding the values together will represent a reliable estimate of the inorganic arsenic present

One of the most comprehensive studies of the quantity of toxic metals, among which is arsenic, is a study that has been conducted by the Food and Drug Administration, which included a large number of food products that could be found on the US market in the period from 2006 to 2013 and 2014 and was called Total Diet Study – Market Baskets 2006–2011 through 2013–2014. The results of the study are shown in Table 6 (US Food and Drug Administration 2017).

Worldwide North America over 30 million people have been reported at risk of exposure to levels that pose a cancer risk.

In the 1960s the Public Health Service has first time advised a safe limit of arsenic presence in drinking water that does not exceed 10 μg/l (Smith et al. 2002). This standard was adopted by the US Environmental Protection Agency (USEPA) in 2002. Canadian standard is the same as the standard in the USA.

Arsenic is predominantly present in ground as inorganic arsenic, and its levels in groundwater are higher than in surface water.

Due to underlying geology, arsenic is known to be a contaminant of water supplies in many parts of North America but is a particular concern in areas where a high proportion of drinking water is sourced from private residential wells (around 45 million people, 15% of the population in the USA) (Chappells et al. 2014). The use of drinking water from private wells is a problem when it comes to arsenic exposure, because the water from the public water supplies is under the constant control of the government and not the private wells.

Some western US states with volcanic rocks and sulfidic mineral deposits have arsenic levels in groundwater exceeding 3 mg/L (Fawell and Mascarenhas 2003).

On the basis of results indicating that the concentration of arsenic in drinking water in areas without natural sources is usually less than 5 μg/L and assuming that the average daily intake of drinking water is 1.5 L, the mean daily intake of arsenic from this source (in the predominantly pentavalent inorganic form) for an adult will generally be less than 7.5 μg. A child (0.5–4.0 years) with an average daily intake of 0.7 L of drinking water would consume less than 3.5 μg.

Babies and young children represent the most sensitive group of toxic effects of inorganic arsenic. Exposure to arsenic in breastfed infants is significantly lower than in formula-fed infants. This is supported by the Cohort of the USA. Previous studies indicate that concentrations in breast milk are relatively low even in areas with high drinking-water arsenic. However, it is uncertain whether breastfeeding leads to reduced infant exposure to arsenic in regions with lower arsenic concentrations. In this study, infants who were fed exclusively with breast milk had lower exposures to arsenic than those fed exclusively with formula or a mix of formula and breast milk. These findings are consistent with the lower median concentration of arsenic measured in breast milk (median 0.31 μg/L) in New Hampshire Birth Cohort Study (NHBCS) compared with the combined concentrations of arsenic in formula powder (median 1.1 μg/L) and tap water (median 0.44 μg/L). These findings suggest that breastfed infants have lower arsenic exposure than formula-fed infants and that both formula powder and drinking water can be sources of exposure for US infants (Carigan et al. 2015).

Table 6 The arsenic content of number of food items from USA from the total diet study conducted by FDA

Element	TDS[a] food no.	TDS[a] food name	N of analysis	N of non-detects	N of trace	Mean (mg/kg)	Std dev (mg/kg)	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
Arsenic	10	Cheese, American, processed	32	31	1	0,001	0,004	0	0	0,022	0,020	0,050
Arsenic	14	Beef roast, chuck, oven roasted	32	31	1	0,0003	0,002	0	0	0,010	0,010	0,040
Arsenic	26	Turkey breast, oven roasted	32	24	7	0,006	0,012	0	0	0,049	0,010	0,040
Arsenic	27	Liver (beef/calf), pan-cooked with oil	32	28	4	0,001	0,004	0	0	0,014	0,010	0,040
Arsenic	28	Frankfurter (beef/pork), boiled	32	30	2	0,001	0	0	0	0,023	0,020	0,050
Arsenic	34	Fish sticks or patty, frozen, oven-cooked	32	0	0	0,504	0,176	0,549	0,055	0,780	0,020	0,040
Arsenic	35	Eggs, scrambled with oil	32	31	1	0,001	0,005	0	0	0,029	0,010	0,040
Arsenic	39	Pork and beans, canned	32	31	1	0,0004	0	0	0	0,012	0,010	0,040
Arsenic	47	Peanut butter, smooth/creamy peanuts	32	28	4	0,004	0	0	0	0,037	0,020	0,050
Arsenic	48	Peanuts, dry roasted, salted	32	26	6	0,005	0,011	0	0	0,032	0,020	0,050
Arsenic	50	Rice, white, enriched, cooked	32	0	1	0,066	0,016	0,063	0,036	0,111	0,010	0,040
Arsenic	51	Oatmeal, plain, cooked	32	30	2	0,001	0,002	0	0	0,01	0,010	0,040
Arsenic	52	Cream of wheat (farina), enriched, cooked	32	31	1	0,0003	0,002	0	0	0,01	0,010	0,040
Arsenic	54	Corn, fresh/frozen, boiled	32	31	1	0,0004	0,002	0	0	0,013	0,010	0,040
Arsenic	60	Cornbread, homemade	32	31	1	0,0003	0,002	0	0	0,011	0,010	0,040
Arsenic	61	Biscuits, refrigerated-type, baked	32	25	7	0,003	0,005	0	0	0,015	0,010	0,040
Arsenic	62	Bread, whole wheat	32	19	13	0,005	0,006	0	0	0,015	0,010	0,040
Arsenic	63	Tortilla, flour	32	31	1	0,001	0,005	0	0	0,027	0,020	0,040
Arsenic	64	Bread, rye	32	31	1	0,0003	0,002	0	0	0,010	0,010	0,040
Arsenic	65	Muffin, blueberry	32	31	0	0,003	0,015	0	0	0,083	0,010	0,040

Arsenic	67	Corn/tortilla chips	32	31	1	0.0004	0.002	0	0	0.014	0.010	0.040
Arsenic	72	Fruit-flavored cereal, presweetened	32	17	5	0.029	0.040	0	0	0.123	0.010	0.040
Arsenic	73	Shredded wheat cereal	32	29	3	0.001	0.004	0	0	0.018	0.010	0.040
Arsenic	74	Raisin bran cereal	32	14	18	0.009	0.009	0.012	0	0.024	0.010	0.040
Arsenic	75	Crisped rice cereal	32	1	0	0.159	0.080	0.156	0	0.505	0.010	0.040
Arsenic	76	Granola with raisins	32	4	27	0.019	0.013	0.017	0	0.061	0.010	0.040
Arsenic	77	Oat ring cereal	32	2	25	0.027	0.013	0.025	0	0.061	0.010	0.040
Arsenic	83	Peach, raw/frozen	32	31	1	0.0003	0.002	0	0	0.009	0.008	0.030
Arsenic	85	Pear, raw (with peel)	32	31	1	0.0003	0.002	0	0	0.010	0.008	0.030
Arsenic	86	Strawberries, raw/frozen	32	31	1	0.0003	0.002	0	0	0.009	0.008	0.030
Arsenic	85	Pear, raw (with peel)	32	31	1	0.0003	0.002	0	0	0.010	0.008	0.030
Arsenic	86	Strawberries, raw/frozen	32	31	1	0.0003	0.002	0	0	0.009	0.008	0.030
Arsenic	87	Fruit cocktails, canned in light syrup	32	31	1	0.001	0.005	0	0	0.029	0.010	0.040
Arsenic	88	Grapes (red/green), raw	32	26	6	0.002	0.005	0	0	0.018	0.008	0.030
Arsenic	89	Cantaloupe, raw/frozen	32	18	14	0.005	0.006	0	0	0.024	0.008	0.030
Arsenic	95	Raisins	32	22	12	0.008	0.012	0	0	0.031	0.020	0.050
Arsenic	97	Avocado, raw	32	31	1	0.001	0.008	0	0	0.044	0.020	0.050
Arsenic	99	Apple juice, bottled	32	28	4	0.002	0.005	0	0	0.022	0.008	0.030
Arsenic	103	Prune juice, bottled	32	24	8	0.004	0.007	0	0	0.028	0.020	0.050
Arsenic	107	Spinach, fresh/frozen, boiled	32	31	1	0.0003	0.00	0	0	0.008	0.008	0.030
Arsenic	108	Collards, fresh/frozen, boiled	32	27	5	0.002	0.005	0	0	0.015	0.008	0.030
Arsenic	113	Broccoli, fresh/frozen, boiled	32	31	1	0.0003	0.002	0	0	0.010	0.010	0.040
Arsenic	115	Asparagus, fresh/frozen, boiled	32	31	1	0.0003	0.002	0	0	0.011	0.010	0.040
Arsenic	117	Tomato, raw	32	31	1	0.0003	0.002	0	0	0.010	0.010	0.040

(continued)

Table 6 (continued)

Element	TDS[a] food no.	TDS[a] food name	N of analysis	N of non-detects	N of trace	Mean (mg/kg)	Std dev (mg/kg)	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
Arsenic	119	Tomato sauce, plain, bottled	32	31	1	0.0004	0.002	0	0	0.012	0.010	0.040
Arsenic	123	Cucumber, peeled, raw	32	32	22	0.011	0.008	0.013	0	0.024	0.010	0.040
	128	Onion, mature, raw	32	31	1	0.002	0.002	0	0	0.011	0.010	0.040
Arsenic	136	Potato, boiled (without peel)	32	31	1	0.0003	0.002	0	0	0.010	0.009	0.030
Arsenic	137	Potato, baked (with peel)	32	29	5	0.001	0.003	0	0	0.012	0.009	0.030
Arsenic	145	Chili con carne with beans, canned	32	30	2	0.001	0.004	0	0	0.017	0.010	0.040
Arsenic	147	Quarter-pound hamburger on bun, fast food	32	30	2	0.001	0.005	0	0	0.023	0.010	0.040
Arsenic	148	Meatloaf, beef, homemade	32	31	1	0.001	0.003	0	0	0.017	0.010	0.040
Arsenic	156	Soup, tomato, canned, condensed, prepared with water	32	31	0	0,001	0,007	0	0	0,039	0,009	0,030
Arsenic	161	Dill cucumber pickles	32	31	1	0,0003	0,002	0	0	0,011	0,010	0,040
Arsenic	178	Cake, chocolate with icing	32	30	0	0,007	0,031	0	0	0,155	0,020	0,050
Arsenic	183	Chocolate chip cookies	32	31	1	0,001	0	0	0	0,021	0,020	0,040
Arsenic	190	Gelatin dessert, any flavor	32	31	1	0,0003	0	0	0	0,011	0,010	0,040
Arsenic	199	Wine, dry table, red/white	32	8	23	0,008	0,006	0,007	0	0,024	0,006	0,020
Arsenic	205	BF, beef, and broth/gravy	32	31	1	0,0003	0,02	0	0	0,010	0,010	0,040
Arsenic	211	BF, vegetables, and beef	32	29	3	0,001	0,003	0	0	0,011	0,010	0,040
Arsenic	212	BF, vegetables, and chicken	32	30	2	0,001	0,004	0	0	0,016	0,010	0,040
Arsenic	214	BF, chicken noodle dinner	32	23	9	0,004	0,006	0	0	0,016	0,010	0,040
Arsenic	215	BF, macaroni, tomato, and beef	32	25	7	0,003	0,005	0	0	0,014	0,010	0,040
Arsenic	216	BF, turkey, and rice	32	31	1	0,0003	0,002	0	0	0,010	0,010	0,040
Arsenic	226	BF, peaches	32	30	2	0,001	0,002	0	0	0,010	0,010	0,040

Arsenic	230	BF, juice, apple	32	23	7	0,009	0,020	0	0	0,086	0,010	0,040
Arsenic	232	BF, custard/pudding	23	18	5	0,003	0,005	0	0	0,013	0,010	0,040
Arsenic	233	BF, fruit dessert/pudding	22	12	10	0,008	0,010	0	0	0,028	0,010	0,040
Arsenic	240	Chicken breast, oven roasted (skin removed)	32	25	7	0.003	0.007	0	0	0.023	0.010	0.040
Arsenic	244	Shrimp, boiled	32	1	0	0.315	0.279	0.236	0	1.400	0.020	0.040
Arsenic	248	Bread, multigrain (formerly cracked wheat)	32	16	16	0.007	0.007	0.005	0	0.022	0.010	0.040
Arsenic	251	Crackers, graham	32	27	5	0.002	0.004	0	0	0.015	0.010	0.040
Arsenic	252	Crackers, butter type	32	31	1	0.0003	0.002	0	0	0.010	0.010	0.040
Arsenic	254	Peach, canned in light syrup	32	31	1	0.0004	0.002	0	0	0.014	0.010	0.040
Arsenic	255	Pear, canned in light syrup	32	31	1	0.0005	0.003	0	0	0.015	0.010	0.040
Arsenic	257	Grape juice, frozen concentrated, reconstituted	32	10	22	0.009	0.007	0.011	0	0.023	0.008	0.030
Arsenic	263	Brussels sprouts, fresh/frozen, boiled	32	31	1	0.0003	0.002	0	0	0.011	0.010	0.040
Arsenic	264	Mushrooms, raw	32	0	16	0.051	0.037	0.040	0.012	0.137	0.010	0.040
Arsenic	265	Eggplant, fresh/frozen, boiled	32	31	1	0.0003	0.002	0	0	0.011	0.010	0.040
Arsenic	267	Okra, fresh/frozen, boiled	32	29	3	0.001	0.003	0	0	0.011	0.010	0.040
Arsenic	269	Beef stroganoff with noodles, homemade	32	19	13	0.007	0.010	0	0	0.031	0.010	0.040
Arsenic	272	Tuna noodle casserole, homemade	32	0	0	0.138	0.063	0.124	0.058	0.321	0.020	0.040
Arsenic	276	Fish sandwich on bun, fast food	32	3	0	0.424	0.212	0.484	0	0745	0.020	0.040
Arsenic	278	Egg, cheese, and ham on English muffin, fast food	32	30	2	0.001	0.004	0	0	0.020	0.010	0.040

(continued)

Table 6 (continued)

Element	TDS^a food no.	TDS^a food name	N of analysis	N of non-detects	N of trace	Mean (mg/kg)	Std dev (mg/kg)	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
Arsenic	285	Clam chowder, New England, canned, condensed, prepared with water	32	1	0	0.127	0.041	0.134	0	0.198	0.020	0.040
Arsenic	286	Ice cream, regular (not low fat), vanilla	32	31	1	0.0004	0.002	0	0	0.012	0.010	0.040
Arsenic	288	Popsicle, fruit-flavored	32	30	2	0.001	0.003	0	0	0.011	0.010	0.040
Arsenic	290	Doughnut, cake-type, any flavor, from donut store	32	31	1	0.001	0.004	0	0	0.025	0.020	0.040
Arsenic	291	Brownie	32	30	2	0.002	0.009	0	0	0.044	0.020	0.040
Arsenic	293	Candy, hard, any flavor	32	31	1	0.001	0.004	0	0	0.022	0.020	0.040
Arsenic	306	Carbonated beverage, fruit-flavored, regular	32	31	1	0.0003	0.002	0	0	0.011	0.008	0.030
Arsenic	317	BF, teething biscuits	31	15	15	0.010	0.013	0.011	0	0.054	0.010	0.040
Arsenic	318	Salmon, steaks/fillets, baked	32	1	0	0.293	0.085	0.289	0	0.436	0.020	0.040
Arsenic	320	BF, squash	32	31	1	0.0004	0.002	0	0	0.013	0.010	0.040
Arsenic	324	BF, cereal, dry, prepared with water	32	0	16	0.042	0.012	0.040	0.019	0.066	0.010	0.040
Arsenic	325	BF, cereal, rice with apples, dry, prepared with water	13	0	9	0.034	0.012	0.034	0.011	0.052	0.010	0.040
Arsenic	334	Beef steak, loin/sirloin, broiled	32	28	3	0.003	0.008	0	0	0.044	0.010	0.040
Arsenic	335	Luncheon meat (chicken/turkey)	32	25	7	0.004	0.008	0	0	0.031	0.010	0.040
Arsenic	336	Chicken breast, fried, fast food (with skin)	32	12	20	0.011	0.010	0.013	0	0.033	0.010	0.040

Arsenic	337	Chicken thigh, oven roasted (skin removed)	32	22	10	0.004	0.007	0	0	0.018	0.010	0.040
Arsenic	338	Chicken leg, fried, fast food (with skin)	32	12	19	0.012	0.012	0.013	0	0.044	0.010	0.040
Arsenic	339	Catfish, pan-cooked with oil	32	21	10	0.008	0.013	0	0	0.051	0.012	0.040
Arsenic	340	Tuna, canned in water, drained	32	0	0	0.999	0.420	0.9	0.349	1.900	0.012	0.040
Arsenic	341	Refried beans, canned	32	31	1	0.001	0.004	0	0	0.025	0.012	0.040
Arsenic	343	Sunflower seeds (shelled), roasted, salted	32	31	1	0.001	0.006	0	0	0.033	0.013	0.050
Arsenic	344	Pancakes, frozen, heated	32	31	1	0.0004	0.002	0	0	0.014	0.010	0.040
Arsenic	350	Fruit juice blend (100% juice) canned, bottled	32	21	11	0.004	0.006	0	0	0.015	0.008	0.030
Arsenic	351	Cranberry juice cocktail, canned/bottled	32	28	4	0.002	0.004	0	0	0.016	0.008	0.030
Arsenic	352	Orange juice, bottled/carton	32	28	4	0.002	0.004	0	0	0.014	0.008	0.030
Arsenic	356	Carrot, baby, raw	32	31	1	0.0004	0.002	0	0	0.013	0.010	0.040
Arsenic	357	Lettuce, leaf, raw	32	27	5	0.002	0.006	0	0	0.027	0.008	0.030
Arsenic	358	Sweet potatoes, canned	32	31	1	0.001	0.005	0	0	0.028	0.010	0.040
Arsenic	361	Lasagna with meat, frozen, heated	32	31	1	0.001	0.005	0	0	0.028	0.010	0.040
Arsenic	362	Beef with vegetables in sauce, from Chinese carry-out	32	26	6	0.003	0.007	0	0	0.024	0.010	0.040
Arsenic	363	Chicken with vegetables in sauce, from Chinese carry-out	32	24	8	0.005	0.009	0	0	0.030	0.010	0.040
Arsenic	364	Fried rice, meatless, from Chinese carry-out	32	0	2	0.069	0.020	0.065	0.033	0.117	0.010	0.040
Arsenic	365	Burrito with beef, beans, and cheese	32	29	3	0.001	0.003	0	0	0.013	0.010	0.040

(continued)

Table 6 (continued)

Element	TDS[a] food no.	TDS[a] food name	N of analysis	N of non-detects	N of trace	Mean (mg/kg)	Std dev (mg/kg)	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
Arsenic	366	Chicken filet (broiled) sandwich on bun	32	31	1	0.001	0.005	0	0	0.029	0.010	0.040
Arsenic	369	Cake, white with icing	32	31	1	0.0004	0.002	0	0	0.012	0.012	0.040
Arsenic	370	Granola bar, with raisins	32	0	26	0.036	0.008	0.034	0.020	0.058	0.012	0.040
Arsenic	371	Candy bar, chocolate, nougat, and nuts	32	31	1	0.0004	0.002	0	0	0.012	0.012	0.040

[a] Totally Diet Study

3.1 Arkansas

A review of As data for public water supply systems currently serving Arkansans reveals that the impact of the new rule will be minimal for current public groundwater supply systems. Only one system out of all systems supplying both small and large communities in Arkansas had an As concentration equaling 10 µg/L. However, results of a recent investigation of groundwater quality in the Bayou Bartholomew watershed in southeastern Arkansas (Kresse and Fazio 2002) revealed elevated levels (>10 µg/L) of As in water from wells completed in the alluvial aquifer of eastern Arkansas (Kresse and Fazio 2003).

The results of the FDA study of several rice varieties show the level of inorganic arsenic in the brown rice marketed in Arkansas ranging from 4.8 to 8.8 mcg/serving with an assumption made that 1 ml = 1 g for the purposes of calculating inorganic arsenic per serving, in instant rice 1.4–2.5 mcg/serving, rice parboiled 3.9–6.9 mcg/serving, white rice, long grain 2.5–5.8 mcg/serving, and white rice medium grain 2.4–7.8 mcg/serving (Food and Drug Administration 2013).

3.2 California

The amount of arsenic taken up is related by rice varies, rice type, and soil concentration (Sommella et al. 2013). Higher arsenic levels in the soil lead to greater uptake and accumulation of arsenic in the rice plant (Zhao et al. 2013). The amount and specific form of arsenic (organic vs inorganic) in the soil depend on several factors, including the amount of water in the soil and soil chemistry (Linquist et al. 2015; Linquist and Ruark 2011).

Rice plants (Oryza sativa) take up arsenic from the soil during the growing process. Arsenic levels are generally more concentrated in the bran or outer coating of the rice grain. The coating is retained in brown (unpolished) rice and removed from white (polished) rice (Meharg et al. 2008).

The source of arsenic in rice is generally from soil and water. A study commissioned by the California Department of Food and Agriculture (CDFA) evaluated the toxic metal content of agricultural soil in California and the potential impact of fertilizers, which can contain trace elements such as arsenic (Chang et al. 2004).

White basmati rice has 1.2 mcg of inorganic arsenic/serving; organic white basmati rice ranges from 2.3 to 2.5 mcg/serving; brown basmati rice ranges from 3.0 to 4.1 mcg/serving; organic brown basmati rice has 4.7 mcg/serving; brown rice ranges from 1.5 to 11 mcg/serving; jasmine rice has 1.5 mcg/serving; rice parboiled has 4.8 mcg/serving; white rice, long grain, has 1.0; white rice, medium grain, ranges from 1.8 to 4.5; and white rice, short grain, ranges from 2.3 to 4.6 mcg/serving (Food and Drug Administration 2013).

3.3 Louisiana

Arsenic is found in well water throughout Louisiana, sometimes at levels that are above the EPA standards of 10 parts per billion (ppb). Testing a water sample is the only way to know if arsenic is present. The Louisiana Department of Health and Hospitals (DHH) recommends that water used for drinking or food preparation contain no more than 10 ppb arsenic (Louisiana Department of Health & Hospitals, Arsenic and Your Private Well, Public Information Series n.d.).

The major source of arsenic from food is rice. Brown rice content of inorganic arsenic ranges from 6.2 to 11 mcg/serving; in white rice, long grain, from 3.1 to 6.1 mcg/serving; and in white rice medium grain from 2.9 to 6.2 mcg/serving (Food and Administration 2013).

3.4 Texas

In Texas the general population is primarily exposed to arsenic and arsenic compounds, through consumption of foods, with an average dietary intake of total arsenic (i.e., arsenic in all forms) of about 58.5 µg/day for males and 50.6 µg/day for females. Drinking water can be a significant source of exposure to inorganic arsenic. In general, adults drinking 2 l of water per day average about 5 µg/day; however, in areas where arsenic is naturally present in the groundwater, intakes can range from 10 to 100 µg/day (Lauwerys and Hoet 1993). Based on the results of the initial investigation, residents of Hebbronville who routinely drink the water likely are at the upper end of this range. Food also may be a significant source of exposure to inorganic arsenic. The National Research Council (NRC) estimates that dietary intake of inorganic arsenic ranges from 8.3 to 14 µg/day. Others have estimated that average daily dietary consumption of inorganic arsenic is about 10.22 µg/day, with a range of 0.93 µg/day to 104.89 µg/day (Agency for Toxic Substances and Disease Registry 2000). The highest levels of dietary arsenic (in all forms) are detected in seafood, rice, rice cereal, mushrooms, and poultry (Agency for Toxic Substances and Disease Registry 2000).

Brown rice contains 5.6–11 mcg of inorganic As/serving; white rice, long grain, from 3.1 to 6.8 mcg/serving; and white rice, medium grain, from 3.5 to 4.9 mcg/serving (Food and Drug Administration 2013).

3.5 Maine

The State of Maine Health and Environmental Testing Laboratory tested 51,347 private wells in Maine, between the years 1999 and 2013. Less than 2% of Maine wells have arsenic levels above 40 µg per liter (Main Environmental Public Health Tracking Network 2016).

In Maine the number of private wells is 250,000 and 42% of the population uses them. Evidence of As presence over the stated guideline (10 μg/L) was found in more than 25% of sampled wells and in 44 towns exceeded 10 μg/L (Chappells et al. 2014).

3.6 Massachusetts

In 2008, the US Geological Survey (USGS) conducted a study to assess concentrations of arsenic and uranium in private bedrock well samples collected by private well owners located in Massachusetts. The USGS researchers analyzed water samples from 478 private bedrock wells in 116 area cities and towns and found that 13% exceeded federal drinking water standards for arsenic and 3% exceeded standards for uranium (Arsenic and uranium in private drinking water wells in Massachusetts 2011).

The number of private wells is 200,000 (8% of homes uses). In east-central Massachusetts 478 wells were sampled, and in 13% concentration of As exceeded 10 μg/L (Chappells et al. 2014).

3.7 Michigan

A few areas in Michigan have naturally higher arsenic levels in groundwater. Exposure to inorganic arsenic typically occurs through groundwater used for drinking and cooking (Michigan Department of Environmental Quality Drinking Water and Municipal Assistance Division 2019).

The US Geological Survey tested 449 drinking water wells in Lapeer County. Of these, 54 exceeded the USEPA standard of 50 μg/L. One hundred and ninety-three of the 449 wells (42.9%) had arsenic concentrations less than or equal to 10 μg/L, and 147 wells had arsenic concentrations less than 5 μ/L. Well drilling records were available for 91 wells. The highest arsenic concentration recorded for a well of known construction was 173.5 μg/L for a well in Lapeer Township completed in the Michigan Formation at a depth of 162 ft. The second highest concentration (100 μg/L) was recorded in Attica Township in a well completed at 262 ft. depth in the Marshall Sandstone (Lapper County Health Department Environmental Health Division 2000).

In Michigan 1 million individual wells are used by 29% of the population. An estimated 8% of the population in southern Michigan are exposed to arsenic in drinking water over 10 μg/L (including public or private system) (Chappells et al. 2014).

3.8 New Hampshire

Water concentrations ranged from 0.002 to 66.6 μg/l. Private drilled or artesian wells had higher water concentrations overall than did public water systems or shallow wells or springs. Public water systems presumably have levels below the current Environmental Protection Agency maximum contaminant level for arsenic; however, private wells are commonly used in rural areas and are not regulated (Karagas et al. n.d.).

The number of individuals wells located in 37.5% of homes in New Hampshire is 190,000. Three hundred forty-three wells were tested, and 19% of samples had an arsenic concentration of more than 10 μg/L (Chappells et al. 2014).

3.9 Minnesota

Arsenic has been detected in about 40% of new wells drilled since 2008 in Minnesota. About 10% of Minnesota's private wells have arsenic levels higher than 10 μg/L (Department of Health 2017).

The way glaciers moved across Minnesota affects where arsenic is found in sediment and groundwater. Arsenic levels can vary between wells, even within a small area. Some wells have arsenic levels as high as 350 μg/L; however, most results are below 50 μg/L (Department of Health 2017).

Minnesota has 480,000 individual wells at 26% of homes. Statewide sampling results indicate that approximately 14% of private wells may exceed 10 μg/L. In western Minnesota 50% of 900 sampled wells are >10 μg/L (Chappells et al. 2014).

3.10 New Jersey

Inorganic arsenic exists naturally at various levels in all geologic formations in the state. Results from testing conducted by the New Jersey Geological Survey indicate that elevated levels of arsenic exist in some aquifers of the Piedmont Province where arsenic has been detected at levels above 5 parts per billion (ppb) or μg/L. Levels as high as 60–80 ppb have been detected in drinking water in this area.

Further, private well testing conducted by the South Branch Watershed Association with the Raritan and Readington Township Environmental Commissions and NJDEP in Hunterdon County shows arsenic levels above 5 ppb in 49 out of 238 wells, or 20%, with the highest concentration being 35 ppb. Beginning in September 2002, all private wells were required to test for arsenic if they were located in the ten counties located in the Piedmont Region of the state. Of the 1928 wells sampled for arsenic between September 2002 and March 2003, 72 wells (3.7%) exceeded the federal drinking water standard of 10 ppb with the highest level reported at 216 ppb (State of New Jersey, Department of Environmental Protection 2003).

In 300,000 individual wells/10% of homes, 3.4% of 17,714 wells tested have arsenic >10 μg/L (12% >5 μg/L, NJ State MCL) (Chappells et al. 2014).

3.11 Wisconsin

In Wisconsin, most arsenic found in groundwater is naturally occurring, released from minerals in bedrock and glacial deposits. Arsenic contamination of groundwater is common in northeastern Wisconsin in areas around Winnebago and Outagamie County, and moderately high levels of arsenic (10–30 ppb) are also common in some parts of southeastern Wisconsin. In northeastern Wisconsin, a geologic formation called the St. Peter Sandstone contains arsenic-rich minerals. When sulfide minerals common in this rock are exposed to oxygen in the air – either at the water table elevation or from drilling activity – chemical reactions solubilize these minerals and lead to very high levels of arsenic in water (exceeding 100 ppb or ten times the ES). In low-oxygen groundwater environments, arsenic can be released from the St. Peter Sandstone at lower concentrations which may still exceed the ES. This more moderate contamination may result from the same sulfide minerals or from arsenic that is bound to iron oxide minerals. In southeastern Wisconsin, most wells draw from glacial sand and gravel deposits or Silurian dolomite formations. While oxidizing conditions tend to release arsenic from sulfide minerals in northeastern Wisconsin, reducing conditions (where dissolved oxygen is low) tend to release arsenic from iron compounds in the glacial deposits and dolomite of southeastern Wisconsin (Wisconsin Groundwater Coordinating Council Report to the Legislature 2018).

In Wisconsin 25% of population has individual wells (680,000 individual wells). Eleven percent of 2233 wells tested in 19 rural townships have arsenic >20 μg/L (Chappells et al. 2014).

4 Latin America

Latin America has a longstanding problem with arsenic (As) exposure with mummified bodies in Chile showing signs of As exposure from as long as 7000 years ago (Arriaza et al. 2010). In many Latin American countries, soil and groundwater are highly enriched with As due to its high density in the region’s abundant volcanic rock and ash. In some countries, mining operations and copper foundries have unearthed As and enhanced its release into groundwater sources for the past few centuries (Ng et al. 2003). Common features of geography and contamination allow Latin America to be classified into three distinct regions: the Chaco-Pampean plain, Andean range, and Central America. While each of these areas has their own defining characteristics, they share the common burden of having been affected by inorganic As transport into drinking water. High concentrations of As have been found in all sources of drinking water in Latin America, including lake, spring, river, and groundwater (Concha et al. 2010). Though this widespread contamination from both natural and anthropological sources has long been a threat to human health in Latin America, relatively little is known about occurrence, distribution, and exposed populations in countries other than Argentina, Brazil, Chile, and Mexico. Only recently has data begun to emerge from such Central American countries as Nicaragua and El Salvador (Cuevas and Bundschuh 2010). Despite this relative lack of detailed exposure data, it is estimated that at least 4.5 million people in Latin America are currently drinking As-contaminated water (>50 μg/L), with some recorded levels as high as 2000 μg/L – roughly 200 times higher than the current World Health Organization (WHO) standard (10 μg/L) for drinking water (Farías et al. 2008; WHO 2003).

4.1 Mexico

4.1.1 Región Lagunera

In the Region Lagunera of Durango and Coahuila States in northern Mexico in 1990, it was estimated that 400,000 people were exposed to As at the concentrations greater than 50 ppb (50% of 129 wells exceeded >50 ppb As with a maximum of 624 ppb As). At 2005, it was suggested that two million people were "at risk." Examining arsenic levels in food and water, Del Razo et al. (1990) concluded that food makes an equal contribution of arsenic to adult dietary intake. Región Lagunera is also an important area for dairy cattle, and Armienta (2003) reported that cow's milk contained up to 27.4 μg/kg, with 10% of samples exceeding the recommended limit of 10 μg/kg As. Although local alfalfa contained up to 316 μg/kg As, it was considered that water was the main source of arsenic in milk (Ravenscroft et al. 2008)

4.1.2 Zimapán Valley, Central Mexico

The Zimapán Valley, an important mining region in Hidalgo State, is the best-documented case of arsenic pollution in Mexico. Pollution was first detected in 1992, when it was found that more than half the wells contained >50 ppb As. Armienta (2003) estimated that most of the 12,000 people were still exposed to concentrations of up to 250 ppb As and had been drinking this water for at least 15 years. Evidence of the amount of arsenic which are residents of the area were exposed was obtained by testing their hair samples (Ravenscroft et al. 2008).

4.1.3 Chihuahua

During 2008–2012 a study was conducted, and 445 well water samples from 94 major rural localities of Chihuahua were collected. Tube well water sampled represent 10% of the tube wells from the 13 municipalities of this study. Three to six water samples in each locality were collected into new plastic bottles from tube wells that served as the primary sources of water for local households. Most of the samples of water collected in this study (97%) contained detectable amounts of As. The concentrations of As in tube water ranged from 0.1 to 419.8 μg/L. Well water from 77 of the 94 Chihuahua localities included in this study (i.e., 81.9%) contained As at levels higher than the MCL value of 10 μg/L; for 33% As levels exceeded 50 μg/L (González-Horta et al. 2015).

4.1.4 Other Regions

In 1998 was described extensive pollution of public water supplies by arsenic and heavy metals in the state of Sonora in northwest Mexico and reported average As concentrations at 29 townships across the state. The water supply to three towns or cities exceeded 50 ppb (the maximum being at Magdalena, with 117 ppb As), and in 19 (66%) townships, the supply exceeded 10 ppb As. Many of the supplies contained elevated concentrations of fluoride, which was positively correlated with arsenic (Ravenscroft et al. 2008).

In the Rio Verde river basin in San Luis Potosi of central Mexico, in 2001 was reported As concentrations of up to 54 ppb in Tertiary–Quaternary basin-fill deposits, bounded by carbonate and acid-volcanic rocks. Arsenic is present dominantly as As(V), and groundwater is subneutral (pH 6.7–7.2) (Ravenscroft et al. 2008).

Natural occurrence of arsenic in groundwater was reported in 2004 in the Guanajuato Mining District, once one of the major silver producers in the world. Both here, and in the San Antonio–El Triunfo mining district, the millions of tonnes of low-grade ore and mine waste, accumulated over hundreds of years, threaten important aquifers (Ravenscroft et al. 2008).

References

Agency for Toxic Substances and Disease Registry (2000) Toxicological profile for arsenic (update). US Department of Health and Human Services, Atlanta. Sept. http://www.atsdr.cdc.gov/toxprofiles/tp2-c5.pdf

Arriaza B, Amarasiriwardenad D, Cornejob L, Standenc V, Byrned S, Bartkusd L et al (2010) Exploring chronic arsenic poisoning in pre-Columbian Chilean mummies. J Archaeol Sci 37:1274–1278

Arsenic and uranium in private drinking water wells in Massachusetts (2011). https://www.mass.gov/service-details/arsenic-and-uranium-in-private-drinking-water-wells-in-massachusetts. Accessed 3 March 2019

Awata H, Linder S, Mitchell L, Delclos G (2012) Association of dietary intake and biomarker levels of arsenic, cadmium, lead, and mercury among Asian populations in the United States. University of Texas Health Science Center, Houston, p 319. https://doi.org/10.1289/EPH28

Boyle D, Turner R, Hall G (1998) Anomalous arsenic concentrations in groundwaters on an island community. Brit Columbia Environ Geochem Health 20:199–212. https://doi.org/10.1023/A:1006597311909

Canadian Food Inspection Agency (2013a) Arsenic speciation in selected foods, Ottawa, pp 14–23

Canadian Food Inspection Agency (2013b) Arsenic, Cadmium, Lead and Mercury in Infant Formulas, Meal Replacement and Nutritional Supplements, Ottawa, pp 14–16

Carigan C, Cottingham K, Jackson B, Farzan S, Gandolfi A, Punshon T, et al (2015) Estimated exposure to arsenic in breastfed and formula-fed infants in a United States Cohort, USA. pp 500–505. https://doi.org/10.1289/EPH.1408789

Chang AC, Page AL Krage NJ (2004) Role of fertilizer and micronutrient applications on arsenic, cadmium and lead accumulation on cropland soils in California. Final Report to CDFA. Department of Environmental Sciences, University of California at Riverside (UCR)

Chappells H, Parker L, Fernandez C, Conrad C, Drage J, O'Toole G et al (2014) Evaluating arsenic remediation approaches for private wells in North America. J Water Health, Canada 12:372–377. https://doi.org/10.2166/WH.2014.054

Chou S, Harper C. (2007) Toxicological profile for arsenic, US Department of Health and Human services, Public Health Service Agency for Toxic Substances and Disease Registry, Atlanta, pp 1–3

Concha G, Broberg K, Grander M, Cardozo A, Palm B, Vahter M (2010) High-level exposure to lithium, boron, cesium, and arsenic via drinking water in the Andes of northern Argentina. Environ Sci Technol 44:6875–6880. PubMed

Cuevas A, Bundschuh J. (2010) Gogenic arsenic in Nicaragua: Occurrence and health effects. Un published data

Department of Health (2017) Well management section environmental health division, arsenic in well water https://www.health.state.mn.us/communities/environment/water/docs/wells/waterquality/arsenic.pdf. Accessed 3 Mar 2019

Dummer TJB,Yu ZM,Nauta L, Murimboh JD, Parker L (2014) Geostatical modeling of arsenic in drinking water wells and related toenail arsenic concentrations across Nova Scotia, Canada

Farías S, Bianco de Salas G, Servant RE, Mitre BG, Escalante J, Ponce RI, et al. (2008) Survey of arsenic in drinking water and assessment of the intake of arsenic from water in Argentinie Pune. Natural Arsenic in Ground Water. In: Bundschuh J, Bhattacharya P, editors. Arsenic in the environment. Volume 1. Chapter 41

Fawell J., Mascarenhas K. (2003) Arsenic in drinking water, United Kingdom. WHO update, pp 41–46

González-Horta C, Ballinas-Casarrubias L, Sánchez-Ramírez B, Ishida M, Barrera-Hernández A, Gutiérrez-Torres D et al (2015) A concurrent exposure to Arsenic and fluoride from drinking water in Chihuahua. Mexico Int J Environ Res Public Health 12:4587–4601. https://doi.org/10.3390/ijerph120504587

Goodwin TA, McIsaac EM, Friske PWB (2009) The North American soil geochemical landscapes project: report on the 2008 sampling program and preliminary 2007 results (no. ME 2009–1). Mineral Resources Branch, report of activities 2008. Government of Nova Scotia

Goodwin TA, Parker L, Fisher BE, Dummer TJB (2010) Toenails, tap water and you: the arsenic connection (no. ME 2010-1).Mineral Resources Branch report of activities 2009, natural resources. Government of Nova Scotia

Government of Canada (2003). https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-arsenic/page-6-guidelines-canadian-drinking-water-quality-guideline-technical-document-arsenic.html. Accessed 26 Aug 2018

IARC Working Group WHO (2004) Some drinking water disinfectants and contaminants, including arsenic, Lyon, p 26

Karagas MR, Tosteson TD, Blum J, Klaue B, Weiss JE et al Measurement of low levels of arsenic exposure: a comparison of water and toenail concentrations. Am J Epidemiol 152(1):86

Kresse TM, Fazio JA (2002) Pesticides, water quality and geochemical evolution of ground water in the alluvial aquifer, bayou bartholomew watershed, Arkansas. Arkansas Dept. of Environmental Quality Water Quality Report WQ02–05-1, Little Rock, AR, 111 p

Kresse T, Fazio J (2003) Occurrence of arsenic in ground waters of arkansas and implications for source and release mechanisms, arkansas ambient ground-water monitoring program arkansas Department of Environmental Quality Water Quality Report WQ03–03-01 March

Lapper County Health Department Environmental Health Division (2000) Arsenic in ground water in lapeer county, Michigan

Lauwerys R., Hoet P. (1993) Industrial chemical exposure, guidelines for biological monitoring. Lewis Publishers. Second Edition

Linquist B, Ruark M (2011) Re-evaluating diagnostic phosphorus tests for rice systems based on soil phosphorus fractions and field level budgets. Agron J 103(2):501–508

Linquist BA, Anders MM, Adviento-Borbe MA, Chaney RL, Nalley LL, Da Rosa EFF, van Kessel C (2015) Reducing greenhouse gas emissions, water use, and grain arsenic levels in rice systems. Glob Change Biol 21:407–417. https://doi.org/10.1111/gcb.12701

Louisiana Department of Health & Hospitals, Arsenic and Your Private Well, Public Information Series (n.d.). http://ldh.la.gov/assets/oph/Center- EH/engineering/PrivateWells/Private_Well_And_Arsenic.pdf

Main Environmental Public Health Tracking Network (2016) Study of arsenic in well water answers important questions about bathing and treatment, https://data.mainepublichealth.gov/tracking/arsenicstudy. Accessed 3 Mar 2019

Meharg AA, Lombi E, Williams PN, Scheckel KG, Feldmann J, Raab A, Zhu Y, Islam R (2008) Speciation and localization of arsenic in white and brown rice grains. Environ Sci Technol 42:1051–1057

Mèranger C, Subramanian S, McCurdy F (1984) Arsenic in Nova Scotia groundwater. Sci Total Environ 39:49

Michigan Department of Environmental Quality Drinking Water and Municipal Assistance Division (2019) ARSENIC IN WELL WATER Guidance

Ng JC, Wang J, Shraim A (2003) A global health problem caused by arsenic from natural sources. Chemosphere 52:1353–1359. PubMed

Nova Scotia Department of the Environment (1998) The state of the Nova Scotia environment. P.18

Ravenscroft P., Brammer H., Richrads K (2008) Arsenic pollution: global Syntesis, pp 422–426

Smith H, Lopipero A, Bates N, Steinmaus M (2002) Arsenic epidemiology and drink water standards. Science 296:2145–2146. https://doi.org/10.1126/science.1072896

Sommella A, Deacon C, Norton G, Pigna M, Violante A, Meharg AA (2013) Total arsenic, inorganic arsenic, and other elements concentrations in Italian rice grain varies with origin and type. Environ Pollut 181:38–43

State of New Jersey, Department of Environmental Protection (2003). https://www.state.nj.us/dep/dsr/arsenic/guide.htm. Accessed 3 Mar 2019

U.S. Department of Health and Human Services Food and Drug Administration Center for Food Safety and Applied Nutrition,(2016) Inorganic arsenic in rice cereals for infants, draft guidance, pp 3–5

U.S. Food and Drug Administration (2013) Analytical results from inorganic arsenic in rice and rice products, https://www.fda.gov/Food/FoodScienceResearch/RiskSafetyAssessment/ucm485278.htm. Accessed 29 Aug 2018

U.S. NRC (1999) Arsenic in drinking water. Subcommittee on arsenic in drinking water, committee on toxicology, board on environmental studies and toxicology commission on life science, U.S. National Research Council. National Academy Press, Washington, DC

US Food and Drug Administration (2017) Total diet study – market baskets 2006–1 through 2013–4, United States, pp 3–12

WHO (2003) Background document for preparation of WHO guidelines for drinking-water quality. World Health Organization (WHO/SDE/WSH/03.04/75), Geneva. Arsenic in drinking-water

Wisconsin Groundwater Coordinating Council Report to the Legislature (2018) p 1

World Health Organization (2001) Arsenic and arsenic compounds, Geneva Environmental Health Criteria 224, 2nd ed. p 915

Zhao F, Zhu Y, Meharg AA (2013) Methylated arsenic species in rice: geographical variation, origin, and uptake mechanisms. Environ Sci Technol 47(9):3957–3966

Arsenic in Latin America: Part I

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Abstract A complete analysis on the occurrence of arsenic (As) in aquifers and several superficial water bodies in Latin America, identified in 13 countries, is presented. The Chaco-Pampean plain in Argentina is the largest area affected by groundwater As contamination. Research on the chemical and hydrogeological processes of release and mobilization of As has also been developed in Mexico, Chile, Bolivia, Peru, and Nicaragua. In most of the contaminated areas, As originates from geogenic sources, mainly volcanic rocks, hydrothermal fluids, and As-bearing minerals. However, anthropogenic sources are also present in certain zones, most of them coming from mining operations and, in some cases, related to agriculture. Mining is indeed the main As source in Brazil. The physicochemical characteristics of the water, such as pH and Eh, and the presence of other ions influence the mobilization of As. Hydrogeological conditions also determine the occurrence of As contamination. It has been found that the element is in the As(V) form in most locations. In all Latin American countries, more research has still to be conducted to determine As concentrations and speciation in water bodies used as drinking water source, to unravel its origin and mobilization processes.

Regarding analytical methods on As determination, 167 papers in scientific journals have been identified in the last 18 years in Latin America. The most widely

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analytical methodologies used for As determination are AAS (57%), specifically HG-AAS, and ICP (26%), mainly coupled with MS. Electrochemical methods have been applied in Chile, Brazil, and Argentina. UV-VIS spectrometry has been used mainly in Cuba and Mexico. XRF spectrometry, principally for solid samples, has been used in Mexico, Cuba, Brazil, Argentina, and Chile. Other used methodologies are INAA, the ARSOlux Biosensor and the SPRN technique.

Keywords Argentina · Arsenic · Brazil · Chile · HG-AAS · XRF spectrometry

Abbreviations

AAS	Atomic absorption spectrometry
AE	Anion exchange
AEC	Anion exchange chromatography
AES	Atomic emission spectrometry
AFS	Atomic fluorescence spectrometry
AS-SWV	Anodic stripping square-wave voltammetry
ASV	Anodic stripping voltammetry
ASV-(CAR-CPE)	Adsorptive stripping voltammetric carrageenan modified carbon paste electrode
BDES	Bi-directional electrostacking system
CPE	Cloud point extraction
CSV	Cathodic stripping voltammetry
CT	Cryotrapping gas
DPP	Differential pulse polarography
EcHG	Electrochemical hydride generation
ETAAS	Electrothermal atomic absorption spectrometry
ETV	Electrothermal vaporizer
EVA	Ethyl vinyl acetate
FI	Flow injection
GC-PFPD	Gas chromatography with pulsed flame photometric detection
GFAAS	Graphite furnace atomic absorption spectrometry
GFH	Granular ferric hydroxide
HG	Hydride generation
HPLC	High pressure liquid chromatography
HR-CS	High-resolution continuum source
HS-SPME	Headspace solid-phase micro-extraction
IC	Ionic chromatography
ICPAES	Inductively coupled plasma atomic emission spectroscopy
ICPMS	Inductively coupled plasma mass spectrometry
ICPOES	Inductively coupled plasma optical emission spectrometry
INAA	Instrumental neutron activation analysis

IXED	Ion exchange/electrodialysis
LA	Laser ablation
LC	Liquid chromatography
MP	Microwave plasma
MS	Mass spectrometry
MSFIA	Multisyringe flow injection analysis
PA-NCu	Copper nanoparticles supported in polyamide pellets
SIA	Sequential injection analysis
SPE	Solid phase extraction
SPRN	Surface plasmon resonance nanosensor
SWCSV	Square wave cathodic stripping voltammetry
UV	Ultraviolet
XRFS	X-ray fluorescence spectrometry

1 Situation of Arsenic in Latin America

The problem of arsenic (As) in drinking water is today very well-known due to the consequences on health all over the world. Arsenic (As) is a natural metalloid abundantly present in the earth's crust.[1] It is one of the most toxic pollutants, present mainly in groundwater by the release of As to soils and aquifers due to natural processes such as volcanic phenomena and rock disintegration, and it can be detected in a wide range of concentrations. Human activities such as industrial processes, metal smelting, pesticide production, and wood preservation increase the contamination of soils and aquifers. The exposure of humans to the element occurs through the consumption of contaminated water and food (International Agency for Research on Cancer (IARC) 2012; Argos et al. 2011; Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018; Murcott 2012; McCarty et al. 2011; Bundschuh et al. 2008, 2010, 2012; Bhattacharya et al. 2006; Smedley et al. 2009; Gomez et al. 2009; Alarcón-Herrera et al. 2013; Nicolli et al. 2009; Mukherjee et al. 2014; Blanes et al. 2011; Zabala et al. 2016; World Health Organization (WHO) 2011; Nicolli et al. 2010; Sigrist et al. 2013; Vázquez et al. 2014; Farias et al. 2016; World Health Organization & International Programme on Chemical Safety 1996; Ormachea Muñoz et al. 2014).

The presence of As in water is a worldwide problem with high impact in the poorest regions, with more than 226 million exposed people (Murcott 2012; McCarty et al. 2011). Its presence has been identified in waters of many areas of Latin America since the twentieth century. Health effects from chronic exposure to As-enriched drinking water were first reported in Bell Ville, Argentina, in 1913 (Bundschuh et al. 2010). Since then, and mainly since the 1960 decade, As

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[1] In this paper, Latin America will be referred to as the region comprising those countries in the Americas where the Spanish or Portuguese languages prevail: Mexico, all countries of Central America with the exception of Belize, all South American countries (with the exception of Guyana, Suriname, and Trinidad and Tobago), and, in the Caribbean, Cuba, Dominican Republic, and Puerto Rico.

occurrence in aquifers and surface water has been found in other parts of Argentina and also in other Latin American countries (Bundschuh et al. 2008, 2012).

2 Distribution of Arsenic in Latin America

2.1 Generalities

Arsenic concentrations and sources vary among sites, although, in most of them, it has a natural origin. The release of As to the water may involve complex geochemical processes that have been unraveled only in certain zones. In many of those sites, most or all drinking water comes from As-enriched aquifers, posing a health threat to the population. Here, an overview of As natural occurrence in Latin American water resources will be presented, including identified sources and geochemical processes involved in its release and mobilization, focusing on water bodies used as a drinking water sources.

2.2 Argentina

A compilation of studies conducted in Argentina related to the As presence in water was recently reported (Bundschuh et al. 2012), being the Chaco-Pampean plain (about 1 million km^2) the largest area affected by groundwater As contamination in Latin America. In this study, the zones with As occurrence were divided in Chaco-Pampean plain, Andean highlands, sub-Andean valleys/Andean foothills, and Patagonia, each one with specific As concentration ranges. Main hydrogeochemical characteristics and geochemical processes influencing As occurrence and mobilization were summarized in this publication. The factors controlling As mobilization in the aquifers of the Río Dulce alluvial cone, where groundwater contains an average As concentration of 743 μg/L, have been identified (Bhattacharya et al. 2006). Arsenic release involves the influx from dissolution of volcanic glass, adsorption of As on Fe and Al mineral phases in relatively low pH zones, and high mobility of As in high pH zones. Processes of As water enrichment and mobility in the Quaternary loess aquifer at the Chaco-Pampean plain were defined (Smedley et al. 2009). Accumulation of As in the groundwater flow toward the depression and lack of flushing seem to be responsible for the high As concentrations, which reach 5300 μg/L. Sorption/desorption on Fe oxides and possibly on Mn oxides were considered as important controls on As mobility. In addition, a high correlation ($R^2 = 0.84$) between As and fluoride (F) contents in the groundwater of the phreatic aquifer of Coronel Moldes has been found (Gomez et al. 2009). Coexistence of As and F in groundwater of the Chaco-Pampean plain was also remarked (Alarcón-Herrera et al. 2013). It has been informed that groundwater flowing through Tertiary and Quaternary loess deposits at Tucumán province contains also high As concentrations (up to 1610 μg/L), with lower concentrations at large depth (Nicolli et al. 2009). Sorption was also considered as a control of As mobility in this study. The role of the tectonic setting in the As concentration increase of groundwater in the Chaco-Pampean plain was evaluated through flow path modeling (Mukherjee et al. 2014). This study included the chemical analysis of major, minor, and trace elements in water from 60 wells. The PHREEQC hydrogeochemical code was used to model reaction flow path for pairs of wells. The simulations considered chemical evolution through silicate weathering, dissolution of evaporites, reversible cation exchange reactions, and oxide phases. Arsenic concentration in water was as high as 7500 μg/L, with As(V) being the dominant species. Volcanic glass was considered to be the primary source of As in the Chaco-Pampean groundwater. In addition, mineralized, hydrothermal zones and hot springs are also a major geogenic source. The As origin may be tectonically controlled; As is transported to the surface aquifers by extrusive volcanism or hydrothermal fluids. Rhyolitic glass in volcanic ash beds and silicate rocks undergo hydrolytic dissolution releasing trace oxy-anions to groundwater that then undergo other geochemical processes in the groundwater flow. Arsenic concentrations and distribution in groundwater of the Central-West region of Chaco have been determined (Blanes et al. 2011). Approximately 88% of 86 groundwater samples collected in 2007 exceeded the WHO guideline value posing a risk to the population since this water is used for human and livestock consumption. Elevated As concentrations were associated to high pH and Na-HCO_3-type groundwater. The processes controlling As and F distribution in groundwater of the Pampeano aquifer and the Del Azul Creek basin, located southeast of the Chaco-Pampean plain, in Buenos Aires province, have been evaluated (Zabala et al. 2016). Concentrations above the present WHO safe drinking level (10 μg/L) (World Health Organization (WHO) 2011) were measured in 92% of 62 samples collected in the years 2011 and 2012. Hydrogeochemical, isotopic, and statistical interpretations within the hydrogeological framework allowed defining two main controls on As distribution. Hydrogeochemical processes control As distribution in low and moderately mineralized water of the middle and lower parts of the basin, while hydrogeological conditions control its distribution northeast and beyond the lower basin. Hydrogeochemical studies have also been performed in the Salí River basin part of the Tucumano-Santiagueña hydrogeological province, where 42 groundwater samples from shallow aquifers, 26 deep samples, and 17 from artesian aquifers were collected (Nicolli et al. 2010). Arsenic concentrations ranged from 11.4 to 1660 μg/L being 100% of the samples above the WHO guideline value. A strong positive correlation among As, F, and V was found in shallow groundwaters. Leaching from pyroclastic materials is favored by high pH and high bicarbonate waters. In another study, the distribution of inorganic arsenic (iAs) species in groundwater used for human consumption was determined in the Santa Fe province (Sigrist et al. 2013). Results showed a prevalence of As(V) and As contents above the WHO limit in all of the samples collected in 27 counties with concentrations up to 186.5 μg/L. Arsenic concentration in water, soils, human, and dog hair was determined at La Matanza District, 31 km away from Buenos Aires City (Vázquez et al. 2014). Average As concentration (measured by total reflection X-ray fluorescence, TXRF) in drinking groundwater was 57 µg/L, while As in human hair was below the reference level, and As in dog hair showed the occurrence of chronic As contamination. The presence of As in surface water and groundwater of the Argentine Altiplano (Puna) and sub-Andean valleys, which is consumed by 355,000 people, was also evaluated (Farias et al. 2016). The concentrations measured in 61% of the 62 samples collected in an area of 30,000 km^2 exceeded the WHO limit. Arsenic occurrence was ascribed to geogenic sources. Results showed that the daily As intake for the majority of the population from La Puna (561 µg/day average in summer and 280.5 µg/day in winter) was higher than the WHO reference value (146 µg/day) (World Health Organization & International Programme on Chemical Safety 1996).

2.3 Bolivia

The presence of As has been identified in various areas of Bolivia, mainly related to mining activities, ore deposits, geothermal manifestations, and leaching of volcanic rocks. Its occurrence in various environmental compartments has been summarized in 2012 (Bundschuh et al. 2008). Many of the studies have focused on the Pilcomayo River basin and the Poopó Lake basin. The As concentration in the less developed area of the basin, where untreated surface water and groundwater are used as drinking water, has been determined (Ormachea Muñoz et al. 2014). General physicochemical characteristics were slightly alkaline with high electrical conductivity and predominance of sodium, chloride, and bicarbonate. Arsenic concentrations were above the WHO guideline value in 95% of the 41 sampled wells and 7 sites along 4 rivers, reaching 623 µg/L. The presence of As was related to water contact with alluvial material in lower terrains, besides arsenopyrite oxidation, and dissolution from volcanic rocks. Arsenic contamination in surface water, groundwater, and soils in the provinces of La Paz and Oruro of the Bolivian highland has been studied (Quintanilla et al. 2009). Groundwater average As concentration was 47 µg/L and ranged from below the detection limit (DL) to 200 µg/L in Kondo K, 245 µg/L in Santuario de Quillacas, 152 µg/L in the central region, and 187 µg/L in Pampa Aullagas. The Poopó lake contained the highest As concentrations of the sampled surface waters with 11,140 µg/L in the dry period. Geothermal processes are the main natural sources of As in the area; anthropogenic contamination is related to mine tailings located around San José, Huanuni, Poopó, Avicaya, Itos, and Llallagua. Arsenic presence in groundwater of the Poopó basin was ascribed to sulfide mineral oxidation. All the rivers that drain the mining area are enriched in As. The sources and geochemical processes controlling the mobilization of As and trace elements in shallow aquifers of the Antequera and Poopó sub-basins in the mining Oruro region have been evaluated (Ramos et al. 2014). In the Antequera sub-basin, As concentration was above the WHO limit in 89% of the samples, with a maximum value of

364 µg/L, while in the Poopó sub-basin, all samples were above that limit, reaching a maximum of 104.4 µg/L. Since high As concentrations were measured far from mining sites in the Antequera sub-basin, a natural origin related to the characteristics of the sediments was ascribed to the presence of the element. Statistical factor analysis showed that four processes could produce the mobilization of As and trace elements: desorption from hydrous ferric oxide surfaces, reductive dissolution of Fe and Mn hydrous oxides, increased trace element concentrations at acidic pH values, and oxidation of sulfide minerals.

2.4 Brazil

Mining has been an important As source in the Iron Quadrangle at the Minas Gerais state. This was assessed through an interdisciplinary project carried out from 1998 to 2007 (Matschullat et al. 2007). The main As source are primary ore deposits containing arsenopyrite and pyrite. Arsenic presence is related to natural leaching of rocks and soils as well as mining operations (Bundschuh et al. 2008). In the Ribeira Valley (southeastern Brazil), Pb and As have contaminated the Ribeira River as a result of Pb-Zn ore production and smelting. The Santana District in the Amazon region is also contaminated with As (up to 2.0 mg/L in some wells) produced from Mn ore benefit. However, low As exposure was identified in this latter area (Figueiredo et al. 2010). The occurrence of As in drinking waters at Paractu was also assessed (Bidone et al. 2014). The results showed that As concentrations in drinking water (surface water and groundwater) were below the WHO standard value in urban and rural communities and most of them below the instrumental DL. However, As reaches up to 40.10 µg/L in freshwater samples at Corrego Rico and Ribeirão Entre-Ribeiros watershed, due to the influence of a gold mining site and abandoned artisanal gold mining sites. In the Itapessoca catchment (northeast Brazil), As pollution due to a shrimp farm and fish ponds in surface waters, with concentrations up to 15.51 µg/L As, has been reported (Santos Pontes et al. 2014).

2.5 Chile

The area of Atacama Desert, northern Chile, is naturally enriched in As. People from the Arica zone have been affected by this metalloid for more than 4500 years (Figueiredo et al. 2010). Nevertheless, As-related health effects from As-rich drinking water pumped from the Loa river were identified only since 1962 at Antofagasta (Bundschuh et al. 2012). Arsenic concentrations up to 2000 µg/L were measured in the Loa river, as a result of high evaporation at alkaline pH and high salinity (Alarcón-Herrera et al. 2013). Arsenic is mainly released from volcanic rocks and sulfide ore deposits at the Andean chain and mobilized by snowmelts and rain to rivers and springs. At the Camarones Valley, about 100 km south of Arica City, drinking water from waterfalls and from the Camarones river contain 48.7 μg/L and 1252 μg/L of As, respectively, mostly as As(V) (Bundschuh et al. 2012). In the Tarapacá region, high As concentrations were determined in surface water and groundwater with a heterogeneous spatial distribution. Arsenic in drinking water of the rural area ranged from 0.1 μg/L in Guatacondo to 345.85 μg/L in Camiña, located at the north and south of the area, respectively. The highest As concentration in the sampled rivers was measured in Pachica. No correlation was found between As, boron (B), and salinity in the Tarapacá area. The occurrence of As was ascribed to the presence of volcanic sediments, salt lakes, thermal areas, predominance of closed basins, and anthropogenic sources like copper mining (Amaro et al. 2014). In the mining region of Antofagasta, high As concentrations were found in river waters (from 10 to 3000 μg/L). In addition, water used for human consumption ranged from 100 to 1900 μg/L. Nevertheless, As exposure has decreased, and As-related problems have been solved in most part of the country (Bundschuh et al. 2012; Figueiredo et al. 2010).

2.6 Colombia

While Colombia geology indicates the presence of rocks containing As minerals, few studies have been developed to assess the actual concentrations in rocks or water. Arsenic was found in the Marmato river water in the Marmato mining district (Bundschuh et al. 2012). In 2010 and 2011, As concentrations were determined in 319 samples of drinking water in Bogotá DC (Patiño-Reyes and Duarte Portocarrero 2014). Concentrations were below the detection level in most of the samples (99.38%), and the rest was below the WHO guideline value. A review of the occurrence and sources of As in Colombia was reported in 2014 (Alonso et al. 2014). The presence of low As levels was determined in the Suratá river waters with concentrations up to 13 μg/L near the municipality of California. Arsenic occurrence was related to mining in the area (Alonso et al. 2014). Information reported in that review showed that As concentrations in surface water and groundwater exceeded national standards at some sites; its presence was ascribed to human activities, mainly to mining and agriculture. This last source of As (up to 255 μg/L) was detected in the phreatic water of several municipalities of the Bogotá savannah with intense irrigation of horticultural crops. Arsenic concentrations above the Colombian drinking water standard of 10 μg/L were also measured in the water near the Muña reservoir, which is used by people (41.8 μg/L average). Although concentrations are low at many of the studied sites, in several cases, the values exceed the national recommended levels for drinking, irrigation, livestock, and aquatic life. The authors of the review highlight the importance of performing more research to understand the occurrence, origin, and distribution of As in Colombia.

2.7 Cuba

Arsenic concentrations have been reported at some sites in Cuba. Studies carried out at Isla de la Juventud, Manzanillo bay, Cienfuegos bay, and Santa Lucía mine have been informed (Bundschuh et al. 2012). At Isla de la Juventud, only one spring close to the Delita mine out of eight sampled points in the watershed was contaminated with 25–250 μg/L As (Toujague et al. 2003). Arsenic concentrations were above the WHO guideline value in wells at other watersheds, representing a risk for noncancerous diseases for children. Streams impacted by acid mine drainage (AMD) from the Santa Lucía mine showed decreasing As contents downstream ranging from 4 to 24 μg/L at around 1500–1700 m from the mine.

2.8 Ecuador

Concentrations of As from 220 to 369 μg/L at the surface and from 289 to 351 μg/L at depth were measured in the water of the Papallacta lake (Cumbal et al. 2009). The authors identified discharges of geothermal waters (containing up to 7853 μg/L of As) to the Tambo river as the main As sources to the lake. Arsenic concentrations ranging from 9 to 126 μg/L were found in wells used as drinking water sources in Tumbaco and Guayabamaba towns in 2006; treatment options were then applied by the municipality (Bundschuh et al. 2012).

2.9 El Salvador

Arsenic is present in the largest lakes of the country (Ilopango, Coatepeque, and Olomega), with the highest concentration (4210 μg/L) measured at the Olomega lake in 2000. While this water is not used for centralized supply, it has been reported to be used by people living in the watersheds (Bundschuh et al. 2012; López et al. 2012). High As contents (up to 770 μg/L) in the waters of the Ilopango lake are linked to hydrothermal fluid interaction with lake sediments. As and B concentrations (up to 8.6 mg/L) were correlated in the lake water with higher values to the south (López et al. 2009). Arsenic in springs and domestic wells of geothermal origin was determined in the Ahucahapán (from 20 to 210 μg/L) and Berlin (from 2 to 285 μg/L) geothermal fields. Arsenic was also found in Las Burras (164 μg/L) and Obrajuelo (16 to 330 μg/L) aquifers (Bundschuh et al. 2012). Water collected in the Bajo Lempa region in October 2012 and March 2013 showed a maximum of 12 μg/L As in surface water and 322 μg/L in groundwater. Arsenic presence is related to natural occurrence in rocks and geothermal fluid and probably to an anthropogenic source due to pesticides and fertilizers used in the area (López et al. 2014). The San Miguel aquifer was recognized to present a high risk due to As presence with up to 162 µg/L. Three rivers of the country (Paz, Sucio, and Jiboa) were identified to contain relatively high As concentrations with up to 123 µg/L in the Jiboa river (Bundschuh et al. 2012).

2.10 Guatemala

In 2007, a concentration of 15 µg/L As, originated from leaching of volcanic rocks, was measured in the water of a well used as drinking water supply at Mexico (Bundschuh et al. 2012; Garrido Hoyos et al. 2007). Later, in the area of the Marlin mine (boundary between San Miguel Ixtahuacán and Sipacapa, San Marcos department, 300 km from Guatemala City), As concentration up to 261 µg/L was measured in wells downgradient from the tailings (Bundschuh et al. 2012).

2.11 Mexico

Chronic As poisoning was first identified in Mexico in 1958 at the Comarca Lagunera, northern México (Cebrián et al. 1994). Since then, As has been detected in many areas of the country. Its presence is mainly related to geogenic sources, mineralization, geothermal systems, sorption and release from minerals, and salinization, but also to anthropogenic activities in some areas. An overview of the As presence in groundwater of Mexico and their possible sources was reported in 2008 (Armienta and Segovia 2008); areas identified with the presence of As and F have been also reported in 2013 (Alarcón-Herrera et al. 2013), and occurrence and mechanisms of As enrichment in geothermal zones were described (Birkle et al. 2010). Here, some of the As-rich areas resulting from diverse sources and recent studies in places where groundwater is used as drinking water are included.

Comarca Lagunera in Durango and Coahuila states has been one of the most studied areas with As concentrations up to 750 µg/L. The zones were where the former lagoons Mayrán and Viesca (currently dried up), in the northeastern part of the basin, are reported as the most As-enriched areas. Higher As concentrations have been determined for thousands of years in old waters with respect to recent infiltrated, young waters. Intensive groundwater abstraction, besides arrest of the Nazas river infiltration due to its canalization, has induced the pumping of deeper As-enriched old waters. As a result, As contents increased in 2010 compared to 1990, mainly in the northern part of the region. A correlation of As concentration with groundwater age, with older waters having higher As contents than the younger ones, has been identified (Boochs et al. 2014). From the interpretation of chemical and isotopic determinations and groundwater flow modeling, evaporation was postulated as the main process producing high As concentrations in the most southeastern part of this area (Ortega-Guerrero 2004). Release of As from sediments to the water due to pH increase was also proposed (Mejía-González et al. 2014). Recently, the geochemical influence of the aquitards on As enrichment at the edges of the Comarca Lagunera has been evaluated (Ortega-Guerrero 2017). Results of this study including geochemical modeling indicated that the advance of As-rich water to the main granular aquifer is due to a reversal of hydraulic gradients resulting from intensive groundwater exploitation and decrease of freshwater runoff from dam construction in the main rivers. Although various sources have been proposed as the origin of As, it was concluded that the most probable source is related to extinct hydrothermal activity and sedimentary process (Boochs et al. 2014). Increased groundwater abstraction and canalization of the Nazas river induced a drawdown of the groundwater level reaching about 100 m in the center of the area. Irrigation with As-rich water contributed also to As increase. Concentrations of As and F above the Mexican drinking water standards (i.e., 25 μg/L for As and 1.5 mg/L for F, Modificación a la Norma Oficial Mexicana 2000) have also been measured in the alluvial aquifer system of the Chihuahua state (Espino-Valdés et al. 2009; Reyes-Gómez et al. 2013). Interpretation of the distribution of concentrations within the hydrogeological and geological framework indicated a natural geogenic source related to the recharge flow coming from mountains presenting arsenopyrite deposits and from the contact of water with the aquifer sediments. Besides, at the Julimes municipality, geothermal water and high evaporation rate are also responsible of As contamination. A review including information from water, soils, and sediments reported natural (related to volcanic processes) and anthropogenic (related to mining and smelting) sources in the Chihuahua and Coahuila states (Mar Camacho et al. 2011). The co-occurrence of F and As in the central part of the Chihuahua state was studied (Reyes-Gómez et al. 2013). Petrographic analyses showed the presence of F as fluorapatite. Distribution maps depicted temporal (since 2003–2010) and spatial concentration variations of As and F. Measured values of pH and Eh indicated that As predominates as $HAsO_4^{2-}$ in groundwater. A geochemical conceptual model was proposed to reflect the mobility of As and F in groundwater. Highly fractured volcanic rocks and alluvial fans at the base of the *sierras* were identified as possible aquifer recharge zones. The alluvial fans contain rhyolites and shales with As and fluorapatite. Weathering releases these elements from the lithology of the area.

Arsenic contamination is related to natural and/or anthropogenic sources in mining zones. At Zimapán, Hidalgo state, two anthropogenic and one natural source were identified as the origin of As groundwater pollution in the aquifer system. Arsenic was determined in rocks, mining wastes, soils, and sediments (Fig. 1); chemical analyses of water included main ions determined by standard methods and isotopic analyses (δ18O, δ2H in water, and δ34S in dissolved sulfates). Interpretation of the results within the hydrogeological framework allowed to define the contamination degree and the As source and mobility. Water interaction with As-bearing minerals in the aquifer matrix releases As to the deep fractured limestone aquifer, while AMD from tailings and infiltration of As-enriched water from smelter stacks contaminated the shallow aquifer (Armienta et al. 2001; Sracek et al. 2010). At the Independencia basin, Guanajuato state, concentrations above drinking water

Fig. 1 Mine tailings at Zimapán, Mexico. Mining residues are one of the main anthropogenic sources of As in water in Latin America

standards have been measured in groundwater. A study to determine the processes involved in the geochemical evolution and mineralization of the area by means of chemical and isotopic (δ18O, 13C, 3H) analyses of groundwater, mineralogical determinations of rocks from boreholes by XRD, geochemical modeling (PHREEQC), and multivariate statistical analysis has been developed (Mahlknecht et al. 2004). Interpretation of the results led to the conclusion that weathering of rhyolites and oxidation of As-bearing minerals produce the high As and F concentrations. The concentrations, distribution, and source of As and F in the same basin were also investigated (Ortega-Guerrero 2009). The study included chemical (major and trace elements) and isotopic (δ18O, δ2H, 13C/14C, 3H) determinations interpreted in the hydrogeological framework. Hydrogeochemical and isotopic results indicated that As originates from the dissolution of silicates, while F is related to the dissolution of fluorite and silicates, thermal water, and a longer residence time of the water. The hydrogeological and geothermal factors related to the origin of As and F in another area of the Guanajuato state, at the Juventino Rosas municipality, were also studied (Morales-Arredondo et al. 2016). Interpretation of the results within the geological and hydrogeological framework using hydrogeochemical plots and statistical methods allowed to relate the water type with concentration ranges and circulation patterns of the groundwater. Rhyolite units appeared to be the most probable source of As and F. At Los Altos de Jalisco, western Mexico, mean As concentration in drinking water varied from 14.7 to 101.9 μg/L, with the highest values in the city of Mexticacán (262.9 μg/L). While most of the surface water has low As contents, the concentrations reach values above the WHO standard value in all sampled wells in the Los Altos de Jalisco towns (Hurtado-Jiménez and Gardea-Torresdey 2006).

2.12 Nicaragua

In the southwestern part of the Sébaco Valley, drinking water has been contaminated by As from geogenic sources (mainly weathering of Tertiary volcanic rocks). The valley is located at the eastern region of the Central American graben and is characterized by intensive tectonic stress, fracturing, presence of active and inactive faults, and hydrothermal alteration. Concentrations range from 10 to 122 μg/L. The high polluted well at El Zapote (As concentration, 1320 μg/L) was closed in 1996; arsenicosis was detected in people consuming that water for 2 years. The aquifer is used by several communities as drinking water source. Changes in redox conditions increase the As mobility. A study developed in 2004 showed that the northern zone of the country presented the highest As contents. In 2005, the presence of geogenic As was identified at San Juan de Limay (Bundschuh et al. 2012; Altamirano Espinoza and Bundschuh 2009; Armienta et al. 2010).

2.13 Peru

The presence of As has been detected at several sites in Peru, mainly in the Andean region, released by weathering and mining operations. The Locumba river and its tributaries contain up to 1680 μg/L. Volcanic rocks and pyroclastic materials release As in the area of the Yucamane volcano to the Collazas and Salado rivers. In the area of Puno, Andean highland As concentrations ranged from 140 to 230 μg/L in river water, mostly present as As(V). East of Lima City, the Rimac river basin has been contaminated by mining activities, leaching of volcanic rocks, and ore deposits. Concentrations present high temporal variations and reached up to 1630 μg/L in 2000 in Puente Santa Rosa (Bundschuh et al. 2012).

2.14 Uruguay

The presence of As (between 25 and 50 μg/L) was reported in the Raigón aquifer, at the southwestern part of the country. Arsenic source was related with the continental sediments containing volcanic ash, also occurring in the Santa Fe province in Argentina (Bundschuh et al. 2012; Guérèquiz et al. 2009). Concentrations below 10 μg/L were only measured in 6 out of 37 samples collected in the Raigón aquifer system since 2007 (Mañay et al. 2014). The importance of a multidisciplinary approach to assess the status of As in health and the environment in Uruguay has been remarked in this study.

3 Analytical Determination of Arsenic in Latin America

Due to the problems that can provoke the presence of As in quantities that can be toxic to human health, the study of the presence of the element and its derivative compounds, together with their quantification, has a great relevance. Arsenic is present in different matrices that impact the different geochemical spheres, i.e., lithosphere (rocks), pedosphere (soils), biosphere (living organisms), atmosphere (air), hydrosphere (water), and anthroposphere (man's effect on the other spheres) (Hounslow 1995). The chemical behavior of As will depend on environmental conditions such as acidity conditions, oxidation-reduction state, presence of iron, organic matter or other ligands (e.g., sulfur), etc. Due to the low concentrations at which As may be present in an environment and its chemical behavior, the selection of an adequate analytical technique will greatly depend on the objectives of the study, the access to the adequate analytical methodology, the cost of the analyses, and the matrix to be studied. The analyst should take all these factors into account when selecting a technique, ensuring a high degree of precision and accuracy, as well as high sensitivity, which allow reaching concentrations below the μg/L range.

The presence of As in the environment has not been regulated until lethal diseases appeared (e.g., skin, lung, bladder cancers). For this reason, permissible limits of As content in water have been established by environmental agencies, and different maximum limits for As in drinking water can exist in each country. These limits are revised and lowered periodically to prevent the serious consequences on the human health.

In this chapter, different analytical methods for the determination of As in different matrices are presented, mainly focused on the studies conducted in Latin American countries. This study is based on a bibliographic research; 167 scientific manuscripts and articles of the last 18 years have been considered. Table 1 shows the different analytical methodologies used for the analysis of As (total or speciation) in different matrices. Classical methods (e.g., atomic flame absorption) and the most advanced methodologies such as the micro-X-ray synchrotron method or electrochemical methods are presented. It includes different matrices of interest such as water, food (e.g., wine, milk, and rice), human fluids (urine and human hair), rock, plants and marine organisms, and natural and synthetic materials.

Figure 2 shows the number of analytical methodologies reported in Latin America for As determination. The data indicate that the most widely analytical technique is AAS (57%), specifically with the method of sample introduction through hydride generation (HG-AAS) (Table 1). The DL using HG-AAS is about 0.1–0.6 μg/L (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). This method has some advantages: the sensitivity and selectivity are improved, and the salinity of the sample does not influence the results (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). Additionally, the methodology is simple and only requires relatively inexpensive and very versatile instrumentation, with excellent detection power for total and iAs (Litter et al. 2009). Figure 2 also shows that the second most used analytical technique is ICP (26%), with emphasis in

Table 1 Methods applied for the determination of As in Latin American countries

	Analytical methodology	Country	Application	References
Electrochemical	ASV-(CAR-CPE)	Chile	Water	Núñez et al. (2018)
	ASV	Ecuador and Venezuela	Water	Carrera et al. (2017)
	AS-SWV	Argentina	Water	Robles et al. (2017)
	ASV	Chile	Water	Núñez et al. (2016)
	CSV	Brazil	Food	Teixeira et al. (2014)
	DPP	Chile	Water	Gamboa et al. (2013)
	SWCSV	Chile	Carrots, beets, and irrigation water	Arancibia et al. (2006)
	SWCSV	Brazil	Water	Barra and Correia dos Santos (2001)
Atomic absorption spectrometry	HG-AAS	Mexico	Thermal spring	Morales-Arredondo et al. (2018)
	HG-AAS	Mexico	Natural zeolitic sorbents	Velázquez-Peña et al. (2019)
	AAS	Mexico	Endophyte-free plants, *Methylobacterium* sp.-colonized plants	Alcántara-Martínez et al. (2018)
	HG-AAS	Brazil	Seawater	Dos Santos et al. (2018)
	HG-AAS	Mexico	Groundwater	Sandoval et al. (2018)
	HR-CS-GFAAS	Brazil-UK	Agricultural soil	Schneider et al. (2018)
	AEC-ICP-MS/ETAAS	Argentina	Olive oils	Torres et al. (2018)
	FIAS-HG-AAS	Argentina	Soil and water	Yáñez et al. (2018)
	GFAAS	Brazil	Natural waters	Alves et al. (2017)
	HG-AAS	USA and Mexico	Urine	Kordas et al. (2017)
	HG-AAS	Mexico	Human urine	López Guzmán et al. (2017)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	HG-AAS	Chile	Food	Muñoz et al. (2017)
	HG-AAS	Mexico	Groundwater	Navarro et al. (2017)
	IXED cell-HG-AAS	Mexico	Wastewater effluents and groundwater	Ortega et al. (2017)
	HG-AAS	Mexico	Soils	Rodríguez Garrido et al. (2017)
	FAAS	Mexico	Soils and plants	Salas-Luévano et al. (2017)
	HG-AAS	Mexico	Fungal biomass	Santos-Domínguez et al. (2017)
	HG-AAS	Mexico	Soils	Sariñana-Ruiz et al. (2017)
	HG-AAS	Mexico	Drinking and potable water, urine, and blood	Arcega-Cabrera and Fargher (2016)
	GFAAS	Mexico	Contaminated soils	Armienta et al. (2016)
	HPLC-HG-AFS	Argentina	Ionic liquids	Castro Grijalba et al. (2016)
	MSFIA-HG-AFS	Brazil	Peanuts	De Santana et al. (2016)
	GFAAS	Mexico-France	Arsenopyrite leachates	Lara René et al. (2016)
	HG-AAS	Brazil	Salmon fish	Oliveira et al. (2016)
	ETAAS	Argentina	Tap water	Peralta Ramos et al. (2016)
	HR-CS-GFAAS	Brazil-UK-Chile	Fish oil	Pereira et al. (2016)
	CPE-HG-AFS	Mexico-Spain	Corn and rice	Rosas-Castor et al. (2016)
	FI-HG-AAS	Argentina	Food samples	Sigrist et al. (2016)
	HPLC-HG-AAS	Mexico	Urine	Torres-Sánchez et al. (2016)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	HG-AAS/ HPLC-HG-ICPMS	Uruguay	Human urine	Bühl et al. (2015)
	EcHG-AAS	Ecuador, Venezuela	Marine sediment	Caiminagua et al. (2015)
	MSFIA-HG-AFS	Mexico-Spain	Agricultural soil	Rosas-Castor et al. (2015)
	ETAAS	Argentina	Water	Castro Grijalba et al. (2015)
	AC-modified KR-ETAAS	Argentina	Medicinal herbs and tea infusions	Castro Grijalba et al. (2015)
	CPE-ETAAS	Brazil	Rice samples	Dos Santos Costa et al. (2015)
	HG-AAS	Mexico	Groundwater	Esteller et al. (2015)
	HG-AAS	Mexico	Groundwater	Morales et al. (2015)
	HG-AAS	Mexico	Water from shallow anddeep wells, irrigation canals and geothermalproduction wells	Armienta et al. (2014)
	HG-AAS	Mexico	Surface waters	Dótor Almazán et al. (2014)
	HG-AAS	Argentina	Human urine	Navoni et al. (2014)
	HG-AAS	Argentina	Water and human urine	De Pietri et al. (2014)
	HG-AFS/IC-HG-AFS	Mexico	Agricultural soil and maize crops	Rosas-Castor et al. (2014)
	Wagtech Arsenator field kit /HG-AAS	Mexico	Water	Avilés et al. (2013)
	HG-AAS	Ecuador	Milk	Ayala and Romero (2013)
	ETAAS	Argentina	Wine	Escudero et al. (2013)
	HG-AAS	Mexico	Soils	Hernández Ordáz et al. (2013)
	HG-AAS	Mexico	Mining acid leachates	Labastida et al. (2013)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	AAS	Mexico	Rocks, sediments and groundwater	Reyes-Gómez et al. (2013)
	Total As: FI-HG-AAS. As speciation: SPE-FI-HG-AAS	Argentina	Water	Sigrist et al. (2013)
	ETAAS	Mexico	Sediment	Álvarez María and Carrillo (2012)
	HG-AAS	Mexico	Tailing deposit	Armienta et al. (2012)
	FI-HG-AAS	Chile and Spain	Algae	Díaz et al. (2012)
	HG-AAS	Mexico	River water	Méndez-Ramírez and Armienta Hernández (2012)
	HG-AAS	Uruguay	Water	Pistón et al. (2012)
	FIAS-HG-AAS	Mexico	Plants, soils, and mine tailings	Ruiz Huerta and Armienta (2012)
	SIA-HPLC-AFS	Brazil	Seafood	Jesus et al. (2011)
	IP-HPLC-HG-AFS	Argentina	Animal feed additives	Monasterio et al. (2011)
	HG-AAS	Mexico	Urine, blood, and bottled water	Rocha-Amador et al. (2011)
	SPE-FI-HG-AAS	Argentina	Groundwater	Sigrist et al. (2011)
	FIAS-HG-AAS	USA and Mexico	Urine	Roy et al. (2011)
	AAS	Mexico-Germany	Geothermal and petroleum reservoir fluids	Birkle et al. (2010)
	HG-CT-AAS	Mexico	Clays	Cervini-Silva et al. (2010)
	HG-AFS	Spain and Brazil	Vegetables, pulses, and cereals	Matos-Reyes et al. (2010)
	HG-AAS/ICPOES	Brazil	Humic acids	Menezes and Maia (2010)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	ETAAS	Argentina	Natural waters	Monasterio and Wuilloud (2010)
	HG-AAS	Argentina	Urine	Navoni et al. (2010)
	HG-AAS	Mexico	Urine	Moreno et al. (2010)
	HG-AFS	Mexico	Urine and drinking water	Salgado-Bustamante et al. (2010)
	FI-HG-AAS	Argentina	Milk	Sigrist et al. (2010)
	FIAS-HG-AAS	USA and Mexico	Shallow wells and shallow river	Sracek et al. (2010)
	HG-AAS	Mexico	Surface sediments	Villalobos-Castañeda et al. (2010)
	AE-FI-HG-AAS/ IC-FI-HG-AAS	Peru	Water	Chávez (2009)
	GFAAS	Mexico	River sediments	Espinosa et al. (2009)
	HG-AAS	Brazil	Phosphate fertilizers and phosphate rocks	Macedo et al. (2009)
	HG-AAS	Mexico	Groundwater	Armienta and Segovia (2008)
	ETAAS	Chile	Marine food	Bruhn et al. (2007)
	BDES-FI-ETAAS	Brazil-Spain	Water	Coelho et al. (2007)
	FIAS-AAS	Brazil	Food	de Souza et al. (2007)
	FI-HG-AAS	Mexico	Water, urine	Valenzuela et al. (2007)
	HG-AAS	Chile	Human urine	Cáceres et al. (2005)
	HG-AAS	Argentina	Water	Martínez and Gazquez (2005)
	ETAAS	Brazil	Petroleum products	Reboucas et al. (2005)
	GFAAS-XRFS	Argentina	Deep and shallow groundwater	García et al. (2004)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	HG-AAS	Mexico	Soil, stream sediment, surface water, and groundwater	Razo et al. (2004)
	HG-AAS	Mexico	Water	Rodríguez et al. (2004)
	LC-UV-HG-AFS	France-Chile	Certified reference fish tissue and sea food samples	Simona et al. (2004)
	GFAAS	Brazil	Environmental samples (sludges, soils, sediments, coal, ashes, and waters)	Lima et al. (2003)
	HG-AAS	Cuba	Water	Quevedo et al. (2003)
	HG-AAS	Brazil	Sediments, coal, and fly ash slurries	Antunes et al. (2002)
	ETAAS	Brazil	Petroleum refinery aqueous streams	Cassella et al. (2002)
	HG-AAS	Mexico	Cooked food and water	Del Razo et al. (2002)
	FI-HG-AAS	Venezuela	Water	Carrero et al. (2001)
	HG-AAS	Brazil	Hair	De Moraes et al. (2001)
	HG-AAS	Germany and Mexico	Groundwater	Planer-Friedich et al. (2001)
	FI-HG-AFS	Chile	Environmental solid reference materials	Vergara Gallardo et al. (2001)
X-ray fluorescence spectrometry	Microwave-assisted distillation-HG-AFS	Brazil	Soils	Barra et al. (2000)
	XRFS	Mexico	Plants	Gómez-Bernal et al. (2018)
	XRFS	Argentina	Water	Aranda et al. (2016)
	XRFS	Chile	Rock	Sepúlveda et al. (2015)
	XFRS	Mexico and UK	Plants and soils	Gómez-Bernal et al. (2014)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	XRFS	Mexico-Bolivia-Spain	Tailings (mine wastes)	Martín et al. (2014)
	Synchrotron micro-X-ray	Mexico	Soil	López-Zepeda et al. (2008)
	XRFS	Brazil	Water	Zucchi et al. (2005)
	XRFS-CSV	Cuba	Water	Valcárcel et al. (2008)
Inductively coupled plasma spectrometry	ICPMS	Argentina	Soil, water, grapevine, and onion	Funes Pinter et al. (2018)
	LC-ICPMS	Mexico and USA	Urine	Quiller et al. (2018)
	HG-MP-AES	Mexico	Forest	Roque-Álvarez et al. (2018)
	HPLC-ICPMS	Brazil	Iron supplements	Araujo-Barbosa et al. (2017)
	ICPOES	Mexico	Soil, irrigation water, and maize samples	Ruíz Huerta et al. (2017)
	ICPMS	USA-Mexico	Urine and water	Cárdenas-González et al. (2016)
	HPLC-ICPMS	Mexico	Human urine	López-Carrillo et al. (2016)
	HG-ICPOES	Mexico	Tap water	Martínez-Acuña et al. (2016)
	ICPOES	Argentina	Tailings (mine wastes)	Nieva et al. (2016)
	LC-ICPMS	Chile and Spain	Carrots (*Daucus carota*), beets (*Beta vulgaris*), and quinoa (*Chenopodium*)	Pizarro et al. (2016)
	MPAES	Mexico	Pure arsenopyrite crystals	Ramírez-Aldaba et al. (2016)
	Total As: ICPMS; As speciation: HPLC-ICP-MS	Brazil	Rice samples	Segura et al. (2016)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	ICPOES	Brazil-Mexico	Tropical peat	de Oliveira et al. (2015)
	ICPMS	Argentina	Biofilm	Rodríguez Castro et al. (2015)
	HPLC-ICPMS	Brazil	Plants	Amaral et al. (2014)
	ICPOES/HG-ICPMS	Chile-USA	Water from hydrothermal transect and sediments	Leiva et al. (2014)
	HPLC-ICPMS	Chile	Human urine	Muñoz et al. (2014)
	ICPOES	Bolivia	Superficial and underground water	Ormachea and Quintanilla (2014)
	ICPMS	México	Water	Martínez-Villegas et al. (2013)
	LC-ICPMS	Brazil	Tissues of bivalve mollusks	Santos et al. (2013)
	Arsenic in water samples was analyzed by ICPMS, and in rocks a sediment was determined by HG-AAS	Mexico	Hydrothermal manifestations, seawater, and sediments	Villanueva-Estrada et al. (2013)
	ICPAES	Mexico	As adsorption by anchor iron nanoparticles onto activated carbon from groundwater	Vitela-Rodriguez and Rangel-Mendez (2013)
	ICPAES	Mexico	Tailings and plants	Santos-Jallath et al. (2012)
	ETV-ICPMS	Brazil	Biological tissue samples	Tormen et al. (2012)
	ICPAES	Mexico	Wetlands	Zurita et al. (2012)
	HPLC-ICPMS	Brazil	Rice samples	Batista et al. (2011)
	LC-ICPMS	Brazil and Germany	Wine	Moreira et al. (2011)
	ICPAES	Mexico	Acid mine leachates	Romero et al. (2011)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	LA-ICPMS	Chile	Hair	Arriaza et al. (2010)
	ICPOES	Brazil	Plants	Melo et al. (2010)
	ICPOES	Argentina	Algae	Pérez et al. (2010)
	ICPOES	Mexico and Cuba	Sulfide-rich waste rocks, surface water, and streambed sediments	Romero et al. (2010)
	ICPOES	Argentina	Groundwater and humic acids	Morgada et al. (2009)
	Total As; ICPOES, iAs: HG-AAS	Argentina and Spain	Macroalgae	Farías et al. (2007)
	EVA column/ HG-ICPOES	Argentina	Water	Gil et al. (2007)
	INAA/ICPOES	USA-Mexico	Soils	Ongley et al. (2007)
	ICPAES	Mexico	Tailings (mine wastes)	Romero et al. (2007)
	LC-ICPMS	USA and Argentina	Algae	Wuilloud et al. (2006)
	ICPMS	Bolivia	Hair, urine, and unfiltered water	Archer et al. (2005)
	HPLC-ICPMS	Brazil-Spain	Beverages (beer, soft drink, and juices)	Coelho et al. (2005)
	HPLC-HG-ICPMS	Chile and USA	Human hair	Yáñez et al. (2005)
	ICPMS	Mexico	Mine tailings	Armienta et al. (2003)
	HG-ICPOES	Argentina	Groundwater	Farías et al. (2003)
	HG-ICPMS	Brazil	Water and plants	Menegário and Gin (2000)
UV-VIS spectrometry	Colorimetry	Mexico	Groundwater	Saldaña-Robles et al. (2018)
	Colorimetry (digital arsenic test kit)	Mexico	Water	Contreras et al. (2017)
	UV-VIS spectrophotometry	Cuba	Water	Ramírez-González et al. (2017)
	Colorimetry	Mexico	Arsenic removal from irrigation water	Saldaña-Robles et al. (2017)

(continued)

Table 1 (continued)

	Analytical methodology	Country	Application	References
	SIA-UV-VIS spectrophotometry	Mexico	Mine tailings	Ramírez Cordero and Cañizares-Macías (2009)
	UV-VIS spectrophotometry	Mexico	Water	Pérez Moreno et al. (2002)
	UV-VIS spectrophotometry	Mexico	Hair	Armienta et al. (1997)
	UV-VIS spectrophotometry	Mexico	Well water	Gómez-Arroyo et al. (1997)
Others	INAA	Chile	Hair	Echeverría et al. (2018)
	Surface plasmon resonance nanosensor	Colombia	Water	Salinas et al. (2014)
	ARSOlux Biosensor	Germany-Argentina	Groundwater	Siegfried et al. (2015)

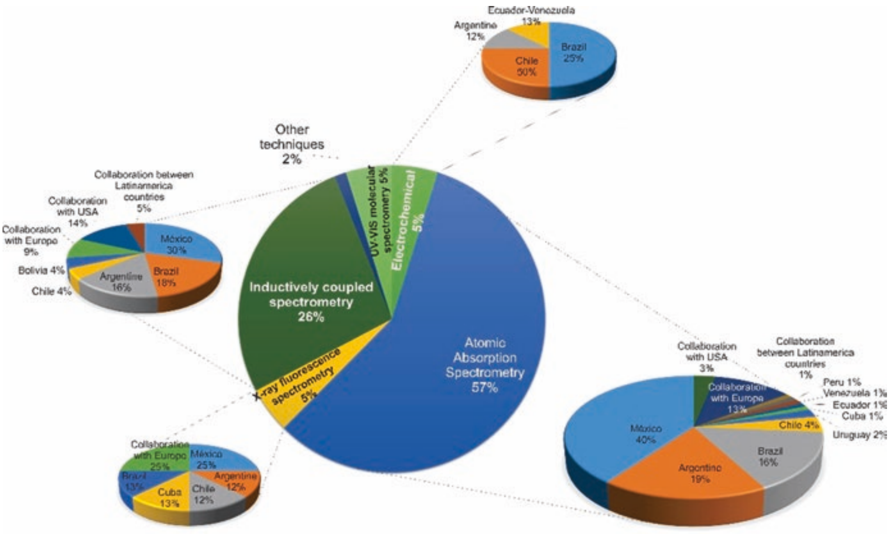

Fig. 2 Analytical instrumentation reported in Latin America for As determination

ICPMS (Table 1). The DL reached by this methodology is 0.1 μg/L, and there is no need of preconcentrating the sample (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). In general, ICP-MS and ICP-OES are robust and sensitive techniques, but they require very expensive equipment, special facilities, and a long and complex training of analysts (Litter et al. 2009). Figure 2 indicates that electrochemical analytical methods are the third most applied methodologies (5%). This method has a high analytical sensitivity, has a low cost, and is easy to use, with a concentration interval between 0.1 and 300 μg/L by anodic voltammetry (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). Chile, Brazil, Argentine, Ecuador, and Venezuela reported the use of electrochemical methodologies for the determination of As mainly in water and food samples (Table 1). The fourth most used method (5%) is UV-VIS molecular spectroscopy. The methods based on this analytical methodology are simple and economical; however, although the sensitivity is high (10–50 μg/L), the accuracy is low (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). Mexico and Cuba are the main countries that reported the use of this methodology for As determination in water and in samples of mine tailings (Table 1).

Regarding speciation, the two most widely methodologies used in Latin America are AAS and ICP spectroscopy combined with separation techniques (chromatography), which has led to the use of hyphenated methodologies (Table 1). These coupled techniques are the best options for the determination of arsenical species, due to their selectivity, their adequate precision, their high level of automation, and their relatively short response (Litter et al. 2009).

XRF spectrometry is mainly used for the identification and determination of As in solid samples. In quartziferous sands, the DL reaches 40 mg/kg (without interferences). Portable equipments can detect up to 60 mg/kg (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). According to reference (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018), the future of this technique, regarding the determination of As in waters at the trace level, will be focused mainly through the development of preconcentration methodologies adaptable to laboratory equipment and to on-site determination.

Other methodologies are the instrumental neutron activation analysis (INAA) (Echeverría et al. 2018) and surface plasmon resonance nanosensor (SPRN) (Salinas et al. 2014). INAA is an accurate and sensitive methodology; it has been used for the determination of total As in biological samples (nail, hair, and other tissues), with a DL of 0.001 μg/g (Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua 2018). It is important to remark that SPRN is an autonomous sensor for mapping and monitoring As concentrations in water (Salinas et al. 2014). This system can be integrated to a portable suitcase, it is of low cost, and it is able to measure As concentrations below 5 μg/L. However, this method has been not yet applied to real cases. The ARSOlux sensor (Siegfried et al. 2015) is a novel method for field measurements of As in groundwater. This biosensor is a robust and accurate method for the detection of total bioavailable As concentrations and uses a lyophilizate containing a bioreporter bacteria strain.

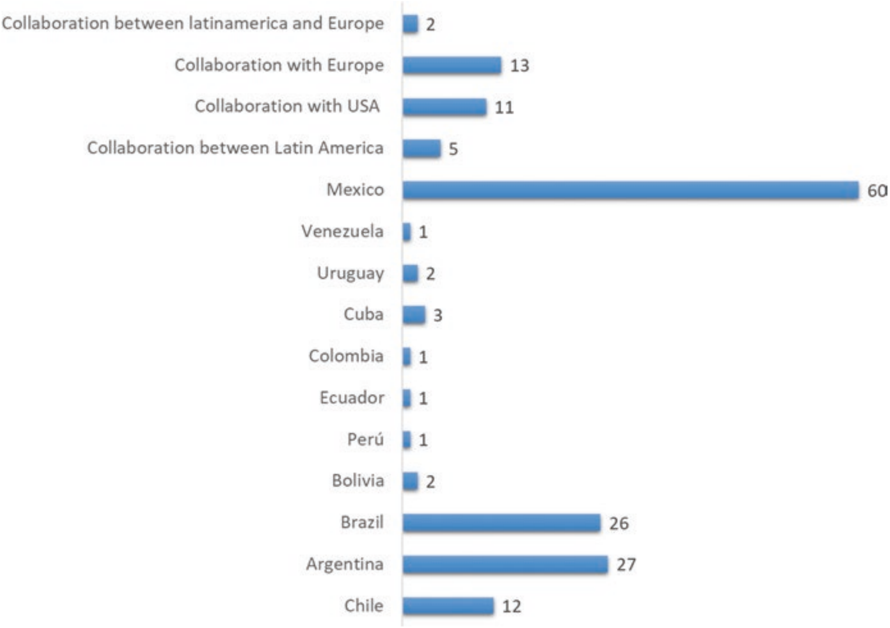

Fig. 3 Number of scientific articles on As analytical methods published by country

Chemical speciation is an area of great importance for assessing the impact of As to evaluate its toxicity and bioavailability. In addition, the technological advance on development of analytical methods in the last two decades has allowed the application of chemical speciation. Chemical speciation is the qualitative and quantitative determination of the different chemical forms in which an element is present under environmental conditions. Some reviews are focused on the preparation of the sample for the chemical speciation of As analytical determination in terrestrial plants through different analytical methodologies (Amaral et al. 2013). A review on chemical analysis and speciation of traces of As in the environment, food, and industrial samples, mainly by the voltammetry technique, has been also published (Cavicchioli et al. 2004). An important review on the different techniques of extraction and derivatization for the chemical speciation of As can be found in the literature (Vieira et al. 2009).

Figure 3 shows the number of scientific articles related to analytical methods for As determination reported in Latin America. The data indicates that Mexico is the country reporting the largest number of studies (Table 1).

Several studies have been conducted in a joint collaborative way between Latin American and European countries (Spain, Germany, the UK, and France) focused on analytical aspects (Fig. 4).

Collaborative works between the United States and Latin American countries regarding analytical methods for As are also reflected in scientific articles (Fig. 5). Mexico, Chile, and Argentina are the main countries collaborating with the United States.

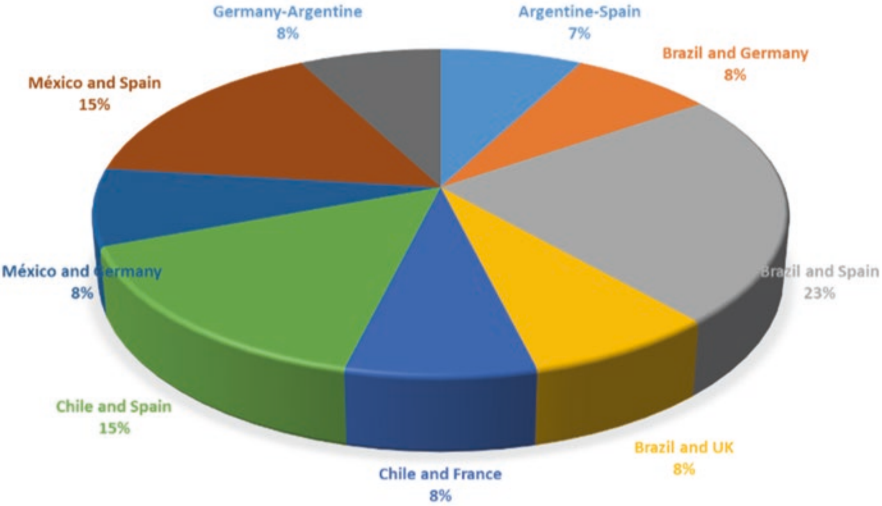

Fig. 4 Collaborative works between Latin America and Europe on development and application of analytical methodologies for As determination

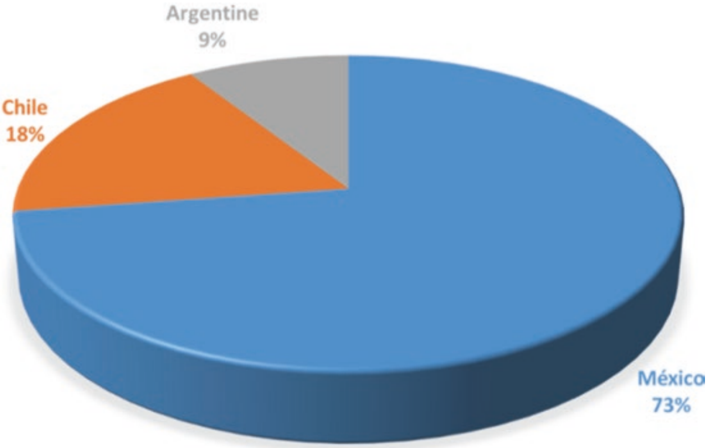

Fig. 5 Collaborative works between Latin America and the United States on development and application of analytical methodologies for As determination

4 Conclusions

Arsenic is present in many aquifers and several superficial water bodies in most of the Latin American countries. Scientific publications related with As occurrence were identified in 13 out of the 19 countries considered in this review. This fact does not imply that concentrations of As above international or national drinking water standards are not present in the rest of the countries. The Chaco-Pampean plain in Argentina is the largest area affected by As contamination in groundwater. Occurrence, sources, geochemical, and mobilization processes of As, including hydrogeological influence, have been studied in diverse parts of this area. Research covering these aspects has also been developed in other countries such as Mexico, Chile, Bolivia, Peru, and Nicaragua. The origin of As in water has been identified in almost all the countries considered in this chapter. In most of the contaminated areas, As originates from geogenic sources, mainly volcanic rocks, hydrothermal fluids, and As-bearing minerals. However, anthropogenic sources are also present in certain zones, most of them as a result of mining operations and, in some cases, related with agriculture. Mining is indeed the main As source in Brazil. Physicochemical characteristics of the water, including pH and Eh, and presence of other ions influence the mobilization of As. Besides, hydrogeological conditions such as lack of flushing, evaporation, and flow-paths related with the tectonic setting also influence the occurrence of As contamination. Although As speciation has only been determined in some areas, it has been found to be mainly as As(V) in those locations. In all Latin American countries, more research has still to be conducted to determine As concentrations and speciation in all water bodies used as drinking water source and to unravel its origin and mobilization processes. This information is essential to develop adequate solutions to avoid the population exposure to this toxic element.

Regarding analytical methods on As determination in Latin American countries, 167 papers in scientific journals have been identified in the last 18 years. The most widely analytical methodology used for As determination is AAS (57%), specifically HG-AAS. The second most used analytical technique is ICP (26%), mainly coupled with MS. Regarding electrochemical methods, Chile, Brazil, and Argentina are the Latin American countries that have published on this topic. Although UV-VIS spectrometry is the least used methodology (5%), it has been employed mainly in Cuba and Mexico, with three reports in 2017 and one in 2018. XRF spectrometry is mainly used for the identification and determination of As in solid samples, and it has been mainly used in Mexico, Cuba, Brazil, Argentina, and Chile. The 2% of other techniques used are INAA and SPRN, with reported studies on As determination in hair and water by Chile in 2018 and Colombia in 2014, respectively. A third novel methodology, ARSOlux Biosensor, developed between Argentine and Germany, is useful for determination of total bioavailable As concentrations in groundwater. Meanwhile, the SPRN technique is at test stage and is used for solid samples.

With respect to scientific publications focused on the analysis of As, it can be concluded that:

- Mexico, Brazil, Argentina, and Chile are the countries presenting the largest number of scientific publications.
- The collaboration between Latin America and Europe is mainly with Spain, Germany, the UK, and France.
- Mexico, Chile, and Argentine are the main countries that have published in collaboration with the United States.

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References

Alarcón-Herrera MT, Bundschuh J, Nath B, Nicolli HB, Gutierrez M, Reyes-Gomez VM, Nunez D, Martín-Dominguez IR, Sracek O (2013) Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: genesis, mobility and remediation. J Hazard Mater 262:960–969

Alcántara-Martínez N, Figueroa-Martínez F, Rivera-Cabrera F, Gutiérrez-Sánchez G, Volke-Sepúlveda T (2018) An endophytic strain of *Methylobacterium* sp. increases arsenate tolerance in *Acacia farnesiana* (L.) Willd: a proteomic approach. Sci Total Environ 625:762–774

Alonso DL, Latorre S, Castillo E, Brandão PFB (2014) Environmental occurrence of arsenic in Colombia: a review. Environ Pollut 186:272–281

Altamirano Espinoza M, Bundschuh J (2009) Natural arsenic groundwater contamination of the sedimentary aquifers of southwestern Sébaco valley, Nicaragua. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 109–122

Álvarez María A, Carrillo G (2012) Simultaneous determination of arsenic, cadmium, copper, chromium, nickel, lead and thallium in total digested sediment samples and available fractions by electrothermal atomization atomic absorption spectroscopy (ETAAS). Talanta 97:505–512

Alves VN, Neri TS, Borges SSO, Carvalho DC, Coelho NMM (2017) Determination of inorganic arsenic in natural waters after selective extraction using *Moringa oleífera* seeds. Ecol Eng 106:431–435

Amaral CDB, Nóbrega JA, Noguiera ARA (2013) Sample preparation for arsenic speciation in terrestrial plants – a review. Talanta 115:291–299

Amaral CDB, Nóbrega JA, Nogueira ARA (2014) Investigation of arsenic species stability by HPLC-ICP-MS in plants stored under different conditions for 12 months. Microchem J 117:122–126

Amaro AS, Venecia Herrera BC, Lictevout E (2014) Spatial distribution of arsenic in the region of Tarapacá, Northern Chile. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 54–55

Antunes VM, Welz B, Curtius AJ (2002) Determination of arsenic in sediments, coal and fly ash slurries after ultrasonic treatment by hydride generation atomic absorption spectrometry and trapping in an iridium-treated graphite tube. Spectrochim Acta Part B 57:2057–2067

Arancibia V, López A, Zuñiga MC, Segura R (2006) Extraction of arsenic as the diethyl dithiophosphate complex with supercritical fluid and quantitation by cathodic stripping voltammetry. Talanta 68:1567–1573

Aranda PR, Llorens I, Perino E, De Vito I, Raba J (2016) Removal of arsenic (V) ions from aqueous media by adsorption on multiwall carbon nanotubes thin film using XRF technique. Environ Nanotechnol Monit Manag 5:21–26

Araujo-Barbosa U, Peña-Vazquez E, Barciela-Alonso MC, Costa Ferreira SL, Pinto dos Santos AM, Bermejo-Barrera P (2017) Simultaneous determination and speciation analysis of arsenic and chromium in iron supplements used for iron-deficiency anemia treatment by HPLC-ICP-MS. Talanta 170:523–529

Arcega-Cabrera F, Fargher LF (2016) Education, fish consumption, well water, chicken coops, and cooking fires: using biogeochemistry and ethnography to study exposure of children from Yucatan, Mexico to metals and arsenic. Sci Total Environ 568:75–82

Archer J, Hudson-Edwards KA, Preston DA, Howarth RJ, Linge K (2005) Aqueous exposure and uptake of arsenic by riverside communities affected by mining contamination in the Río Pilcomayo basin, Bolivia. Min Mag 69:719–736

Argos M, Kalra T, Pierce BL, Chen Y, Parvez F, Islam T, Ahmed A, Hasan R, Hasan K, Sarwar G, Levy D, Slavkovich V, Graziano JH, Rathouz PJ, Ahsan H (2011) A prospective study of arsenic exposure from drinking water and incidence of skin lesions in Bangladesh. Am J Epidemiol 174:185–194

Armienta MA, Segovia N (2008) Arsenic and fluoride in the groundwater of Mexico. Environ Geochem Health 30:345–353

Armienta MA, Rodríguez R, Cruz O (1997) Arsenic content in hair of people exposed to natural arsenic polluted groundwater at Zimapán, México. Bull Environ Contam Toxicol 59:583–589

Armienta MA, Villaseñor G, Rodriguez R, Ongley LK, Mango H (2001) The role of arsenic-bearing rocks in groundwater pollution at Zimapán Valley, México. Environ Geol 40:571–581

Armienta MA, Talavera O, Morton O, Barrera M (2003) Geochemistry of metals from Mine Tailings in Taxco, Mexico. Bull Environ Contam Toxicol 71:387–393

Armienta MA, Rodríguez R, Segovia N, Monteil M (2010) Medical geology in Mexico, Central America and the Caribbean. In: Selinus O, Finkelman RB, Centeno JA (eds) Medical geology a regional synthesis. Springer, New York, pp 59–78

Armienta MA, Villaseñor G, Cruz O, Ceniceros N, Aguayo A, Morton O (2012) Geochemical processes and mobilization of toxic metals and metalloids in an As-rich base metal waste pile in Zimapán, Central Mexico. Appl Geochem 27:2225–2237

Armienta MA, Rodríguez R, Ceniceros N, Cruz O, Aguayo A, Morales P, Cienfuegos E (2014) Groundwater quality and geothermal energy. The case of Cerro Prieto geothermal field, México. Renew Energy 63:236–254

Armienta MA, Mugica V, Reséndiz I, Gutierrez AM (2016) Arsenic and metals mobility in soils impacted by tailings at Zimapán, México. J Soils Sediments 16:1267–1278

Arriaza B, Amarasiriwardena D, Cornejo L, Standen V, Byrne S, Bartkus L, Bandak B (2010) Exploring chronic arsenic poisoning in pre-Columbian Chilean mummies. J Archaeol Sci 37:1274–1278

Arsénico en agua, informe Grupo Ad-Hoc Arsénico en agua (2018) Red de Seguridad Alimentaria, CONICET. https://www.rsa.conicet.gov.ar/wp-content/uploads/2018/08/Informe-Arsenico-en-agua-RSA.pdf. Accessed Oct 2018

Avilés M, Garrido SE, Esteller MV, De La Paz JS, Najera C, Cortés J (2013) Removal of groundwater arsenic using a household filter with iron spikes and stainless steel. J Environ Manag 131:103–109

Ayala AJ, Romero BH (2013) Presencia de metales pesados (arsénico y mercurio) en leche de vaca al sur de Ecuador. LA GRANJA. Rev Cienc Vida 17:36–46

Barra CM, Correia dos Santos MM (2001) Speciation of inorganic arsenic in natural waters by square-wave cathodic stripping voltammetry. Electroanalysis 13:1098–1104

Barra CM, Cervera ML, De la Guardia M, Erthal Santelli R (2000) Atomic fluorescence determination of inorganic arsenic in soils after microwave-assisted distillation. Anal Chim Acta 407:155–163

Batista BL, Souza JMO, De Souza SS, Barbosa F Jr (2011) Speciation of arsenic in rice and estimation of daily intake of different arsenic species by Brazilians through rice consumption. J Hazard Mater 191:342–348

Bhattacharya P, Claesson M, Bundschuh J, Sracek O, Fagerberg J, Jacks G, Martin RA, Storniolo A, Thir JM (2006) Distribution and mobility of arsenic in the Rio Dulce alluvial aquifers in Santiago del Estero Province. Sci Total Environ 358:97–120

Bidone ED, Castillos ZC, Santos MCB, Silva RSV, Cesar RG, Ferreira M (2014) Arsenic levels in natural and drinking waters from Paracatu, MG, Brazil. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 162–164

Birkle P, Bundschuh J, Sracek O (2010) Mechanisms of arsenic enrichment in geothermal and petroleum reservoirs fluids in Mexico. Water Res 44:5605–5617

Blanes PS, Buchamer EE, Giménez MC (2011) Natural contamination with arsenic and other trace elements in groundwater of the Central–West region of Chaco, Argentina. J Environ Sci Health, A 46:1197–1207

Boochs PW, Billib M, Gutiérrez C, Aparicio J (2014) Groundwater contamination with arsenic, Región Lagunera, México. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 132–134

Bruhn CG, Bustos CJ, Sáez KL, Neira JY, Álvarez SE (2007) A comparative study of chemical modifiers in the determination of total arsenic in marine food by tungsten coil electrothermal atomic absorption spectrometry. Talanta 71:81–89

Bühl V, Álvarez C, Kordas K, Pistón M, Mañay N (2015) Development of a simple method for the determination of toxicologically relevant species of arsenic in urine using HG-AAS. J Environ Pollut Human Health 3:46–51

Bundschuh, J., Pérez-Carrera, A., Litter, M. 2008. Distribución del arsénico en las regiones Ibérica e Iberoamericana. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo

Bundschuh J, Litter M, Ciminelli V, Morgada ME, Cornejo L, Garrido Hoyos S, Hoinkis J, Alarcón-Herrera MT, Armienta MA, Bhattacharya P (2010) Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Iberoamerica – a critical analysis. Water Res 44:5828–5845

Bundschuh J, Litter MI, Parvez F, Román-Ross G, Nicolli HB, Jiin-Shuh J, Chen-Wuing L, López D, Armienta MA, Guilherme LRG, Gomez Cuevas A, Cornejo L, Cumbal L, Toujaguez R (2012) One century of arsenic exposure in Latin America: a review of history and occurrence from 14 countries. Sci Total Environ 429:2–35

Cáceres DD, Pino P, Montesinos N, Atalah E, Amigo H, Loomis D (2005) Exposure to inorganic arsenic in drinking water and total urinary arsenic concentration in a Chilean population. Environ Res 98:151–159

Caiminagua A, Fernández L, Romero H, Lapo B, Alvarado J (2015) Electrochemical generation of arsenic volatile species using a gold/mercury amalgam cathode, determination of arsenic by atomic absorption spectrometry. Anal Chem Res 3:82–88

Cárdenas-González M, Osorio-Yáñez C, Gaspar-Ramírez O, Pavković M, Ochoa-Martínez A, López-Ventura D, Medeiros M, Barbier OC, Pérez-Maldonado IN, Sabbisetti VS, Bonventre JV, Vaidya VS (2016) Environmental exposure to arsenic and chromium in children is associated with kidney injury molecule-1. Environ Res 150:653–662

Carrera P, Espinoza-Montera PJ, Fernández L, Romero H, Alvarado J (2017) Electrochemical determination of arsenic in natural waters using carbon fiber ultra-microelectrode modified with gold nanoparticles. Talanta 166:198–206

Carrero P, Malave A, Burguera JL, Burguera M, Rondon C (2001) Determination of various arsenic species by flow injection hydride generation atomic absorption spectrometry: investigation of the effects of the acid concentration of different reaction media on the generation of arsines. Anal Chim Acta 438:195–204

Cassella RJ, de Sant'Ana OD, Santelli RE (2002) Determination of arsenic in petroleum refinery streams by electrothermal atomic absorption spectrometry after multivariate optimization based on Doehlert design. Spectrochim Acta B 57:1967–1978

Castro Grijalba A, Escudero LB, Wuilloud RG (2015) Capabilities of several phosphonium ionic liquids for arsenic species determination in water by liquid–liquid microextraction and electrothermal atomic absorption spectrometry. Anal Methods 7:490–499

Castro Grijalba A, Fiorentini EF, Martinez LD, Wuilloud RG (2016) A comparative evaluation of different ionic liquids for arsenic species separation and determination in wine varietals by liquid chromatography – hydride generation atomic fluorescence spectrometry. J Chromat A 1462:44–54

Cavicchioli A, La-Scalea M, Gutz IGR (2004) Analysis and speciation of traces of arsenic in environmental, food and industrial samples by voltammetry: a review. Electroanalysis 16:697–711

Cebrián ME, Albores A, García-Vergas G, Del Razo LM (1994) Chronic arsenic poisoning in humans: the case of Mexico. In: Nriagu JO (ed) Arsenic in the environment part II. Wiley, New York, pp 93–107

Cervini-Silva J, Hernández-Pineda J, Rivas-Valdés MT, Cornejo-Garrido H, Guzmán J, Fernández-Lomelín P, Del Razo LM (2010) Arsenic (III) methylation in betaine–nontronite clay–water suspensions under environmental conditions. J Hazard Mater 178:450–454

Chávez M (2009) Evaluación de dos técnicas analíticas para la especiación de arsénico en aguas superficiales del sur del Perú. Rev Peru Med Exp 26:20–26

Coelho NMM, Coelho LM, De Limac ES, Pastord A, De la Guardia M (2005) Determination of arsenic compounds in beverages by high-performance liquid chromatography-inductively coupled plasma mass spectrometry. Talanta 66:818–822

Coelho LM, Coelho NMM, Arruda MAZ, De la Guardia M (2007) On-line bi-directional electrostacking for As speciation/preconcentration using electrothermal atomic absorption spectrometry. Talanta 71:353–358

Contreras S, Henríquez-Vargas L, Álvarez PI (2017) Arsenic transport and adsorption modeling in columns using a copper nanoparticles composite. J Water Proc Eng 19:212–219

Cumbal LH, Bundschuh J, Aguirre V, Murgueitio E, Tipán I, Chávez C (2009) The origin of arsenic in sediments from Papallacta lake area in Ecuador. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 81–90

De Moraes FÉM, Cirne da Silva LL, Smanioto BJ, Fleig Saidelles AP, Zanella VR, Dressler L, Gottfried Paniz JN (2001) Minimization of volatile nitrogen oxides interference in the determination of arsenic by hydride generation atomic absorption spectrometry. Spectrochim Acta Part B 56:1883–1891

de Oliveira LK, Melo CA, Goveia D, Lobo FA, Armienta Hernández MA, Fraceto LF, Rosa AH (2015) Adsorption/desorption of arsenic by tropical peat: influence of organic matter, iron and aluminium. Environ Technol 36:149–159

De Pietri DE, Navoni JA, Olmos V, Giménez C, Bovi Mitre G, de Titto E, Villaamil Lepori EC (2014) Geospatial human health risk assessment in an Argentinean region of hydroarsenicism. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, Taylor and Francis Group, London, pp 597–601

De Santana FA, Portugal LA, Serra AM, Ferrer L, Cerdà V, Ferreira SLC (2016) Development of a MSFIA system for sequential determination of antimony, arsenic and selenium using hydride generation atomic fluorescence spectrometry. Talanta 156–157:29–33

de Souza SVC, Pinto CT, Junqueira RG (2007) In-house method validation: application in arsenic analysis. J Food Compos Anal 20:241–247

Del Razo LM, Garcia-Vargas GG, Garcia-Salcedo J, Sanmiguel MF, Rivera M, Hernández MC, Cebrian ME (2002) Arsenic levels in cooked food and assessment of adult dietary intake of arsenic in the Region Lagunera, Mexico. Food Chem Toxicol 40:1423–1431

Díaz O, Tapia Y, Muños O, Montoro R, Velez D, Almela C (2012) Total and inorganic arsenic concentrations in different species of economically important algae harvested from coastal zones of Chile. Food Chem Toxicol 50:744–749

Dos Santos Costa BE, Melo Coelho NM, Melo Coelho L (2015) Determination of arsenic species in rice samples using CPE and ETAAS. Food Chem 178:89–95

Dos Santos QO, Silva Junior MM, Lemos VA, Ferreira SLC, de Andrade JB (2018) An online preconcentration system for speciation analysis of arsenic in seawater by hydride generation flame atomic absorption spectrometry. Microchem J 143:175–180

Dótor Almazán A, Armienta Hernández MA, Árcega Cabrera F, Talavera Mendoza O (2014) Arsenic and metals transport processes in surface waters from the mining district of Taxco, Mexico: stable isotopes application. Hidrobiol 24:245–256

Echeverría J, Niemeyer HM, Muñoz L, Uribe M (2018) Arsenic in the hair of mummies from agro-ceramic times of Northern Chile (500 BCE–1200 CE). J Archaeol Sci Rep 21:175–182

Escudero LB, Martinis EM, Olsina RA, Wuilloud RG (2013) Arsenic speciation analysis in monovarietal wines by on-line ionic liquid-based dispersive liquid–liquid microextraction. Food Chem 138:484–490

Espinosa E, Armienta MA, Cruz O, Aguayo A, Ceniceros N (2009) Geochemical distribution of arsenic, cadmium, lead and zinc in river sediments affected by tailings in Zimapán, a historical polymetalic mining zone of México. Environ Geol 58:1467–1477

Espino-Valdés MS, Barrera-Prieto Y, Herrera-Peraza E (2009) Arsenic presence in North section of Meoqui–Delicias aquifer of State of Chihuahua, Mexico. Tecnociencia Chihuahua 3:8–17

Esteller MV, Domínguez-Mariani E, Garrido SE, Avilés M (2015) Groundwater pollution by arsenic and other toxic elements in an abandoned silver mine, Mexico. Environ Earth Sci 74:2893–2906

Farías SS, Casa VA, Vázquez C, Ferpozzi L, Pucci GN, Cohen IM (2003) Natural contamination with arsenic and other trace elements in groundwaters of Argentine Pampean Plain. Sci Total Environ 309:187–199

Farías S, Smichowski P, Vélez D, Montoro R, Curtosi A, Vodopívez C (2007) Total and inorganic arsenic in Antarctic macroalgae. Chemosphere 69:1017–1024

Farias SS, Bianco de Salas G, Servant RE, Bovi Mitre G, Escalante J, Ponce RI, Ávila Carrera ME (2016) Survey of arsenic in drinking water and assessment of the intake of arsenic from water in Argentine Puna. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 397–407

Figueiredo BR, Litter MI, Silva CR, Mañay N, Londono SC, Rojas AM, Garzón C, Tosiani T, Di Giulio GM, De Capitani EM, Dos Anjos JASA, Angélica RS, Morita MC, Paoliello MMB, Cunha FG, Sakuma AM, Licht OA (2010) In: Selinus O, Finkelman RB, Centeno JA (eds) Medical geology studies in South America. Springer, New York, pp 79–106

Funes Pinter I, Salomon MV, Gil R, Mastrantonio L, Bottini R, Piccoli P (2018) Arsenic and trace elements in soil, water, grapevine and onion in Jáchal, Argentina. Sci Total Environ 615:1485–1498

Gamboa JCM, Cornejo L, Acarapi J, Squella JA (2013) Determination of arsenic (III) by differential pulse polarography in the waters of Camarones area, Chile. J Chil Chem Soc 58:2031–2034

García MG, D'Hiriart J, Giullitti J, Hurng L, Custo G, Hidalgo M d V, Litter MI, Blesa MA (2004) Solar light induced removal of arsenic from contaminated groundwater: the interplay of solar energy and chemical variables. Sol Energy 77:601–613

Garrido Hoyos SE, Avilés Flores M, Rivera Huerta ML, Nájera Flores MC (2007) Diagnóstico de la presencia de arsénico en agua de pozo, Mixco, Guatemala, Final report TC-0711.3. Instituto Mexicano de Tecnología del Agua, Jiutepec

Gil RA, Ferrúa N, Salonia JA, Olsina RA, Martinez LD (2007) On-line arsenic co-precipitation on ethyl vinyl acetate turning-packed mini-column followed by hydride generation-ICP OES determination. J Hazard Mater 143:431–436

Gomez ML, Blarasin MT, Martínez DE (2009) Arsenic and fluoride in a loess aquifer in the central area of Argentina. Environ Geol 57:143–155

Gómez-Arroyo S, Armienta MA, Cortés-Eslava J, Villalobos-Pietrini R (1997) Sister chromatid exchanges in *Vicia faba* induced by arsenic-contaminated drinking water from Zimapan, Hidalgo, Mexico. Mutat Res 394:1–7

Gómez-Bernal JM, Morton Bermea O, Ruíz-Huerta EA, Armienta-Hernández MA, González DO (2014) Microscopic evidences of heavy metals distribution and anatomic alterations in breaching-leaves of *Cupressus lindleyi* growing around mining wastes. Microsc Res Tech 77:714–726

Gómez-Bernal JM, Ruiz-Huerta EA, Armienta Hernández MA, Luna-Pabello VM (2018) Heavy metals and arsenic phytoavailability index in pioneer plants from a semipermanent natural wetland. Environ Prog Sustain Energy 37:980–988

Guérèquiz R, Mañay N, Goso-Aguilar C, Fernández-Turiel JL, García-Valles M (2009) Environmental risk assessment of arsenic in the Raigon aquifer. Uruguay. Biologist (Lima) 7.. Special issue:C0130

Hernández Ordáz G, Segura Castruita MA, Álvarez González Pico LC, Aldaco Nuncio RA, Fortis Hernández M, González Cervantes G (2013) Behavior of arsenic in soils of the región lagunera of Coahuila, Mexico. Terra Latinoam 31:291–303

Hounslow AW (1995) Water quality data. Analysis and interpretation. Taylor & Francis Group. E.U.A

Hurtado-Jiménez R, Gardea-Torresdey JL (2006) Contamination of drinking water supply with geothermal arsenic in Los Altos de Jalisco, Mexico, pp. 179–190. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 179–190

International Agency for Research on Cancer (IARC) (2012) Arsenic, metals, fibres, and dusts. Volume 100 C. A review of human carcinogens. IARC monographs on the evaluation of carcinogenic risks to humans. Arsenic, metals, fibres, and dusts. International Agency for Research on Cancer, World Health Organization, Lyon. http://monographs.iarc.fr/ENG/Monographs/vol100C/mono100C.pdf

Jesus JP, Suárez CA, Ferreira JR, Giné MF (2011) Sequential injection analysis implementing multiple standard additions for As speciation by liquid chromatography and atomic fluorescence spectrometry (SIA-HPLC-AFS). Talanta 85:1364–1368

Kordas K, Roy AR, López P, García Vargas G, Cebrian ME, Vera-Aguilar E, Rosado JL (2017) Iron and zinc supplementation does not impact urinary arsenic excretion in Mexican school children. Nutr Res 185:205–210

Labastida I, Armienta MA, Lara-Castro RH, Aguayo A, Cruz O, Ceniceros N (2013) Treatment of mining acidic leachates with indigenous limestone, Zimapan Mexico. J Hazard Mater 262:1187–1195

Lara René H, Velázquez Leticia J, Vazquez-Arenas J, Mallet M, Dossot M, Labastida I, Sosa-Rodríguez FS, Espinosa-Cristóbal LF, Escobedo-Bretado MA, Cruz R (2016) Arsenopyrite weathering under conditions of simulated calcareous soil. Environ Sci Pollut Res 23:3681–3706

Leiva ED, Rámila CDP, Vargas IT, Escauriaza CR, Bonilla CA, Pizarro GE, Regan JM, Pasten PA (2014) Natural attenuation process via microbial oxidation of arsenic in a high Andean watershed. Sci Total Environ 466–467:490–502

Lima EC, Brasil JL, Vaghetti JCP (2003) Valuation of different permanent modifiers for the determination of arsenic in environmental samples by electrothermal atomic absorption spectrometry. Talanta 60:103–113

Litter MI, Armienta MA, Farías SS (2009) Metodologías analíticas para la determinación y especiación de arsénico en aguas y suelos. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo

López Guzmán D, Costilla Salazar R, Pelallo Martínez N, Alcaraz Contreras Y, Bocanegra Salazar M, Rocha Amador DO (2017) Micronucleus in exfoliated buccal cells of children, from Durango, Mexico, exposed to arsenic through drinking water. Rev Int Contam Amb 33:281–287

López DL, Ransom L, Monterrosa J, Soriano T, Barahona F, Olmos R, Bundschuh J (2009) Volcanic arsenic and boron pollution of Ilopango lake, El Salvador. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 129–143

López DL, Bundschuh J, Birkle P, Armienta MA, Cumbal L, Sracek O, Cornejo L, Ormachea M (2012) Arsenic in volcanic geothermal fluids of Latin America. Sci Total Environ 429:57–75

López DL, Ribó A, Quinteros E, Mejía R, López A, Orantes C (2014) Arsenic in soils, sediments, and water in area with high prevalence of chronic kidney disease of unknown etiology. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 251–254

López-Carrillo L, Gamboa-Loira B, Becerra W, Hernández-Alcaraz C, Hernández-Ramírez RU, Jay GA, Franco-Marina F, Cebrián ME (2016) Dietary micronutrient intake and its relationship with arsenic metabolism in Mexican women. Environ Res 151:445–450

López-Zepeda JL, Villalobos M, Gutiérrez-Ruiz M, Romero F (2008) The use of synchrotron micro-X-ray techniques to determine arsenic speciation in contaminated soils. In: Bundschuch J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of latinoamerica, vol 1. CRC Press, London, pp 255–264

Macedo SM, de Jesus RM, Garcia KS, Hatje V, Queiroz AF d S, Ferreira SLC (2009) Determination of total arsenic and arsenic (III) in phosphate fertilizers and phosphate rocks by HG-AAS after multivariate optimization based on Box-Behnken design. Talanta 80:974–979

Mahlknecht J, Steinich B, Navarro de León I (2004) Groundwater chemistry and mass transfers in the Independence aquifer, Central Mexico, by using multivariate statistics and mass-balance models. Environ Geol 45:781–795

Mañay N, Pistón M, Goso C (2014) Arsenic environmental and health issues in Uruguay: a multidisciplinary approach. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 485–487

Mar Camacho L, Gutierrez M, Alarcon-Herrera MT, Villalba ML, Deng S (2011) Occurrence and treatment of arsenic in groundwater and soil in northern Mexico and southwestern USA. Chemosphere 83:2011–2225

Martín R, Canet C, Alfonso P, Zambrana RN, Soto N (2014) The role of cassiterite controlling arsenic mobility in an abandoned stanniferous tailings impoundment at Llallagua, Bolivia. Sci Total Environ 481:100–107

Martínez LD, Gazquez JA (2005) Determinación de arsénico en aguas: diferentes técnicas y metodologías. II° Seminario Hispano-Latinoamericano sobre temas actuales de hidrología subterránea. IV° Congreso Hidrogeológico Argentino

Martínez-Acuña MI, Mercado-Reyes M, Alegría-Torres JA, Mejía-Saavedra JJ (2016) Preliminary human health risk assessment of arsenic and fluoride in tap water from Zacatecas, México. Environ Monit Assess 188:476

Martínez-Villegas N, Briones-Gallardo R, Ramos-Leal JA, Avalos-Borja M, Castañón-Sandoval AD, Razo-Flores E, Villalobos M (2013) Arsenic mobility controlled by solid calcium arsenates: a case study in Mexico showcasing a potentially widespread environmental problem. Environ Pollut 176:114–122

Matos-Reyes MN, Cervera ML, Campos RC, de la Guardia M (2010) Total content of As, Sb, Se, Te and Bi in Spanish vegetables, cereals and pulses and estimation of the contribution of these foods to the Mediterranean daily intake of trace elements. Food Chem 122:188–194

Matschullat J, Birmann K, Borba RP, Ciminelli V, Deschamps EM, Figueiredo BR, Gabrio T, Haßler S, Hilscher A, Junghänel I, de Oliveira NJ, Raßbach H, Schmidt H, Schwenk M, de Oliveira Vilhena MJ, Weidner U (2007) Long-term environmental impact of arsenic-dispersion in Minas Gerais, Brazil. In: Trace metals and other contaminants in the environment, vol 9. Elsevier, Amsterdam, pp 355–382

McCarty KM, Hanh HT, Kim KW (2011) Arsenic geochemistry and human health in South East Asia. Rev Environ Health 26:71–78

Mejía-González M, González L, Briones R, Cardona A, Soto P (2014) Mecanismos que liberan arsénico al agua subterránea de la Comarca Lagunera, estados de Coahuila y Durango. México, Tecnología Ciencias del Agua 5:71–82

Melo RF, Dias LE, Vargas de Mello JW, Oliveira JA (2010) Behavior of *Eucalyptus grandis* and *E. cloeziana* seedlings grown in arsenic-contaminated soil. Soc Bras Ciênc Solo 34:985–992

Méndez-Ramírez M, Armienta Hernández MA (2012) Distribución de Fe, Zn, Pb, Cu, Cd y As originada por residuos mineros y aguas residuales en un transecto del Río Taxco en Guerrero, México. Rev Mex Cienc Geológicas 29:450–462

Menegário AA, Gin MF (2000) Rapid sequential determination of arsenic and selenium in waters and plant digests by hydride generation inductively coupled plasma-mass spectrometry. Spectrochim Acta B 55:355–362

Menezes HA, Maia G (2010) Specific adsorption of arsenic and humic acid on Pt and PtO films. Electrochim Acta 55:4942–4951

Modificación a la Norma Oficial Mexicana (2000) NOM-127-SSA1-1994, Salud Ambiental. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a los que debe someterse el agua para su potabilización. Diario Oficial de la Federación, 22 noviembre de 2000, México City, México

Monasterio RP, Wuilloud RG (2010) Ionic liquid as ion-pairing reagent for liquid–liquid microextraction and preconcentration of arsenic species in natural waters followed by ETAAS. J Anal At Spectrom 25:1485–1490

Monasterio RP, Londinio JA, Farías SS, Smichowski P, Wuilloud RG (2011) Organic solvent-free reversed-phase ion-pairing liquid chromatography coupled to atomic fluorescence spectrometry for organoarsenic species determination in several matrices. J Agric Food Chem 59:3566–3574

Morales I, Villanueva-Estrada RE, Rodríguez R, Armienta MA (2015) Geological, hydrogeological and geothermal factors associated to the origin of arsenic, fluoride and groundwater temperature in a volcanic environment. Environ Earth Sci 74:5403–5415

Morales-Arredondo I, Rodríguez R, Armienta MA, Villanueva-Estrada RE (2016) The origin of groundwater arsenic and fluorine in a volcanic sedimentary basin in Central Mexico: a hydrochemistry hypothesis. Hydrogeol J 24:1029–1044

Morales-Arredondo JI, Esteller-Alberich MV, Armienta Hernández MA, Martínez-Florentino TAK (2018) Characterizing the hydrogeochemistry of two low-temperature thermal systems in Central Mexico. J Geochem Explor 185:93–104

Moreira CM, Duarte FA, Lebherz J, Pozebon D, Flores EMM, Dressler VL (2011) Arsenic speciation in white wine by LC-ICP-MS. Food Chem 126:1406–1411

Moreno ME, Acosta-Saavedra LC, Meza-Figueroa D, Vera E, Cebrian ME, Ostrosky-Wegmand P, Calderon Aranda ES (2010) Biomonitoring of metal in children living in a mine tailings zone in Southern Mexico: a pilot study. Int J Hyg Environ Health 213:252–258

Morgada ME, Levy IK, Salomone V, Farías SS, López G, Litter MI (2009) Arsenic (V) removal with nanoparticulate zerovalent iron: effect of UV light and humic acids. Catal Today 143:261–268

Mukherjee A, Raychowdhury N, Bhattacharya P, Bundschuh J, Johannesson K (2014) Tectonic-sourced groundwater arsenic in Andean foreland of Argentina: insight from flow path modeling. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 22–25

Muñoz L, Meneses M, Pismante P, Andonie O, Queirolo F, Stegen S (2014) Methodological validation for the determination of toxic arsenic species in human urine using HPLC with ICP-MS. J Chil Chem Soc 59:2432–2436

Muñoz O, Zamorano P, Garcia O, Bastías JM (2017) Arsenic, cadmium, mercury, sodium, and potassium concentrations in common foods and estimated daily intake of the population in Valdivia (Chile) using a total diet study. Food Chem Toxicol 109:1125–1134

Murcott S (2012) Arsenic contamination in the world – an international sourcebook. IWA Publishing, London

Navarro O, González J, Júnez-Ferreira HE, Bautista C-F, Cardona A (2017) Correlation of arsenic and fluoride in the groundwater for human consumption in a semiarid region of Mexico. Procedia Eng 186:333–340

Navoni JA, Olivera NM, Villaamil Lepori EC (2010) Cuantificación de arsénico por inyección de flujo-generación de hidruros-espectrometría de absorción atómica (IF-GH-EAA) previa derivatización con L-cisteína. Validación y comparación intermetodológica utilizando dos técnicas de referencia. Acta Toxicol Argent 18:29–38

Navoni JA, De Pietri D, Olmos V, Gimenez C, Bovi Mitre G, Titto d, Villaamil Lepori E (2014) Human health risk assessment with spatial analysis: study of a population chronically exposed to arsenic through drinking water from Argentina. Sci Total Environ 499:166–174

Nicolli HB, Tineo A, Falcón CM, García JW, Merino MH, Etchichury MC, Alonso MS, Tofalo OR (2009) Arsenic hydrogeochemistry in groundwater from the Burruyacú basin, Tucumán province, Argentina. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 47–59

Nicolli HB, Bundschuh J, García JW, Falcón CM, Jean J (2010) Sources and controls for the mobility of arsenic in oxidizing groundwaters from loess-type sediments in arid/semi-arid dry climates – evidence from the Chaco Pampean plain (Argentina). Water Res 44:5589–5604

Nieva NE, Borgnino L, Locati F, García MG (2016) Mineralogical control on arsenic release during sediment–water interaction in abandoned mine wastes from the Argentina Puna. Sci Total Environ 550:1141–1151

Núñez C, Arancibia V, Gómez M (2016) Determination of arsenic in the presence of copper by adsorptive stripping voltammetry using pyrrolidine dithiocarbamate or diethyl dithiophosphate as chelating-adsorbent agents. Effect of CPB on the sensitivity of the method. Microchem J 126:70–75

Núñez C, Arancibia V, Triviño JJ (2018) A new strategy for the modification of a carbon paste electrode with carrageenan hydrogel for a sensitive and selective determination of arsenic in natural waters. Talanta 187:259–264

Oliveira A, Henrique Gonzalez M, Müller Queiroz H, Cadore S (2016) Fractionation of inorganic arsenic by adjusting hydrogen ion concentration. Food Chem 213:76–82

Ongley LK, Sherma L, Armienta A, Concilio A, Ferguson Salinas C (2007) Arsenic in the soils of Zimapán, Mexico. Environ Pollut 145:793–799

Ormachea Muñoz M, Huallpara L, Coariti E, García Aróstegui JL, Kohfahl C, Estévez M, Bhattacharya P (2014) Natural arsenic occurrence in drinking water and assessment of water quality in the southern part of the Poopó lake Basin, Bolivia Altiplano. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 154–151

Ormachea MM, Quintanilla AJ (2014) Distribution of geogenic arsenic in superficial and underground water in Central Bolivian Highlands. Rev Boliviana Quím 31:54–60

Ortega A, Oliva I, Contreras KE, González I, Cruz-Díaz MR, Rivero EP (2017) Arsenic removal from water by hybrid electro-regenerated anion exchange resin/electrodialysis process. Sep Purif Technol 184:319–326

Ortega-Guerrero MA (2004) Abstract at the International Geologic Congress, Florence

Ortega-Guerrero A (2009) Presencia, distribución, hidrogeoquímica y origen de arsénico, fluoruro y otros elementos traza disueltos en agua subterránea, a escala de cuenca hidrológica tributaria de Lerma-Chapala, México. Rev Mex Cienc Geol 26:143–161

Ortega-Guerrero A (2017) Evaporative concentration of arsenic in groundwater: health and environmental implications, La Laguna Region, Mexico. Environ Geochem Health 39:987–1003

Patiño-Reyes N, Duarte Portocarrero E (2014) Analysis of mercury and arsenic in drinking water in Bogotá DC (Colombia) in 2010 and 2011. In: Litter MI, Nicolli HB, Meichtry JM, Quici

N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 187–188

Peralta Ramos ML, González JA, Albornoz SG, Pérez CJ, Villanueva ME, Giorgieri SA, Copello GJ (2016) Chitin hydrogel reinforced with TiO_2 nanoparticles as an arsenic sorbent. Chem Eng J 285:581–587

Pereira ER, De Almeida TS, Borges DLG, Carasek E, Welz B, Feldmann J, Del Campo Menoyo J (2016) Investigation of chemical modifiers for the direct determination of arsenic in fish oil using high-resolution continuum source graphite furnace atomic absorption spectrometry. Talanta 150:142–147

Pérez Moreno F, Prieto García E, Barrado Estebán E, Roas Heranández A, Méndez Marzo MA (2002) Optimización del método de determinación de arsénico en aguas potables por espectrofotometría UV-Vis con dietilcarbamato de plata. Rev Soc Quími Méx 46:175–179

Pérez AA, Pérez LB, Strobl AM, Camarda S, Farias SS, López CM, Fajardo MA (2010) Variación estacional de arsénico total en algas comestibles recolectadas en el Golfo San Jorge (Chubut, Argentina). Rev Latinoam Biotecnol Amb Algal 1:16–30

Pistón M, Silva J, Pérez-Zambra R, Dol I, Knochen M (2012) Automated method for the determination of total arsenic and selenium in natural and drinking water by HG-AAS. Environ Geochem Health 34:273–278

Pizarro I, Gómez-Gómez M, León J, Román D, Palacios MA (2016) Bioaccessibility and arsenic speciation in carrots, beets and quinoa from a contaminated area of Chile. Sci Total Environ 565:557–563

Planer-Friedich B, Armienta MA, Merkel BJ (2001) Origin of arsenic in the groundwater of the Río Verde Basin, México. Environ Geol 40:1290–1298

Quevedo O, Luna B, Carballeira E, Rodríguez AC (2003) Determinación de As(III) y As (V) en aguas naturales por generación de hidruro con detección por espectrometría de absorción atómica. Rev CENIC Cienc Químicas 34:133–137

Quiller G, Mérida-Ortega Á, Rothenberg SJ, Cebrián MEA, Gandolfi J, Franco-Marina F, López-Carrillo L (2018) Dietary flavonoids improve urinary arsenic elimination among Mexican women. Nutr Res 55:65–71

Quintanilla J, Ramos O, Ormachea M, García ME, Medina H, Thunvik R, Bhattacharya P, Bundschuh J (2009) Arsenic contamination, speciation and environmental consequences in the Bolivian plateau. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 91–99

Ramírez Cordero BE, Cañizares-Macías MP (2009) Determination of bioavailable soluble arsenic and phosphates in mine tailings by spectrophotometric sequential injection analysis. Talanta 78:1069–1076

Ramírez-Aldaba H, Valles OP, Vazquez-Arenas J, Rojas-Contreras JA, Valdez-Pérez D, Ruiz-Baca E, Meraz-Rodríguez M, Sosa-Rodríguez FS, Rodríguez AG, Lara RH (2016) Chemical and surface analysis during evolution of arsenopyrite oxidation by *Acidithiobacillus thiooxidans* in the presence and absence of supplementary arsenic. Sci Total Environ 566–567:1106–1119

Ramírez-González S, Jiménez-Prieto Y, Esperanza-Pérez G, Ribalta-Quesada JA, Rodríguez-Rivero RA (2017) Determinación de arsénico por el método de azul de molibdeno en muestras de aguas provenientes de una planta de procesamiento de minerales auríferos. Rev Cub Quim 29:3–12

Ramos OE, Quino I, Quintanilla J, Bhattacharya P, Bundschuh J (2014) Geochemical processes controlling mobilization of arsenic and trace elements in shallow aquifers in mining regions, Bolivian Altiplano. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 239–241

Razo I, Carrizales L, Castro J, Díaz-Barriga F, Monroy M (2004) Arsenic and heavy metal pollution of soils, water and sediments in a semi-arid climate mining area in México. Water Air Soil Pollut 152:129–152

Reboucas MV, Ferreira SLC, De Barros NB (2005) Behaviour of chemical modifiers in the determination of arsenic by electrothermal atomic absorption spectrometry in petroleum products. Talanta 67:195–204

Reyes-Gómez V, Alarcón M, Gutiérrez M, Nuñez D (2013) Fluoride and arsenic in an alluvial aquifer system in Chihuahua, Mexico: contaminant levels, potential sources, and co-occurrence. Water Air Soil Pollut 224:1433–1448

Robles AD, Vetterelo SN, Gerpe M, Garay F (2017) The electrochemical reaction mechanism of arsenic on gold analyzed by anodic stripping square-wave voltammetry. Electrochim Acta 10:447–454

Rocha-Amador DO, Calderón J, Carrizales L, Costilla-Salazar R, Pérez-Maldonado IN (2011) Apoptosis of peripheral blood mononuclear cells in children exposed to arsenic and fluoride. Environ Toxicol Pharmacol 32:399–405

Rodríguez Castro MC, Urrea G, Guasch H (2015) Influence of the interaction between phosphate and arsenate on periphyton's growth and its nutrient uptake capacity. Sci Total Environ 503–504:122–132

Rodríguez Garrido NE, Segura Castruita MA, Orozco Vidal JA, Fortis Hernández M, Preciado Rangel P, Olague Ramírez J, Yescas Coronado P (2017) Arsénico edáfico y su distribución en el distrito de riego 017: uso de métodos de interpolación. Terra Latinoam 35:19–28

Rodríguez R, Ramos JA, Armienta A (2004) Groundwater arsenic variations: the role of local geology and rainfall. Appl Geochem 19:245–250

Romero FM, Armienta MA, González-Hernández G (2007) Solid-phase control on the mobility of potentially toxic elements in an abandoned lead/zinc mine tailings impoundment, Taxco, Mexico. Appl Geochem 22:109–127

Romero FM, Prol-Ledesma RM, Canet C, Núñez Alvares L, Pérez-Vázquez R (2010) Acid drainage at the inactive Santa Lucia mine, Western Cuba: natural attenuation of arsenic, barium and lead, and geochemical behavior of rare earth elements. Appl Geochem 25:716–727

Romero FM, Núñes L, Gutiérrez ME, Armienta MA, Ceniceros-Gómez AE (2011) Evaluation of the potential of indigenous calcareous shale for neutralization and removal of arsenic and heavy metals from acid mine drainage in the Taxco Mining Area, Mexico. Arch Environ Contam Toxicol 60:191–203

Roque-Álvarez I, Sosa-Rodríguez FS, Vázquez-Arenas J, Escobedo-Bretado MA, Labastida I, Corral-Rivas JJ, Aragón-Piña A, Armienta MA, Ponce-Peña P, Lara RH (2018) Spatial distribution, mobility and bioavailability of arsenic, lead, copper and zinc in low polluted forest ecosystem in Northwestern, Mexico. Chemosphere 210:320–333

Rosas-Castor JM, Guzmán-Mar JL, Alfaro-Barbosa JM, Hernández-Ramírez A, Pérez-Maldonado IN, Caballero-Quintero, Hinojosa-Reyes L (2014) Evaluation of the transfer of soil arsenic to maize crops in suburban areas of San Luis Potosi, Mexico. Sci Total Environ 497–498:153–162

Rosas-Castor JM, Portugal L, Ferrer L, Guzmán-Mar JL, Hernández-Ramírez A, Cerdà V, Hinojosa-Reyes L (2015) Arsenic fractionation in agricultural soil using an automated three-step sequential extraction method coupled to hydride generation-atomic fluorescence spectrometry. Anal Chim Acta 874:1–10

Rosas-Castor JM, Portugal L, Ferrer L, Hinojosa-Reyes L, Guzmán-Mar JL, Hernández-Ramírez A, Cerdà V (2016) An evaluation of the bioaccessibility of arsenic in corn and rice samples based on cloud point extraction and hydride generation coupled to atomic fluorescence spectrometry. Food Chem 204:475–482

Roy A, Kordas K, López P, Rosado JL, Cebrian ME, García Vargas G, Ronquillo D, Stoltzfus RJ (2011) Association between arsenic exposure and behavior among first-graders from Torreón, Mexico. Environ Res 111:670–676

Ruiz Huerta EA, Armienta MA (2012) Acumulación de arsénico y metales pesados en maíz en suelos cercanos a jales o residuos mineros. Rev Int Contam Amb 28:103–117

Ruíz Huerta EA, De la Garza Varela A, Gómez-Bernal JM, Castillo F, Avalos-Borja M, Sen Gupta B, Martínez-Villegas N (2017) Arsenic contamination in irrigation water, agricultural soil and maize crop from an abandoned smelter site in Matehuala. J Hazard Mater 339:330–339

Salas-Luévano MA, Mauricio-Castillo JA, González-Rivera M, Vega-Carrillo HR, Salas-Muñoz S (2017) Accumulation and phytostabilization of As, Pb and Cd in plants growing inside mine tailings reforested in Zacatecas, Mexico. Environ Earth Sci 76:806

Saldaña-Robles A, Saldaña-Robles N, Saldaña-Robles AL, Damian-Ascencio C, Rangel-Hernández VH, Guerra-Sánchez R (2017) Arsenic removal from aqueous solutions and the impact of humic and fulvic acids. J Clean Prod 159:425–431

Saldaña-Robles A, Damian-Ascencio CE, Guerra-Sanchez RJ, Saldaña-Robles AL, Saldaña-Robles N, Gallegos-Muñoz A, Cano-Andrade S (2018) Effects of the presence of organic matter on the removal of arsenic from groundwater. J Clean Prod 183:720–728

Salgado-Bustamante M, Ortiz-Pérez MD, Calderón-Aranda E, Estrada-Capetillo L, Niño-Moreno P, González-Amaro R, Portales-Pérez D (2010) Pattern of expression of apoptosis and inflammatory genes in humans exposed to arsenic and/or fluoride. Sci Total Environ 408:760–767

Salinas S, Mosquera N, Yate L, Coy E, Yamhure G, González E (2014) Surface plasmon resonance nanosensor for the detection of arsenic in water. Sensors Transducers 183:97–102

Sandoval MA, Fuentes R, Navab JL, Coreño O, Lid Y, Hernández JJ (2018) Simultaneous removal of fluoride and arsenic from groundwater by electrocoagulation using a filter-press flow reactor with a three-cell stack. Sep Purif Technol 208:208–216

Santos Pontes BM, de Albuquerque Menor E, Figueiredo JA (2014) Arsenic, selenium and lead contamination from the waters in surface Itapessoca catchment, northeastern Brazil. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 65–67

Santos CMM, Nunes MAG, Barbosa IS, Santos GL, Peso-Aguiar MC, Korn MGA, Flores EMM, Dressler VL (2013) Evaluation of microwave and ultrasound extraction procedures for arsenic speciation in bivalve mollusks by liquid chromatography–inductively coupled plasma-mass spectrometry. Spectrochim Acta Part B 86:108–114

Santos-Domínguez EE, Vargas-Morales JM, Cárdenas-González JF, Acosta-Rodríguez I (2017) Removal of arsenic (V) in aqueous solution by modified fungal biomass of *Aspergillus niger*. Inf Tecnol 28:45–51

Santos-Jallath J, Castro-Rodríguez A, Huezo-Casillas J, Torres-Bustillos L (2012) Arsenic and heavy metals in native plants at tailings impoundments in Queretaro, Mexico. Phys Chem Earth 37–39:10–17

Sariñana-Ruiz YA, Vazquez-Arenas J, Sosa-Rodríguez FS, Labastida I, Armienta MA, Aragon-Piña A, Escobedo-Bretado MA, González Valdez LS, Ponce-Peña P, Ramírez-Aldaba H, Lara RH (2017) Assessment of arsenic and fluorine in surface soil to determine environmental and health risk factors in the Comarca Lagunera, Mexico. Chemosphere 178:391–401

Schneider M, Cadorim HR, Welz B, Carasek E, Feldmann J (2018) Determination of arsenic in agricultural soil samples using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sample analysis. Talanta 188:722–728

Segura FR, de Oliveira Souza JM, De Paula ES, da Cunha Martins A Jr, Paulelli ACC, Barbosa F Jr, Batista BL, Lemos Batista B (2016) Arsenic speciation in Brazilian rice grains organically and traditionally cultivated: is there any difference in arsenic content? Food Res Int 89(Part 1):169–176

Sepúlveda M, Gutiérrez S, Carcamo J, Oyaneder A, Valenzuela D, Montt I, Santoro CM (2015) In situ X-ray fluorescence analysis of rock paintings along the coast and valleys of the Atacama Desert, Northern Chile. J Chil Chem Soc 60:2822–2826

Siegfried K, Hahn-Tomer S, Koelsch A, Osterwalder E, Mattusch J, Staerk HJ, Meichtry JM, De Seta GE, Reina FD, Panigatti C, Litter MI, Harms H (2015) Introducing simple detection of bioavailable arsenic at Rafaela (Santa Fe Province, Argentina) using the ARSOlux Biosensor. Int J Environ Res Publ Health 12:5465–5482

Sigrist M, Albertengo A, Beldoménico H, Repetti MR (2010) Evaluation of the influence of arsenical livestock drinking waters on total arsenic levels in cow's raw milk from Argentinean dairy farms. Food Chem 121:487–491

Sigrist M, Albertengo A, Beldoménico H, Tudino M (2011) Determination of As(III) and total inorganic As in water samples using an on-line solid phase extraction and flow injection hydride generation atomic absorption spectrometry. J Hazard Mater 188:311–318

Sigrist M, Albertengo A, Brusa L, Beldoménico H, Tudino M (2013) Distribution of inorganic arsenic species in groundwater from Central-West part of Santa Fe Province, Argentina. Appl Geochem 39:43–48

Sigrist M, Hilbe N, Brusa L, Campagnoli D, Beldoménico H (2016) Total arsenic in selected food samples from Argentina: estimation of their contribution to inorganic arsenic dietary intake. Food Chem 210:96–101

Simona S, Lobos G, Pannier F, De Gregori I, Pinochet H, Potin-gautier (2004) Speciation analysis of organoarsenical compounds in biological matrices by coupling ion chromatography to atomic fluorescence spectrometry with on-line photooxidation and hydride generation. Anal Chim Acta 521:99–108

Smedley PL, Nicolli HB, MacDonald DMJ, Kinniburgh DG (2009) Arsenic in groundwater and sediments from La Pampa province, Argentina. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwaters of Latin America. CRC Press, London, pp 35–45

Sracek O, Armienta MA, Rodríguez R, Villaseñor G (2010) Discrimination between diffuse and point sources of arsenic at Zimapán, Hidalgo state, Mexico. J Environ Monit 12:329–337

Teixeira MC, Tavares EFL, Saczk AA, Okumura LL, Cardoso M d G, Magriotis ZM, Oliveira MF (2014) Cathodic stripping voltammetric determination of arsenic in sugarcane brandy at a modified carbon nanotube paste electrode. Food Chem 154:38–43

Tormen L, Gil RA, Frescura VLA, Martinez LD, Curtius AJ (2012) The use of electrothermal vaporizer coupled to the inductively coupled plasma mass spectrometry for the determination of arsenic, selenium and transition metals in biological samples treated with formic acid. Anal Chim Acta 717:21–27

Torres S, Martínez LD, Pacheco PH (2018) Determination of arsenic species distribution in extra virgin olive oils from arsenic-endemic areas by dimensional chromatography and atomic spectroscopy. J Food Compos Anal 66:121–126

Torres-Sánchez L, López-Carrillo L, Rosado JL, Rodriguez VM, Vera-Aguilar E, Kordas K, García-Vargas GG, Cebrian ME (2016) Sex differences in the reduction of arsenic methylation capacity as a function of urinary total and inorganic arsenic in Mexican children. Environ Res 151:38–43

Toujague R, Leonarte T, Reyes Verdecia A, Miravet BL, Leal RM (2003) Arsénico y metales pesados en aguas del área Delita, Isla de la Juventud. Cuba, Cienc Tierra Espacio 4:27–33

Valcárcel LA, Montero A, Estévez JR, Pupo I (2008) Arsenic speciation study using X-ray Fluorescence and cathodic stripping voltammetry. In: Bundschuch J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latinoamerica, vol 1. CRC Press, London, pp 265–271

Valenzuela OL, Germolec DR, Borja-Aburto VH, Contreras-Ruiz J, García-Vargas GG, Del Razo LM (2007) Chronic arsenic exposure increases TGFalpha concentration in bladder urothelial cells of Mexican populations environmentally exposed to inorganic arsenic. Toxicol Appl Pharmacol 222:264–270

Vázquez C, Marcó L, Rodríguez Castro MC, Boeykens S, Maury AM (2014) Integrated study of arsenic contamination in different matrices and targets in La Matanza, Buenos Aires province, Argentina. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 49–51

Velázquez-Peña GC, Solache-Ríos M, Olguina MT, Fall C (2019) As(V) sorption by different natural zeolite frameworks modified with Fe, Zr and FeZr. Microporous Mesoporous Mater 273:133–141

Vergara Gallardo M, Bohari Y, Astruc A, Potin-Gautier M, Astruc M (2001) Speciation analysis of arsenic in environmental solids reference materials by high-performance liquid chromatography–hydride generation–atomic fluorescence spectrometry following orthophosphoric acid extraction. Anal Chim Acta 441:257–268

Vieira MA, Grinberg P, Bobeda CRR, Reyes MNM, Campos RC (2009) Non-chromatographic atomic spectrometric methods in speciation analysis: a review. Spectrochim Acta B 64:459–476

Villalobos-Castañeda B, Alfaro-Cuevas R, Cortés-Martínez R, Verónica Martínez M, Márquez-Benavides L (2010) Distribution and partitioning of iron, zinc, and arsenic in surface sediments in the Grande River mouth to Cuitzeo Lake, Mexico. Environ Monit Assess 166:331–346

Villanueva-Estrada RE, Prol-Ledesma RM, Rodríguez-Díaz AA, Canet C, Armienta MA (2013) Arsenic in hot springs of Bahía Concepción, Baja California Peninsula, México. Chem Geol 348:27–36

Vitela-Rodriguez AV, Rangel-Mendez JR (2013) Arsenic removal by modified activated carbons with iron hydro(oxide) nanoparticles. J Environ Manag 114:225–231

World Health Organization & International Programme on Chemical Safety (1996) Guidelines for drinking-water quality. Vol. 2, health criteria and other supporting information, 2nd. World Health Organization, Geneva. http://www.who.int/iris/handle/10665/38551. Accessed Nov 2017

World Health Organization (WHO) (2011) Guidelines for drinking-water quality, 4th edn. World Health Organization, Geneva. http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf?ua=1. Accessed Nov 2017

Wuilloud RG, Altamirano JC, Smichowski PN, Heitkempera DT (2006) Investigation of arsenic speciation in algae of the Antarctic region by HPLC-ICP-MS and HPLC-ESI-Ion Trap MS. J Anal At Spectrom 21:1214–1223

Yáñez J, Fierro V, Mansilla H, Figueroa L, Cornejo L, Barnes RM (2005) Arsenic speciation in human hair: a new perspective for epidemiological assessment in chronic arsenicism. J Environ Monit 7:1335–1341

Yáñez LM, Alfaro JA, Bovi Mitre G (2018) Absorption of arsenic from soil and water by two chard (Beta vulgaris L.) varieties: a potential risk to human health. J Environ Manag 218:23–30

Zabala ME, Manzano M, Vives L (2016) Assessment of processes controlling the regional distribution of fluoride and arsenic in groundwater of the Pampeano aquifer and the Del Azul Creek basin (Argentina). J Hydrol 541:1067–1087

Zucchi OLAD, Moreira S, Salvador MJ, Santos LL (2005) Multielement analysis of soft drink by X-ray fluorescence spectrometry. J Agric Food Chem 53:7863–7869

Zurita F, Del Toro-Sánchez CL, Gutierrez-Lomelí M, Rodriguez-Sahagún A, Castellanos-Hernández OA, Ramírez-Martínez G, White JR (2012) Preliminary study on the potential of arsenic removal by subsurface flow constructed mesocosms. Ecol Eng 47:101–104

Arsenic in Latin America: Part II

Marta I. Litter, María A. Armienta, Ruth E. Villanueva Estrada, Edda C. Villaamil Lepori, and Valentina Olmos

Abstract Long-term exposure to As through drinking water is an important health problem in Latin America (LA), causing both carcinogenic and non-carcinogenic effects (McClintock TR, Chen Y, Bundschuh J, Oliver JT, Navoni J, Olmos V, Villaamil Lepori E, Ahsan H, Parvez F (2012) Arsenic exposure in latinamerica: biomarkers, risk assessments and related health effects. Sci Total Environ 429:76–91). This chapter reviews information on health effects conducted in LA. It is estimated that, in this region, 14 million people are chronically exposed to As through drinking water and food. Lung cancer is the most studied adverse effect of As exposure in LA, followed by skin lesions, bladder cancer, and the effects of early exposure to As. Studies on As exposure and cancer development are well described in Chile, Mexico, and Argentina. According to studies conducted mainly in Mexico, an association between As exposure and diabetes is reported.

Arsenic removal technologies investigated in LA over the last few decades rely on adaptation and improvement of methods involving simple physicochemical processes like adsorption, coagulation/precipitation, or ion exchange, all of them being more suitable for As(V) than for As(III) removal, which usually implies a preliminary oxidation step. However, new technologies are constantly under investigation, and several of them have been reported. For rural communities in LA, small-scale

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and household level, As removal systems are the only feasible short-term solution. Natural geological materials like iron oxides and hydroxides, calcite, clays, etc. can be used as effective, simple, and low-cost materials for As removal at the household level and for small communities. Natural organic materials are also the basis for suitable low-cost technologies. Sorption agents coming from plants and animal residues are also useful. Procedures using zerovalent iron from diverse materials are affordable and easy to operate and maintain. Other alternatives are capacitive deionization, phytoremediation, and constructed wetlands. An overview of the state of the art of technologies for As removal studied in LA will be given in this chapter.

Keywords Arsenic removal technologies · Biotransformation · Cancer · Diabetes · Immunotoxicity

1 Analysis of Human Health Impacts Associated with Arsenic Exposure in Latin America

1.1 Health Impacts of Arsenic on Humans

Arsenic is highly toxic for humans. As said before, long-term exposure to As through drinking water is an important health problem, causing both carcinogenic and non-carcinogenic effects in many regions of the world, including LA (McClintock et al. 2012; Armienta and Segovia 2008; Pérez-Carrera and FernándezCirelli 2010; Flora 2015; Bundschuh et al. 2009; Castro de Esparza 2009). Arsenic is a known human carcinogen (International Agency for Research on Cancer (IARC) 2012), and inorganic arsenic (iAs) has been related to the development of skin, lung, liver, kidney, bladder, and prostate cancer (Smith et al. 1992; Martinez et al. 2011; Hong et al. 2014). Among the pathologies produced by As, the arsenicosis is a disease with characteristic skin lesions such as melanosis, leucomelanosis, and keratosis. Other pathologies include diabetes mellitus, peripheral vascular disease, cardiovascular and respiratory diseases, and a wide variety of clinical manifestations including neurological effects, anemia, leukopenia, liver dysfunction, and high blood pressure. Many of these effects are known through studies in Southeast Asia, where the greatest number of people chronically exposed to As reside. However, it is estimated that, in LA, 14 million people are chronically exposed to As through drinking water and food (Bardach et al. 2015; Arsénico en agua, informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018).

While the carcinogenicity of As has been confirmed, the mechanisms behind the disease are still not well understood. To date, the majority of research has examined cancer incidence after exposure to high As concentrations. However, numerous studies have reported various health effects caused by chronic exposure to low concentrations of As (Hong et al. 2014). More systematic studies are needed to determine the link between As exposure and its related cancer and non-cancer end points

(Rahman et al. 2009; Agency for Toxic Substances and Disease Registry (ATSDR) 2013; Parvez et al. 2013).

1.2 Biotransformation of Inorganic Arsenic

The biotransformation of iAs generates metabolites of different toxicities, and this is one of the factors that determine the nature and magnitude of the harmful effects. Trivalent species (arsenite (As^{III}), monomethylarsonous acid (MMA^{III}), and dimethylarsinious acid (DMA^{III})) showed to be more toxic than pentavalent species (arsenate (As^{V}), monomethylarsonic acid (MMAV), and dimethylarsinic acid (DMA^{V})), due to their ability to bind to more than 200 enzymes (Khairul et al. 2017). MMA^{III} is, among all As metabolites, the most toxic metabolic intermediate (Styblo et al. 2000; Petrick et al. 2001), while DMA^{V} is the least toxic (Styblo et al. 2000). However, the quantification of the As metabolic intermediates based on its oxidation state is not feasible in many cases due to the lability of the trivalent intermediates, which are rapidly oxidized to pentavalent forms. Therefore, the urinary metabolic profile of As is usually considered as the proportions of arsenite, arsenate, monomethylated arsenic (MMA^{III} + MMA^{V}), and dimethylated arsenic (DMA^{III} + DMA^{V}). Then, a protective metabolism of As is the one that leads to an increase in urinary DMA, at the expense of a decrease in the rest of the metabolites, but mainly of MMA. On the contrary, an unfavorable metabolism will be the one that leads to an increase in the MMA percentage at the expense of a decrease in the DMA percentage.

In humans, iAs is metabolized to methylated metabolites mainly by arsenite methyltransferase (As3MT). There is a wide variability in the relative proportions of urinary iAs metabolites between individuals. Percentages of the major three As species can vary from 5 to 25% for iAs (As^{III} + As^{V}), 10 to 30% for monomethylated metabolites (MMA^{III} + MMA^{V}), and 50 to 85% for dimethylated metabolites (DMA^{III} + DMA^{V}) (Bailey et al. 2013; Olmos et al. 2015).

Genetic factors (presence of polymorphism in genes linked to the metabolism of As) and non-genetic factors (age, gender, nutritional status, social habits, among others) have been studied in relation to their influence on the processes of biotransformation of As and, consequently, on its toxicity (Olmos et al. 2015; Tseng 2009; Hall and Gamble 2012; Olmos et al. 2014; Fu et al. 2014; Jain 2015; Yáñez et al. 2015; Recio-Vega et al. 2016).

Polymorphism in genes encoding enzymes related to As metabolism accounts for the interindividual variability in the ability to metabolize As (Olmos et al. 2015; Engström et al. 2011; Harari et al. 2013). Among the studies of the impact of the presence of genetic polymorphism on the ability to metabolize As conducted in LA, some findings have been produced. In a study conducted between 1994 and 2008, the hypothesis of the existence of a protective haplotype in the native population of the Argentine Puna (a region with a high natural content of As in the water available for consumption, Litter et al. 2019) has been proposed (Schlebusch et al. 2013).

This population presents a unique metabolism of As, with a greater efficiency of methylation and elimination of DMA. For this population, it was found a strong association between the haplotype linked to the AS3MT gene and a hypothetical protective haplotype designed as a reference haplotype (Schlebusch et al. 2015). Carrying such haplotype would be linked to favorable metabolism of As and would demonstrate an adaptation to tolerate the As-rich environment. However, while urinary metabolic profile in individuals from the Argentine Puna showed an efficient metabolism (Engström et al. 2011; Harari et al. 2013; Schlebusch et al. 2015), people from other regions of the Chaco-Pampean plain showed a less efficient metabolism (Olmos et al. 2015).

The influence of variants in AS3MT on iAs metabolism can also vary by level of exposure. Associations between genotypes and methylation capacity were for some variants significantly stronger among subjects exposed to As in water with As contents lower than 50 μg/L (Xu et al. 2016) and, for other variants, significantly stronger among subjects exposed to As in water above 50 μg/L and higher (Olmos et al. 2015; Xu et al. 2016). Other genes were evaluated in relation to their influence on As methylation. Methyltransferase-encoding gene and N-6 adenine-specific DNA methyltransferase 1 (N6AMT1) polymorphisms did not show clear association with As methylation (de la Rosa et al. 2017). In Mexican population, among the one-carbon metabolizing gene polymorphisms (FOLH1 c.223 T > C, MTHFD1 c.1958 G > A, MTHFR c.665 C > T, MTR c.2756 A > G, and MTRR c.66 A > G), only FOLH1 c.223 T > C demonstrated association with a lower percentage of iAs and a higher DMA/iAs ratio (Gamboa-Loira et al. 2018).

Other studies conducted in Mexico and Argentina investigated the influence of gender (Olmos et al. 2015; Recio-Vega et al. 2016), level of exposure (Olmos et al. 2014), and ethnic origin (Bobillo et al. 2014) on the metabolism of As. These studies identified the male gender and the level of exposure as factors that decrease the methylation efficiency (leading to unfavorable metabolism) and, therefore, contribute to an increased risk of developing the toxic effects of As (Olmos et al. 2015; Olmos et al. 2014; Recio-Vega et al. 2016). Ethnic origin was not found to be associated with differential metabolism (Bobillo et al. 2014). This study included 70 children from the Chaco-Pampean plain who were chronically exposed to high As levels and were evaluated for genetic markers of maternal, paternal, and biparental ancestry.

1.3 Carcinogenicity

The International Agency for Research on Cancer (IARC) has confirmed that chronic exposure to iAs causes cancers of the skin, lung, and bladder (International Agency for Research on Cancer (IARC) 2012). The IARC also states the positive association between iAs and cancer of liver, kidney, and prostate (International Agency for Research on Cancer (IARC) 2012; National Research Council 2001). Epidemiological studies conducted in Chile and Argentina, where population is chronically exposed to As through drinking water (concentrations of 150 μg/L and above), have demonstrated the association of As exposure and lung and bladder cancers (Ferreccio et al. 1998; Hopenhayn-Rich et al. 1998; Smith et al. 1998; Ferreccio et al. 2000; Steinmaus et al. 2010).

Several mechanisms have been implicated in the development of As-associated cancers, including the generation of reactive oxygen species (ROS), the inhibition of DNA repair process, alterations in cellular signal transduction, and alterations in DNA methylation. No single mechanism has emerged as a key event, and it is likely that iAs exerts carcinogenic effects through multiple mechanisms (Bailey et al. 2016). A recent review (Cohen et al. 2016) proposes that iAs is a non-genotoxic carcinogen and concludes that induction of cancer by iAs involves cytotoxicity and regenerative proliferation rather than genotoxicity. A transcriptomic study, conducted in newborn cord blood of Mexican women with different levels of exposure to As, has identified that prenatal exposure to As was linked to microRNA (miRNA) expression changes, mainly associated with cancer development, among other pathologies (Rager et al. 2014).

1.4 Early Exposure and Cancer and Non-cancer Pathologies Development

The health effects resulting only from the early exposure to As are difficult to evaluate since the majority of the population continues exposed until adult life, that is, they do not interrupt their exposure. For example, it would be necessary to identify and evaluate adults who have resided in areas of hydroarsenicism during their childhood, which would make the selection of the study population very difficult. The region of Antofagasta, in the north of Chile, has presented a unique framework of human exposure to As through drinking water. Between 1958 and 1970, As concentration in water was above 800 μg/L. In 1970, with the installation of a treatment plant, As concentration in water decreased to values close to 10 μg/L. The population born in the period between 1958 and 1970, in that area, presents the characteristics of having been early exposed to As. A steep increase in adult mortality due to lung cancer, bladder cancer, and kidney cancer was observed in the Chilean population probably due to in utero and early-life exposure to As (Yuan et al. 2010; Steinmaus et al. 2014).

Many studies have been conducted in people of LA to assess the influence of an early exposure to As. In Chile, it was found that in utero and childhood exposure to As through drinking water was linked to long-term lung function impairment and nonmalignant lung diseases in humans and that early-life exposure has irreversible respiratory effects of a magnitude similar to smoking throughout adulthood (Dauphiné et al. 2011). In Mexico, decrease in forced vital capacity and a restrictive spirometric pattern were observed in the lungs of children exposed to high As levels in drinking water (mean value 152.13 μg/L) during in utero and early-life stages

(Recio-Vega et al. 2015). In Antofagasta, Chile, As in drinking water has resulted in the greatest increase in mortality by non-cancer diseases in adults under 50 years of age, ever associated with early-life exposure (Smith et al. 2012). Also in Chile, exposure to drinking water with less than 50 μg/L of As during pregnancy was associated with reduction in birth weight (Hopenhayn et al. 2003).

1.5 Skin Lesions and Skin Cancer

The first description of dermatological lesions caused by As is more than a century old. Bell Ville disease, the former name for hydroarsenicism or arsenicosis, was presented and described for the first time in Argentina by Dr. Ayerza in 1917 (Ayerza 1917, 1918a, b; Litter 2010) based on the description of a case (Círculo Médico del Rosario 1917). Since that moment, hydroarsenicism was recognized as a disease due to chronic exposure to As through drinking water. Several studies conducted in Mexico, Chile, and Argentina related the consumption of As through drinking water with the development of dermatological lesions and skin cancer (Cebrián et al. 1983; Smith et al. 2000; Cabrera and Gómez 2003; Castro de Esparza 2004; Ferreccio and Sancha 2006; Mercado de Scaglione and Llapur 2006; Ochoa Reyes et al. 2009).

The specific dermal lesions of hydroarsenicism are the alteration of pigmentation and keratosis. The alteration of pigmentation appears as a pattern of fine freckles particularly pronounced on the torso and limbs. The alteration of the pigmentation can also appear in mucous membranes such as the lower surface of the tongue and buccal mucosa. Other patterns include diffuse hyperpigmentation, localized in patches and also leucomelanosis, with hypopigmented macules with the appearance of moles. The leucomelanosis usually appears in patients with arsenicosis who for a time have stopped consuming water with As. Keratosis appears as a diffuse thickening in palms and soles, alone or in combination with usually symmetrically distributed nodules. Nodular forms are most commonly found on the palm and its edges, or at the birth or lateral surface of fingers, heel, and toes, some of which form larger, wartlike lesions. Keratoderma was the skin lesion most frequently observed in studies conducted in LA. Melanosis, leucomelanoses, and carcinomas (squamous cell carcinoma and Bowen's disease) were also described, although not for all cases. The basal cell carcinoma (BCC) and squamous cell carcinoma (SqCC) are the most common forms of skin cancer found in patients with long-term exposure to As. A dose-response relationship and cell-type specificity have been described in patients of northern Chile for As-related skin cancer (Martinez et al. 2010).

1.6 Lung Cancer and Respiratory Disease

Chronic exposure to As via drinking water is related to respiratory alterations and lung cancer. Studies conducted in Argentina and Chile revealed a clear trend in lung cancer standardized mortality rates (SMR) and odds ratios with increasing As concentration in drinking water ranging from less than 10 μg/L to a 65-year average concentration of 200–400 μg/L (Hopenhayn-Rich et al. 1998; Ferreccio et al. 2000).

Case-control studies conducted from 2007 to 2010 showed very high odds ratios for lung cancer and evidence of additive effects in people exposed to As concentrations higher than 335 μg/L and who were tobacco smokers (Ferreccio et al. 2013a), or in people exposed to more than 800 μg/L, and had elevated body mass index (BMI) (Steinmaus et al. 2015). Other studies also from Argentina and Chile provided evidence that people who are less effective at methylating MMA to DMA (unfavorable metabolism) are at greater risk of As-related cancer than others (Steinmaus et al. 2010; Melak et al. 2014).

In relation to the type of lung cancer, a study made in Taiwan found that patients from an endemic area had higher proportions of squamous cell and small cell carcinomas but a lower proportion of adenocarcinomas (Guo et al. 2004). Concordantly, in Antofagasta, where population was exposed to high levels of As and the mortality for lung cancer is the highest in Chile (Roco et al. 2013), a study showed that the rates for squamous cell carcinoma were the highest, accounting for approximately two-thirds of all lung cancer cases in the region (Buys et al. 2010).

There are also studies that investigated the impairment of lung function and its association to As exposure through drinking water. A study conducted in Mexico in a population of 275 children found a relationship between As exposure and the frequency of abnormal spirometry pattern and lung inflammation biomarkers (Olivas-Calderón et al. 2015). Nonmalignant lung disease (bronchiectasis) was observed in a study on the Chilean population of Antofagasta, exposed to high As levels in drinking water (870 μg/L) (Smith et al. 2006).

An association between nonmalignant respiratory diseases, high body mass index (BMI), and As exposure was described in adults of northern Chile (Nardone et al. 2017). In addition, new evidence in Chilean population shows that prolonged exposure to moderate levels of As (60 μg/L) could be associated with pulmonary impairment (Steinmaus et al. 2016).

1.7 Bladder Cancer

Numerous studies from Chile and Argentina have reported the association of chronic exposure to As with bladder cancer. The development of bladder cancer was related to As concentrations of more than 100 μg/L, and odds ratios increased significantly with the level of exposure (Hopenhayn-Rich et al. 1998; Steinmaus et al. 2014; Ferreccio et al. 2013a). It was also demonstrated that a less effective methylation of

MMA to DMA (unfavorable metabolism) leads to an increased probability of developing bladder cancer (Melak et al. 2014). In a study conducted in Chile, large time intervals (more than 25 years) were found between the cessation of exposure to As and the peak of the mortality rates due to bladder cancer (Marshall et al. 2007). There are also other studies in Chile (Smith et al. 2012; Fernández et al. 2012) that observed higher mortality rates from bladder cancer after 20 years from cessation of exposure and found differences between women and men, with a higher mortality rate for women.

A new potential connection between exposure to iAs and bladder cancer was investigated in a study on 46 residents of Chihuahua, Mexico. The study examined epigenetic alterations (DNA methylation patterns) and their association with intracellular concentrations of total As and with the different As species. It was found that iAs exposure and specific As metabolites retained in exfoliated urothelial cells were associated with the altered promoter methylation of key cancer and metabolic disease-associated genes (Rager et al. 2015).

1.8 Other Cancers

Inorganic As compounds, including arsenic trioxide, arsenite, and arsenate, cause cancer of lung, urinary bladder, and skin. Also, a positive association has been observed between exposure to As and iAs compounds and cancer of kidney, liver, and prostate (International Agency for Research on Cancer (IARC) 2012).

Three studies investigated the association of As exposure and kidney cancer (Yuan et al. 2010; Ferreccio et al. 2013b; Smith et al. 2018). All of them were conducted in Chile in the same region, but data were collected in different periods of time. Two of the studies (Yuan et al. 2010; Smith et al. 2018) found evidence of increased adjusted rate ratios for kidney cancer mortality in exposed population compared to unexposed population. Elevated odds ratios and dose-response relationships between renal pelvis and ureter cancers (transitional cell carcinoma) and various metrics of As intake (highest 5-year daily average of arsenic intake, highest daily arsenic intake before 1971, and cumulative arsenic exposure) have been found (Ferreccio et al. 2013b). In this study, no associations were found for renal cell cancer.

A study in 26 counties of Córdoba, Argentina, where there has been a well-documented history of As exposure from well water drinking, investigated mortality from lung, skin, kidney, and liver cancers in counties which were categorized into low (40–140 μg/L), medium (140–178 μg/L), and high (>178 μg/L) As-exposure areas. The authors found significant increasing trend, in dose-response relations, in SMR for kidney cancer (0.87, 1.33, and 1.57 for men, 1.00, 1.36, and 1.81 for women, [$p = 0.001$ for both]). A slight trend was also seen for liver cancer, with elevated SMR in all exposure groups (Hopenhayn-Rich et al. 1998).

Other studies found evidence of association of development of liver cancer and exposure to As. Increased childhood liver cancer mortality possibly related to As exposure has been found (Liaw et al. 2008). The study, conducted in Chile, included childhood (0–19 years old) cancer mortality data of As-exposed and As-unexposed areas, in the period 1950–2000. They found statistically significant differences in mortality rates between exposed and non-exposed boys and girls born just before (1950–1957) the high As-exposure period began (1957–1970). A link between As exposure and liver cancer deaths for adults (30–39 years old, males and females) exposed during childhood to near 1000 μg/L of As has been also found (Smith et al. 2012). Both studies analyzed liver cancer mortality rates in the same region of Chile (Region II), during the period 1958–1970, when population was exposed to very high As levels in water (800–1300 μg/L).

In a recent case-control study, conducted in Argentina (Roman et al. 2018), both exposure to As in drinking water above 10 μg/L and occupational exposure in rural workers contributed to a significant increase in prostate cancer (PC) occurrence (OR 5.07; 95% CI 2.074–12.404). The same study found that the time of consumption of groundwater in regions with As above 10 μg/L was also positively associated with PC incidence.

Additionally, the relationship between exposure to As and the development of other cancers (leukemia, brain, colon, breast, larynx, stomach, cervix, and endometrium) was also investigated. No relationship was found between As exposure and brain cancer or leukemia in Chilean children (Liaw et al. 2008). No evidence of association between As exposure and breast, cervix, endometrium, prostate, colon, or stomach cancers was found in a study relating As levels in water with cancer frequency, conducted in La Pampa province, Argentina (Molina et al. 2014). Evidence of increased laryngeal cancer mortality among men with early-life exposure to As had been reported (Smith et al. 2012). In another study performed in Argentina, increased risk for colon cancer in women was associated with As exposure (Aballay et al. 2012). In the same study, no association of As exposure and breast cancer was observed. The fact that these studies included population with wide levels of As exposure, from non-detectable to near 800 μg/L and from 800 to 1300 μg/L for Argentina and Chile, respectively, gives more weight to the negative results.

1.9 Diabetes

In the last decade, a growing interest has been noted in evaluating the potential role of low-to-moderate dose exposure to As in the development of type 2 diabetes in humans. In LA, most studies were conducted in Mexico. Exposure to low-to-moderate levels of As through drinking water has shown to be associated with markers of diabetes fasting plasma glucose (FPG) and 2-h plasma glucose (2HPG) (Coronado-González et al. 2007; Del Razo et al. 2011; Mendez et al. 2016). Individuals with total As concentration in urine (63.5–104 μg/g creatinine) had odds ratio (OR 2.16) and 95% confidence interval (95% CI 1.23–3.79) (Coronado-González et al. 2007). Exposure to iAs through drinking water was positively associated with diabetes (OR, 1.13 per 10 μg/L; 95% CI, 1.05–1.22, $p < 0.01$) (Del Razo et al. 2011). The association of As exposure with fasting plasma insulin levels and insulin resistance is still not clear (Del Razo et al. 2011). Two cross-sectional studies, conducted in Mexico, have reported that the relationship between As and markers of diabetes, FPG and 2HPG, seems to be at the expense of the As dimethylated metabolite, DMA (OR, 1.24; 95% CI, 1.00–1.55) (Del Razo et al. 2011) and (OR, 2.61; 95% CI, 1.22–5.57) (Mendez et al. 2016). A third cross-sectional study, also conducted in Mexico, found association between both urinary DMA/MMA ratio (OR, 1.37; 95% CI, 1.03–1.84) and urinary DMA (OR, 1.34; 95% CI, 1.02–1.76) and FPG and 2HPG (Currier et al. 2014).

In a recent study involving metabolomic analysis, 103 metabolite shifts were identified in diabetic and nondiabetic individuals exposed to As. Of the 103 altered metabolite, 59 were unique to diabetic individuals (42 urinary and 14 plasma metabolites) possibly indicating a metabolomics fingerprint of As-associated diabetes (Martin et al. 2015).

As a conclusion, despite it seems to be an association between As exposure and diabetes, more studies should be conducted, specially focusing on the potential mechanisms of As-induced diabetes in humans.

1.10 Cardiovascular Disease

According to the World Health Organization (2017), cardiovascular diseases (CVDs) are disorders of the heart and blood vessels and include coronary heart disease, cerebrovascular disease, rheumatic heart disease, and other conditions. CVD deaths are due to heart attacks, myocardial infarction, and strokes. Individuals at risk of CVD may demonstrate raised blood pressure, glucose, and lipids as well as overweight and obesity. The generation of ROS and reactive nitrogen species (RNS) is one of the proposed mechanisms related to cardiovascular effects due to chronic exposure to As. This redox imbalance leads to endothelial dysfunction, an early-effect marker of atherosclerosis, hypertension, or peripheral vascular disease.

In LA, studies investigating the association of As exposure and the development of CVDs have been conducted in Chile and Mexico. In Chile, acute myocardial infarction (AMI) has been identified as the major CVD related to chronic exposure to As (13 years, 580 μg/L, average) (Yuan et al. 2007). AMI resulted in the main cause of death in the first years after exposure, overcame, in later years, by lung and bladder cancer (Smith et al. 2018; Yuan et al. 2007). In another study in Chile, statistically significant associations between drinking water As exposure (median As water concentrations of 10 μg/L, 178 μg/L, and 860 μg/L) and hypertension among study participants have been found (Hall et al. 2017). In Mexico, a cross-sectional study was conducted in 199 children exposed to 3–135 μg/L of As through drinking water (Osorio-Yáñez et al. 2013). The children were examined using a cardiovascular ultrasound system, and carotid intima media thickness (cIMT) was calculated. cIMT, a widely accepted indicator of subclinical atherosclerotic burden, was significantly associated with urinary As (Osorio-Yáñez et al. 2013). Although it could not be confirmed, the influence of the in utero exposure could not be ruled out either. Then, and according to those authors, the association between cIMT and exposure to As during childhood could include in utero exposure. In a recent study conducted in adults (>18 years old) in Mexico, As exposure (concentrations of urinary As from 0.52 to 491.5 μg/L, with a median of 55.8 μg/L) was associated with several markers of increased cardiometabolic risk (triglyceridemia and cholesterolemia), but no correlation with hypertension and low-density lipoprotein (LDL) cholesterol has been found (Mendez et al. 2016).

The aforementioned studies covered a wide range of exposure; however, the available information on exposure to As and CVDs in LA is still partial, scarce, and even inconclusive.

1.11 Liver Dysfunction

Worldwide, it has been described that non-cirrhotic portal hypertension is related to chronic arsenic exposure (Schouten et al. 2015) and that As toxicity can also be expressed as non-cirrhotic portal fibrosis (Mazumder 2005). However, in LA, there is a lack of studies investigating these effects. Only one study was found, conducted in Chile in 1990, which reported hepatic cirrhosis and hemangioendothelioma of the liver in ten autopsied children with chronic arsenical dermatosis from Antofagasta, Chile (Zaldivar 1980).

1.12 Chronic Kidney Disease

Urinary excretion represents the major route of As elimination. Since a large fraction of absorbed As is filtered by the kidney, it is an important site of As uptake and accumulation. Epidemiological and experimental studies evaluating As nephrotoxicity have tested the following markers of renal toxicity: glomerular filtration rate (GFR), proteinuria, albuminuria, N-acetyl-b-D-glucosaminidase (NAG), β2-microglobulin, and α-1-microglobulin and retinol-binding protein (Robles-Osorio et al. 2015).

A cross-sectional study conducted in Mexico, in a population exposed to low-to-moderated levels of As (median urinary As levels were of 15.0 μg/g of creatinine, range 0.56–89.2 μg/g), found association between urinary As and urinary excretion of α-1-microglobulin, a marker of early renal injury (Robles-Osorio et al. 2012). However, no associations with urinary albumin or serum urea, creatinine, and uric acid were found. In Chile, an ecological design study found evidence of increased mortality from chronic renal disease (Smith et al. 2012).

Although As may be considered as a risk factor, the evidence linking As exposure and chronic kidney disease is still scarce and limited to studies in a few countries, and only the results of two studies are available for LA.

1.13 Neurological Effects and Cognitive Impairment

In the last years, various epidemiological reports have investigated the influence of environmental exposure to As on neurological and cognitive functions. Four studies, conducted in Mexico, investigated the association of environmental exposure to As (and to other pollutants as lead and fluoride) with central nervous system (CNS) effects. The associations between first-grade children's urinary arsenic levels, As metabolite concentrations, and behavior and cognition function have been investigated (Roy et al. 2011). The authors found marginal associations between total urinary As and the As metabolite DMA and select measures of children's behavior.

A study to explore the influence of both F and As on IQ in first-to-third grade children living in three rural areas with contrasting levels of F and As has been conducted. An inverse association of As exposure with full, performance and verbal IQ scores was observed (Rocha-Amador et al. 2007).

Two more studies conducted in children found that As exposure affected children's cognitive function (Calderón et al. 2001; Rosado et al. 2007). The urinary As was inversely correlated to verbal intelligent quotient (IQ), verbal comprehension, and long-term memory (Calderón et al. 2001).

1.14 Immunotoxicity

The effects of iAs on the immune system are complex and apparently divergent, since they include evidence of immunosuppression and inflammation. Chronic As exposure seems to be related to immunosuppression, a process which strongly enhances cancer development. It also increases the incidence of diabetes mellitus, an autoimmune-mediated disease, and it is related to impaired lung function probably via inflammation processes. In LA, several studies have been conducted to assess the effects of As on immunological status of As-exposed populations. Inflammation and immunosuppression, both markers of effect, have been observed simultaneously in children exposed population from Zimapán, Mexico (Soto-Peña et al. 2006). Secretion of granulocyte-macrophage colony-stimulating factor (GM-CSF) was found to be directly associated with urinary As levels. On the other hand, urinary As levels were inversely associated with interleukin 2 levels, suggesting immunosuppression (Soto-Peña et al. 2006).

Evidence of the complex impairment of the immune response was observed in a study conducted in Mexico, where a significant negative correlation between As urinary levels and the proportion of natural T regulatory (nTreg) cells in peripheral blood was observed in individuals exposed to As, via drinking water, while, in vitro tests, low concentration of As enhanced the proportions of nTreg cells (Hernández-Castro et al. 2009).

In another study also conducted in Mexico, biomarkers of inflammation, soluble receptor for advanced glycation end products (sRAGE), matrix metalloproteinase 9 (MMP-9), and tissue inhibitor of metalloproteinase 1 (TIMP-1), were evaluated in children with different levels of exposure to As (Olivas-Calderón et al. 2015). Results indicated that chronic As exposure modifies negatively sRAGE, MMP-9, and MMP-9/TIMP-1 levels, leading to a chronic lung inflammatory response (Olivas-Calderón et al. 2015).

Two "omic" studies were conducted in Mexico to investigate the effects of As exposure on the immune system. At transcriptomic level, prenatal exposure to As was linked to 12 microRNA (miRNA) expression changes, which are known to be associated with inflammatory response and inflammatory disease, among other pathologies (Rager et al. 2014). The study, conducted in Mexico, focused on investigation of innate and adaptive immune signaling in newborn cord blood of women with different levels of exposure to As. An epigenomic study examining the relationship between gene-specific promoter DNA methylation levels of peripheral blood leukocytes (PBLs) and urinary arsenical concentrations was conducted in individuals from Zimapán, Mexico. More than 800 genes were found where promoter DNA methylation was associated with the urinary concentration of As. Major functions associated with these genes include cellular growth and development, inflammatory response, and immune response (Bailey et al. 2014). More recently, a study from Argentina found an association between As exposure and expression and differential methylation of genes linked to immune response (Engström et al. 2017).

1.15 Preventive and Curative Options to Deal with Chronic Arsenic Exposure in Humans

There is not curative treatment for arsenicosis and its clinical manifestations. However, national guidelines for the treatment of arsenicosis have been published by the Ministries of Health of Argentina (2011), Chile (2014) and Peru (2012). For all cases, first-line actions should be focused on avoiding exposure by means of providing alternative sources of safe water. In Chile, the therapeutic decisions are based on urinary As levels (Ministerio de Salud (MINSAL) 2014) and presence of symptoms. Indications include education, nutritional assessment, urinary As monitoring, antioxidant intake, and referral to specialist, if applicable. In Peru, treatment recommendations are based on avoiding exposure and nutritional assessment (Ministerio de Salud (MINSA) 2012). Nutritional assessment includes the intake of antioxidant-rich foods as vegetable oils (nut, cereals, peanut, lupine, and olive) and fruits and vegetables (orange, lemon, kiwi, broccoli, and pepper). In Argentina, the national guidelines recommend avoiding the exposure and symptomatic support treatment consisting of healthy protein foods diet (Ministerio de Salud (MSAL) 2011). In addition, the guideline indicates that specific symptoms should receive the corresponding treatment measures as follows: stop smoking in case of chronic bronchitis, topical keratolytics for keratosis, and surgical exeresis for skin tumors (Ministerio de Salud (MSAL) 2011).

Few studies were conducted in LA to investigate the influence of nutritional factors and dietary habits on As-related toxicity. A study from Mexico, investigating the relationship between nutrition and As exposure, found that both culinary practices and the quality of food not only did not contribute to avoid exposure but did not provide the minimum necessary contribution of antioxidants to the diet (Monroy Torres et al. 2016). Another study conducted in Argentina found an elevated OR for prostate cancer linked to a high adherence to a dietary pattern characterized by fat and processed meat and starchy vegetables (Roman et al. 2018). Both studies attribute a higher probability of development of specific toxicity to the composition of the diet, which could mean that a change in diet could contribute to reduce the risk of appearance of certain toxic effects. However, in LA, studies proving this statement are lacking.

Nevertheless, there are studies that investigate the influence of nutrients on As metabolism, which could, in turn, influence the toxicity of As. Studies conducted in Mexico and Uruguay investigated whether the differences in dietary intake of selected micronutrients and foods are associated with the metabolism of iAs. The daily intake of methionine, choline, folate, vitamin B12, vitamin C, Fe, Zn, Se, and Na was significantly associated with the reduction of % iAs and/or % DMA increase in one study conducted in Mexico (López-Carrillo et al. 2016). Higher meat and folate consumption, diet rich in green leafy and red-orange vegetables, and eggs contributed to a higher methylation capacity according to the study conducted in Uruguayan children (Kordas et al. 2016). Zinc and iron seemed not to influence arsenic metabolism in Mexican children (Kordas et al. 2017).

A very recent review reported the clinical and epidemiological studies that have evaluated different treatments for arsenicosis conducted around the world (Sharma and Flora 2018). They include vitamins (A, C, E, folic acid), minerals (iron, zinc, selenium), amino acids (methionine, choline), and medicinal plant oils (*Nigella sativa*, *Allium sativum*) treatments. The results indicated that the nutritional intervention represents a valid and economical alternative for the alleviation of the symptoms of arsenicosis.

In conclusion, in LA, research focusing on curative options for chronic As exposure is beginning, and it is aligned to latest international research.

2 Arsenic Removal Technologies in Latin America

2.1 Generalities

Economic aspects are the most important factors for the selection of a technology for As abatement, taking into account the size of the population, the incidence of chronic illnesses, the lack of safe water, the sustainability of the water resources, poverty conditions, and other socioeconomic variables. Although many attempts to solve the As problem in drinking water have been made in many large urban areas in LA by the installation of water treatment plants, many of them are not working properly or are proving to be too expensive to operate. In contrast, practically no action has been taken by the authorities, or international and bilateral cooperation agencies, to mitigate the As problem affecting rural or peri-urban populations. This makes the dispersed population the most disadvantaged group because they often depend on As-contaminated water as their only available drinking water resource. Furthermore, typically, these communities are not aware of As toxicity. In addition, As treatment units require special monitoring and maintenance arrangements, which fall far beyond the economic scope of rural communities and peri-urban localities where the income level and sanitation conditions are rather low. Moreover, a number of cultural and political factors play deciding roles in implementing new technologies (Bundschuh et al. 2009; Litter et al. 2010a).

The physicochemical and microbiological characteristics of the waters and the available materials in the region will determine the most convenient technology for As removal in each site. From a technical point of view, the selection of the removal method depends greatly on As speciation; chemical composition of the water matrix; oxidation-reduction potential; hardness; presence of silica, sulfate, phosphate, iron, and other chemical species; volumes to be treated; and degree of sophistication that may be applied. Additionally, the volume, handling, and final disposal of the generated wastes should be considered (Sancha and Castro 2001; Hering et al. 1997; McNeill and Edwards 1995; Meng et al. 2000; Sancha 2003). However, due to the length of this chapter, the treatment and disposal of As wastes will not be included in this chapter.

All technologies rely on a few basic chemical processes, which can be applied simultaneously or in sequence: oxidation/reduction, coagulation-filtration, precipitation, adsorption and ion exchange, solid/liquid separation, physical exclusion, membrane technologies, biological methods, etc. It is important to note that boiling does not remove As from water and, on the contrary, the process will increase the As concentration by evaporation, a fact commonly ignored by the potentially affected people. Most As removal technologies are efficient when the element is present in the pentavalent state, since the trivalent form is uncharged at pH below 9.2. This is the reason why many As remediation methods use, previously to other processes, an oxidation step. However, oxidation without help of other physical or chemical transformations does not remove As from water (Höll and Litter 2010).

Table 1 Classification in groups of the different methodologies for As removal from water

(1) *Adsorption*	(5) *Ionic exchange*
Activated alumina	
Sorbents based on iron and nanomaterials	
Geological materials	
(2) *Oxidation and reduction*	(6) *Lime softening*
Photochemical oxidation/reduction	
In situ oxidation	
Oxidation/reduction with iron nanoparticles	
(3) *Precipitation*	(7) *Membrane filtration*
Removal with Fe/Mn	Reverse osmosis
	Nanofiltration
	Electrodialysis
(4) *Coagulation-filtration*	(8) *Bioremediation*
	Biosorbents
	Biological oxidation

A simplified scheme of the most common technologies for As removal from water is shown in Table 1. For the full description, please see the corresponding references (e.g., Litter et al. 2010a; Höll and Litter 2010; Pirnie 2000; Ravenscroft et al. 2009; Sharma and Sohn 2009; www.physics.harvard.edu/~wilson/arsenic/conferences/Feroze_Ahmed/Sec_3.htm n.d.; Morgada et al. 2008; Bundschuh and Litter 2010).

2.2 Technologies Employed in Latin America

The most used processes for As removal in LA are adsorption, chemical precipitation, activated alumina, use of ion exchange resins, membrane technologies, distillation, and coagulation/filtration, which can be employed alone or in combination (Castro de Esparza 2004; Litter et al. 2010a; Sancha and Castro 2001; Litter 2010; Alarcón-Herrera et al. 2013; Litter and Bundschuh 2012). However, the use of geo-adsorbents, natural materials, iron-based technologies, and solar applications can be also mentioned (Litter et al. 2012).

2.2.1 Argentina

In Argentina, the accepted maximum level for As in drinking water is still under discussion. In 2007, a joint resolution (No. 68 and 196/2007) modified the articles 982 (about drinking water of public supply and domestic use) and 983 (about bottled drinking water) of the Argentine Food Code (CAA) (Código Alimentario Argentino 2012), reducing the allowable value of As in drinking water from of 50 to

10 µg/L to comply with the WHO recommendations (World Health Organization (WHO) 2011). In 2012, a new extension period to attain this level was adopted, waiting for the conclusions of an epidemiological study to be performed by governmental authorities to establish the guideline value for Argentina (Secretaría de Políticas, Regulación e Institutos y Secretaría de Agricultura, Ganadería y Pesca, Código Alimentario Argentino, Resolución Conjunta 2012). It has been estimated that, according to the last WHO recommendations (10 µg/L), approximately 4 million people can be at risk in Argentina due to consumption of water with high As levels (Litter 2010).

Since the 1970s, studies on As removal have been reported (Sancha and Castro 2001; Trelles et al. 1970; Callegaro et al. 1976; Dodero et al. 1978). The patented ALUFLOC technology developed by PAHO-CEPIS (see Sect. 2.2.11) has been tested in the 1990s in Salta and Tucumán at the household level (Sancha and Castro 2001; Esparza 1996).

Today, the use of membranes (mainly reverse osmosis, RO) is the most employed alternative for As treatment in large-medium plants of Argentina, followed by coagulation/adsorption/filtration processes (Litter et al. 2010a; Alarcón-Herrera et al. 2013; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; D'Ambrosio 2005; Bundschuh et al. 2010).

Several RO plants have been installed in the Santa Fe, Cordoba, and La Pampa provinces (Litter et al. 2010a; Alarcón-Herrera et al. 2013; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Bundschuh et al. 2010; Ingallinella and Fernández 2010; Cortina et al. 2016; Hering et al. 2017). In Santa Fe, there are more than 80 RO plants; 32 of them treat flows between 10 and 100 m^3/h, which are supplied to the distribution network, and 50 are small plants (0.2–5 m^3/h) from which the water is distributed in bottles to the population. The plants provide an As removal efficiency around 92%. An industrial scale plant that uses Ultra-Osmosis (URO) special membranes has been installed in the locality of Venado Tuerto and treats approximately 4800 m^3/day of water, reducing As levels to less than 10 µg/L (Armas et al., 2014). Although several RO plants have been installed in Buenos Aires, the only documented results are those from the company AySA (Aguas y Saneamientos Argentinos), which has installed a large potabilizing plant to treat waters from the southern periphery of Buenos Aires City, benefiting 400,000 inhabitants (Bardach et al. 2015; AySA 2014a). A similar plant is being installed at present in the district of Ezeiza (AySA 2014b).

Coagulation/adsorption/filtration processes are the second technology most used in Argentina for As removal. In Santa Fe, several studies were made since the 1990s (Fernández et al. 2009a). In 1998, a direct coagulation treatment was evaluated for reducing the As levels from an initial concentration of 0.27 mg/L (Sancha and Castro 2001; Mozziconacci et al. 1998). At the Centro de Ingeniería Sanitaria-Universidad Nacional de Rosario (CIS-UNR), the patented ArCIS-UNR® process for the removal of As and F in groundwater with low total salinity has been developed. The process is based on coagulation-adsorption on aluminum hydroxide flocs, using polyaluminum chloride (PAC) as coagulant, and two filtration stages, i.e., a first coarse upflow gravel prefiltration followed by a rapid filtration. This technology achieves concentrations of As less than 0.05 mg/L and 1.5 mg/L of F, and it has been applied to real scale in populations up to 10,000 inhabitants. The process was implemented in Santa Fe (Villa Cañás, López, Santa Isabel) and in Buenos Aires (Lezama). Recently, the ArCIS-UNR® process was improved to treat groundwater containing phosphates by adding the PAC coagulant in two stages. For cities with a larger population and higher F concentrations in the water, the original process has been modified replacing the coarse prefiltration stage by an upflow rapid filtration (Litter et al. 2010a; Alarcón-Herrera et al. 2013; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; D'Ambrosio 2005; Bundschuh et al. 2010; Ingallinella and Fernández 2010; Cortina et al. 2016; Hering et al. 2017; Ingallinella et al. 2003a, b; Ingallinella, 2006; Litter et al. 2008; Fernández et al. 2009b; González et al. 2014a, b, 2016).

In Jáchal (San Juan province), a conventional plant, previously designed to remove turbidity, consisting of five lagoons as equalization vessels followed by settlers and slow sand filters, was modified with a second step to remove As adding aluminum sulfate as coagulant and an organic flocculant at two points before the lagoon inlet. The technology could reduce As concentrations from 70 to 110 to less than 10 μg/L (Ingallinella and Fernández, 2010; Cortina et al. 2016; OSE (Obras Sanitarias del Estado, Provincia de San Juan, Argentina 2006).

In San Antonio de los Cobres (Salta), a coagulation filtration system with $FeCl_3$ passing through a series of sand filters was installed at the water treatment plant of Pompeya (Sancha and Castro 2001; Figueroa and Montes 1995). Water with As levels ranging 0.27–0.30 mg/L was treated with aluminum sulfate, lime, and a polyelectrolyte. As concentration was reduced to 0.12–0.15 mg/L, but could not reach the 10 μg/L level. In 2006, the company AdEdge Water Technologies LLC designed and built a new system consisting of a two-step process, a first step using an ADGS+ filtration media (a silica-based media with a hybrid MnO_2 component) followed by a second polishing step which uses GFO+ granular ferric oxide (GFO) adsorptive-based media. Final As levels were less than 5 μg/L (Bonillas, 2012).

The removal of As from synthetic waters and surface water by nanofiltration (NF) membranes was investigated using a NF-300 membrane module. Arsenic was removed 93–99% from synthetic feed waters containing between 100 and 382 μg/L As(V), resulting in permeate As concentrations of about 5 μg/L. In surface water, the mean rejection of As(V) was 95% (Saitua et al. 2005).

On the other hand, in the Chaco-Pampean plain of Argentina, about 12% of the population is living in dispersed settlements consisting of less than 50 inhabitants, which belong mostly to the poorest members of the regional population. To solve the problem, several works have been conducted, using conventional and emergent technologies with commercial adsorbents or natural materials at the laboratory scale, with some applications on real waters. Iron or aluminum materials have been the most tested. A description of the technologies follows.

A hydrogel of activated aluminum hydroxide was tested and found effective to treat 64 artificial water samples (As 100–5,000 mg/L) and 200 groundwater samples from Tucumán (As 40–800 mg/L), reaching in all cases As concentrations below 10 mg/L (Litter et al. 2010a; Litter and Bundschuh 2012; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Luján and Graieb 1994; Luján and Graieb 1995; Luján 2001a, b).

Later, different clay-rich soils and sediments have been tested as adsorbents at a laboratory scale to remove As from groundwater of the Río Dulce aquifer in Santiago del Estero. In laboratory experiments, high As removal at household scale was achieved using a Fe-rich laterite (an acidic soil from the Misiones province, composed by hydrous oxides of Fe and Al). In experiments with natural groundwaters (As concentration: 500 mg/L), As concentration was decreased to 10–30 mg/L within 40 min (94–98% efficiency). However, the high transport costs of the laterite from Misiones to Santiago del Estero (1100 km far) make the technology not convenient for the isolated settlements of the province. Natural clays from Santiago del Estero, Tucumán, and Salta were also evaluated as adsorbents, but As(V) removal was found less efficient than the Misiones material (99 vs. 40–53%) (Claesson and Fagerberg 2003; Mellano and Ramirez 2004; Lindbäck and Sjölin 2006; Storniolo et al. 2005; Bundschuh et al. 2011). A compressed laterite from Misiones with a high content of iron has been tested recently in rural areas of the Chaco province. It was shown that As removal with the ground laterite used in the form of spheres was around 95–99%. However, to avoid disintegration and obstructions, laterite was used in the form of tablets, showing excellent results (90% removal) (Hryczyñski et al. 2014).

Arsenic removal using a low-cost synthetic 4-Na-mica ($Na_4Si_4Al_4Mg_6O_{20}F_4 \cdot xH_2O$) and its product of mechanical treatment (4-Na-micaMT) was evaluated. With an As concentration of 550 μg/L at pH 7 and 1 g/L of the mineral, the removal capacities were 60.7% for 4-Na-mica and 96.5% for the mechanically activated mica. Both materials were also found very efficient for natural contaminated waters from Salta (ca. 200 μg As/L) (Litter et al. 2012; Lorenzo et al. 2008).

Granular ferric hydroxides/oxides (GFH/GFO) were used in a fixed bed for As removal in a mobile plant in waters from Romera Pozo and Agua Azul (Tucumán). The As content reached 10 μg/L after 10,000 bed volumes (BV) for groundwater with an initial content of 65 μg/L, after 8000 BV for water with 110 μg/L, and 1000 BV for water with 920 μg/L (Graieb and Lujan 2014). Small systems based on adsorption on fixed GFH beds have been also implemented in four localities: Junín, Suipacha and Chivilcoy (Buenos Aires), and Villa María (Córdoba) (Bardach et al. 2015; Bahr and Ewy 2014).

The As removal capacity of low-cost materials, such as a natural clay (laterite from Misiones), microparticulate ZVI (μFe(0)), and commercial iron wool, was studied using As(III) and As(V) (As initial concentration, 5 mg/L, at pH 7). The results indicate that concentrations of 2.5% m/v for clay or 0.05% m/v for both Fe(0) materials are required for As removal higher than 95% for As(V) and As(III) (Meichtry et al. 2014; Meichtry et al. 2015).

In another study, the aptitude of two residual lateritic soils for the remediation of groundwater contaminated with As was tested in batch and column tests. Permeable soil columns were prepared with mixtures of sand (90%) and two soils (10%). As removal in batch ranged 95–99% when using a 1 : 10 solid/liquid ratio depending on the As concentration and the flow rate, and the maximum adsorption capacities were related to the amount of iron compounds in the solid phase (Carro Perez and Francisca 2013).

Synthetic iron oxide pillared clays developed from montmorillonite (Mt) were tested as a new material for As removal. Arsenic(V) was completely removed at pH 4.0 and 6.5 using the modified clays, while low adsorption was observed using Mt (Iriel et al. 2014).

Natural zeolites from Neuquén and Misiones were also tested, in pure form, and modified with iron (T-CZ) and compared with commercial zeolites. Although the pure material presented a higher adsorption capacity than the commercial one, the capacity of T-CZ was better, achieving As concentrations lower than 3 μg/L from initial concentrations as high as 500 μg/L (Camerotto Andreani et al. 2014).

Adsorption on iron oxyhydroxides like goethites was also studied. As(V) adsorption on pure and Sn-substituted goethites was compared. It was found that Sn(IV)-for-Fe(III) substitution duplicated the adsorption value of pure goethite (Larralde et al. 2014). In another study, the adsorption of As(V) onto several Al-substituted goethites was analyzed by STEM micrographs, which indicated the structure of the products of the reaction as bidentated complexes (Tufo et al. 2014).

The modification of diatomaceous earth (diatomite) with ferric oxide after impregnation with $FeCl_3$ followed by calcination increased 50 times the uptake of arsenite and arsenate compared to raw diatomite (Danil de Namor et al. 2014).

Recently, an ergonomic, portable, and household device for As removal has been designed to obtain As concentrations in water below the limits recommended by the WHO. The system uses natural clays, bentonites, and zeolites from the Buenos Aires province. The system was composed of a plastic container containing inside the sorbent in separate multilayers (Yonni et al. 2016).

The effectiveness of adsorption technology for As removal in drinking water was analyzed in seven samples from different wells of Buenos Aires City. It was concluded that, within the range of technologies used for As removal, the adsorption methods provide 80% removal of As in 60% of cases, leading to water quality within the parameters required by the existing legislation in Argentina (Borneo and Barrionuevo 2014).

Biomaterials have been also tested. The effects of pH, hardness, alkalinity, salinity, and bone calcination temperature for As(V) adsorption onto natural biogenic hydroxyapatite obtained from charred cow bones have been studied. Up to 75% As(V) removal from a 1000 μg As/L laboratory solution was obtained after 24-h contact with a 5 g/L suspension of the material (Litter et al. 2012; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Bundschuh et al. 2010; Ingallinella 2006; Czerniczyniec et al. 2007).

As removal from aqueous solutions employing low-cost adsorbents based on hydroxyapatite, nacre, and external surface of shells showed that hydroxyapatite exhibited the highest adsorption performance (43%) (García et al. 2014).

Adsorption studies of arsenate using chitosan were also reported. The maximum percentage removal of As(V) was 82% after 60-min contact time starting from 1 mg/L of As(V), 1 g/L adsorbent dose, and pH 5 (Giménez et al. 2016).

A preliminary study on the use of untreated biomass coming from dead aquatic macrophytes, *Pistia stratiotes*, *Limnobium* sp., *Azolla pinnata*, and *Lemna* sp. for adsorption of As(V) from aqueous solutions indicated that *Azolla pinnata* presented the best adsorption capacity (0.16 mg As/g biomass) (Saralegui et al. 2014).

Arsenic removal (0.25 mg/L) using *Pseudomonas aeruginosa* isolated from Presidencia Roque Sáenz Peña groundwater (Chaco) reached 50% after 3 months. Strains were immobilized in natural stone and cultivated in salts broth and 1 mg As/L. The arsenic resistance and biofilm formation were observed, obtaining interaction between cells, rock, and arsenic. Arsenic removal was evaluated during 3 months, and the final removal percentage was 60%. The bacteria are easy to handle and do not require strict temperature and pH controls, and the reactors can be easily assembled and require low maintenance (Giménez and Pellizzari 2014; Pellizzari et al. 2015).

Phytofiltration (phytoremediation), i.e., the use of plants to remove As from water, has also been reported. Aquatic macrophytes such as *Lemna minor* have been tested allowing As adsorption from the soil through the roots of plants, with incorporation to the vegetal biomass. It was found that the submerged species are more efficient that the emergent ones. Arsenic is absorbed by the roots, and it is accumulated principally in leaves. The removal percentage is higher at higher As concentrations and depends on climatic conditions. In the case of *Lemna minor*, the highest removal was reached at 0.5 mg As/L (Ingallinella 2006; Pérez Carrera et al. 2010).

Removal of As using raw and trihexyltetradecylphosphonium chloride ionic liquid-impregnated polymeric resins was evaluated for removal of As(V), reaching 95% extraction efficiency under the optimal experimental conditions (Escudero et al. 2014).

An intervention model was developed by the Instituto Nacional de Tecnología Industrial (INTI), to provide solutions for the As problem to communities connected to a public water network and to private wells. The study included the construction of a simple and low-cost rural device (Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Instituto Nacional of Tecnología Industrial (INTI) 2009; Frangie et al. 2014). The device uses an optimized coagulation/filtration technology, with a previous oxidation step, and does not require electrical supply. Both the intervention model and the rural device were applied in groundwaters of Taco Pozo (Chaco province) and of Lobos (Buenos Aires province). By request of sponsors of rural schools, 18 rural devices for As removal have been installed from 2009 to 2014 in schools of El Impenetrable, close to Taco Pozo. The initial As concentration was in the 500–2000 μg/L range during 2011–2014, and, in the schools where the device was correctly used, final As concentrations in the treated water were lower than 10 μg/L (Fig. 1).

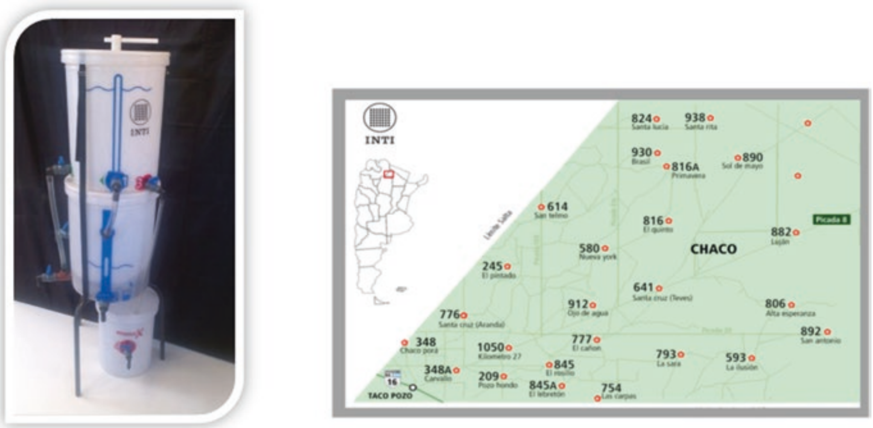

Fig. 1 Rural device for As removal designed by INTI and map of identification of rural schools where the devices were installed

A simple and low-cost technology for As elimination from water using geoadsorbents was developed and implemented. The technology uses iron-rich mineral species, and, for this purpose, mineral deposits localized in nine Argentine provinces have been evaluated. The process was complemented with a coagulation-sedimentation stage, using PAC as the coagulant. Laboratory experiments with waters containing 100–500 μg/L As gave values lower than 10 μg/L after the treatment. The process has been scaled at pilot level for application in small localities, and experimental prototypes for treating 2000 L/day were installed in rural schools of the Buenos Aires province. The As values in the raw water were in the range 150–200 μg/L, and values lower than 10 μg/L after the treatment were always obtained. An upscale to treat higher water volumes (20,000 L) is planned (Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; González 2015; Botto et al. 2013).

A novel module for As removal of using a geoadsorbent was reported. The adsorptive material is a granular media from Cuesta Colorada, La Calera (Córdoba), composed of 26% graves, 66% sand, and 8% montmorillonite, with significant presence of iron oxides. A commercial 25 L water container was modified to include a reactive filter of this material. With this device, removal efficiencies from 12% to 92% (0.1–15 mg/L) were obtained. A natural water with As concentration of 0.05 mg/L was also evaluated. The developed filters successfully reduced As concentration in drinking water during more than 100 days (Francisca et al. 2014).

Arsenic removal with zerovalent iron (ZVI) has been the object of different studies at low scale, especially for households. There are results from basic experiments using ZVI, which use local iron materials, iron wool and packing wire, as well as iron nanoparticles. The use of ZVI can be improved by solar irradiation. A study using extremely reactive commercial nanoparticles (nZVI) produced by an Argentine industry was performed. A rapid As(V) removal was found using very low amounts of iron (0.005–0.1 g/L) with more than 90% As removal after 150 min of contact time at the optimal nZVI concentration. After a 3-h contact time between nZVI (0.025 mg/L) and a real groundwater sample (As concentration, 174 mg/L, circumneutral pH), the concentration decreased to 42 mg/L in the dark and to levels lower than 10 mg/L under UV irradiation. Additionally, removal of As with nZVI in the dark and under UV-Vis light was studied at different As/Fe ratios, in the presence of O_2 or anoxic conditions. Solid products were analyzed by Mössbauer and XANES spectroscopy. From the point of view of the application, the most favorable conditions for As(III) removal with nZVI are in O_2 under UV-Vis irradiation, whereas, for As(V) removal, irradiation is not necessary to achieve a high removal extent (Litter et al. 2010a; Morgada et al. 2008; Litter and Bundschuh 2012; Litter et al. 2012; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Ingallinella 2006; Leupin and Hug 2005; Levy et al. 2014a; Kanel et al. 2005; Su and Puls2001; Morgada et al. 2009; Morgada de Boggio et al. 2006; Morgada et al. 2010). In a recent work, toxicity of As(V) solutions has been also evaluated after treatment with nZVI. After 60 min of treatment, where As(V) removal was 77%, neither lethal nor sublethal effects were observed. However, nZVI had to be eliminated before the bioassay because they caused adverse effects in both embryos and larvae. This work highlights the utility of the test for monitoring toxicity changes in As(V) solutions after nZVI treatment (Pérez Coll et al. 2018).

Treatment systems for As removal based on coprecipitation-filtration through a sand bed containing different iron materials (nails, wires, etc.) were developed in Salta. The iron materials have been activated to generate a layer of iron oxyhydroxides. Two treatment plants were scaled in two schools of the Chaco Salteño region, allowing a production of 1000 L/day of water containing less than 0.05 mg/L As. Later, other ten systems were installed in Rivadavia, Banda Sur, Joaquín V. González, Quebrachal, and El galpón counties (Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Secretaría de Obras Públicas; Ministerio de Planificación Federal, Inversión Pública y Servicios n.d.).

A water treatment plant for As removal at small scale, based on the use of ZVI, was designed to treat continuously (500 mL/min) groundwater with high As content and with minimal electric energy requirements, applicable in rural areas. The system involves three stages: (1) water circulation from an overhead tank to a tubular reactor filled with commercial iron wool; (2) aeration/contact tank for Fe oxidation and additional precipitation and coprecipitation; and (3) removal of the precipitated particles through a slow sand filter (composed of a coarse gravel layer, a fine gravel middle layer, a sand bed, and a geotextile fabric). A pilot plant (700 L/day) was constructed later to test the efficiency using groundwater of the Buenos Aires province with high As levels (130 μg/L). Arsenic removal attained 90–95%, with concentrations lower than 10 μg/L in the treated water. In a second field test, two treatment cycles were included renewing the iron wool after depletion during the first cycle; 95–100% removal with As concentrations below 3 μg/L was obtained. The design and construction of a plant for 20 m^3/day are envisaged during 2019

(Arsénico en agua, informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Einschlag and Triszcz 2008; Triszcz et al. 2009; Berardozzi et al. 2014; Berardozzi and Einschlag 2017).

A method using the electrochemical corrosion of a fixed bed of metallic iron was developed and applied in San Juan for small-scale applications (households to a few hundred people).The system consisted of a first oxidative chlorination step, a second step using a bed filled with iron fillings or small pieces of iron, conditioning of the flocs, and filtration. An As removal above 90% was obtained (Litter and Bundschuh 2012; Ingallinella 2006; Cáceres et al. 2010).

Treatment systems for As removal based on coprecipitation-filtration through a sand bed containing different iron materials (nails, wires, etc.) were developed in Salta. The iron materials have been activated to generate a layer of iron oxyhydroxides. Two treatment plants were scaled in two schools of the Chaco Salteño region, allowing a production of 1000 L/day of water containing less than 0.05 mg/L As. Later, other ten systems were installed in Rivadavia, Banda Sur, Joaquín V. González, Quebrachal and El galpón counties (Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Secretaría de Obras Públicas, 2018).

Iron materials such as commercial GFO and iron nanoparticles were tested for their ability to remove As in samples of well waters from Copo, Santiago del Estero. Nanoparticles gave very good results after 30 min of treatment, while the granular materials resulted in a low removal, even after 3 h of treatment (Litter et al. 2015; Pereyra et al. 2014; Litter and Pereyra 2016).

Photochemical technologies are also important methods for As transformation, either by oxidation of As(III) or by reduction of As(III) or As(V). Some reviews on the subject can be found in the literature written by Latin American researchers (Litter 2009, 2017; Litter and Quici 2014; Morgada and Litter 2010; Litter et al. 2016, 2018; Quici et al. 2018).

Photooxidation of As(III) (200 μg/L) to As(V) was performed in a laboratory batch reactor with two 40 W tubular germicidal lamps ($\lambda = 253.7$ nm) operating inside a recycling system with H_2O_2 addition. The effectiveness of As oxidation was evaluated using a raw groundwater sample (Lescano et al. 2011). In a further study, a kinetic model for the system has been presented (Lescano et al. 2012).

A combined technology employing photochemical oxidation (UV/H_2O_2) and adsorption was evaluated. A middle scale photochemical annular reactor was developed, connected alternately to a pair of adsorption columns filled with titanium dioxide (TiO_2) and GFH. The combined technology resulted effective and promising for removal at small and medium scale. A sample spiked with 150 and 50 μg/L of As(V) and As(III), respectively, was treated with 3 mg/L H_2O_2 under 254 nm irradiation, and the resulting solution was passed through an adsorbing TiO_2 column. Under these conditions, complete As removal was obtained (Lescano et al. 2014).

The Solar Oxidation and Removal of As (SORAS) technology, a very simple process for poor, isolated populations, used with partial success in Bangladesh and India, was tested in Argentina (Wegelin et al. 2000; Hug et al. 2001; Hug and Leupin

2003). In this method, water in transparent PET bottles is irradiated under sunlight, and, in the presence of small amounts of dissolved iron, precipitation of iron(III) (hydr)oxides, As(III) oxidation, and As(V) adsorption take place; clear water is obtained by further decantation or filtration. The addition of small amounts of citric acid – in the form of drops of lemon juice – enhances the effectiveness of As removal due to the coupling of photo-Fenton processes. As groundwaters of most regions of LA do not have enough iron to make the SORAS technology efficient, iron has to be externally added employing some natural Fe-containing minerals or ZVI in different forms. In Argentina, experiments in laboratory waters and natural well waters from Los Pereyra (Tucumán) were performed adding iron wool and packing wire or nZVI. Natural dissolved organic matter promoted Fenton reactions without the need of adding lemon juice. The capacity of As removal using this method at the household level has been well proven (Bundschuh et al. 2009; Litter et al. 2010a; Morgada et al. 2008; Litter and Bundschuh 2012; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Bundschuh et al. 2010; Ingallinella and Fernández 2010; Ingallinella 2006; García et al. 2003, 2004a, b; d'Hiriart et al. 2009) (Fig. 2).

TiO_2 heterogeneous photocatalysis is also a promising emergent technology that allows the simultaneous oxidation of As(III) and removal of organic pollutants, toxic metals, and microbiological contamination. An iron source should be added to retain As on a solid surface. PET plastic bottles have been impregnated with TiO_2 and used to remove As from well waters of Las Hermanas (Santiago del Estero Province, As concentration, 500–1800 mg/L, circumneutral pH). More than 94% removal of As(III) and As(V) was obtained when the bottles were exposed to artificial UV light in the presence of Fe(III) salts (Litter et al. 2010a; Morgada et al. 2008; Litter and Bundschuh 2012; Arsénico en agua, Informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET 2018; Bundschuh et al. 2010; Ingallinella 2006; Morgada et al. 2010; Meichtry et al. 2007; de la Fuente et al. 2006; Hurng et al. 2004; Mateu 2007; Morgada de Boggio et al. 2009; Morgada de Boggio et al. 2010; Litter et al. 2010b). TiO_2 photocatalytic oxidation of As(III) in the presence of Hg(II) was also attempted in the absence of oxygen, as a convenient alternative for simultaneous As and Hg removal. Formed

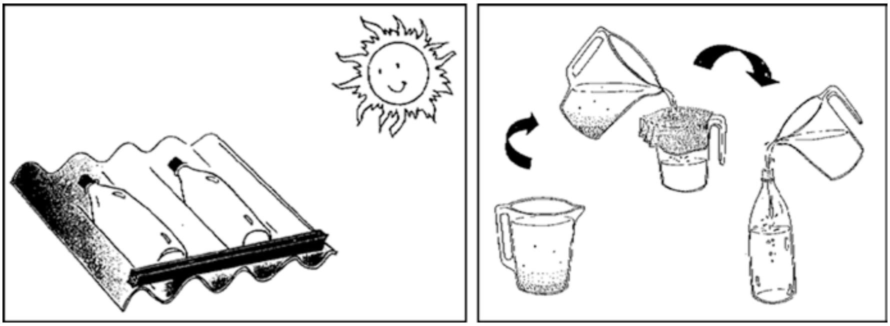

Fig. 2 Scheme of SORAS technology

As(V) can be then removed by other techniques (adsorption, ZVI, etc.) and, at the same time, Hg deposits as a solid, which can be separated by a subsequent physical step (Rodríguez et al. 2014).

In other experiments, reduction of As(V) and As(III) over TiO_2 under UV light was conducted in deoxygenated aqueous suspensions. For the first time, As(0) was unambiguously identified together with arsine (AsH_3) as reaction products. Arsenic(V) reduction requires the presence of an electron donor (methanol in this case), which is not needed for As(III) reduction. The reductive photocatalytic process is very efficient at the lowest As (III or V) concentrations (e.g., 0.013 mM ≡ 1 mg L^{-1}), and As levels lower than 10 μg L^{-1} were attained. As(0) formation results in a definite way to make less mobile As(V) and As(III) present in water. However, AsH_3 formation must be controlled due to the high toxicity of this gas. For this purpose, adsorption on suitable catalysts or treatment by a second TiO_2 photocatalytic oxidative step in the gas phase using supported TiO_2 can be applied (Levy et al. 2012; Litter et al. 2014). On the other hand, scientific evidences of the occurrence of the otherwise forbidden reduction of As(V) by electrons stored in TiO_2 nanoparticles were observed in the UV irradiation of an ethanolic sol of TiO_2 nanoparticles in the presence of As(V) (Levy et al. 2013, 2014b). In another work, the dynamics of the transfer of electrons stored in TiO_2 nanoparticles to As(III) and As(V) was investigated by using the stopped-flow technique. Suspensions of TiO_2 nanoparticles with stored trapped electrons were mixed with solutions of acceptor species to evaluate the reactivity by following the temporal evolution of the trapped electrons through the decrease in the absorbance at $\lambda = 600$ nm. The results indicate that As(V) and As(III) cannot be reduced by the trapped electrons under the reaction conditions (Meichtry et al. 2016).

2.2.2 Bolivia

The concentration limit for As in drinking water according to the normative (NB 512) is 10 μg/L (Instituto Boliviano de Normalización y Calidad 2010). Some removal experiences in Bolivia are reported.

A filter using iron oxide-coated sand and a filter using a composite iron matrix have been tested for their As removal capacity using synthetic water mimicking real groundwater of the Bolivian high plain; As concentrations lower than 10 μg/L were reached (Van den Bergh et al. 2010).

The development and application of a semicircular section tubular solar continuous flow photoreactor for As removal using a modified SORAS method with ferrous and citrate salts were assessed (Escalera and Ormachea 2012a). The reactor and solar concentrator were constructed with locally available, low-cost, recycled materials: fluorescent glass tubes and sewage PVC pipes cut in half and covered by aluminum foil. The reactor concentrates solar radiation up to 2.8 times its natural intensity. Continuous flow experiments with As concentrations of 1000 μg/L showed an efficiency of 98.4% for As(V) removal, reaching a final concentration of 16.5 μg As/L. The photoreactor was able to treat approximately 130 L/m^2 within a 5-h period with UVA irradiation intensities of 50–70 W/m^2. The performance of the pilot plant was assessed in 18 deepwater wells located in the peri-urban area of Cochabamba (at the center of the country), where As concentrations exceeded the regulations in approximately 50% of the wells. The performance was satisfactory even in cloudy days, leading to As removals higher than 80% and As concentrations below the regulations. Aeration with domestic commercial sprinklers led to an effective oxidation of arsenite to arsenate (Ormachea et al. 2012; Escalera Vásquez et al. 2014; Escalera and Ormachea 2012b).

Empiric relationships on the kinetics of the growth of $Fe(OH)_3$ flocs in function of the effective UVA radiation intensities using solar concentrators of higher capacity and reducing exposure times for achieving high As removal were also investigated. The performance of a filtration system for the simultaneous removal of As and Fe was carried out in wells of a school during 40 days, treating groundwater containing low total iron concentrations. The system comprised an aeration tank with a commercial spray and two commercial polypropylene microfilters (5 μm) arranged in series (Escalera Vásquez 2016).

The effectiveness and suitability of dried macro-algae (*Spirogyra* spp.) for As removal from acid mine drainage (AMD) and other contaminated waters in the Poopó Lake basin were investigated and compared with those of totora (*Schoenoplectus californicus*) and paja brava (*Festuca orthophylla*) (Bundschuh et al. 2007, 2010). Experiments were performed with synthetic solutions containing 7.5 mg/L As and with a real AMD effluent taken from the Bolivar mine (40 km SE of Oruro), having 5.75 mg/L As. Both solutions gave similar results regarding As removal: within 4 days, macro-algae removed 80–90% of As, being found more efficient than totora, while paja brava was found unsuitable.

2.2.3 Brazil

In Brazil, the limit for As in drinking water established by Regulation 2914 is 10 μg/L (Health Brazil 2011). Although high As concentrations have been found in soils and sediments of the most problematic zone, the Iron Quadrangle (south-center of the Minas Gerais state), the enriched iron environment creates favorable conditions for natural mitigation that has contributed to reduce the potential impact of As release from tailings and residues. However, for some cases, soil liners have been used at contaminated sites, owing to their ability to sorb As, forming a mineral barrier inhibiting infiltration to surrounding soils, groundwater, and the environment.

Arsenic adsorption on soils has been extensively studied (Cortina et al. 2016; Ladeira et al. 2002; Vasconcelos et al. 2004; Esper et al. 2007; Ladeira and Ciminelli 2004; Deschamps et al. 2003; Deschamps et al. 2005; Duarte et al. 2012). For example, the adsorption and desorption of As(III) and As(V) on an oxisol and its main mineral constituents indicated that, among the soil constituents, goethite was the most efficient As adsorbent (12.4 mg/g for As(V) and 7.5 mg/g for As(III)), superior to gibbsite. Thus, goethite and the oxisol were shown to be adequate to be used as protective liners in waste dams (Ladeira and Ciminelli 2004).

Precipitation with trivalent iron salts and lime (CaO or $Ca(OH)_2$) is a two-step As removal technique commonly employed in mining effluents. The resulting residues (arsenical slimes) are disposed of in lined pits located in the area under influence of the metallurgical operation. The long-term stability of these As residues has been investigated by determining As phases remaining in gold mining residues after two decades of impoundment (Pantuzzo et al. 2007; Pantuzzo and Ciminelli 2010; Bundschuh et al. 2012).

Regarding As removal from water, Al-Fe (hydr)oxides were precipitated from Al and ferrous sulfates at different Fe/Al ratios in the presence of As at different concentrations. The resulting suspensions were aged for 3 months, and As was periodically analyzed in the supernatant. At the end of the aging period, the precipitates were collected and oven dried at 50 °C. Results showed that all treatments were efficient to remove As from water; the resulting precipitates were considered non-toxic and stable residues under acidic or reducing conditions (de Mello et al. 2014).

Recently, the application of a steel waste, basic oxygen furnace sludge (BOFS), rich in iron, to treat water contaminated with As and sulfate was studied and compared with commercial ZVI. Three doses (10, 60, and 80 g/L) of BOFS were tested to investigate As(III) and As(V) removal (67 mg/L) from an aqueous solution. The use of BOFS achieved As removal up to 92% after 72 h of contact time, and similar results were achieved with ZVI. The results of this study will be used for the investigation of the efficiency of the steel waste in the removal of metals present in AMD (Araujo et al. 2018).

The possibility of obtaining enriched As precipitates in the form of scorodite ($FeAsO_4 \cdot 2H_2O$) from industrial solutions with initial As concentration as low as 0.1 g/L was studied, taking advantage of the presence of Fe(II)/Fe(III) in solution. As(III) was oxidized first with H_2O_2. Arsenic removal varied from 80.5 to 94.6%, and scorodite was the only As phase identified by XRD and micro-Raman analyses of the precipitates (Caetano et al. 2009).

Technologies based on coprecipitation by the use of selective coagulants/flocculants have been studied to be applied in mining and other effluents. The raw water used for the experiments was provided by a company that produces gold, and their resulting wastewater presents As concentrations between 300 and 1600 mg/L. Tests were carried out with 1 L samples of raw water, at $pH > 10.5$. The additions of removal agent to the As solution were made in stepwise to optimize its removing action. The use of coagulants and an As removal agent was developed for As removal from effluents generated during gold mining processes to a level below the 0.2 mg/L discharge criteria established by the Brazilian Environmental Legislation; 0.1885 mg As/L has been reached (Langsch et al. 2012).

Removal of As(V)/As(III) (from 32 to 157 µg/L) from natural waters of low and high turbidity by clarification with PAC and aluminum sulfate, with a chlorine pre-oxidation step, has been described. Removal was better when PAC was used as primary coagulant. As(V) removal yielded a concentration lower than 10 µg/L. Oxidation preceding the clarification led to As(III) removal efficiencies from 80 to 90% for both coagulants and types of water (Pires et al. 2015).

Adsorbents have been also explored. For example, application of pisolite, a sedimentary rock composed of iron and manganese hydrated oxides occurring as waste material from manganese ore mining, was tested in column and batch for As removal with solutions prepared with Velhas River water. In columns system, 1.0 g of pisolite removed 1.41 mg of As (4.05% As extraction) from 630 ml of the aqueous feed solution, and 1.0 g of activated pisolite (heating natural pisolite to extract the crystallized water) extracted 3.51 mg of As (11.6% As extraction). In batch tests with 100 ml of aqueous solution and 1.0 g of pisolite, 1.29 mg of As (24.7% As extraction) was removed, while 1.0 g of activated pisolite extracted 3.17 mg (58.2% As extraction) (Pereira et al. 2007).

Magnetic δ-FeOOH nanoparticles were also tested, and adsorption capacities for As(III) and As(V) of 40 and 41 mg/g, respectively, were observed. The adsorbent was highly efficient to purify As-contaminated water from a Brazilian river, leading to concentrations close to zero. Approximately 85% of the total adsorbed As could be recovered and used as a precursor to produce Ag_3AsO_4, a compound with excellent photocatalytic activity under visible light (Hott et al. 2016).

The mechanism of As(III) oxidation and removal using nanosized birnessite (Mn(IV)) was also investigated. It was shown to involve a reduction to hausmannite (Mn(II) and Mn(III)),with precipitation of $Mn_3(AsO_4)_2.4H_2O$, correlated with the very high As removal (up to 110 mg/g) (Dias et al. 2008).

As(III) oxidation to As(V) and As(V) removal from water were assessed by using TiO_2 immobilized in PET bottles (Meichtry et al. 2007) in the presence of natural sunlight and iron salts. Using 10% TiO_2 of the coating solution, 7.0 mg/L Fe(II), and solar exposure for 120 min, As(III) and total As concentrations at the end were lower than 2 μg/L, showing a removal over 99% and giving evidence that As(III) was effectively oxidized to As(V) (Fostier et al. 2008).

Regarding biomaterials, an activated waste biomass with a high fibrous protein content (keratin) obtained from chicken feathers was developed for the selective removal of As(III), yielding As uptake of 270 mmol As(III)/g of biomass (Teixeira and Ciminelli 2005).

A detailed investigation of As complexation with an iron-loaded vegetable biomass (dried lettuce leaves) was carried out, reaching a maximum sorption capacity of 9.74 mg/g As(V) using 12.0 mg Fe/g (Silva et al. 2009).

Arsenite immobilization using sulfate-reducing bacteria (SRB) grown in sulfate containing liquid medium supplemented with powdered chicken feathers was reported. As(III) is immobilized by precipitation with the H_2S produced by the microorganisms and by adsorption on the powdered chicken feathers. This approach may be useful for passive and active As-contaminated site bioremediation (Moreira et al. 2012).

Arsenic absorption by plants like *Eichhornia crassipes* (water hyacinth) and *Lemna valdiviana* (valdivia duckweed) has been studied, cultivating the plants in nutrient solutions containing different As concentrations up to 1.4 mg/L. Monitoring of As removal by the plants was performed by sampling at intervals up to 240 h for the water hyacinth and 168 h for *Lemna*. For *Eichhornia*, absorption was observed after 96 h of culture, while for *Lemna*, absorption was at 48 h. Arsenic concentrations above 1 mg/L implied deleterious effects on both plant species and on the phytoremediation process (Litter and Bundschuh 2012; de Souza et al. 2018).

The potential of As(III) decontamination by *Microcystis novacekii* has been reported. In this study, the potential decontamination of As(III) and As(V) using cyanobacteria cultures was assessed. *M. novacekii* showed normal growth in concentrations of As(V) similar to those found in natural environments contaminated with As, demonstrating its resistance to As(V). After exposure to 14.7 mg/L As(III), 21.2% of As was removed from the culture medium (Ferreira et al. 2018).

2.2.4 Chile

The Chilean guideline (NCh 409/1, 2005) was modified in 2005 establishing 10 μg/L as the maximum allowable amount of As in drinking water. However, a period of 10 years was set to reach this value (NCh 409/1, 2005). At present, no data are reported regarding the compliance of this value.

In Northern Chile, water treatment plants based on the coagulation technology have been installed since 1970 for removing As from drinking water in small and medium cities with centralized water supply (Bundschuh et al. 2009; Litter et al. 2010a; Sancha and Castro 2001; Hering et al. 1997; Alarcón-Herrera et al. 2013; Bundschuh et al. 2010; Cortina et al. 2016; Hering et al. 2017; Latorre 1966; Alonso 1992; Ruiz et al. 1992; Sancha 1996, 2000, 2006; Karcher et al. 1999). A coagulation process with $FeCl_3$ addition was applied, and plants with treatment capacities of about 40,000 m^3/day were built, boosted by the Chilean government. The first plant was built and began to be operative in 1970 in Complejo Salar del Carmen, and other plants were built later in the same locality, in Calama (Cerro Topater), Chuquicamata, and Taltal, with successive improvements (Sancha 1986, 2003, 2006, 2010a, b, c; Sancha and Ruiz 1984; Barahona and González 1987; Sancha 1999; Fuentealba 2003; Sancha and Fuentealba 2009; Granada et al. 2003; Sancha et al. 2000). Removal of As(V) was generally 80–100%, while only 40–70% was obtained for As(III). Thus, an oxidation step with Cl_2 was included to transform As(III) to As(V) before the treatment (Sancha et al. 1992). The use of $Al_2(SO_4)_3$ showed removal efficiencies lower than $FeCl_3$ (75% for As(V) and only 5–20% for As(III)) (Sancha and Ruiz 1984).

Regarding mining activities, the copper metallurgical processes (extremely important in Chile) produce effluents that have to be treated due to the presence of As in the processed ores. In 2012, an industrial plant for the treatment of 1250 m^3/day of mining effluents was inaugurated by Codelco and its Chilean subsidiary EcoMetales for dusts from three copper smelters in the Chuquicamata and Ministro Hales mines. Ferric sulfate was used for the stabilization of As forming scorodite, the most stable As industrial form. By-products of the iron mining industry, such as magnetite, hematite, iron hydroxides, and/or foundry slag, were also used. The unit was designed to treat up to 10,000 tons of As per year, to be disposed of in a deposit with the capacity of 1.1 million tons of waste over a 15-year period. The concentrated copper solution, free from the impurities, is sent back to the metallurgical plant (Cortina et al. 2016; Reporte de Sustentabilidad de EcoMetales 2012; Superneau 2012).

Another possibility for Northern Chile is to replace some sources of surface water with desalinized sea water, option only applicable in coastal cities (Gonzalez 1997; O'Ryan and Sancha 2000). Thus, in 2003, a project to install a seawater RO desalination plant in Antofagasta by the company ESSAN (Empresa de Servicios Sanitarios de Antofagasta) was approved, with an initial water production capacity of 13,000 m^3/day, expanded later to 52,000 m^3/day (IADB 2003). Another desalination plant was installed in 2011 in the copper-gold mine Esperanza (180 km from Antofagasta), where desalinated seawater is pumped 150 km to the mine site (2300 m a.s.l.); Severn Trent Services improved the plant with 16-in. membranes, replacing the conventional 8-in. membranes (Global Water Intelligence 2011; WaterWorld 2010). In 2013, another RO water treatment plant was built and is, at present, operative in Pago de Gómez (Arica) (Adedge Water Technologies, LLC 2012). A 2,500-L/s seawater desalination plant was also inaugurated in April 2018 in Escondida mine (Puerto Coloso, 170 km SE of Antofagasta) (Global Water Intelligence 2011; Petry et al. 2007; International Mining 2018), and another desalination plant will be built by Codelco, and it will be the second-largest desalination plant in Chile, behind the one supplying BHP Escondida copper mine, the largest in the world (Cambero and Cohen 2018).

For small settlements, the SORAS method has been modified and tested in natural waters of the Camarones river (Arica), where As(V) concentration (1000–1300 μg/L) has been successfully decreased using iron wool. The optimal conditions when using solar radiation were 1.3 g/L of iron wool and one drop (ca. 0.04 mL) of lemon juice, and removal percentages higher than 99.5%, with final As concentration below 10 mg/L, were obtained (Bundschuh et al. 2009; Litter et al. 2010a; Litter and Bundschuh 2012; Litter et al. 2012; Bundschuh et al. 2010; Cornejo et al. 2004, 2006a, b, 2008, 2010; Lara et al. 2006; Mansilla et al. 2003).

As(V) biosorption using dried algae (*Lessonia nigrescens*) collected in Valparaiso bay has been studied. Experiments were performed with laboratory solutions containing 200 mg/L As(V) at different pH values. Maximum adsorption capacities were estimated to be 45.2, 33.3, and 28.2 mg/g at pH 2.5, 4.5, and 6.5, respectively (Bundschuh et al. 2009; Litter et al. 2012; Hansen et al. 2006).

Three Fe-Cu bimetallic nanomaterials were prepared at the University of Santiago, and the effect of the Cu content on the removal of As(V) was evaluated. The material without Cu presented the best efficiency for As removal because Cu provoked an interference effect on the removal process (Sepúlveda et al. 2016).

Arsenic removal by horizontal subsurface flow constructed wetlands was found a cost-effective, environment-friendly treatment technology. Horizontal flow wetlands were used to verify the effectiveness of two media types, zeolite and a mixture of limestone and cocopeat. Inflow water had 2.6 mg As/L, 97.3 mg Fe/L, and 30.8 mg B/L at pH 2. Zeolite removed 99.9 and 96.1% of As and Fe, respectively, whereas the limestone/cocopeat wetlands removed 99.8 and 87.3%. Limestone/cocopeat wetlands offer a more suitable treatment, given the neutral pH achieved, but zeolite wetlands were able to achieve lower concentrations of Fe, despite the acidic pH. Metals were mainly retained in the media rather than in the plants (Lizama Allende et al. 2010, 2012a, b, 2014).

2.2.5 Colombia

The threshold adopted by Colombia in 2007 as the maximum permissible concentration of As in drinking water is 10 µg/L (Ministerio de la Protección Social y Ministerio de Ambiente, Vivienda y Desarrollo Territorial 2007).

Only one study is reported about As removal from water. The As precipitation efficiency of two native SRB strains was evaluated. One strain was previously isolated and adapted in vitro, and another strain was isolated from agricultural soils from the Bogotá savannah. The first one showed a precipitation efficiency of 83%, while the other one presented 63% (Rodríguez et al. 2016).

2.2.6 Costa Rica

Costa Rica was considered as a country without As in drinking water. However, polluted groundwater resources (up to 200 µg/L) in the north and North Pacific regions were detected in 2008 (Romero et al. 2014). The maximum amount of As permissible in Costa Rica is 10 µg/L (Ministerio de Salud, Costa Rica 2005).

In 2013, the German company GTWE installed a filter for As elimination in Cañas, Guanacaste. The filter unit has a capacity of up to 2,000 L/h and provides As-free drinking water for an office building of an international company. A special granulate, which does not have to be regenerated and is active up to 5 years, was used as adsorbent (GTWE German Technology for Water and Energy n.d.).

Low-cost alternatives for As removal were explored, evaluating coagulation with $FeCl_3$, a synthetic or a natural flocculant, SORAS, and local adsorbents. The coagulation experiments showed 96% removal from around 200 µg/L As spiked water. The SORAS experiments showed similar results with a residual As concentration below 10 µg/L after 4 h of sunlight. In both cases, coagulation and SORAS, a further sand filtration step to reduce turbidity, suspended iron hydroxides and color was needed. Among the local adsorbents tested, a soil-rich biotite (iron(II)-bearing silicates) was promising as powder application, with more than 94% removal from 200 µg/L spiked water, dosing 8 g/L of the soil (Romero et al. 2014).

Another SORAS system was tested with 200 µg/L As(V) and 0.6 g/L of iron wool, reaching As concentrations less than 10 µg/L after 2 h and 4 h of exposure in a sunny or cloudy day, respectively (Rojas-Chaves et al. 2015).

A coagulation-flocculation system was tested at laboratory scale finding optimal pH, coagulant and flocculant doses, and the optimal flocculation time. The best conditions were achieved at pH 6 using 1 mg/L FK-930-S, a commercial polymer of polydiallyldimethylammonium chloride as flocculant and 12 mg/L $FeCl_3$; the natural flocculant mozote (*Triumfetta semitriloba*) was also tested at pH 6 (at 250 mg/L) with 14 mg/L $FeCl_3$. A prototype consisting in a coagulation-flocculation container and a sand filtration step was able to treat 15 L of synthetic water with 200 μg As/L and natural water with 10 and 50 μg As/L. In all cases, As concentrations less than 10 μg/L were obtained (Rojas-Chaves et al. 2015).

Five natural local low-cost adsorbents from the area of Guanacaste for As removal in drinking water have been selected, having relatively high content of iron oxides, aluminum, and titanium, and identified as biotite, limestone, diatomite, magnetite enriched sands, and pyroclastic rocks of basaltic composition (Acuña-Piedra et al. 2016). No data about their utilization is reported so far.

A novel treatment for As removal under natural conditions using in-line electrochlorination to oxidize water constituents without the need for external chemical supply was tested in groundwater. Electrochlorination produces hypochlorous acid and oxidizes As and Fe that coprecipitated and were filtered via a Greensand Plus™ granular filter. Although the contaminant removal during a field test was impaired by strong fluctuations in water quality including low iron concentrations, the system was able to remove on average 68% As (from average 40 to 13 μg/L), with Fe 93% removal (from average 2.8 to 0.2 mg/L) (Kunz et al. 2017).

2.2.7 Ecuador

According to the Instituto Ecuatoriano de Normalización, the maximum allowable As concentration in drinking water in Ecuador is 10 μg/L (INEN (Instituto Ecuatoriano de Normalización) 2006).

Nanoscale hydrated Fe(III) oxide (HFO) particles were supported on polymeric beads using commercially available cation and anion exchangers as host materials, the latter exhibiting a much higher As removal capacity. This technology is adequate for As removal in small communities upward, but, due to economic limitations, not for household scale. HFO particles offer very high As removal capacity; less than 10% of influent arsenic broke through after 10,000 BV. This system has been applied in rural communities of India and Cambodia and can be useful to be applied in LA (Bundschuh et al. 2010; Cumbal et al. 2003; Cumbal 2004; Cumbal and Sengupta 2005, 2009; SenGupta and Cumbal 2005; Cumbal and Shengheng 2014). Later, the municipal company for drinking water of Tumbaco installed As treatment plants for two wells having water with high As concentrations, which included an oxidation stage with chlorine, followed by a filtration unit loaded with ArsenXnp, the commercial As sorbent developed before (Cumbal and Sengupta 2005). No results have been obtained so far (Bundschuh et al. 2012).

Chitosan beads impregnated with iron particles were found to be a very efficient adsorbent for As removal from waters (laboratory and natural). Sorption is different for As(III) and As(V) because at $pH < 6.3$ As(V) oxyanions are removed by electrostatic and Lewis acid-base interaction, while As(III) is removed only by Lewis acid-base interaction. A pilot plant was designed and built, and waters of the Papallacta lake (which provides drinking water to the 1.2 million inhabitants of Quito, the capital city, as well as to local communities) were tested. The treatment reduced the

As concentration from 192 to 50 μg/L after 12,500 L of water were circulated (Cumbal Flores and Zúñiga Salazar 2010).

An initiative for the treatment of water from hot springs feeding the Papallacta lake with adsorption columns composed of a layer of iron oxides followed by a layer of activated carbon was proposed in 2004 with a grant from TWAS, the Academy of Sciences for the Developing World. The activated carbons have the capability of removing also other metals and organic contaminants present in solution. A calculation indicates that each adsorption column, with a treatment capacity of 20 L/min, will cost less than USD 2000, with an operating cost of USD 100 per month. No new advances on this project were reported so far (Muñoz-Rivadeneira et al. 2004).

A technosol, elaborated using a clay-silty soil (iron-rich) collected in a mining area, and iron nanoparticles synthetized with the extract of orange peel were tested as adsorbent for As removal. The technosol was composed of a ferralsol with 25,531 mg/kg of Fe (associated with Fe and Mn oxides) and multicomponent nanoparticles from orange peel residues. An adsorption model was also developed to simulate the real application of the sorbents to the remediation of AMD As-rich water using the software Vensim PLE. The scaling up of the remediation procedure for field application in a gold mining area in Portovelo (South Ecuador) was proposed. The technosol achieves elimination of more than 96% of As in water entering the remediation tank at each water discharge (216 L), using only 5 kg of soil and 0.025 kg of nanoparticles (Bolaños-Guerrón et al. 2018).

2.2.8 Guatemala

In Guatemala, the COGUANOR NGO 29.001 normative establishes the value of 10 μg/L as the limit for As in drinking water (Guatemala, Ministerio de Salud Pública y Asistencia Social 2001).

Only one example of As removal has been reported. A plant was installed to supply As-free water to the Naranjo County (3000 inhabitants, Mixco, close to the capital city) (Sancha and Castro 2001; Bundschuh et al. 2010; Cortina et al. 2016; Garrido and Avilés 2008; Cardoso et al. 2010; Garrido Hoyos et al. 2013). The plant is composed of a coagulation-filtration system with $FeCl_3$ to treat approximately 4400 m^3/day of groundwater from two wells with an average As concentration of 150 μg/L. The plant consisted of a preoxidation unit, pH regulation, a fast mixing unit, four flocculation basins, two sedimentation basins, four pressure filter units (0.15 MPa) with a ceramic medium (Microlite-Kinetico® filtration rate of 25 m/h), and a disinfection unit. The optimal operational conditions were 12 mg/L $FeCl_3$, 1 mg/L Poliflocal-CH, and pH adjustment at 7.5, providing an As removal efficiency higher than 90% (Garrido and Avilés 2008). An increase of the color and iron of 100% in the filter influent was observed (80 UPt-Co and 1.6 mg/L, respectively), due to the $FeCl_3$ dosage, and the problem was solved using Microlite-Kinetico® filters. A full-scale treatment plant was built in 2008 (Río Azul Plant), which gave excellent results, achieving an effluent with As concentration below 10 μg/L at an operating and maintenance cost of 0.2 USD/m^3 treated drinking water.

2.2.9 Mexico

In Mexico, the guideline value for As in drinking water is presently 25 μg/L (Modificacion a la Norma Oficial Mexicana NOM-127-SSA1-1994 2000). Many technologies for As removal from water have been tested in the country.

An early study for the Pan American Health Organization (PAHO) reports some technologies to be applied in the Durango state in the 1980s. For rural areas, technologies based on the use of crushed bones, lime, and aluminum sulfate were recommended. For urban areas, water treatments using crushed bones, activated alumina, and reverse osmosis were proposed (Solsona 1985, 1986). A study in Durango city reported As removal efficiencies greater than 77% using aluminum sulfate (Flóres-Montenegro 1998). Other laboratory studies reported that the process is effective for the removal of As and F, as long as their concentrations do not exceed 0.19 and 6 mg/L, respectively (Alarcón-Herrera et al. 2013; Alarcón-Herrera et al. 1999; Camacho et al. 2011).

In 1999, the Instituto Mexicano de Tecnología del Agua (IMTA) adopted a methodology based on a coagulation-flocculation process using $Al_2(SO_4)_3$ as coagulant and other solid materials (zeolites, clays, bone carbon) as coagulation coadjuvants, defining the optimal dose of the coadjuvant, the coagulant, and the oxidant. The As content at the end of the procedure was very close to that indicated by the guideline at that time (50 μg/L). The systems were tested then in natural waters of Zimapán (Litter et al. 2010a; Sancha and Castro 2001; Bedolla et al. 1999; Avilés and Pardón 2000).

The behavior of two filter media (manganese greensand and sand-anthracite) to remove As from groundwater in Torreón (Coahuila), with As concentrations averaging 0.070–0.085 mg/L, was studied at laboratory and pilot plant scale. A maximum adsorption capacity of 0.007 mg As/g was obtained (Garrido et al. 2013). Derived from this study, the governments of Coahuila and Durango have invested in the installation of ten filtration plants in the wells in the Comarca Lagunera (Coahuila), to comply with Mexican regulations (Cortina et al. 2016).

In Zimapán (Hidalgo state), several studies were undertaken since the 1990s. Some materials with high Fe content have been identified as As adsorbents: iron-manganese, hematite, manganese oxide, and carbon activated with copper sulfate presented high removal efficiencies. A pilot study performed on water from a well from the town, which supplied 47% of the water to the population and contained 500–900 μg/L As, identified natural hematite as the best material. A pilot plant was designed later with two filters, hematite and zeolite, attaining removal from 0.62 to 0.875 mg/L to less than 0.050 mg/L of As (Sancha and Castro 2001; Petkova Simeonova 1999; Simeonova 2000).

Two mobile pilot plants (0.8 L/s) were installed in Zimapán for As removal. Arsenic was oxidized by sodium hypochlorite, followed by HCl acidification, addition of activated alumina, and readjustment of pH with NaOH. The removal efficiency was 90–100%, reaching As levels lower than the regulated limit. The produced water was introduced in a tank to be distributed to six 2,500 L containers to different quarters (Rivera-Huerta et al. 2000).

The combined use of cake alum (aluminum sulfate octadecahydrate) and a polymeric anionic flocculant (PAF) prepared from acrylamide for removal of As and F from drinking water has been evaluated in water from two wells at Meoqui City (Chihuahua). Arsenic concentration (0.134 mg/L) may be reduced by this method up to 99% at the optimal pH (7.1), at a cost of 0.38 USD/m^3 (Alarcón-Herrera et al. 2013; Piñón-Miramontes et al. 2003).

A conventional (flocculation with $Fe_2(SO_4)_3$, sedimentation, and filtration) mobile treatment plant was designed and tested. Silica sand and anthracite were used as filtering agents in one of the tanks and activated charcoal in the other. The As content decreased from around 800 to less than 30 μg/L. A plant was later installed at Zimapán to treat polluted well water (Litter and Bundschuh 2012; Armienta et al. 2007).

An indigenous limestone from Zimapán (Soyatal) was tested in batch and packed column tests for As removal from well water (around 500 mg/L of As). Batch experiments using 10 g/L limestone showed 90% As removal within the first 5 min; the same particles could be used for five separate cycles (Litter et al. 2012; Bundschuh et al. 2010; Ongley et al. 2001; Romero et al. 2004; Armienta et al. 2009, 2016; Labastida et al. 2013).

Iron-coated LECA (commercial light expanded clay aggregates, a gardening material) was tested for As removal under batch and flow conditions. More than 80% of As was sorbed to Fe-LECA within 1-h contact. The maximum As sorption capacity was 3.3 mg/g when the Fe content on LECA was 0.93 mg/g at a 10 mL/min flow rate (Cano-Aguilera et al. 2009).

Goethite (α-FeO(OH)) was also tested as an adsorbent for As(V) spiked tap water from Comarca Lagunera. The highest efficiency was obtained using a Fe/As molar ratio of 20; the adsorbent was used for treating a well water containing 210 mg/L of As from El Mayrán (Coahuila) (Bundschuh et al. 2010; Alvarez-Silva et al. 2009).

The removal of As(III) by red clays from Huayacocotla (Hidalgo-Veracruz region), using 2.5 g/L of material and As(III) solutions at 0.1–10 mg/L at pH 4, 6, 8, and 10, was evaluated. The highest As(III) sorption occurred at pH 8 in 2 h (Rivera-Hernández and Green-Ruiz 2014).

Natural zeolites, volcanic stone, and the cactaceous powder CACMM were tested as adsorbents for As(III), As(V), DMA, and phenylarsonic acid (PHA). The sorption of the As species onto zeolites was studied on both non-activated and activated zeolites, as well as on zeolites hydrogenated or iron-modified. Arsenic sorption takes place more slowly on zeolites in comparison to ferrihydrite. Arsenate was sorbed on volcanic stone and on cactaceous powder, while DMA was retained to a greater extent by zeolites. Among the unmodified zeolite samples, the natural clinoptilolite ZMS was effective for arsenite retention, while the mixed phase zeolite

ZMA showed the highest efficiency in the iron-modified group (Elizalde-González et al. 2001).

Natural zeolites of the clinoptilolite type were tested in another study at small pilot scale to remove As from a well water supplying Mazatlán (Sinaloa state), using ion exchange followed by an oxidation process using Cl_2, which forms a Mn oxide coating on the zeolite. This coating then adsorbs dissolved Fe and Mn (Bundschuh et al. 2010; Rivera and Piña 2004).

Synthetic goethite and Fe(III)-coated silica sand were also tested. The most efficient medium was synthetic goethite with 98.61% removal and a concentration in treated water of 0.005 mg As/L. The goethite used in the study had a higher adsorption rate constant compared with those of other investigations (Garrido and Romero 2014).

Metallic wool was oxidized through an extensive washing process and then periodically moistened with water to induce its oxidation and test its applicability to remove As(III) from water. The obtained magnetic, microporous nanomaterial was composed mainly of lepidocrocite (γ-FeO(OH)). As(III) was removed from water up to undetectable levels (< 5 μg/L) in a retention time of 7 minutes by using 0.55 g/L at pH 7.8, showing a removal capacity of 2.9×10^{-2} mmol As/g. Arsenic was adsorbed onto the iron nanoparticles and separated efficiently from water by applying an external magnetic field (Alarcón-Herrera et al. 2014a).

A surfactant-modified zeolite (SMZ) prepared by adsorbing the cationic surfactant hexadecyltrimethylammonium (HDTMA) bromide on a clinoptilolite showed an As(V) adsorption capacity 12.5 times greater than that of the pure clinoptilolite at concentrations of As(V) below 300 μg/L (Mendoza-Barrón et al. 2011).

A sample of metallurgical slag, a by-product generated from the production of iron and steel, generated in an electric arc furnace (containing goethite, maghemite, and/or magnetite) was found to be an efficient and economical As adsorbent. The best adsorption conditions obtained in the treatment of a 6.0 mg As/L solution using slags (pH 10, adsorbent dose of 7.0 g/L) produced an effluent with 0.002 mg As/L. The material was compared with a commercial nZVI sample (pH 8, 1.5 g/L), and the same residual concentration was found. However, calculation of unit costs was 0.72 USD/m^3 for nZVI and 0.55 USD/m^3 for the slag, which also presented a lower water treatment cost (Mercado-Borrayo et al. 2014).

Different types of low-cost organic materials have been proposed by Mexican researchers to remove As, including cellulose, milled bones, sedges, sorghum biomass, and waste biomass. Filters using a combination of iron-enriched activated carbon from lignite and acetylated cellulose synthesized from low-cost cotton and Kraft cellulose were tested in a continuous flow cell with synthetic As solutions (200 and 400 mg/L As(V)) (Bundschuh et al. 2010; Muñiz et al. 2009). Bone char modified by supporting iron nanoparticles was also found very efficient for As(V) removal (Villela-Martínez et al. 2016).

Adsorption of As on sorghum biomass (SB) was investigated in batch experiments in a pH range of 2.0–10.0. A strong influence of pH was demonstrated with a maximum As removal at pH 5.0. Farm waste SB from Guanajuato was used to immobilize SB, and column experiments were performed to obtain the breakthrough curves for both non-immobilized sorghum biomass (NISB) and immobilized sorghum biomass (ISB) under different flow conditions (pump and gravity flow). Arsenic removal below 50 g/L was observed for up to 31 and 27 pore volumes for the NISB and ISB columns, respectively, for an influent As concentration of 5 mg/L. Breakthrough (> 60 and > 65 g/L for NISB and ISB, respectively) occurred after 33 and 27 h, respectively (Haque et al. 2007). Later, field experiments were conducted for As removal from the groundwater of a well located in Guanajuato using NISB as the sorbent. The columns were run under gravity and pump flow conditions. The maximum As accumulation measured was 3.2 and 3.3 mg of As/g of NISB for gravity and pump flow conditions, respectively (Haque et al. 2005).

In another study with SB, As adsorption capacities at pH 4.5 and 60 min of contact time of 8.43 mg/g and 6.99 mg/g for NISB and ISB, respectively, were found. In flow conditions, the adsorption capacity of the immobilized biomass packed in a column was 143 mg/cm^3 when the input rate of the As solution was 3 mL/min. Using two columns in series and one of reserve, the water cost after this treatment was 0.002 and 0.011 USD/L for NISB and ISB, respectively (González-Acevedo et al. 2005).

Materials obtained from maracuya shell and fiber of maracuya shell allowed an efficient As removal from water samples from the Lagunera region, as well as from artificial water samples containing As(III) or As(V), without the necessity of additional treatments. The higher adsorption capacity was detected for Fe(III)-loaded materials (Iliná et al. 2009). In another study, a bioadsorbent medium using passion fruit was evaluated, using synthetic water (As concentration, 0.22 mg/L). The pectin was extracted using two methods, conventional acid extraction and alkali treatment with steam drag. Arsenic removal percentages were 91% for acidic pectin and 81% for alkaline pectin (Paredes and Garrido 2014).

Another study reported As removal using a bioadsorbent obtained from orange albedo coated with Fe(III). The obtained adsorption capacity was 0.5498 g/(mg min) for Fe(III)-coated pectin (Gómez and Garrido 2014).

Sequential batch experiments were conducted to study the efficiency of As removal by means of an oxidation process using ZVI fillings. Experiments were done in three sequential steps with recirculation of acid-arsenic mists, using a 0.4 (w/v) iron fillings/water ratio at pH 3, 5, and 7, different As concentrations (2000, 4000, and 8000 mg/L), and 950 mL/min air flow. Efficiencies greater than 70% As removal were observed in the first batch step. At concentrations of 2000 and 4000 mg/L, 99% removal efficiencies were obtained in the second batch reactor. Therefore, it was inferred that the third phase in the sequential reactors was not needed (Garcés Mendoza et al. 2014).

In Chihuahua, more than 280 small RO plants have been installed in rural communities to alleviate the problem of high As and F concentrations in drinking water (Alarcón-Herrera et al. 2013; Alarcón-Herrera et al. 2007). In 2007, the first desalination plant was installed in Los Cabos, Mexico, with a capacity of 21,000 m^3/day (Bundschuh et al. 2010).

A study of As adsorption over metallic precipitates produced by electrotreatment with Fe electrodes was performed with synthetic water samples (0.5–2 mg/L) using a voltage of 13.5–14 V. Removals higher than 90% were obtained (Alvarez and Rosas 1999).

Other studies optimized As removal by capacitive deionization, a technology involving electrostatic attraction and adsorption onto the surface of electrodes. In a second stage, the polarity of the cell is automatically reversed, causing the capacitor to release the contaminants into the cell channels, and, in a third stage, the contaminants are removed from the cell by flushing with a small quantity of liquid forming a concentrated solution. At laboratory scale, 99% and 65% of As were removed from water with initial As concentrations of 900 and 10,000 mg/L, respectively, by adding 1 g/L goethite at pH 6 (Litter and Bundschuh 2012; Litter et al. 2012; Garrido et al. 2009; Garrido Hoyos et al. 2010). Maximum As removal efficiencies of 96.06, 82.76, and 67.30% were obtained with synthetic water, rejection waters of capacitive deionization and reverse osmosis processes, in As concentrations of 1.0, 5.0, and 0.198 mg/L, respectively (Ramírez Alvarado et al. 2014).

Experiments of dispersion and sorption of As in a biofilter with *Eicchornia crassipes* biomass were compared with numerical simulations done with the COMSOL Multiphysics code with the aim at finding the best fitting between the experimental breakthrough curve and the simulated curve (Alvarado-Rodríguez et al. 2012).

Arsenic removal using magnetic nanoparticles obtained by alcohol catalytic chemical vapor deposition (ACCVD) was reported. ACCVD use an ultrasonic nebulizer for atomizing a precursor solution in droplet form, tailoring the size and composition of magnetic nanoparticles by variation of the flow ratio Ar-Air and the furnace temperature. Different types of nanoparticles (195–272 nm) were obtained, composed of metallic Fe and different iron oxides including Fe_2O_3. The magnetic nanoparticles showed a high capacity to completely remove As simply by putting in contact a solution (0.02 mg As/L) with the materials (0.25 mg/L) and submitting to ultrasound for some minutes (Barrientos et al. 2013).

Two Cyperaceae species, *Schoenoplectus americanus* and *Eleocharis macrostachya*, were studied regarding their As tolerance and removal capacity. The studies were conducted in a subsurface wetland prototype system with three operated units in parallel under continuous flow. Water solutions with As (1000 mg/L) were continuously pumped using peristaltic pumps. The artificial wetland prototype units planted with *S. americanus* were 90% efficient in removing As from water, reducing the As concentration to 100 mg/L. A study with *E. macrostachya* was conducted over a period of 7.5 months (Alarcón-Herrera et al. 2007; Alarcón-Herrera et al. 2009; Olmos-Márquez et al. 2009), reaching 99% As removal from 500 mg As/L and 89% from 100 mg As/L, attaining the required concentration of As for drinking water according to Mexican regulations. Three constructed wetland prototypes, two planted with *E. macrostachya* and *S. americanus*, respectively, and a third unplanted used as control, were continuously operated inside of a greenhouse for 343 days, fed by groundwater with As concentration at 90.66 μg/L, and a hydraulic retention time of 2 days. Planted prototypes had higher As retention (87–90% of the total As inflow) than the prototype without plants (27%) (Fu et al. 2014; Valles-Aragón and Alarcón-Herrera 2014; Alarcón-Herrera et al. 2014b).

Subsurface flow constructed wetlands (SSFCW) are currently under evaluation. The removal of total As(34 μg/L) in a subsurface flow constructed wetland mesocosm containing an iron oxide substrate (tezontle) both without plants and containing two plant species, *Zantedeschia aethiopica* and *Anemopsis californica*, for phytoremediation was evaluated. The total As mass removal efficiencies during the first 3 months were 57.7, 75.2, and 77.8% in the control (not planted), *Z. aetiopica*-planted, and A. *californica*-planted cells, respectively. The presence of plants increased As removal in a batch-fed subsurface flow constructed wetland system (Zurita et al. 2009; Zurita et al. 2011; Zurita et al. 2012).

The feasibility of the ultrafiltration (UF) technology in a municipal water treatment plant in Celaya, a small city in Guanajuato (340,400 inhabitants), was tested. The Celaya plant has a production capacity of 108 m^3/h, based on 32 UF modules, a system recovery higher than 98%, and a design flux of 66 L/m h. The UF technology uses hydrophilic PVDF polymeric hollow fiber membranes and allows the removal of the As flocks, reducing the amount of coagulant needed in the process. Additionally, the method is capable of removing bacteria and virus without using a secondary step, decreasing the amount of waste to be disposed of (De Carvalho et al. 2014).

The SORAS technology was tested for three different concentrations of iron, five concentrations of lemon juice, four concentrations of hardness, and various removal times. The best removal conditions in laboratory tests yielded an efficiency of about 80% with 10 mg/L of iron, 0.6 mL/L lemon juice, 3 h exposure, and hardness above 200 mg/L. Field experiments were carried out in two sites from the San Luis Potosí and Zacatecas states (As concentrations between 300 and 900 μg/Lin wells), using the most efficient removal conditions tested. The system removed more than 95% of As, reaching values below the threshold established for water for human consumption (25 μg/L) (Gelover et al. 2006).

Photocatalytic oxidation of As(III) using TiO_2-Cr_2O_3 semiconductors in basic pH under UV-Vis light irradiation was studied. Improved photoactivity was found with the TiO_2-Cr_2O_3 photocatalyst compared with bare TiO_2. The results showed that the addition of Cr_2O_3 significantly improved As(III) photooxidation, in which the Cr(III)/Cr(VI) pair play an important role as electron acceptor in the process (May-Ix et al. 2014).

The use of heterogeneous photocatalysis in water for As removal and disinfection under UV (solar radiation) and ferric chloride was used in the simultaneous removal of As as well as pathogens from water. With the optimized conditions determined in a batch process, a continuous flow system was developed. It was demonstrated that the heterogeneous photocatalysis process in the presence of iron salts is a viable method for oxidizing and removing As while achieving a high level of disinfection, and it can be scaled to a full-scale continuous flow system to treat larger volumes of water (Córdova-Villegas and Alarcón-Herrera 2014).

2.2.10 Nicaragua

The limit value for As in drinking water in Nicaragua is 10 μg/L (INAA 2001). Some studies on As removal in this country can be mentioned.

The biopolymer chitosan was studied as a potential adsorption material for the removal of As from aqueous solutions for water treatment design purposes, because the use of local produced chitosan for As removal from water is of great interest in Nicaragua, since there is abundant raw material for the production of the polymer. The chitosan was extracted from shrimp shells with an overall yield of 40% and a deacetylation grade of 59%. The maximum adsorption capacity was determined to be 20.9 mg As/g at pH 5.5 (Westergren 2006).

Another work studied As removal in chitosan packed columns. Removal experiments were carried out with an As standard solution (1.0 mg/L) and drilled well water samples from Limon Mine Community at different pH, water flowrate, and volume of adsorbent material. The experiments showed that As adsorption depended mainly on pH as well as the activity of functional groups that compose the chitosan structure. At pH 3 and 337.8 cm^3 of adsorbent, 94% adsorption was obtained. The highest As concentration detected was 8.40 μg/L. However, these waters were not suitable for human consumption because the calcium concentration and total solids exceeded the permissible limits (Benavente et al. 2006).

The WHO and the United Nations Children's Fund (UNICEF) developed the RADWQ (Rapid Assessment of Drinking Water Quality) low-cost method for rapidly assessing the quality of drinking water in a country. Nicaragua was one of the six countries that volunteered to host pilot projects to test the new method, and As was one of the elements included in the study, whose results provided a statistically representative snapshot of the water and sanitation status of Nicaragua. In November 2010, ACI As reduction filters, manufactured by the US Aqua Clara International organization, consisting in a hollow fiber membrane tabletop filter that can include one or two buckets for safe water storage, were installed in the Camoapa region in Nicaragua. The used filter was smaller than the traditional ACI biosand filter and was used as a secondary filtration device after water is first cleaned by a biosand filter. The Department of Chemistry of the National Engineering University registered a total elimination of As from water at the end of the campaign. In April 2015, the Nicaraguan company AquaNIC built ACI Household Arsenic Filters for households in Achuapa, León. Together with a local Nicaraguan NGO, El Porvenir, 14 ACI Household Arsenic Filters were provided to go along with their recently made ACI biosand filters. At the end of April 2017, a team of the Grand Rapids Rotarians, whose club had supplied funding for the first 110 ACI Arsenic Household Filters (ACI As HHFs) to be built in an area of San Juan, Tipitapa, Nicaragua, came down to perform the initial installations. All 110 filters were prepared, and the first 29 were implemented into homes. San Juan, Tipitapa, has been dealing with natural As contamination from the well. This problem in the area was found by World Vision, who plans to fit all 200+ homes of the town eventually with As remediation filters. ACI has fit this role, and the remaining filters will be installed throughout these next few months as village members become more informed of As and its implications (Arsenic in Nicaragua n.d.).

The National Water Authority and the NGO Nuevas Esperanzas conducted a research about As removal in Nicaragua in cooperation with TU Delft. A NF treatment plant powered by solar energy was constructed in the rural community of Nuevo Amanecer, next to the active volcano Telica. Arsenic content was measured with the portable kit Arsenator (Inteccon.inc 2018), and, at the end of the treatment, 99% As removal was achieved, with values<10 µg/L (TUDelft 2018).

2.2.11 Peru

Since 2011, the maximum allowable limit for As in drinking water established by the Peruvian normative is 10 µg/L. However, a period (not established yet) has been recommended by the Sanitary Application Plans to attain this maximum (Ministerio de Salud 2011).

A treatment plant in the city of Ilo was built in 1982 designed to eliminate As and turbidity. The treatment used initially massive doses of 90% lime (CaO), but it was improved by the use of ferric chloride, ferric hydroxide plus sulfuric acid, or removal at high pH through coagulation and flocculation with natural $Mg(OH)_2$ (Sancha and Castro 2001; Cortina et al. 2016; Kirchmer and Castro de Esparza 1978; Castro de Esparza 2006).

Later, the ALUFLOC product, a mixture of an oxidant, activated clays and a coagulant (aluminum sulfate or ferric chloride), was developed by CEPIS/SDE/OPS, constituting a simple and low-cost methodology for household use in rural zones. Removal up to 98% was obtained using $FeCl_3$ as coagulant, for initial concentrations of 1 mg/L. For lower concentrations, $Al_2(SO_4)_3$ have been recommended. Three reactors were tested; the best mixers were a bucket with vertical axis and a 20 L bottle with paddle instead of a reactor with a hand crank (Litter et al. 2010a; Sancha and Castro 2001; Litter and Bundschuh 2012; Bundschuh et al. 2010; Esparza and Wong 1998; Castro de Esparza 2010). In Pelipeline and Jallamilla (Puno region), ALUFLOC was evaluated at household scale, testing 20 L of well water in paddle reactors. After the treatment, As values lower than maximum allowable limit (at that time, i.e., 50 µg/L) were obtained with removal percentages between 85% and 99%. ALUFLOC could remove turbidity, bacteria, As, Al, Zn, Cu, Fe, Mn, and Pb (Castro de Esparza 2010).

The SORAS technology was tested in laboratory and in field using a UV lamp and solar irradiation. It was found that for As concentrations up to 500 µg/L and a Fe^{2+}/citrate ratio of 1.8:1, As was removed to 95% after 4 h under solar irradiation or UV of ~7.5 mW/cm^2 (Bundschuh et al. 2009; Jorge et al. 2003). Later, laboratory and field tests have been performed to study the application of SORAS in Sama Las Yaras, Tacna, with As natural contamination. Removal up to 95% (initial As concentrations, 0.012–0.016 mg/L) was obtained using 3 g of iron wire, 3 drops of lemon juice, and 4 h irradiation (Jorge et al. 2006).

Another study using SORAS was later tested, using iron wires and lemon juice. Experimental tests were carried out with synthetic waters at pH around 6.7 and 0.2 mg/L As; a 98.5% reduction of total As under solar irradiation for 6 h was obtained. For the treatment of 1 L of water, 6 grams of iron wire No. 16 and 1.3 mL of lemon juice (variety *Citrus aurantifolia* swingle (subtle)) were used. Field experiments were carried out in the waters of the Iscahuaca-Colcabamba river (Apurímac region), which contained 0.05 mg/L As, yielding a reduction of 88% of total As, under solar irradiation (Chávez Quijada and Miglio Toledo 2011).

Iron nanoparticles impregnated on chitosan extracted from squid pen (*Dosidicus gigas*) were prepared and characterized. The material was found excellent for As removal (1000 μg/L) to less than 10 μg/L in 120 min. Groundwater and surface waters from Tacna were treated successfully reducing As concentration from 500 μg/L to less than 10 μg/L (Villa et al. 2016).

2.2.12 Venezuela

The only reported study of As removal in Venezuela is phytoremediation using water hyacinth (*Eichhornia crassipes*) and lesser duckweed (*Lemna minor*). Arsenic initial concentration was 0.15 mg/L. Plant densities were 1 kg/m^2 for lesser duckweed and 4 kg/m^2 for water hyacinth on a wet basis. Arsenic was monitored as a function of time during 21 days. No significant differences were found in the bioaccumulation capability of both species. The removal rate for *L. minor* was 140 mg As/ha.day with a removal recovery of 5%. The water hyacinth had a removal rate of 600 mg As/ha d and a removal recovery of 18%, under the conditions of the assay. The climatic conditions of the experiment area were more adequate for the water hyacinth and influence the removal capability of the species. The water hyacinth represents a reliable alternative for As bioremediation in waters under the climatic conditions of very dry tropical forest in Tarabana, Edo. Lara, Venezuela (Alvarado et al. 2008).

3 Conclusions

Contamination of surface and groundwaters by As in LA is a relevant problem for the region due to dramatic consequences on health. Lung cancer is the most studied adverse effect of As exposure, followed by skin lesions, bladder cancer, and the effects of early exposure to As. Chile is the country with the highest number of scientific publications related to As health effects, followed by Mexico and Argentina. The studies on As exposure and cancer development are well described in these three countries. Sufficient evidence of the association between As exposure and skin, lung, and bladder cancers has been reported in Argentina, Chile, and Mexico. Evidence of association between As exposure and kidney and liver cancer mortality rates was also reported in Chile and Argentina. For other types of cancers (prostate, leukemia, brain, colon, breast, larynx, stomach, cervix, and endometrium), the evidence is scarce or absent. While the carcinogenicity of As has been confirmed for several cancers, the mechanisms behind the disease are still not well understood, and, therefore, more well-designed studies are needed in that area. According to several studies, conducted mainly in Mexico, an association between As exposure and diabetes seems to occur. However, more studies should be conducted, specially focusing on the potential mechanisms of As-induced diabetes in humans. Metabolomic studies seem to be a way to discover the biochemical pathways that relate As exposure to diabetes. The available information on the association of exposure to arsenic and cardiovascular disease, liver dysfunction, and chronic kidney disease covered a wide range of levels of exposure. However, this information is still partial, scarce, and even inconclusive.

As remediation can proceed through adequate treatments. However, most of the technologies are rather complicated, and they can only be applied in regions where the population has enough economical resources and at large or medium scale, where the supply is centralized. These technologies are not accessible in small communities or disperse settlements of low economical resources, where simple and economical equipments are required that can be easily handled and maintained by the population.

Although there are several sustainable solutions developed by local researchers, the authorities, industries, or international agencies have not practically developed any financial and technical cooperation action for mitigating the As problem in isolated rural and peri-urban LA populations.

Technologies investigated in LA over the last few decades rely on adaptation and improvement of methods involving simple physicochemical processes like adsorption, coagulation/precipitation, or ion exchange, all of them being more suitable for As(V) than for As(III) removal, which usually implies a preliminary oxidation step. For rural communities in LA, small-scale and household level As removal systems are the only feasible short-term solution. Specific reactants used in coagulation/sorption processes for As removal are suitable for addition to small volumes of water and can be easily applied at a household level. Natural geological materials like iron oxides and hydroxides, calcite, clays, and soils may yield effective, simple, and low-cost As removal at the household level and for small communities. Natural organic materials are also the basis for suitable low-cost technologies. Sorption agents coming from plants and animal residues are more attractive for small-scale, rural, household applications, while the use of As-tolerant and As-accumulating plants is more suitable for community applications. Procedures using zerovalent iron from diverse materials are affordable and easy to operate and maintain. They require daily attention, but most of them are nevertheless adequate for family use, and, furthermore, sunlight may be used to improve their effectiveness. Other alternatives, like capacitive deionization, require electricity that may be produced from environment-friendly sources like wind or sunlight. Phytoremediation and wetland construction are also promising technologies. In all cases, water composition and socioeconomic features should be carefully taken into account for selecting the technology.

Since experiences with innovative emerging As removal processes in LA remain scarce and are generally limited to laboratory studies, there is a great need for further research to determine how the technologies for As removal described previously can be effectively applied as As mitigation interventions in rural and urban isolated communities. However, one aspect that should be addressed prior to its implementation for regular use is the acceptance by the local people, since some of the materials (like soils) may be associated with the pollution rather than with the decontamination.

Other examples of As removal plants have been reported in Peru and in Guatemala. In the first case, a technology using coagulation/coprecipitation with $FeCl_3$ has been used, whereas in the second case, $FeCl_3$, a flocculant plus ceramic-based filtering media were employed.

Concerning removal and disposal of As from industrial effluents containing high levels of the element in solution (copper and gold mining and metallurgical plants of Chile and Brazil), coprecipitation methods with iron salts precipitated either as amorphous (arsenical ferrihydrite) or crystalline arsenates are the predominant technologies.

In spite of all the difficulties and problems that had to be faced, the LA experience gives valuable information that could be used to solve the As problem in other regions of the world, especially in countries of Asia where the first option is to find other water sources not contaminated with As.

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References

Aballay LR, Díaz M d P, Francisca FM, Muñoz SE (2012) Cancer incidence and pattern of arsenic concentration in drinking water wells in Córdoba, Argentina. Int J Environ Health Res 22:220–231

Acuña-Piedra A, Araya-Obando A, Romero-Esquivel LG (2016) Selección teórica de adsorbentes potenciales naturales de bajo costo para la remoción de arsénico en el agua de consumo humano en Costa Rica (Potential natural low-cost adsorbents for the removal of arsenic in drinking water in Costa Rica). Tecnol Marcha 29:23–34

Adedge Water Technologies, LLC (2012) Arica Pago de Gomez, Chile – case study. http://www.siss.gob.cl/586/w3-article-9785.html. Accessed Sept 2018

Agency for Toxic Substances and Disease Registry (ATSDR) (2013) Course: arsenic toxicity. Environmental Health and Medicine Education. https://www.atsdr.cdc.gov/csem/csem.asp?csem=1&po=1.1. Accessed Oct 2013

Alarcón-Herrera M T, Flores Montenegro I, Sánchez I. (1999) Remoción de flúor y arsénico del agua potable por precipitación química. Cátedra del Medio Ambiente, Contribución a la Educación y la Protección Ambiental, La Habana, pp 168–172

Alarcón-Herrera M T, Martín-Domínguez I R, Benavides Montoya A (2007) Wetlands for arsenic removal. In: WETPOL 2007 2nd International Symposium on Wetland Pollutant Dynamics and Control, Tartu

Alarcón-Herrera MT, Nuñez-Montoya OG, Melgoza-Castillo A, Royo-Márquez MH, Rodriguez Almeida FA (2009) Potential use of sedges (Cyperaceae) in arsenic phytoremediation. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 649–655

Alarcón-Herrera MT, Bundschuh J, Nath B, Nicolli HB, Gutierrez M, Reyes-Gomez VM, Nunez D, Martín-Dominguez IR, Sracek O (2013) Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: genesis, mobility and remediation. J Hazard Mater 262:960–969

Alarcón-Herrera MT, López Paraguay MZ, Martín Domínguez IR (2014a) Arsenic removal from groundwater using magnetic nanoparticles. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 792–796

Alarcón-Herrera MT, Llorens i, Ribes E, Olmos-Márquez MA, Martín-Domínguez IR (2014b) Arsenic retention and distribution in treatment wetlands. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 856–857

Alonso H (1992) Arsenic enrichment in superficial waters. II. Región Northern Chile. In: Sancha A (ed) Proceedings of the international seminar on arsenic in the environment and its incidence on health. Universidad de Chile, Santiago, pp 101–108

Alvarado S, Guédez M, Marcó P L-M, Graterol N, Anzalone A, Arroyo CJ, Záray Gyula J (2008) Arsenic removal from waters by bioremediation with the aquatic plants Water Hyacinth (Eichhornia crassipes) and Lesser Duckweed (Lemna minor). Bioresour Technol 99:8436–8440

Alvarado-Rodríguez CE, Duarte Pérez R, Klapp-Escribano J, Romero Guzmán ET, de Marín Allende MJ (2012) Dispersion and sorption of Arsenic in a biofilter with a not living biomass (Eicchornia crassipes): comparison of experimental and numerical results. In: Klapp J, Cros A, Velasco Fuentes O, Stern C, Rodriguez Meza MA (eds) Experimental and theoretical advances in fluid dynamics. Springer, Berlin, pp 349–358

Alvarez J, Rosas L (1999) Adsorción de Arsénico Electrotratamiento, IPN Ciencia, Arte: Cultura, Enero-Febrero, Hemeroteca Virtual ANUIES

Alvarez-Silva M, Uribe-Salas A, Nava-Alonso F, Pérez Garibay R (2009) Adsorption of As(V) onto goethite: experimental statistical optimization. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 527–534

Araujo SF, Caldeira CL, Ciminelli VST, Silva A, Amorim CC (2018) Versatility of iron-rich steel waste for the removal of high arsenic and sulfate concentrations in water. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-018-3168-7

Armas A, Olivieri V, Mauricci JJ, Silva V (2014) Reduction of arsenic from groundwater by using a coupling of RO and processes. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 759–761

Armienta MA, Segovia N (2008) Arsenic and fluoride in the groundwater of Mexico. Environ Geochem Health 30:345–353

Armienta MA, Rodríguez CR, Ongley LK, Brust H, Morales F, Aguayo A, Cruz O, Ceniceros N (2007) Origin and fate of arsenic in a historic mining area of Mexico. In: Trace metals and other contaminants in the environment, vol 9. Elsevier, Amsterdam, pp 461–486

Armienta MA, Micete S, Flores-Valverde E (2009) Feasibility of arsenic removal from contaminated water using indigenous limestone. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 505–510

Armienta MA, Labastida I, Lara RH, Cruz O, Aguayo A, Ceniceros N (2016) Removal of arsenic from acid mine drainage by indigenous limestones. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 594–595

Arsenic in Nicaragua (n.d.) http://aquaclara.org/where-we-work/nicaragua/arsenic/. Accessed Aug 2018

Arsénico en agua, informe del Grupo Ad-Hoc Arsénico en agua de la Red de Seguridad Alimentaria de CONICET (2018) https://rsa.conicet.gov.ar/wp-content/uploads/2018/08/Informe-Arsenico-en-agua-RSA.pdf. Accessed Nov 2018

Avilés M, Pardón M (2000) Remoción de Arsénico de Agua Mediante Coagulación-Floculación a Nivel Domiciliario, Federación Mexicana de Ingeniería Sanitaria y Ciencias del Ambiente, FEMISCA, pp 1–10

Ayerza A (1917) Noticias Universitarias en la Academia de Medicina. Premios del Centenario. Interesante disertación del Dr. Ayerza. La Prensa Médica Argentina N° 13. Buenos Aires, 10 de octubre de 1917, pp. 170–171

Ayerza A (1918a) Arsenicismo regional endémico (keratodermia y melanodermia combinadas). Bol Acad Med 2(3):11–24

Ayerza A (1918b) Arsenicismo regional endémico (keratodermia y melanodermia combinadas) (continuación). Bol Acad Med 2(3):41–55

AySA (2014a) http://www.aysa.com.ar/index.php?id_seccion=562. Accessed June 2014.

AySA (2014b) http://www.aysa.com.ar/index.php?id_contenido=1550&id_seccion=570. Accessed Aug 2018

Bahr C, Ewy W (2014) Drinking water dearsenification with granular ferric hydroxide: comparison of field experience with waterworks units in Germany and POU units in Argentina. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the Discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 667–669

Bailey KA, Wu MC, Ward WO, Smeester L, Rager JE, García-Vargas G, Del Razo LM, Drobná Z, Stýblo M, Fry RC (2013) Arsenic and the epigenome: interindividual differences in arsenic metabolism related to distinct patterns of DNA methylation. J Biochem Mol Toxicol 27:106–115

Bailey KA, Laine J, Rager JE, Sebastian E, Olshan A, Smeester L, Drobná Z, Stýblo M, Rubio-Andrade M, García-Vargas G, Fry RC (2014) Prenatal arsenic exposure and shifts in the newborn proteome: interindividual differences in tumor necrosis factor (TNF)- responsive signaling. Toxicol Sci 139:328–337

Bailey KA, Smith AH, Tokar EJ, Graziano JH, Kim KW, Navasumrit P, Ruchirawat M, Thiantanawat A, Suk WA, Fry RC (2016) Mechanisms underlying latent disease risk associated with early-life arsenic exposure: current research trends and scientific gaps. Environ Health Perspect 124:170–175

Barahona J, González Z (1987) Estudio a nivel de planta piloto sobre abatimiento de arsénico del agua de Taltal. Proceedings VII Congreso Chileno de Ingeniería Sanitaria y Ambiental, pp 880–896

Bardach AE, Ciapponi A, Soto N, Chaparro MR, Calderon M, Briatore A, Cadoppi N, Tassara R, Litter MI (2015) Epidemiology of chronic disease related to arsenic in Argentina: a systematic review. Sci Total Environ 538:802–816

Barrientos E, Matutes J, Miki M (2013) Arsenic removal from water using magnetic nanoparticles obtained by ACCVD. Momento, Rev Fís 46:28–37

Bedolla L, Avilés M, Tirado L, Cortés J M C (1999) Remoción de arsénico del agua para consumo humano mediante coagulación-floculación a nivel domiciliario. Instituto Mexicano de Tecnología del Agua (IMTA), México, Report

Benavente M, Arévalo M, Martínez J (2006) Speciation and removal of Arsenic in column packed with chitosan, Water practice & technology, 1 IWA Publishing. https://doi.org/10.2166/WPT.2006089

Berardozzi E, Einschlag FSG (2017) Development of a water treatment plant for arsenic removal based on the zero-valent iron technology. In: Knežević R (ed) Arsenic: risks of exposure, behavior in the environment and toxicology. Nova Science Publishers, New York, pp 115–148

Berardozzi E, Galindez JM, García Einschlag FS (2014) Effects of changes in operating conditions on the iron corrosion rate in zerovalent iron columns. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 675–677

Bobillo C, Navoni JA, Olmos V, Merini LJ, Villaamil Lepori E, Corach D (2014) Ethnic characterization of a population of children exposed to high doses of arsenic via drinking water and a possible correlation with metabolic processes. Int J Mol Epidemiol Genet 17:1–10

Bolaños-Guerrón D R, Sánchez-Gómez V P, Paz J, Izquierdo A R, Stael C, Balseiro-Romero M (2018) Arsenic retention on technosols prepared with nanoparticles and ferric soil from mine drainage water. J Nanotechnol: 6840856, 8 pages. https://doi.org/10.1155/2018/6840856.

Bonillas E (2012) Arsenic free in Argentina. https://sgc-wqpmag.s3.amazonaws.com/s3fs-public/14_app_adedge_0512WQP.pdf. Accessed Aug 2018

Borneo G, Barrionuevo L (2014) Adsorption technology for removal of arsenic in water. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 722–723

Botto IL, González MJ, Gazzolli D, Soto E (2013) Iron activation of natural aluminosilicates to remove arsenic from groundwater. J Environ Sci Eng A 2(12A):744–752

Bundschuh J, Litter MI (2010) Opciones sustentables para resolver los problemas de arsénico en Iberoamérica. In: Litter MI, Bundschuh J (eds) Situación del arsénico en la Región Ibérica e Iberoamericana. Posibles acciones articuladas e integradas para el abatimiento del As en zonas aisladas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 37–54

Bundschuh J, García M E, Alvarez M T (2007) Arsenic and heavy metal removal by phytofiltration and biogenic sulfide precipitation – a comparative study from Poopó Lake Basin, Bolivia. 3rd International Groundwater Conference IGC-2007, Water, Environment & Agriculture – Present Problems & Future Challenges, p 152

Bundschuh J, García ME, Birkle P, Cumbal LH, Bhattacharya P, Matschullat J (2009) Occurrence, health effects and remediation of arsenic in groundwaters of Latin America. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 3–15

Bundschuh J, Litter M, Ciminelli V, Morgada ME, Cornejo L, Garrido Hoyos S, Hoinkis J, Alarcón-Herrera MT, Armienta MA, Bhattacharya P (2010) Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Iberoamerica – a critical analysis. Water Res 44:5828–5845

Bundschuh J, Bhattacharya P, Sracek O, Mellano MF, Ramírez AE, Storniolo AdR, Martín RA, Cortés J, Litter MI, Jean J-S (2011) Arsenic removal from groundwater of the Chano-Pampean plain (Argentina) using natural geological materials as adsorbents. J Environ Sci Health Part A 46:1297–1310

Bundschuh J, Litter MI, Parvez F, Román-Ross G, Nicolli HB, Jiin-Shuh J, Chen-Wuing L, López D, Armienta MA, Guilherme LRG, Gomez Cuevas A, Cornejo L, Cumbal L, Toujaguez R (2012) One century of arsenic exposure in Latin America: a review of history and occurrence from 14 countries. Sci Tot Environ 429:2–35

Cabrera HN, Gómez ML (2003) Skin cancer induced by arsenic in the water. J Cutan Med Surg 2:106–111

Cáceres R, Aguirre L, Cáceres CX (2010) Experiencias de remoción of arsénico realizadas en Argentina por corrosión electroquímica de un lecho fijo of hierro. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico in aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 209–217

Caetano ML, Ciminelli VST, Rocha SDF, Spitale MC, Caldeira CL (2009) Batch and continuous precipitation of scorodite from diluted industrial solutions. Hydrometallurgy 95:44–52

Calderón J, Navarro ME, Jimenez-Capdeville ME, Santos-Diaz MA, Golden A, Rodriguez-Leyva I, Borja-Aburto V, Díaz-Barriga F (2001) Exposure to arsenic and lead and neuropsychological development in Mexican children. Environ Res 85:69–76

Callegaro R, Deambrosis N, Cusimano N, Cotta E (1976) Arsénico, flúor y vanadio en aguas de bebida. Técnicas para corregir su exceso. XV Congreso de Ingeniería Sanitaria, Buenos Aires

Camacho LM, Gutierrez M, Alarcón-Herrera MT, Villalba ML, Deng S (2011) Occurrence and treatment ofarsenic in groundwater and soil in northern Mexico and southwestern USA. Chemosphere 83:211–225

Cambero F A, Cohen L (2018) Chile's Codelco receives approval for $1 billion desalination plant. https://www.reuters.com/article/us-chile-codelco/chiles-codelco-receives-approval-for-1-billion-desalination-plant-idUSKCN1GK26Y. Accessed Aug 2018

Camerotto Andreani PA, Trinelli MA, Leal PR, Rodriguez AV, Rodriguez AI, Llano J, dos Santos Afonso M (2014) Adsorptive removal of arsenic from waters using natural and modified Argentine zeolites. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 711–713

Cano-Aguilera AF, Aguilera-Alvarado AF, de la Rosa G, Fuentes Ramírez F, Cruz-Jiménez G, Gutiérrez-Valtierra M, Ramírez-Ramírez ML (2009) The use of iron-coated LECA for arsenic removal from aqueous solutions under batch and flow conditions. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 565–570

Cardoso S, Grajeda C, Argueta S, Garrido S (2010) Experiencia satisfactoria para la remoción de arsénico en Mixco, Guatemala. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 179–189

Carro Perez ME, Francisca FM (2013) Arsenic entrapment in reactive columns of residual soils. J Environ Eng 139:788–795

Castro de Esparza, M.L. 2004. Remoción del arsénico en el agua para bebida y biorremediación de suelos. Tercer Seminario Internacional sobre Evaluación y Manejo de las Fuentes de Agua de Bebida contaminadas con Arsénico. Santiago: Universidad de Chile, November 08–11. http://www.bvsde.paho.org/bvsacd/arsenico/Arsenic2004/theme1/Esparza2.pdf. Accessed Nov 2018

Castro de Esparza ML (2006) Removal of arsenic from drinking water and soil bioremediation. In: International Congress Mexico City, Natural Arsenic in Groundwaters of Latin America

Castro de Esparza ML (2009) The presence of arsenic in drinking water in Latin America and its effect on public health. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 17–29

Castro de Esparza ML (2010) Remoción de arsénico del agua de pozos de zonas rurales de Puno, Perú empleando ALUFLOC. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 243–255

Cebrián ME, Albores A, Aguilar M, Blakely E (1983) Chronic arsenic poisoning in the north of Mexico. Hum Toxicol 2:121–133

Chávez Quijada ML, Miglio Toledo M (2011) Remoción de arsénico por oxidación solar en aguas para consumo humano. Rev Soc Quím Perú 77:307–314

Círculo Médico del Rosario (1917) Sobre la nueva enfermedad descubierta en Bell Ville. Sesión extraordinaria del Círculo Médico del 15 de octubre de 1917. Rev Med de Rosario 7:485–489

Claesson M, Fagerberg J (2003) Arsenic in groundwater of Santiago del Estero – Sources, Mobility Patterns and Remediation with Natural Materials. Master thesis, Department of Land and Water Resources Engineering, KTH, Stockholm, Sweden, TRITALWREX-03-05

Código Alimentario Argentino (2012) Bebidas hídricas, aguas y aguas gasificadas. Capítulo XII. http://www.anmat.gov.ar/alimentos/codigoa/CAPITULO_XII.pdf. Accessed Jan 2018

Cohen SM, Chowdhury A, Arnold LL (2016) Inorganic arsenic: a non-genotoxic carcinogen. J Environ Sci 49:28–37

Córdova-Villegas LG, Alarcón-Herrera MT (2014) Use of heterogeneous photocatalysis in water for arsenic removal and disinfection. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 844–846

Cornejo L, Mansilla HD, Arenas MJ, Flores M, Flores V, Figueroa L, Yañez J (2004) Removal of arsenic from water of Río Camarones, Arica, Chile, using the modified SORAS technology. In: Litter MI, Jiménez González A (eds) Advances in economic solar technologies for disinfection, decontamination, and removal of arsenic from water of rural communities of Latin America, OAS AE 141 Project. Digital Graphic Publisher, La Plata, pp 84–97

Cornejo L, Lienqueo H, Arenas M, Acarapi J, Mansilla H, Yañez J (2006a) Remoción de arsénico de aguas naturales del río de Camarones y su utilización para consumo humano, mediante la tecnología SORAS Modificada-Hierro Cero (Removal of arsenic from natural waters of the Camarones River and their use for human consumption by the modified SORAS – zerovalent iron technology). In: Litter MI (ed) Resultados finales del Proyecto OEA/AE141: investigación, desarrollo, validación y aplicación de tecnologías solares para la potabilización de agua en zonas rurales aisladas de América Latina y el Caribe. Editorial OEA, Buenos Aires, pp 139–157

Cornejo L, Lienqueo H, Arenas M, Acarapi J, Mansilla H, Yañez J (2006b) Transferencia de la metodología SORAS Modificada – Hierro Cero a los poblados que carecen de agua potable de la Comuna de Camarones, Arica, Chile (Transference of the modified SORAS – zerovalent iron methodology to communities that lack drinking water in the Commune of Camarones, Arica, Chile). In: Litter MI (ed) Resultados finales del Proyecto OEA/AE141: investigación, desarrollo, validación y aplicación de tecnologías solares para la potabilización de agua en zonas rurales aisladas de América Latina y el Caribe. Editorial OEA, Buenos Aires, pp 159–198

Cornejo L, Lienqueo H, Arenas M, Acarapi J, Contreras D, Yáñez J, Mansilla HD (2008) In field arsenic removal from natural water by zero valent iron. Environ Poll 156:827–831

Cornejo L, Acarapi J, Lienqueo H, Arenas M (2010) Métodos solares. Tecnología Hierro Cero para la remoción de arsénico en aguas naturales con altos niveles de salinidad. Experiencias en implementación y transferencia tecnológica comunidades rurales del norte de Chile. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 229–241

Coronado-González JA, Del Razo LM, García-Vargas G, Sanmiguel-Salazar F, Escobedo-de la Peña J (2007) Inorganic arsenic exposure and type 2 diabetes mellitus in Mexico. Environ Res 104:383–389

Cortina JL, Litter MI, Gibert O, Valderrama C, Sancha AM, Garrido S, Ciminelli VST (2016) Latin American experiences in arsenic removal from drinking water and mining effluents. In: Kabay N, Bryjak M (eds) Innovative materials and methods for water treatment-separation of Cr and As. CRC-Taylor & Francis, Boca Raton, pp 391–416

Cumbal LH (2004) Polymer-supported hydrated ferric oxide nanoparticles: characterization and environmental applications. Lehigh University, Bethlehem

Cumbal Flores L, Zúñiga Salazar M (2010) Quitosano impregnado con partículas de óxido de hierro: un biosorbente que remueve selectivamente arsénico de aguas. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 269–289

Cumbal L, Sengupta AK (2005) Arsenic removal using polymer-supported hydrated iron(III) oxide nanoparticles: role of Donnan membrane effect. Environ Sci Technol 39:6508–6515

Cumbal LH, Sengupta AK (2009) Polymer-supported Fe(III) oxide particles: an arsenic-selective sorbent. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee

AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 571–580

Cumbal L, Shengheng H (2014) Robust and reusable hybrid nanosorbent to mitigate arsenic crisis: from laboratory to masses in the field. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 797–800

Cumbal L, Greenleaf J, Leun D, SenGupta AK (2003) Polymer supported inorganic nanoparticles: characterization and environmental applications. React Funct Polym 54:167–180

Currier JM, Ishida MC, González-Horta C, Sánchez-Ramírez B, Ballinas-Casarrubias L, Gutiérrez-Torres DS, Hernández Cerón R, Viniegra Morales D, Baeza Terrazas FA, Del Razo LM, García-Vargas GG, Saunders RJ, Drobná Z, Fry RC, Matoušek T, Buse JB, Mendez MA, Loomis D, Stýblo M (2014) Associations between arsenic species in exfoliated urothelial cells and prevalence of diabetes among residents of Chihuahua, Mexico. Environ Health Perspect 122:1088–1094

Czerniczyniec M, Farías S, Magallanes J, Cicerone D (2007) Arsenic (V) Adsorption onto biogenic hydroxyapatite: solution composition effects. Water Air Soil Pollut 180:75–82

D'Ambrosio C (2005) Evaluación y selección de tecnologías disponibles para remoción de arsénico. In: Galindo G, Fernández Turiel JL, Parada MA, Torrente DG (eds) Arsénico en aguas: origen movilidad y tratamiento. Taller II Seminario Hispano-Latinoamericano sobre temas actuales de hidrología subterránea-IV Congreso Hidrogeológico Argentino. Río Cuarto, pp. 28–38

d'Hiriart J, Hidalgo MV, García, Litter MI, Blesa MA (2009) Arsenic removal by solar oxidation in groundwater of Los Pereyra, Tucumán province, Argentina. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 615–624

Danil de Namor AF, Cartwright JR, Abou Hamdan W, Webb OA, Al Hakawati N, Valiente L, Korfali S (2014) From a modified naturally occurring material to the design of novel receptors for the removal of arsenic from water. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 787–791

Dauphiné DC, Ferreccio C, Guntur S, Yuan Y, Hammond SK, Balmes J, Smith AH, Steinmaus C (2011) Lung function in adults following in utero and childhood exposure to arsenic in drinking water: preliminary findings. Int Arch Occup Environ Health 84:591–600

De Carvalho F, Masetto N, Lima A, Arbelaez J, Ramos RG, Avalos C (2014) Arsenic removal enhanced by the use of ultrafiltration. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 775–777

de la Fuente L, Soria MC, Blesa MA, Litter MI (2006) Acciones de difusión del Proyecto OEA/AE/141, Tecnologías económicas para la desinfección y descontaminación de aguas en zonas rurales de América Latina. In: Litter MI (ed) Resultados finales del Proyecto OEA/AE141: investigación, desarrollo, validación y aplicación de tecnologías solares para la potabilización de agua en zonas rurales aisladas de América Latina y el Caribe. Editorial OEA, Buenos Aires, pp 379–409

de la Rosa R, Steinmaus C, Akers NK, Conde L, Ferreccio C, Kalman D, Zhang KR, Skibola CF, Smith AH, Zhang L, Smith MT (2017) Associations between arsenic (+3 oxidation state) methyltransferase (AS3MT) and N-6 adenine-specific DNA methyltransferase 1 (N6AMT1) polymorphisms, arsenic metabolism, and cancer risk in a Chilean population. Environ Mol Mutagen 58:411–422

de Mello JWV, Gasparon M, Silva J (2014) Treatment of As contaminated water from mining industry by precipitation of Al-Fe (hydr)oxides. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 678–680

de Souza TD, Carraro Borges A, Teixeira de Matos A, Veloso RW, Fernandes Braga A (2018) Kinetics of arsenic absorption by the species *Eichhornia crassipes* and *Lemna valdiviana* under optimized conditions. Chemosphere 209:866–874

Del Razo LM, García-Vargas GG, Valenzuela OL, Castellanos EH, Sánchez-Peña LC, Currier JM, Drobná Z, Loomis D, Stýblo M (2011) Exposure to arsenic in drinking water is associated with increased prevalence of diabetes: a cross-sectional study in the Zimapán and Lagunera regions in Mexico. Environ Health 10:73. https://doi.org/10.1186/1476-069X-10-73

Deschamps E, Ciminelli VST, Weidler PG, Ramos AY (2003) Arsenic sorption onto soils enriched in Mn and Fe minerals. Clays Clay Miner 51:197–204

Deschamps E, Ciminelli VST, Höll W (2005) Removal of As(III) and As(V) from water using a natural Fe and Mn enriched sample. Water Res 39:5212–5220

Dias A, Sá RG, Spitale MC, Athayde M, Ciminelli VST (2008) Microwave-hydrothermal synthesis of nanostructured Na-birnessites and phase transformation by arsenic(III) oxidation. Mater Res Bull 43:1528–1538

Dodero E, Pirosky A, Guberman J, Martínez L, Tarquini G (1978) Tratamiento por ósmosis inversa de aguas con alto contenido de arsénico y fluor. XVI Congreso Interamericano de Ingeniería Sanitaria y Ambiental, Santo Domingo

Duarte G, Ciminelli V, Gasparon M, Mello JWV (2012) Evaluation of 10 years stability of concentrated arsenic-sulfide tailings. In: Ng JC, Noller BN, Naidu R, Bundschuh J, Bhattacharya P (eds) Understanding the Geological and Medical Interface of Arsenic. Taylor and Francis Group, London, pp 423–425

Einschlag FSG, Triszcz JM (2008) Arsenic removal in continuous systems using zero – valent iron fixed beds. In: Masotti A (ed) Arsenic: sources, toxicity and environmental impact. Nova Science Publishers, New York, pp 305–324

Elizalde-González MP, Mattusch J, Einicke W-D, Wennrich R (2001) Sorption on natural solids for arsenic removal. Chem Eng J 81:187–195

Engström K, Vahter M, Mlakar SJ, Concha G, Nermell B, Raqib R, Cardozo A, Broberg K (2011) Polymorphisms in arsenic (+III oxidation state) methyltransferase (AS3MT) predict gene expression of AS3MT as well as arsenic metabolism. Environ Health Perspect 119:182–188

Engström K, Wojdacz TK, Marabita F, Ewels P, Käller M, Vezzi F, Prezza N, Gruselius J, Vahter M, Broberg K (2017) Transcriptomics and methylomics of CD4-positive T cells in arsenic-exposed women. Arch Toxicol 91:2067–2078

Escalera R, Ormachea OA (2012a) Solar oxidation and removal of arsenic from groundwater utilizing a semicircular section Tubular Photoreactor. J Environ Sci Eng A 1:1071–1082

Escalera CR, Ormachea OA (2012b) Solar oxidation and removal of arsenic from groundwater utilizing a semicircular section tubular photoreactor. J Environ Sci Eng A1:1071–1082

Escalera Vásquez R (2016) Remoción de arsénico en aguas subterráneas con bajas concentraciones de hierro mediante microfiltros comerciales. Investig Desarro 16:39–48

Escalera Vásquez R, Ormachea M, Ormachea O, Heredia M (2014) Presencia de arsénico en aguas de pozos profundos y su remoción usando un prototipo piloto basado en colectores solares de bajo costo. Investig Desarro 14:83–91

Escudero LB, Castro Grijalba A, Wuilloud RG (2014) Removal of arsenic using a phosphonium ionic liquid impregnated-resin. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 740–741

Esparza M L (1996) Abatimiento de Arsénico en Aguas Subterráneas para zonas rurales. Experiencias del CEPIS en Salta y Tucumán. Seminario Potabilización de Aguas con Arsénico y Flúor. AIDIS-Córdoba

Esparza M L, Wong M (1998) Abatimiento de Arsénico en Aguas Subterráneas para Zonas Rurales, CEPIS. Congreso Interamericano de Ingeniería Sanitaria y Ambiental

Esper J A M M, Amaral R D, Ciminelli V S T (2007) Cover design performance at a Kinross gold mine in Brazil. In: XXII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa, Proceedings VII Meeting of the Southern Hemisphere on Mineral Technology, Ouro Preto, Vol. II, Ouro Preto, p 607–612

Fernández RG, Petrusevski B, Schippers J, Sharma S (2009a) Arsenic removal from groundwater using ferric chloride and direct filtration. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 555–564

Fernández RG, Ingallinella AM, Stecca LM (2009b) Arsenic removal from groundwater by coagulation with polyaluminum chloride and double filtration. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 589–594

Fernández MI, López JF, Vivaldi B, Coz F (2012) Long-term impact of arsenic in drinking water on bladder cancer health care and mortality rates 20 years after end of exposure. J Urol 187:856–861

Ferreccio C, Sancha AM (2006) Arsenic exposure and its impact on health in Chile. J Health Popul Nutr 24:164–175

Ferreccio C, Gonzalez C, Milosavjlevic V, Marshall G, Sancha AM (1998) Lung cancer and arsenic exposure in drinking water: a case-control study in northern Chile. Cad Saúde Pública 14(Suppl 3):S193–S198

Ferreccio C, González C, Milosavjlevic V, Marshall G, Sancha AM, Smith AH (2000) Lung cancer and arsenic concentrations in drinking water in Chile. Epidemiology 11:673–679

Ferreccio C, Yuan Y, Calle J, Benitez H, Parra RL, Acevedo J, Smith AH, Liaw J, Steinmaus C (2013a) Arsenic, tobacco smoke, and occupation associations of multiple agents with lung and bladder cancer. Epidemiology 24:898–905

Ferreccio C, Smith AH, Durán V, Barlaro T, Benítez H, Valdés R, Aguirre JJ, Moore LE, Acevedo J, Vásquez MI, Pérez L, Yuan Y, Liaw J, Cantor KP, Steinmaus C (2013b) Case-control study of arsenic in drinking water and kidney cancer in uniquely exposed Northern Chile. Am J Epidemiol 178:813–818

Ferreira FAG, Franco MW, De Oliveira DM, Magalhães SMS, Rodrigues Barbosa FA (2018) Arsenic tolerance of *Microcystis novacekii* and its arsenic decontamination potential. Braz Arch Biol Technol 61:e18160644. https://doi.org/10.1590/1678-4324-2018160644

Figueroa ME, Montes F (1995) Remoción de arsénico por coagulación química. Departamento de Los Andes, Dirección General de Obras Sanitarias, Salta

Flora SJS (2015) Arsenic: chemistry, occurrence and exposure. Handbook of arsenic toxicology. Academic, London, pp 1–49

Flóres-Montenegro I (1998) Evaluación de las concentraciones de flúor y arsénico en el agua del valle del Guadiana: alternativas de remoción. Master of Science thesis, Instituto Tecnológico de Durango, Química y Bioquímica, Durango

Fostier AH, Pereira MDSS, Rath S, Guimarães JR (2008) Arsenic removal from water employing heterogeneous photocatalysis with TiO_2 immobilized in PET bottles. Chemosphere 72:319–324

Francisca FM, Carro Perez ME, Krapp A, Panique Lazcano DR (2014) Adsorptive filter for removal of arsenic from drinking water. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 708–710

Frangie MS, Hernández A, Orsini MP (2014) Intervention model on removal of arsenic from drinking water. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 894–896

Fu S, Wu J, Li Y, Liu Y, Gao Y, Yao F, Qiu C, Song L, Wu Y, Liao Y, Sun D (2014) Urinary arsenic metabolism in a Western Chinese population exposed to high-dose inorganic arsenic in drinking water: influence of ethnicity and genetic polymorphisms. Toxicol Appl Pharmacol 274:117–123

Fuentealba C (2003) Planta piloto para remover arsénico en una fuente subterránea de agua potable. Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile

Gamboa-Loira B, Hernández-Alcaraz C, Gandolfi AJ, Cebrián ME, Burguete-García A, García-Martínez A, López-Carrillo L (2018) Arsenic methylation capacity in relation to nutrient intake and genetic polymorphisms in one-carbon metabolism. Environ Res 164:18–23

Garcés Mendoza ID, Vaca Mier M, López Callejas R (2014) Evaluation of arsenic removal process in water using zerovalent iron oxidation. In: Litter MI, Nicolli HB, Meichtry JM, Quici

N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 662–663

García MG, Hidalgo MV, Litter MI, Blesa MA (2003) Remoción de As mediante el método RAOS en Los Pereyra, Provincia de Tucumán, Argentina (As removal by SORAS in Los Pereyra, Province of Tucumán, Argentina). In: Litter MI, Mansilla H (eds) Arsenic removal assisted by solar light in rural communities of Latin America, OAS Project AE/141. Digital Grafic, La Plata, pp 9–33

García MG, D'Hiriart J, Giullitti J, Lin H, Custo G, Hidalgo MV, Litter MI, Blesa MA (2004a) Solar light induced removal of arsenic from contaminated groundwater: the interplay of solar energy and chemical variables. Sol Energy 77:601–613

García MG, Lin HJ, Custo G, d'Hiriart J, Hidalgo MV, Litter MI, Blesa MA (2004b) Avances en remoción de arsénico por oxidación solar en aguas de Tucumán, Argentina (Advances in arsenic removal by solar oxidation from water of Tucumán, Argentina). In: Litter MI, Jiménez-González A (eds) Advances in economic solar technologies for disinfection, decontamination, and removal of Arsenic from Water of Rural Communities of Latin America. Digital Graphic Publisher, La Plata, pp 43–63

García JI, Boeykens S, Saralegui A, Gobbi A, Fernandez C, Ozols A (2014) Arsenic removal feasibility from aqueous solutions using shells and bone derivatives as adsorbents: a preliminary study. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 738–739

Garrido S, Avilés M (2008) Análisis de la información técnica y evaluación del funcionamiento de la planta para remoción de arsénico, Mixco, Guatemala, Final report. Instituto Mexicano de Tecnología del Agua, Jiutepec

Garrido Hoyos SE, Avilés Flores M, Pargaru I, Santos de La Paz J, Segura Beltrán N, Narváez YG, Ortiz F (2010) México: Método electroquímico. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 257–267

Garrido Hoyos S, Avilés Flores M, Ramírez Gonzalez A, Grajeda Fajardo C, Cardoso Zoloeta S, Velásquez Orozco H (2013) Comparing two operating configurations in a full-scale arsenic removal plant: case study Guatemala. Water 5:834–851

Garrido SE, Romero L (2014) Synthesis of adsorbents with iron oxide and hydroxide contents for the removal of arsenic from water for human consumption. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 693–695

Garrido S, Avilés M, Ramírez A, Calderón C, Ramírez-Orozco A, Nieto A, Shelp G, Seed L, Cebrián M, Vera E (2009) Arsenic removal from water of Hualtla, Morelos, Mexico using a capacitive deionization. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 665–679

Garrido S, Piña M, López I, De La OD, Rodríguez R (2013) Behavior of two filter media for to remove arsenic from drinking water. The Filtration Society. Int J Filtrat Separ 13:21–26

Gelover S, Leal Ascencio MT, Tonnerieux JB (2006) Implementación de la remoción de arsénico por oxidación solar en México. In: Litter MI (ed) Resultados finales del Proyecto OEA/AE141: investigación, desarrollo, validación y aplicación de tecnologías solares para la potabilización de agua en zonas rurales aisladas de América Latina y el Caribe. Editorial OEA, Buenos Aires, pp 243–277

Giménez MC, Pellizzari EE (2014) Arsenic decrease using *Pseudomonas aeruginosa* on mineral matrix for bioremediation. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 762–763

Giménez MC, Varela NM, Blanes PS (2016) Bioadsorption studies of arsenate from aqueous solutions using chitosan. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad

A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 474–475

Global Water Intelligence (2011) Water for mining. Opportunities in scarcity and environmental regulation. A Global Water Intelligence publication. Water management and technologies. Water supply, treatment and reuse in mines, pp 64–65. https://www.globalwaterintel.com/client_media/uploaded/Water%20for%20Mining/GWI_Water_for_Mining_sample_pages-.pdf. Accessed Oct 2018

Gómez V, Garrido SE (2014) Removal of arsenic from water for human consumption using a bioadsorbent obtained from orange wastes. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 735–737

Gonzalez K (1997) Alternativas de remoción de arsénico desde fuentes de agua potable en la II Región Antofagasta y costos asociados. Dissertation, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile

González MJ (2015) Desarrollo de adsorbentes a partir de especies minerales para eliminación de contaminantes inorgánicos. Tesis doctoral. Facultad de Ciencias Exactas, Universidad Nacional de La Plata

González A, Ingallinella AM, Pacini V, Fernández R, Sanguinetti G, Quevedo H (2014a) Remoción de arsénico (As) y fluoruros (F^-) en aguas subterráneas mediante coagulación, adsorción y doble filtración. Cuad CURIHAM 20:59–72

González A, Ingallinella AM, Sanguinetti GS, Pacini VA, Fernández RG, Quevedo H (2014b) Enhancing arsenic removal by means of coagulation—adsorption—filtration processes from groundwater containing phosphates. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 705–707

González A, Ingallinella AM, Sanguinetti GS, Quevedo H, Pacini VA, Fernández RG (2016) Influence of silica on arsenic removal from groundwater by coagulation, adsorption and filtration. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 486–488

González-Acevedo ZI, Cano-Aguilera I, Aguilera-Alvarado AF (2005) Removal and recovery of arsenic from aqueous solutions bysorghum biomass In Bundschuh J, Bhattacharya P, Chadraseharam D (eds) Natural arsenic in groundwater: occurrence, remediation and management. 32nd international geological congress, Florence, Italy, Taylor and Francis/Balkema, Leiden, pp 255–261.

Graieb OJ, Lujan JC (2014) Arsenic reduction levels in drinking water using granular ferric hydroxide oxide. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 673–674

Granada J, Cerda W, Godoy D (2003) ESSAN: El camino para reducir notoriamente el arsénico en el agua potable. Rev AIDIS-Chile 34:44–49

GTWE German Technology for Water and Energy (n.d.) http://www.gtwe-nu.com/costa-rica-gtwe-installs-filter-for-arsenic-removal-from-drinking-water/. Accessed Nov 2018

Guatemala, Ministerio de Salud Pública y Asistencia Social, Unidad Ejecutora del Programa de Acueductos Rurales (2001) Norma guatemalteca obligatoria, agua potable (especificaciones), CONGUANOR, NGO, 29.001. UNEPAR, Guatemala

Guo HR, Wang NS, Hu H, Monson RR (2004) Cell type specificity of lung cancer associated with arsenic ingestion. Cancer Epidemiol Biomark Prev 13:638–643

Hall MN, Gamble MV (2012) Nutritional manipulation of one-carbon metabolism: effects on arsenic methylation and toxicity. J Toxicol 2012:595307,. 11 pages. https://doi.org/10.1155/2012/595307

Hall EM, Acevedo J, López FG, Cortés S, Ferreccio C, Smith AH, Steinmaus CM (2017) Hypertension among adults exposed to drinking water arsenic in Northern Chile. Environ Res 153:99–105

Hansen H, Ribeiro AB, Mateus EP (2006) Biosorption of arsenic(V) with *Lessonia nigrescens*. Miner Eng 19:486–490

Haque N, Morrison G, Perrusquía G, Cano-Aguilera I, Aguilera-Alvarado AF, Gutiérrez-Valtierra M (2005) Sorption of arsenic on sorghum biomass: a case study. In: Bundschuh J, Bhattacharya P, Chadraseharam D (eds) Natural arsenic in groundwater: occurrence, remediation and management, 32nd international geological congress, Florence, Italy. Taylor and Francis/Balkema, Leiden, pp 246–253

Haque MN, Morrison GM, Perrusquía G, Gutierrez M, Aguilera AF, Cano-Aguilera I, Gardea-Torresdey JL (2007) Characteristics of arsenic adsorption to sorghum biomass. J Hazard Mater 145:30–35

Harari F, Engström K, Concha G, Colque G, Vahter M, Broberg K (2013) N-6-Adenine-Specific DNA Methyltransferase 1 (N6AMT1) polymorphisms and arsenic methylation in Andean women. Environ Health Perspect 121:797–803

Health Brazil (2011) Standards and drinkability standard of water intended for human consumption. Administrative Rule 2914, Brasília

Hering JG, Chen PY, Wilkie JA, Elimelech M (1997) Arsenic removal from drinking water during coagulation. J Environ Eng ASCE 123:800–807

Hering JG, Katsoyiannis IA, Ahumada Theoduloz G, Berg M, Hug SJ (2017) Arsenic removal from drinking water: experiences with technologies and constraints in practice. J Environ Eng 143:1–1

Hernández-Castro B, Doníz-Padilla LM, Salgado-Bustamante M, Rocha D, Ortiz-Pérez MD, Jiménez-Capdeville ME, Portales-Pérez DP, Quintanar-Stephano A, González-Amaro R (2009) Effect of arsenic on regulatory T cells. J Clin Immunol 29:461–469

Höll W, Litter MI (2010) Ocurrencia y química del arsénico en aguas. Sumario de tecnologías de remoción de arsénico de aguas. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 17–31

Hong Y-S, Song K-H, Chung J-Y (2014) Health effects of chronic arsenic exposure. J Prev Med Public Health 47:245–252

Hopenhayn C, Ferreccio C, Browning SR, Huang B, Peralta C, Gibb H, Hertz-Picciotto I (2003) Arsenic exposure from drinking water and birth weight. Epidemiology 14:593–602

Hopenhayn-Rich C, Biggs ML, Smith AH (1998) Lung and kidney cancer mortality associated with arsenic in drinking water in Córdoba, Argentina. Int J Epidemiol 27:561–569

Hott RC, Andrade TG, Santos MS, Lima ACF, Faria MCS, Bomfeti CA, Barbosa F, Maia LFO, Oliveira LCA, Pereira MC, Rodrigues JL (2016) Adsorption of arsenic from water and its recovery as a highly active photocatalyst. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-016-7441-3

Hryczyñski E, López WG, Alegre J, Giménez MC (2014) Arsenic removal with compressed laterite. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 717–718

Hug SJ, Leupin O (2003) Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. Environ Sci Technol 37:2734–2742

Hug S, Canonica L, Wegelin M, Gechter D, Von Gunten U (2001) Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. Environ Sci Technol 35:2114–2121

Hurng L, Meichtry JM, Piperata G, Apella MC, Hidalgo MV, Powell P, Litter MI (2004) Resultados de la aplicación de la tecnología FH para potabilizar aguas de la República Argentina (Results of the application of the HP technology for water purification in Argentina). In: Litter MI, Jiménez-González A (eds) Advances in Economic Solar Technologies for Disinfection, Decontamination, and Removal of Arsenic from Water of Rural Communities of Latin America. Digital Graphic Publisher, La Plata, pp 15–41

IADB (2003) Antofagasta desalination plant, Project Abstract, CH-0171. Interamerican Development Bank, Washington, DC. http://idbdocs.iadb.org/wsdocs/getdocument.aspx?docnum=410882. Accessed Aug 2018

Iliná A, Martínez-Hernández JL, Segura-Ceniceros P, Villarreal-Sánchez JA, Gregorio-Jáuregui KM (2009) Biosorción de arsénico en materiales derivados de maracuyá. Rev Int Contam Ambient 25:201–216

INAA (2001) Normas Técnicas para el diseño de abastecimiento y potabilización de agua. Normas NTON 09003-99

INEN (Instituto Ecuatoriano de Normalización) (2006) Norma 1108: Sobre requisitos del agua potable. Registro Oficial N° 231, Quito, Ecuador

Ingallinella AM (2006) Remoción de Arsénico y Flúor en Aguas Subterráneas Mediante Doble Filtración, Doctoral Thesis, Universidad Nacional de Rosario, Santa Fe

Ingallinella AM, Fernández RG (2010) Experiencia argentina en la remoción de arsénico por diversas tecnologías. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 155–167

Ingallinella AM, Fernández RG, Stecca LM (2003a) Proceso ARCIS-UNR para la remoción de As y flúor en aguas subterráneas: una experiencia de aplicación. Part 1. Rev Ing Sanit Ambient 66:36–39

Ingallinella AM, Fernández RG, Stecca LM (2003b) Proceso ARCIS-UNR para la remoción de As y flúor en aguas subterráneas: una experiencia de aplicación. Part 2. Rev Ing Sanit Ambient 67:61–65

Instituto Boliviano de Normalización y Calidad A Norma Boliviana NB 512-2010 (n.d.) Agua potable – Requisitos

Instituto Nacional of Tecnología Industrial (INTI) (2009) Modelo de intervención para el abatimiento de arsénico en aguas de consumo. Informe INTI Química, Centro de investigación y desarrollo en química. https://www.inti.gob.ar/quimica/pdf/asenagua.pdf. Accessed Nov 2017

Inteccon.inc (2018) Arsenator®: Digital Arsenic Test Kit Product code: WAG-WE10500http://www.intecconinc.com/index.php?option=com_content&view=article&id=266&Itemid=121. Accessed Nov 2018

International Agency for Research on Cancer (IARC) (2012) Arsenic, metals, fibres, and dusts. volume 100 C. A review of human carcinogens, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Arsenic, metals, fibres, and dusts. International Agency for Research on Cancer, World Health Organization, Lyon. http://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Evaluation-Of-Carcinogenic-Risks-To-Humans/Arsenic-Metals-Fibres-And-Dusts-2012. Accessed Apr 2018

International Mining (2018) BHP opens Escondida Water Supply, the largest desalination plant in Latin America. https://im-mining.com/2018/04/07/bhp-opens-escondida-water-supply-largest-desalination-plant-latin-america/. Accessed Sept 2018

Iriel A, Fernández Cirelli A, Marco-Brown JL, Trinelli MA, Pérez AL, dos Santos Afonso M (2014) Arsenic removal in polluted water using pillared clays. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One Century of the Discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 670–672

Jain RB (2015) Association of arsenic exposure with smoking, alcohol, and caffeine consumption: data from NHANES 2005–2010. Environ Toxicol Pharmacol 39:651–658

Jorge C, Nieto J, Ponce S, Rodríguez J, Solís J, Estrada W (2003) Remoción de arsénico del agua mediante irradiación solar en Lima, Perú (Arsenic removal of water using solar radiation in Lima, Peru). In: Litter MI, Mansilla H (eds) Arsenic removal assisted by Solar Light in Rural Communities of Latin America, OAS Project AE/141. Digital Grafic, La Plata, pp 55–64

Jorge C, Venero J, Díaz J, Carpio E, Zúñiga P, Maurtua D, Cristóbal R, Galarza P, Quintana M, Ponce S, Solís J, Rodríguez J, Estrada W (2006) La experiencia peruana en la desinfección y descontaminación de agua utilizando energía solar. In: Litter MI (ed) Resultados finales del Proyecto OEA/AE141: investigación, desarrollo, validación y aplicación de tecnologías solares para la potabilización de agua en zonas rurales aisladas de América Latina y el Caribe. Editorial OEA, Buenos Aires, pp 279–334

Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. Environ Sci Technol 39:1291–1298

Karcher S, Cáceres I, Jekel M, Contreras R (1999) Arsenic removal from water supplies in northern Chile using ferric chloride coagulation. Water Environ Manag 13:164–168

Khairul I, Wang QQ, Jiang YH, Wang C, Naranmandura H (2017) Metabolism, toxicity and anticancer activities of arsenic compounds. Oncotarget 8(14):23905–23926

Kirchmer C, Castro de Esparza ML (1978) Remoción de Arsénico en aguas con alto contenido de Magnesio. CEPIS, Lima

Kordas K, Queirolo EI, Mañay N, Peregalli F, Hsiao PY, Lu Y, Vahter M (2016) Low-level arsenic exposure: nutritional and dietary predictors in first-grade Uruguayan children. Environ Res 147:16–23

Kordas K, Roy A, López P, García-Vargas G, Cebrián ME, Vera-Aguilar E, Rosado JL (2017) Iron and zinc supplementation does not impact urinary arsenic excretion in Mexican School Children. J Pediatr 185:205–210

Kunz S, Romero L G, Otter P, Feller J (2017) Treatment of arsenic-contaminated water using in-line electrolysis, co-precipitation and filtration in Costa Rica. Water Sci Technol Water Supply 18(1):ws2017089 https://doi.org/10.2166/ws.2017.089.

Labastida I, Armienta MA, Lara-Castro RH, Aguayo A, Cruz O, Ceniceros N (2013) Treatment of mining acidic leachates with indigenous limestone, Zimapan Mexico. J Hazard Mater 262:1187–1195

Ladeira ACQ, Ciminelli VST (2004) Adsorption and desorption of arsenic on an oxisol and its constituents. Water Res 38:2087–2094

Ladeira ACQ, Ciminelli VST, Nepomuceno AL (2002) Seleçao de solos para a immobilizaçao de arsênio. REM 55:215–221

Langsch JE, Costa M, Moore L, Morais P, Bellezza A, Falcão S (2012) New technology for arsenic removal from mining effluents. J Mater Res Technol 1:178–181

Lara F, Cornejo L, Yanez J, Freer J, Mansilla HD (2006) Solar-light assisted removal of arsenic from natural waters: effect of iron and citrate concentrations. J Chem Technol Biotechnol 81:1282–1287

Larralde AL, Tufo AE, Sileo EE (2014) Sorption and chemical stability of As(V) onto tin doped goethites. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 714–716

Latorre C (1966) Estudio fisico-químico para la remoción del arsénico en el rio Toconce. Santiago: Rev Ing Sanit:12–21

Lescano M, Zalazar C, Cassano A, Brandi R (2011) Arsenic(III) oxidation of water applying a combination of hydrogen peroxide and UVC radiation. Photochem Photobiol Sci 19:1797–1803

Lescano M, Zalazar C, Cassano A, Brandi R (2012) Kinetic modelling of arsenic (III) oxidation in water employing the UV/H_2O_2 process. Chem Eng J 211– 212:360–368

Lescano MR, Zalazar CS, Brandi RJ (2014) A combined system for arsenic removal from water by photochemical oxidation and adsorption technology. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 664–666

Leupin OX, Hug SJ (2005) Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. Water Res 39:1729–1740

Levy IK, Mizrahi M, Ruano G, Requejo F, Zampieri G, Litter MI (2012) TiO_2-photocatalytic reduction of pentavalent and trivalent arsenic: production of elemental arsenic and arsine. Environ Sci Technol 46:2299–2308

Levy IK, Brusa MA, Aguirre ME, Custo G, San Román E, Litter MI, Grela MA (2013) Exploiting electron storage in TiO_2 nanoparticles for dark reduction of As(V) by accumulated electrons. Phys Chem Chem Phys 15:10335–10338

Levy IK, Ramos C, Custo G, Litter MI, Mizrahi M, Requejo F (2014a) Removal of arsenic with zerovalent iron nanoparticles in the dark and under UV-vis light. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 805–807

Levy IK, Quici N, Custo G, Litter MI (2014b) Dark reduction of As(V) by accumulated electrons stored in alcoholic TiO_2 nanoparticles. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914-2014). CRC Press, London, pp 802–804

Liaw J, Marshall G, Yuan Y, Ferreccio C, Steinmaus C, Smith AH (2008) Increased childhood liver cancer mortality and arsenic in drinking water in northern Chile. Cancer Epidemiol Biomark Prev 17:1982–1987

Lindbäck K, Sjölin A M (2006) Arsenic in Groundwater in the Southwestern Part of the Río Dulce Alluvial Cone, Santiago del Estero Province, Argentina. Master thesis. Department of Land and Water Resource Engineering, KTH, Stockholm, Sweden, TRITA-LWREX- 06-26

Litter MI (2009) Treatment of chromium, mercury, lead, uranium and arsenic in water by heterogeneous photocatalysis. Adv Chem Eng 36:37–67

Litter MI (2010) La problemática del arsénico en la Argentina: el HACRE. Rev Soc Argent Endocrinol Ginecol Reprod (SAEGRE) 17:5–10

Litter MI (2017) Last advances on TiO_2-photocatalytic removal of chromium, uranium and arsenic. Curr Opin Green Sustain Chem 6:150–158

Litter MI, Bundschuh J (2012) Emerging options for solving the arsenic problems of rural and periurban areas in Latin America. In: Ng JC, Noller BN, Naidu R, Bundschuh J, Bhattacharya P (eds) Understanding the geological and medical interface of arsenic. Taylor and Francis Group, London, pp 267–270

Litter MI, Pereyra S (2016) Evaluation of safe drinking water access for dispersed rural populations in the Santiago del Estero province, Argentina – a challenge for arsenic removal. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability. CRC Press/Balkema, Taylor and Francis Group, London, pp 642–643

Litter MI, Quici N (2014) New advances of heterogeneous photocatalysis for treatment of toxic metals and arsenic. In: Kharisov BI, Kharissova OV, Rasika Dias HV (eds) Nanomaterials for environmental protection. Wiley, Hoboken, pp 145–167

Litter M, Fernández R, Cáceres R, Grande Cobián D, Cicerone D, Fernández Cirelli A (2008) Tecnologías de bajo costo para el tratamiento de arsénico a pequeña y mediana escala. Rev Ing Sanit Ambient 100:41–50

Litter MI, Morgada ME, Bundschuh J (2010a) Possible treatments for arsenic removal in Latin American waters for human consumption. Environ Pollut 158:1105–1118

Litter MI, Morgada ME, Lin H, García MG, Hidalgo MV, d'Hiriart J, Giullitti J, Blesa MA, Levy IK, López G, Mateu M (2010b) Experiencias de remoción de arsénico por tecnologías fotoquímicas y solares en Argentina. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 191–207

Litter MI, Armienta MA, Villanueva Estrada RE, Villaamil Lepori EC, Olmos V (2019) Arsenic in Latin America – Part I. In: Srivastava S (ed) Arsenic in drinking water and food. Springer. In press

Litter MI, Alarcón-Herrera MT, Arenas MJ, Armienta MA, Avilés M, Cáceres RE, Cipriani HN, Cornejo L, Dias LE, Fernández Cirelli A, Farfán EM, Garrido S, Lorenzo L, Morgada ME, Olmos-Márquez MA, Pérez-Carrera A (2012) Small-scale and household methods to remove arsenic from water for drinking purposes in Latin America. Sci Total Environ 429:107–122

Litter MI, Levy IK, Requejo F, Mizrahi M, Ruano G, Zampieri G (2014) Titanium dioxide-photocatalytic reduction of pentavalent and trivalent arsenic: production of elemental arsenic and arsine. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 820–824

Litter MI, Pereyra S, López Pasquali CE, Iriel A, Senn AM, García FE, Blanco Esmoris MF, Rondano K, Pabón DC, Dicelio LE, Lagorio MG, Noel GD (2015) Remoción de arsénico en localidades de la provincia de Santiago del Estero, Argentina. Evaluación del acceso, uso y calidad de agua en poblaciones rurales con problemas de arsénico. Rev Ing Sanit Amb 125:13–25

Litter MI, Quici N, Meichtry JM, Senn AM (2016) Photocatalytic removal of metallic and other inorganic pollutants. In: Dionysiou DD, Li Puma G, Ye J, Schneider J, Bahnemann (eds) Photocatalysis: applications. Royal Society, London, pp 35–71

Litter MI, Quici N, Meichtry JM, Montesinos VN (2018) Photocatalytic treatment of inorganic materials with TiO2 nanoparticles. In: Nalwa HS (ed) Encyclopedia of nanoscience and nanotechnology, vol 29. American Scientific Publishers, Valencia, pp 303–336

Lizama Allende K, Fletcher TD, Sun G (2010) Removal processes for arsenic in constructed wetlands. Chemosphere 84:1032–1043

Lizama Allende K, Fletcher TD, Sun G (2012a) The effect of substrate media on the removal of arsenic, boron and iron from an acidic wastewater in planted column reactors. Chem Eng J 179:119–130

Lizama Allende K, Fletcher TD, Sun G (2012b) Arsenic removal by subsurface flow constructed wetlands. In: Ng JC, Noller BN, Naidu R, Bundschuh J, Bhattacharya P (eds) Understanding the Geological and Medical Interface of Arsenic. Taylor and Francis Group, London, pp 278–279

Lizama Allende K, McCarthy DT, Fletcher TD (2014) The removal of arsenic by horizontal subsurface flow constructed wetlands. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 764–765

López-Carrillo L, Gamboa-Loira B, Becerra W, Hernández-Alcaraz C, Hernández-Ramírez RU, Gandolfi AJ, Franco-Marina F, Cebrián ME (2016) Dietary micronutrient intake and its relationship with arsenic metabolism in Mexican women. Environ Res 151:445–450

Lorenzo L, Farfán Torres E M, Naranjo P M, Torres Sánchez R (2008) Adsorción de As en 4-NaMica sintética y su producto de tratamiento mecánico. In: Blesa MA, Dos Santos Afonso M, Torres Sánchez RM (eds) Las Fronteras de la Física y Química Ambiental en Ibero América. Buenos Aires, pp 314–9

Luján J (2001a) Hidróxido de aluminio coloidal para eliminar el arsénico del agua. Rev. Panam Salud Pública 9:302–305

Luján JC (2001b) Desarsenicación del agua utilizando hidrogel activado de hidróxido de aluminio. Cienc, Tecnol Medio Ambiente Univ Tecnol Nac, Tucumán I:9–13

Luján JC, Graieb OJ (1994) Eliminación del arsénico en agua por destilación a escala doméstica en zonas rurales. Rev Méd Tucumán 1:247–255

Luján JC, Graieb OJ (1995) Eliminación del arsénico en agua por destilación a escala doméstica en zonas rurales. Rev Cien Tecnol Univ Tecnol Nac, Tucumán 3:13

Mansilla, H.D., Cornejo, L., Lara, F., Yáñez, J., Lizama, C., Figueroa, L. 2003. Remoción de arsénico de aguas del Río Camarones, Arica, Chile (Arsenic removal from waters from the Camarones River, Arica, Chile). Litter, M.I., Mansilla, H. Arsenic Removal Assisted by Solar Light in Rural Communities of Latin America, OAS Project AE/141. Digital Grafic, La Plata, 35–53.

Marshall G, Ferreccio C, Yuan Y, Bates MN, Steinmaus C, Selvin S, Liaw J, Smith AH (2007) Fifty-year study of lung and bladder cancer mortality in Chile related to arsenic in drinking water. J Natl Cancer Inst 99:920–928

Martin E, González-Horta C, Rager J, Bailey KA, Sánchez-Ramírez B, Ballinas-Casarrubias L, Ishida MC, Gutiérrez-Torres DS, Hernández Cerón R, Viniegra Morales D, BaezaTerrazas FA, Saunders RJ, Drobná Z, Mendez MA, Buse JB, Loomis D, Jia W, García-Vargas GG, Del Razo LM, Stýblo M, Fry R (2015) Metabolomic characteristics of arsenic-associated diabetes in a prospective cohort in Chihuahua, Mexico. Toxicol Sci 144:338–346

Martinez VD, Buys TP, Adonis M, Benítez H, Gallegos I, Lam S, Lam WL, Gil L (2010) Arsenic-related DNA copy-number alterations in lung squamous cell carcinomas. Br J Cancer 103:1277–1283

Martinez VD, Vucic EA, Becker-Santos DD, Gil L, Lam WL (2011) Arsenic exposure and the induction of human cancers. J Toxicol:431287,. 13 pages. https://doi.org/10.1155/2011/431287

Mateu M (2007) Remoción de arsénico por fotocatálisis heterogénea, Master thesis, Universidad de Buenos Aires

May-Ix LA, Gomez R, López R (2014) Photocatalytic oxidation of As(III) using TiO_2-Cr_2O_3 semiconductors. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 811–813

Mazumder DN (2005) Effect of chronic intake of arsenic-contaminated water on liver. Toxicol Appl Pharmacol 206:169–175

McClintock TR, Chen Y, Bundschuh J, Oliver JT, Navoni J, Olmos V, Villaamil Lepori E, Ahsan H, Parvez F (2012) Arsenic exposure in latinamerica: biomarkers, risk assessments and related health effects. Sci Total Environ 429:76–91

McNeill LS, Edwards M (1995) Soluble arsenic removal in full-scale water treatment plants. J AWWA 87:105–113

Meichtry JM, Lin HJ, Fuente L, Levy IK, Gautier EA, Blesa MA, Litter M (2007) Low-cost TiO_2 photocatalytic technology for water potabilization in plastic bottles for isolated regions. J Sol Energ-T ASME 129:119–126

Meichtry JM, De Seta EG, López AR, Reina FD, Mugrabi FI, Lan LE, Lavezzari E, Domingo EJ, Tojo N (2014) Arsenic removal using low-cost materials. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 684–686

Meichtry J, Castiglia M, Mugrabi F, Lan L, Reina F, De Seta E, López A, Domingo E (2015) Remoción de arsénico en agua mediante materiales de bajo costo y segura disposición final. Proyecciones 13:47–58

Meichtry JM, Levy IK, Mohamed HH, Dillert R, Bahnemann DW, Litter MI (2016) Mechanistic features of TiO_2-heterogeneous photocatalysis of arsenic and uranyl nitrate in aqueous suspensions studied by the stopped flow technique. Chem Phys Chem 17:885–892

Melak D, Ferreccio C, Kalman D, Parra R, Acevedo J, Pérez L, Cortés S, Smith AH, Yuan Y, Liaw J, Steinmaus C (2014) Arsenic methylation and lung and bladder cancer in a case-control study in northern Chile. Toxicol Appl Pharmacol 274:225–231

Mellano MF, Ramirez AE (2004) Groundwater Arsenic in the Area around Maria Elena in Santiago del Estero Province, Northwestern Argentina, TRITA-LWREX-04-40. Department of Land and Water Resources Engineering KTH, Stockholm

Mendez MA, González-Horta C, Sánchez-Ramírez B, Ballinas-Casarrubias L, Cerón RH, Morales DV, Terrazas FA, Ishida MC, Gutiérrez-Torres DS, Saunders RJ, Drobná Z, Fry RC, Buse JB, Loomis D, García-Vargas GG, Del Razo LM, Stýblo M (2016) Chronic exposure to arsenic and markers of cardiometabolic risk: a cross-sectional study in Chihuahua, Mexico. Environ Health Perspect 124:104–111

Mendoza-Barrón J, Jacobo-Azuara A, Leyva-Ramos R, Berber-Mendoza MS, Guerrero-Coronado RM, Fuentes-Rubio L, Martínez-Rosales JM (2011) Adsorption of arsenic (V) from a water solution onto a surfactant-modified zeolite. Adsorption 17:489–496

Meng XG, Bang S, Korfiatis GP (2000) Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. Water Res 34:1255–1261

Mercado de Scaglione S, Llapur M (2006) Hidroarsenicismo crónico. Comentario de los casos diagnosticados en el Hospital Independencia de Santiago del Estero en el período 1998–2005. Arch Argent Dermatol 56:177–183

Mercado-Borrayo B M, Schouwenaars R, Litter M I, Ramírez-Zamora R M (2014) Metallurgical slag as an efficient and economical adsorbent of arsenic. In: Ahuja S (ed) Water reclamation and sustainability, Elsevier, San Diego, pp 95–114

Ministerio de la Protección Social y Ministerio de Ambiente, Vivienda y Desarrollo Territorial. Resolución 2115 (2007) República de Colombia, Bogotá

Ministerio de Salud (2011) Reglamento de la calidad del agua para consumo humano. Lima: Dirección General de Salud Ambiental. http://www.digesa.minsa.gob.pe/publicaciones/descargas/Reglamento_Calidad_Agua.pdf. Accessed Nov 2018

Ministerio de Salud (MINSA) (2012) Guia de practica clinica para el diagnostico y tratamiento de la intoxicacion por arsenico 2012 Peru. http://bvs.minsa.gob.pe/local/MINSA/2109.pdf. Accessed Nov 2018

Ministerio de Salud (MINSAL) (2014) Guia Clinica: Vigilancia Biologica de la Poblacion Expuesta a Arsenico, beneficiarios de la ley 20.590. Santiago: MINSAL. https://www.minsal.cl/sites/default/files/files/Guia_Clinica_Vigilancia_Arsenico_final.pdf. Accessed Nov 2018.

Ministerio de Salud (MSAL) (2011) Hidroarsenicismo crónico regional endémico (HACRE). Módulo de capacitación para atención primaria. Programa Nacional para la Prevención y Control de las Intoxicaciones (PRECOTOX). Ministerio de Salud. http://www.msal.gob.ar/images/stories/bes/graficos/0000000332cnt-03-Capacit_hidroarsenicismo.pdf. Accessed Nov 2018

Ministerio de Salud, Costa Rica (2005) Reglamento para la Calidad del Agua Potable. Pub. L. No. 32327-S

Modificacion a la Norma Oficial Mexicana NOM-127-SSA1-1994 (2000) Salud Ambiental. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a los que debe someterse el agua para su potabilización. Diario Oficial de la Federación, 22 noviembre de 2000, Mexico City

Molina R, Schulz C, Bernardos J, Dalmaso M (2014) Association between arsenic in groundwater and malignant tumors in La Pampa, Argentina. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 644–645

Monroy Torres R, Espinoza Pérez JA, Pérez González RM (2016) Evaluación de las prácticas de alimentación y nutrición en una población expuesta a arsénico: una propuesta para integrar indicadores de exposición nutricional. Nutr Clín Diet Hosp, ISSN 0211-6057 36:140–149

Moreira M, Costa PF, Teixeira Sun MC (2012) Arsenite (bio) immobilization using Sulfur Reducing Bacteria (SRB). In: Ng JC, Noller BN, Naidu R, Bundschuh J, Bhattacharya P (eds) Understanding the Geological and Medical Interface of Arsenic. Taylor and Francis Group, London, pp 303–304

Morgada de Boggio ME, Levy IK, Mateu M, Litter MI (2006) Tecnologías económicas basadas en la fotocatálisis heterogénea y el hierro cerovalente para la remoción de arsénico en la Llanura Chacopampeana, Argentina (Low-cost technologies based on heterogeneous photocatalysis and zerovalent iron for arsenic removal in the Chaco-Pampean Plain, Argentina). In: Litter MI (ed) Resultados finales del Proyecto OEA/AE141: investigación, desarrollo, validación y aplicación de tecnologías solares para la potabilización de agua en zonas rurales aisladas de América Latina y el Caribe. Editorial OEA, Buenos Aires, pp 11–37

Morgada de Boggio ME, Levy IK, Mateu M, Bhattacharya P, Bundschuh J, Litter MI (2009) Low-cost technologies based on heterogeneous photocatalysis and zerovalent iron for arsenic removal in the Chacopampean plain, Argentina. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 677–686

Morgada de Boggio ME, Levy IK, Mateu M, Meichtry JM, Farías S, López GD, Bahnemann D, Dillert R, Litter MI (2010) Low-cost solar technologies for arsenic removal in drinking water. In: Kabay N, Bundschuh J, Hendry B, Bryjak M, Yoshizuka K, Bhattacharya P, Anaç S (eds) The global Arsenic problem: challenges for safe water production. CRC Press/Balkema, Taylor & Francis Group, Londres, pp 209–218

Morgada ME, Litter MI (2010) Tecnologías fotoquímicas y solares para la remoción de arsénico de soluciones acuosas. Estado del arte. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 73–89

Morgada ME, Mateu M, Bundschuh J, Litter MI (2008) Arsenic in the Iberoamerican Region. The Iberoarsen Network and a possible economic solution for arsenic removal in isolated rural zones. e-Terra, vol 5 – n° 5. http://e-terra@geopor.pt. ISSN 1645-0388

Morgada ME, Levy IK, Salomone V, Farías SS, López G, Litter MI (2009) Arsenic(V) removal with nanoparticulate zerovalent iron: effect of UV light and humic acids. Catal Today 143:261–268

Morgada ME, Levy IK, Salomone V, Farías SS, López G, Litter MI (2010) Arsenic (V) removal with zerovalent iron nanoparticles: Effect of UV light and humic acid. In: Shuh Jean J-J, Bundschuh J, Bhattacharya P (eds) Arsenic in geosphere and human diseases. Taylor and Francis Group, London, pp 535–537

Mozziconacci D, Madiec H, Cepero E (1998) Abatimiento de arsénico por coagulación sobre filtro. Rev Ing Sanit Ambient 40:25

Muñiz G, Manjarrez-Nevárez LA, Pardo-Rueda J, Rueda-Ramírez A, Torres-Muñoz V, Ballinas-Casarrubias ML (2009) Filter development from low cost materials for arsenic removal from water. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 657–663

Muñoz-Rivadeneira GA, de la Torre E, Guevara A, Criollo E, Díaz V (2004) Removing arsenic: Ecuador. http://tcdc2.undp.org/GSSDAcademy/SIE/Docs/Vol11/SIE.v11_CH19.pdf. Accessed Nov 2018

Nardone A, Ferreccio C, Acevedo J, Enanoria W, Blair A, Smith AH, Balmes J, Steinmaus C (2017) The impact of BMI on non-malignant respiratory symptoms and lung function in arsenic exposed adults of Northern Chile. Environ Res 158:710–719

National Research Council (2001) Arsenic in the drinking water: 2001 update. National Academy Press, Washington, DC. https://www.nap.edu/download/10194. Accessed Nov 2018

NCh 409/1 Instituto nacional de Normalización, INN-Chile (2005) Drinking water- part 1- requirements.

O'Ryan R, Sancha A (2000) Controlling hazardous pollutants in a developing contex: the case of arsenic in Chile. In: Lehr JH (ed) McGraw-Hill Standard handbook of environmental science, health and technology. Global perspectives and trends. McGraw-Hill, New York, pp 22.13–22.28

Ochoa Reyes J, Vidal Lozano A, Lerma Santana A, Gómez Reza L, Reta Sánchez A, Fernández Escajeda D, Vidal Flores A, Trevizo Ortiz L, González Piñeyro DM, Ornelas Reynoso M, Fernández Luna F, Hernández García A, del Rosal Díaz C, Chavira Renova J, Orozco Domínguez LR (2009) Arsenicismo subagudo y crónico en una población rural. Dermatol Rev Mex 53:63–69

Olivas-Calderón E, Recio-Vega R, Gandolfi AJ, Lantz RC, González-Cortes T, Gonzalez-De Alba C, Froines JR, Espinosa-Fematt JA (2015) Lung inflammation biomarkers and lung function in children chronically exposed to arsenic. Toxicol Appl Pharmacol 287:161–167

Olmos V, Navoni JA, Villaamil Lepori EC (2014) High levels of exposure to arsenic and its influence on arsenic urinary methylated metabolites. A study from Argentina. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 501–503

Olmos V, Navoni JA, Calcagno ML, Sassone AH, Villaamil Lepori EC (2015) Influence of the level of arsenic exposure on its metabolic profile, in a population from an endemic area of Argentina. Association with the presence of the T860C polymorphism in arsenic 3-Methyl Transferase Gene. Hum Exp Toxicol 34:170–178

Olmos-Márquez M A, Benavides-Montoya A, Rosette M, Alarcón-Herrera M T (2009) The arsenic removal efficiency of Eleocharis Macrostachya in constructed wetlands with subsurface flow. In Proceedings of the 3rd wetland pollutant dynamics and control WETPOL, Barcelona

Ongley LK, Armienta MA, Heggeman K, Lathrop A, Mango H, Miller W, Pickelner S (2001) Arsenic removal from contaminated water by the Soyatal Formation, Zimapán mining district, Mexico da potential low-cost low-tech remediation system. Geochem: Explor, Environ, Anal 1:23–31

Ormachea M, Huallpara L, Quintanilla J, Ormachea O, Escalera R, Bhattacharya P (2012) Natural arsenic occurrence and its removal from drinking water using a tubular photo-reactor enhanced with a solar concentrator in Cochabamba, Bolivia. In: Ng JC, Noller BN, Naidu R, Bundschuh J, Bhattacharya P (eds) Understanding the geological and medical interface of arsenic. Taylor and Francis Group, London, pp 305–306

OSE (Obras Sanitarias del Estado), Provincia de San Juan, Argentina (2006) Personal Communication

Osorio-Yáñez C, Ayllon-Vergara JC, Aguilar-Madrid G, Arreola-Mendoza L, Hernández-Castellanos E, Barrera-Hernández A, De Vizcaya-Ruiz A, Del Razo LM (2013) Carotid intima-media thickness and plasma asymmetric dimethylarginine in Mexican children exposed to inorganic arsenic. Environ Health Perspect 121:1090–1096

Pantuzzo FL, Ciminelli VST (2010) Arsenic association and stability in long-term disposed arsenic residues. Water Res 44:5631–5640

Pantuzzo F L, Ciminelli V S T, Braga I (2007) Arsenic Speciation in arsenic slimes. In: Meeting of the Southern hemisphere on mineral technology, 7, Ouro Preto, Proceedings, Ouro Preto, 1, pp 107–114

Paredes J, Garrido SE (2014) Development of a bio-adsorbent medium to remove arsenic from water. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 730–732

Parvez F, Chen Y, Yunus M, Olopade C, Segers S, Slavkovich AM, Hasan R, Ahmed A, Islam T, Akter MM, Graziano JH, Ahsan H (2013) Arsenic exposure and impaired lung function. Findings from a Large Population-based Prospective Cohort Study. Am J Resp Crit Care Med 188:813–819

Pellizzari EE, Marinich LG, Flores SA, Giménez MC (2015) Degradación de arsénico por *Pseudomonas aeruginosa* para bioremediación de agua. Estudio preliminar (Arsenic degradation by *Pseudomonas aeruginosa* for water bioremediation. Preliminary study). Av Cien Ing 6:1–5

Pereira PAL, Dutra AJB, Martins AH (2007) Adsorptive removal of arsenic from river waters using pisolite. Minerals Eng 20:52–59

Pereyra S, Litter MI, López Pasquali CE (2014) Access, use and quality of water: water economy and policy in rural populations with arsenic problems in Santiago del Estero, Argentina. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of arsenicosis in Latin America (1914–2014). CRC Press, London, pp 900–901

Pérez Carrera A, Cayla C, Fabre J, Fernández Cirelli A (2010) Uso de plantas acuáticas para la remoción de arsénico del agua. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 219–228

Pérez Coll CS, Pabón-Reyes C, Meichtry JM, Litter MI (2018) Monitoring of toxicity of As(V) solutions by AMPHITOX test without and with treatment with zerovalent iron nanoparticles. Environ Toxicol Pharmacol 60:138–145

Pérez-Carrera A, FernándezCirelli A (2010) Arsenic and water quality challenges in South America. In: Schneier-Madanes G, Courel MF (eds) Water and sustainability in arid regions. Springer, Dordrecht, pp 275–293

Petkova Simeonova V (1999) Pilot studies for arsenic removal, State of Hidalgo. Rev Ing Hidráulica Méx 14:65–77

Petrick JS, Jagadish B, Mash EA, Aposhian HV (2001) Monomethylarsonous acid (MMA(III)) and arsenite: LD(50) in hamsters and in vitro inhibition of pyruvate dehydrogenase. Chem Res Toxicol 14:651–656

Petry M, Sanz MA, Langlais C, Bonnelye V, Durand J-P, Guevara D, Mantovani Nardes W, Homma Saemi C (2007) The El Coloso (Chile) reverse osmosis plant. Desalination 203:141–152

Piñón-Miramontes M, Bautista-Margulis RG, Perez-Hernandez A (2003) Removal of arsenic and fluoride from drinking water with cake alum and a polymeric anionic flocculent. Fluoride 35:122–128

Pires VGR, Lima DRS, Aquino SF, Libânio M (2015) Evaluating arsenic and manganese removal from water by chlorine oxidation followed by clarification. Braz J Chem Eng 32:409–419

Pirnie M (2000) Technologies and costs for removal of arsenic from drinking water, US EPA Report 815-R-00-028

Quici N, Meichtry M, Montesinos VN (2018) Use of nanoparticulated iron materials for chromium, arsenic, and Uranium removal from water. In: Litter MI, Quici N, Meichtry M (eds) Iron nanomaterials for water and soil treatment. Pan Stanford Publishing Pte. Ltd, Singapore, pp 177–200

Rager JE, Bailey KA, Smeester L, Miller SK, Parker JS, Laine JE, Drobná Z, Currier J, Douillet C, Olshan AF, Rubio-Andrade M, Stýblo M, García-Vargas G, Fry RC (2014) Prenatal arsenic exposure and the epigenome: altered microRNAs associated with innate and adaptive immune signaling in newborn cord blood. Environ Mol Mutagen 55:196–208

Rager JE, Miller S, Tulenko SE, Smeester L, Ray PD, Yosim A, Currier JM, Ishida MC, González-Horta MC, Sánchez-Ramírez B, Ballinas-Casarrubias L, Gutiérrez-Torres DS, Drobná Z, Del Razo LM, García-Vargas GG, Kim WY, Zhou Y-H, Wright FA, Stýblo M, Fry RC (2015) Identification of novel gene targets and putative regulators of arsenic-associated DNA methylation in human urothelial cells and bladder cancer. Chem Res Toxicol 28:1144–1155

Rahman MM, Ng JC, Naidu R (2009) Chronic exposure of arsenic via drinking water and its adverse health impacts on humans. Environ Geochem Health 31(Suppl 1):189–200

Ramírez Alvarado JA, Garrido SE, Baeza Reyes A (2014) Recovery of elemental arsenic using electrodeposition with rejection water from capacitive deionization and reverse osmosis. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 772–774

Ravenscroft P, Brammer H, Richards K (2009) Arsenic pollution: a global synthesis. Wiley-Blackwell, Hoboken, p 588

Recio-Vega R, Gonzalez-Cortes TD, Olivas-Calderon E, Lantz RC, Gandolfi AJ, Gonzalez-De Alba C (2015) In utero and early childhood exposure to arsenic decreases lung function in children. J Appl Toxicol 35:358–366

Recio-Vega R, González-Cortes T, Olivas-Calderón E, Clark Lantz R, Jay Gandolfi A, Michel-Ramirez G (2016) Association between polymorphisms in arsenic metabolism genes and urinary arsenic methylation profiles in girls and boys chronically exposed to arsenic. Environ Mol Mutagen 57:516–525

Reporte de Sustentabilidad de EcoMetales (2012) https://www.ecometales.cl/wp-content/uploads/2016/09/EcoMetales_Espanol2012.pdf. Accessed Oct 2018

Rivera ML, Piña M (2004) A pilot study for arsenic removal from water by adsorption in natural zeolite adsorption in presence of iron and manganese. In: Sancha A M (ed) Third international seminar on evaluation, and management of drinking water resources contamin ated by arsenic. http://www.cepis.ops-oms.org/bvsacd/arsenico/Arsenic2004/theme3/paper3.14.pdf. Accessed Dec 2009

Rivera-Hernández JR, Green-Ruiz CR (2014) Effect of pH on As^{3+} sorption from aqueous solution by red clays. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 702–704

Rivera-Huerta M L, Cortés-Muñoz J E, Piña-Soberanis M, Martín Domínguez A (2000) Remoción de hierro y arsénico de agua de consumo humano mediante precipitación y adsorción en Zimapán, Hidalgo, México. In: Anales del XXVII Congreso Interamericano de Ingeniería Sanitaria y Ambiental: Las Américas y la Acción por el Medio Ambiente en el Mundo, Río de Janeiro, ABES, p 1–8

Robles-Osorio ML, Pérez-Maldonado IV, del Campo DM, Montero-Perea D, Avilés-Romo I, Sabath-Silva E, Sabath E (2012) Urinary arsenic levels and risk of renal injury in a cross-sectional study in open population. Rev Invest Clin 64:609–614

Robles-Osorio ML, Sabath-Silva E, Sabath E (2015) Arsenic-mediated nephrotoxicity. Ren Fail 37:542–547

Rocha-Amador D, Navarro ME, Carrizales L, Morales R, Calderón J (2007) Decreased intelligence in children and exposure to fluoride and arsenic in drinking water. Cad Saude Publica 23(Suppl 4):S579–S587

Roco A, Quiñones L, Acevedo C, Zagmutt O (2013) Cancer Status in Chile 2000 – 2010. Cuad Méd Soc (Chile) 53:83–94

Rodríguez DJ, Quici N, Custo G, Cherchiet L, Ortiz M, Litter MI (2014) TiO_2 photocatalytic oxidation of As(III) in the presence of Hg(II). In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 808–810

Rodríguez CM, Castillo E, Brandão PFB (2016) Evaluation of native sulphate-reducing bacteria for arsenic bioremediation. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 488–489

Rojas-Chaves P, Vargas-Benavides MJ, Araya-Obando A, Valverde-Cerdas J, Romero-Esquivel LG (2015) Estudio de remoción de arsénico en agua potable a nivel domiciliar mediante oxidación solar y coagulación-floculación (Study of arsenic removal in drinking water at household level using solar oxidation and coagulation-flocculation techniques). Tecnol Marcha 28:54–65

Roman MD, Niclis C, Aballay LR, Lantieri MJ, Díaz MDP, Muñoz SE (2018) Do exposure to arsenic, occupation and diet have synergistic effects on prostate cancer risk? Asian Pac J Cancer Prev 19:1495–1501

Romero FM, Armienta MA, Carrillo-Chavez A (2004) Arsenic sorption by carbonate-rich aquifer material, a control on arsenic mobility at Zimapán, Mexico. Archiv Environ Contam Toxicol 47:1–13

Romero LG, Valverde J, Rojas P, Vargas MJ, Araya JA (2014) Exploring low-cost arsenic removal alternatives in Costa Rica. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 853–855

Rosado JL, Ronquillo D, Kordas K, Rojas O, Alatorre J, Lopez P, Garcia-Vargas G, Caamaño MC, Cebrián ME, Stoltzfus RJ (2007) Arsenic exposure and cognitive performance in Mexican schoolchildren. Environ Health Perspect 115:1371–1375

Roy A, Kordas K, Lopez P, Rosado JL, Cebrian ME, Vargas GG, Ronquillo D, Stoltzfus RJ (2011) Association between arsenic exposure and behavior among first-graders from Torreón, Mexico. Environ Res 111:670–676

Ruiz G, Perez O, Sancha A M (1992) Filtración directa para el Tratamiento de Aguas Subterráneas con arsénico. In: Proceedings XXIII Congreso de la Asociación Interamericana de Ingeniería Sanitaria y Ambiental (AIDIS), AIDIS Cuba, La Habana, pp 729–39

Saitua H, Campderros M, Cerutti S, Padilla AP (2005) Effect of operating conditions in removal of arsenic from water by nanofiltration membrane. Desalination 172:173–180

Sancha A (1986) Experiencia Chilena en remoción de arsénico en fuentes de agua potable. Sección Ingenieria Sanitaria y Ambiental, Universidad de Chile, Santiago

Sancha A M (1996) Experiencia Chilena en Abatimiento de Arsénico. Seminario Potabilización de Aguas con Arsénico y Flúor. 9°. Congreso Argentino de Saneamiento y Medio Ambiente. Córdoba- Argentina

Sancha A (1999) Full-scale application of coagulation processes for arsenic removal in Chile: a successful case study. In: Chappell W, Abernathy C, Calderon R (eds) Arsenic exposure and health effects. Elsevier, Amsterdam, pp 373–378

Sancha A (2000) Removal of arsenic from drinking water supplies: Chile experience. Water Supp 18:621–625

Sancha AM (2003) Removing arsenic from drinking water: a brief review of some lessons learned and gaps arisen in Chilean water utilities. In: Chappell WR, Abernathy CO, Calderon RL, Thomas DJ (eds) Arsenic exposure and health effects V. Elsevier B.V, Amsterdam, pp 471–481

Sancha AM (2006) Review of coagulation technology for removal of arsenic: Case of Chile. J Health Popul Nutr 24:267–272

Sancha AM (2010a) Remoción de arsénico por coagulación y precipitación. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 33–41

Sancha AM (2010b) Importancia de la matriz de agua a tratar en la selección de las tecnologías de abatimiento de arsénico. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 145–153

Sancha AM (2010c) Experiencia chilena en la remoción de arsénico a escala de planta de Tratamiento. In: Litter MI, Sancha AM, Ingallinella AM (eds) Tecnologías económicas para el abatimiento de arsénico en aguas. Editorial Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo, Buenos Aires, pp 169–178

Sancha AM, Castro ML (2001) Arsenic in Latin America: occurrence, exposure, health effects and remediation. In: Chappell WR, Abernathy CO, Calderon RL (eds) Arsenic exposure and health effects IV. Elsevier B.V., Amsterdam, pp 88–96

Sancha AM, Fuentealba C (2009) Application of coagulation-filtration processes to remove arsenic from low-turbidity waters. In: Bundschuh J, Armienta MA, Birkle P, Bhattacharya P, Matschullat J, Mukherjee AB (eds) Natural arsenic in groundwater of Latin America. CRC Press/Balkema Publisher, Leiden, pp 581–588

Sancha A, Ruiz G (1984) Estudio del proceso de remoción de arsénico de fuentes de agua potable empleando sales de aluminio. In: Proceedings XIX Congreso Interamericano de Ingeniería Sanitaria y Ambiental (AIDIS) Chile, Tema I Agua Potable 2:380–410

Sancha A M, Vega F, Fuentes S (1992) Speciation of arsenic present in water inflowing to the Salar del Carmen treatment plant in Antofagasta, Chile, and its incidence on the removal process. In: International Seminar Proceedings. Arsenic in the environment and its incidence on health. Universidad de Chile, Chile, p 183–186

Sancha A M, O'Ryan R, Pérez O (2000) The removal of arsenic from drinking water and associated costs: the Chilean case. Interdisciplinary Perspectives on drinking water risk assessment and management. IAHS Publ 260, pp 17–25

Saralegui A, García JI, Gobbi A, Boeykens S (2014) Dead macrophyte biomass utilization for the adsorption of arsenic from aqueous solutions. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 742–744

Schlebusch CM, Lewis CM Jr, Vahter M, Engström K, Tito RY, Obregón-Tito AJ, Huerta D, Polo SI, Medina ÁC, Brutsaert TD, Concha G, Jakobsson M, Broberg K (2013) Possible positive selection for anarsenic-protective haplotype in humans. Environ Health Perspect 121:53–58

Schlebusch CM, Gattepaille LM, Engström K, Vahter M, Jakobsson M, Broberg K (2015) Human Adaptation to Arsenic-Rich Environments. Mol Biol Evol 32:1544–1555

Schouten JN, Verheij J, Seijo S (2015) Idiopathic non-cirrhotic portal hypertension: a review. Orphanet J Rare Dis 10:67. https://doi.org/10.1186/s13023-015-0288-8

Secretaría de Obras Públicas; Ministerio de Planificación Federal, Inversión Pública y Servicios (n.d.) Proyecto S10068 y S10064. http://www.vivienda.gob.ar/adjuntos/0b04f1260de41f646bb678aca593b6aa.pdf. Accessed Jul 2018.

Secretaría de Políticas, Regulación e Institutos y Secretaría de Agricultura, Ganadería y Pesca, Código Alimentario Argentino, Resolución Conjunta 34/2012 y 50/2012 Modificación (2012) https://www.ecolex.org/details/legislation/resolucion-conjunta-no-342012-y-502012-prorrogase-el-plazo-de-cinco-anos-previsto-en-los-articulos-982-y-983-del-codigo-alimentario-argentino-lex-faoc110418/. Accessed Jul 2018.

SenGupta A K, Cumbal L H (2005) Method of manufacture and use of hybridanion exchanger for selective removal of contaminating ligands from fluids. US Patent Appl. 156136 (07/21/05)

Sepúlveda P, Muñoz Lira D, Suazo J, Arancibia-Miranda N, Rubio MA (2016) Synthesis of Fe-Cu bimetallic nanoparticles: effect of percentage of Cu in the removal of As present in aqueous matrices. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 503–504

Sharma A, Flora SJS (2018) Nutritional management can assist a significant role in alleviation of arsenicosis. J Trace Elem Med Biol 45:11–20

Sharma VK, Sohn M (2009) Aquatic arsenic: toxicity, speciation, transformations, and remediation. Environ Int 35:743–759

Silva GC, Vasconcelos IF, Carvalho RP, Dantas MSS, Ciminelli VST (2009) Molecular modeling of iron and arsenic interactions with carboxyl groups in natural biomass. Environ Chem 6:1–7

Simeonova V (2000) Pilot study for arsenic removal. Water Supply 18:636–640

Smith AH, Hopenhayn-Rich C, Bates NM, Goeden HM, Hertz-Picciotto I, Dugdan HM, Wood R, Kosnett MJ, Smith MTE (1992) Environ Health Persp ECT97:259–267

Smith AH, Goycolea M, Haque R, Biggs ML (1998) Marked increase in bladder and lung cancer mortality in a region of Northern Chile due to arsenic in drinking water. Am J Epidemiol 147:660–669

Smith AH, Arroyo AP, Mazumder DN, Kosnett MJ, Hernandez AL, Beeris M, Smith MM, Moore LE (2000) Arsenic-induced skin lesions among Atacamenio people in Northern Chile despite good nutrition and centuries of exposure. Environ Health Perspect 108:617–620

Smith AH, Marshall G, Yuan Y, Ferreccio C, Liaw J, von Ehrenstein O, Steinmaus C, Bates MN, Selvin S (2006) Increased mortality from lung cancer and bronchiectasis in young adults after exposure to arsenic in utero and in early childhood. Environ Health Perspect 114:1293–1296

Smith AH, Marshall G, Liaw J, Yuan Y, Ferreccio C, Steinmaus C (2012) Mortality in young adults following in utero and childhood exposure to arsenic in drinking water. Environ Health Perspect 120:1527–1531

Smith AH, Marshall G, Roh T, Ferreccio C, Liaw J, Steinmaus C (2018) Lung, bladder, and kidney cancer mortality 40 years after arsenic exposure reduction. J Natl Cancer Inst 110:241–249

Solsona F (1985) Informe final de la consultoría sobre remoción de flúor y arsénico de las aguas de bebida. Panamerican Health Organization, Durango

Solsona F (1986) Solución al problema del hidroarsenicismo en la Región Lagunera (Coahuila y Durango). Organización Panamericana de la Salud, México

Soto-Peña GA, Luna AL, Acosta-Saavedra L, Conde P, López-Carrillo L, Cebrián ME, Bastida M, Calderón-Aranda ES, Vega L (2006) Assessment of lymphocyte subpopulations and cytokine secretion in children exposed to arsenic. FASEB J 20:779–781

Steinmaus, C-, Yuan, Y-, Kalman, D-, Rey, O.A., Skibola, C.F., Dauphiné, D., Basu, A., Porter, K.E., Hubbard, A., Bates, M.N., Smith, M.T., Smith, A.H. 2010. Individual differences in arsenic metabolism and lung cancer in a case-control study in Cordoba, Argentina. Toxicol Appl Pharmacol 247:138–145.

Steinmaus C, Ferreccio C, Acevedo J, Yuan Y, Liaw J, Durán V, Cuevas S, García J, Meza R, Valdés R, Valdés G, Benítez H, VanderLinde V, Villagra V, Cantor KP, Moore LE, Perez SG, Steinmaus S, Smith AH (2014) Increased lung and bladder cancer incidence in adults after in utero and early-life arsenic exposure. Cancer Epidemiol Biomark Prev 23:1529–1538

Steinmaus C, Castriota F, Ferreccio C, Smith AH, Yuan Y, Liaw J, Acevedo J, Pérez L, Meza R, Calcagno S, Uauy R, Smith MT (2015) Obesity and excess weight in early adulthood and high risks of arsenic-related cancer in later life. Environ Res 142:594–601

Steinmaus C, Ferreccio C, Acevedo J, Balmes JR, Liaw J, Troncoso P, Dauphiné DC, Nardone A, Smith AH (2016) High risks of lung disease associated with early-life and moderate lifetime arsenic exposure in northern Chile. Toxicol Appl Pharmacol 313:10–15

Storniolo A, Martín R, Thir M, Cortes J, Ramirez A, Mellano F, Bundschuh J, Bhattacharya P (2005) Reduction of the arsenic content in water using natural geological materials. In: Galindo G, Fernández-Turiel JL, Parada MA, Gimeno Torrente D (eds) Arsenic in water: origen, mobility and treatment. Taller. II Seminario Hispano-Latinoamericano sobre temas actuales de hidrología subterránea – IV Congreso Hidrogeológico Argentino, pp 173–182

Styblo M, Del Razo LM, Vega L, Germolec DR, LeCluyse EL, Hamilton GA, Reed W, Wang C, Cullen WR, Thomas DJ (2000) Comparative toxicity of trivalent and pentavalent inorganic and methylated arsenicals in rat and human cells. Arch Toxicol 74:289–299

Su C, Puls RW (2001) Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation. Environ Sci Technol 35:1487–1492

Superneau L (2012) Codelco, EcoMetals launch arsenic treatment plant. www.ecometales.cl. http://www.bnamericas.com/news/mining/codelco-ecometals-launch-arsenic-treatment-plant. Accessed Jan 2015

Teixeira MC, Ciminelli VST (2005) Development of a biosorbent for arsenite: structural modeling based on x-ray spectroscopy. Environ Sci Technol 39:895–900

Trelles R, Larghi A, Paez J (1970) El problema sanitario de las aguas destinadas a la bebida humana con contenidos elevados de arsénico, vanadio y flúor. Universidad de Buenos Aires. Facultad de Ingeniería Sanitaria, Publicación No. 4

Triszcz JM, Porta A, García Einschlag FS (2009) Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal. Chem Eng J 150:431–439

Tseng CH (2009) A review on environmental factors regulating arsenic methylation in humans. Toxicol Appl Pharmacol 235:338–350

TUDelft (2018) Arsenic removal in Nicaragua. https://www.tudelft.nl/en/ceg/about-faculty/departments/watermanagement/education/marc-van-eekeren-reisfonds/aanvragen-en-procedure-studenten/completed-projects/2016/arsenic-removal-in-nicaragua/. Accessed Nov 2018

Tufo AE, Marchi MC, dos Santos Afonso M, Sileo EE, Landi SM (2014) Influence of the Al-for-Fe substitution in the adsorption of As(V) onto goethites—morphological surface characterization. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 699–701

Valles-Aragón MC, Alarcón-Herrera MT (2014) Seasonal variation of redox potential and arsenic removal from water in a constructed wetland mesocosm. In: Litter MI, Nicolli HB, Meichtry JM, Quici N, Bundschuh J, Bhattacharya P, Naidu R (eds) One century of the discovery of Arsenicosis in Latin America (1914–2014). CRC Press, London, pp 748–750

Van den Bergh K, Du Laing G, Montoya JC, De Deckere E, Tack F (2010) Arsenic in drinking water wells on the Bolivian high plain: Field monitoring and effect of salinity on removal efficiency of iron-oxides containing filters. J Environ Sci Health Part 45:1741–1749

Vasconcelos FM, Ciminelli VST, Oliveira RP, Silva RJ (2004) Determination of chemical speciation and the potential of As remobilization in mining sites. Geochim Bras 18:115–120

Villa G, Huamaní C, Charvez M, Huamaní J (2016) In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability, Proceedings 6th. International Congress on Arsenic in the Environment (As2016), Stockholm, Sweden. CRC Press/Balkema, Taylor and Francis Group, London, pp 531–532

Villela-Martínez DE, Leyva-Ramos R, Mendoza-Barron J (2016) Removal of As(V) supported on bone char. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 507–509

WaterWorld (2010) Desalination plant to serve Chilean mine. https://www.waterworld.com/articles/2010/03/desalination-plant-to-serve-chilean-mine.html

Wegelin M, Gechter D, Hug S, Mahmud A, Motaleb A (2000) SORAS-a simple arsenic removal process. In: Water, sanitation, hygiene: challenges of the millennium. 26th WEDC Conference, Dhaka, Bangladesh, p 379–382

Westergren R (2006) Arsenic removal using biosorption with Chitosan Evaluating the extraction and adsorption performance of Chitosan from shrimp shell waste. A Minor Field Study, MSc. Thesis KTH, the Royal Institute of Technology, Stockholm

World Health Organization (WHO) (2011) Guidelines for drinking-water quality, 4th edn. World Health Organization, Suiza. [en línea]. Disponible en: http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf?ua=1. Consulta: noviembre 2017.

World Health Organization (WHO) (2017) Cardiovascular diseases (CVDs) key facts. http://www.who.int/en/news-room/fact-sheets/detail/cardiovascular-diseases-(cvds). Accessed July 2018

www.physics.harvard.edu/~wilson/arsenic/conferences/Feroze_Ahmed/Sec_3.htm (n.d.) Accessed Nov 2018

Xu X, Drobná Z, Voruganti VS, Barron K, González-Horta C, Sánchez-Ramírez B, Ballinas-Casarrubias L, Cerón RH, Morales DV, Terrazas FA, Ishida MC, Gutiérrez-Torres DS, Saunders RJ, Crandell J, Fry RC, Loomis D, García-Vargas GG, Del Razo LM, Stýblo M, Mendez MA (2016) Association between variants in arsenic (+3 oxidation state) methyltranserase (AS3MT) and urinary metabolites of inorganic arsenic: role of exposure level. Toxicol Sci 153:112–123

Yáñez J, Mansilla HD, Santander IP, Fierro V, Cornejo L, Barnes RM, Amarasiriwardena D (2015) Urinary arsenic speciation profile in ethnic group of the Atacama desert (Chile) exposed to variable arsenic levels in drinking water. J Environ Sci Health A 50:1–8

Yonni F, Fasoli HJ, Fernández AE, Martínez LC, Alvarez JH (2016) Ergonomic design of a system for removal of arsenic for household use. In: Bhattacharya P, Vahter M, Jarsijö J, Kumpiene J, Ahmad A, Sparrenborm C, Jacks G, Donselaar ME, Bundschuh J, Naidu R (eds) Arsenic research and global sustainability (As2016). CRC Press/Balkema, Taylor and Francis Group, London, pp 545–546

Yuan Y, Marshall G, Ferreccio C, Steinmaus C, Selvin S, Liaw J, Bates MN, Smith AH (2007) Acute myocardial infarction mortality in comparison with lung and bladder cancer mortality in arsenic-exposed region II of Chile from 1950 to 2000. Am J Epidemiol 166:1381–1391

Yuan Y, Marshall G, Ferreccio C, Steinmaus C, Liaw J, Bates M, Smith AH (2010) Kidney cancer mortality: fifty- year latency patterns related to arsenic exposure. Epidemiology 21:103–108

Zaldivar R (1980) A morbid condition involving cardio- vascular, bronco pulmonary, digestive and neural lesions in children and young infants after dietary arsenic exposure. Zbl Bakt I Abt Orig B 170:44–56

Zurita F, De Anda J, Belmont MA (2009) Treatment of domestic wastewater and production of commercial flowers in vertical and horizontal subsurface-flow constructed wetlands. Ecol Eng 35:861–869

Zurita F, Belmont MA, De Anda J, White JR (2011) Seeking a way to promote the use of constructed wetlands for domestic wastewater treatment in developing countries. Water Sci Technol 63:654–659

Zurita F, Del Toro-Sánchez CL, Gutierrez-Lomelí M, Rodriguez-Sahagún A, Castellanos-Hernandez OA, Ramírez-Martínez G, White JR (2012) Preliminary study on the potential of arsenic removal by subsurface flow constructed mesocosms. Ecol Eng 47:101–104

Arsenic Contamination Status in Europe, Australia, and Other Parts of the World

Gordana Medunić, Željka Fiket, and Maja Ivanić

Abstract This chapter presents latest research in Australia, Europe, and other parts of the world on environmental issues related to As, particularly in water, but the viewpoints of food, health, and soil professionals are presented too. Having summarized more than 150 ecogeochemistry papers, the text is showcasing developments in this fast-moving field of research witnessing inadvertent arsenic poisoning on mass scale. In Europe, there are several regional hotspots of As contamination which warrant further detailed investigations. Most notable is the case of the Pannonian Basin (Hungary, Serbia, and Romania), where more than 600,000 residents are at risk of drinking water containing high As concentrations. Other regions threatened by waterborne As include Czech Republic, Croatia, Finland, Greece, Italy, Spain, and Turkey. While the majority of problems associated with arsenic mobilization in Asian regions are linked to natural processes, those recorded in Australia and New Zealand arise from both the natural processes and anthropogenic activities related to the mining industry, waste disposal, usage of arsenic pesticides and herbicides, atmospheric deposition, and timber treatment practices. Not only have the mining of mostly gold deposits and the associated gold extraction activities increased the release of As into the environment, but they also left a long-lasting legacy of the As-contaminated environment. In Africa, elevated As levels are found only sporadically across the continent, more as a result of the lack of research than a real absence of the problem. Although elevated arsenic concentrations have been reported in both the surface and groundwater of Africa, high As levels in surface waters generally are linked to mining operations, as well as to agricultural drains, local sediments, and disposal and incineration of municipal and industrial waste. Conversely, in groundwater, As occurrence is generally related to local geology, mineralization, geothermal water, etc. In Russia, drinking water quality is, in general, rather low due to surface contamination; lack of sanitary protection; delayed repair, cleaning, and disinfection of wells; and interruptions. The

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occurrences of high arsenic in soil and drinking water, although based on small number of studies, are associated with both the geogenic and anthropogenic sources. Similar situation is also found in many countries of Eastern, Central, and Western Asia where As contamination is evidenced, although only sporadically, in both drinking water and food.

Keywords Arsenic · Drinking water · Food · Contamination · Europe · Australia · Africa · Russia

1 Introduction

Arsenic is a toxic, non-essential element, used as a pigment, a livestock growth promoter, and as a component in pesticides and wood preservatives. It has caused considerable environmental pollution due to the frequent and long-term use of its compounds in industry and agriculture. It is ubiquitous in nature and is found in detectable levels in nearly all environmental media (Reimann et al. 2009). It is concentrated in volcano-sedimentary ore deposits in various mineralizations. Its freshwater content is typically 2 μg/L. Arsenic is mobile in low pH and reductive conditions. In humans, due to its chemical similarity with P, it can disrupt metabolic pathways involving P. Since adults drink on average 1.5 L/day drinking water, they are more likely affected by pollutants from this route than from the diet. Drinking water laden with As is slowly poisoning humans, starting with keratoses and discoloration of the skin, while later these turn into cancers, and liver and kidneys deteriorate.

The reasons why aquifers are contaminated by As are manifold. Mostly, it is associated with iron-rich sediments from the rivers like Ganges, Brahmaputra, Meghna, etc. Also, As is included in sulphide minerals; e.g. pyrite is the most widespread source of As. Reducing conditions lead to solubilization of Fe and the concomitant release of the adsorbed arsenate. The problem of the release of As from sediments into the groundwater is found in many parts of the world, which is elaborated in this chapter.

Strong regulatory safe drinking water standards have prompted scientists and technologists in search for water treatment schemes to remove As and other contaminants from wells used by communities in affected regions (Katsoyiannis et al. 2014; Sharma et al. 2017). Furthermore, some scientific groups employ redox active molecules against As toxicity in rice, in order to cut down the As load in rice grains and enhance their tolerance capacity along with nutritional quality (Upadhyay et al. 2018).

Environmental contamination with arsenic on global, regional, and local levels has been increasingly recognized by scientists and public authorities across the

Table 1 Arsenic maximum concentrations in different sampling water media in European (EU) regions/countries

Region	Country	µg As/L	Sample media	References
Balkan	Croatia	611	Drinking water	Ćavar et al. (2005)
	Serbia	8000	Mineral and thermal water	Dangić (2007)
		420	Public water supply	Jovanović et al. (2011)
	Greece	1840	Public water supply	Kouras et al. (2007)
	Romania	175	Drinking water	Neamtiu et al. (2015)
	Turkey	911	Groundwater	Gemici et al. (2008)
		594	Geothermal water	Gunduz et al. (2010)
East EU	Czech Republic	1141	Groundwater	Drahota et al. (2009)
	Slovakia	90,000	Sb-As-Au mine borehole	Flakova et al. (2012)
		2150	Mine surface water	Hiller et al. (2012)
	Hungary	28.6	Drinking water	Hough et al. (2010)
		88.0	Drinking water	Lindberg et al. (2006)
North EU	Sweden	17.0	Lakes	Jacks et al. (2013)
		14.0	Unimpacted surface water	Routh et al. (2007)
	Finland	2230	Drilled bedrock well	Parviainen et al. (2015)
South EU	Spain	890	Spoil heap surface water	Alvarez et al. (2006)
		118	Drinking water	Medrano et al. (2010)
	Portugal	7.8	Well water	Candeias et al. (2014)
		24.3	Surface water	Luís et al. (2011)
West EU	UK	21.0	Surface water	Camm et al. (2004)
	Ireland	234	Drinking water	McGrory et al. (2016)
	Denmark	25.3	Drinking water	Monrad et al. (2017)

world recently. Namely, arsenic contamination of underground water reservoirs has gone unrecognized for decades. Arsenic contamination of groundwater and plants in India is well documented (Srivastava et al. 2016). According to some estimates, only in West Bengal the population of 6×10^6 has been exposed to unacceptably high levels of As in drinking water (Nordstrom 2002), while many times more in Bangladesh. Since there are countless reservoirs plagued by high As levels across the world, mitigation plans require massive efforts and knowledge of a current arsenic status in the environment. The aim of this chapter is to present latest research in Europe (selected papers summarized in Table 1), Australia, and other parts of the world (selected papers shown in Table 2) on environmental issues related to As, particularly in water, but the viewpoints of food and health professionals are presented too. Through a summary of more than 150 ecogeochemistry papers, the text is showcasing developments in this fast-moving field of research witnessing inadvertent arsenic poisoning on mass scale.

Table 2 Arsenic maximum concentrations in different sampling water media in Australia, New Zealand, Africa, Russian Federation, and selected Asian countries

Region	Country/state	µg As/L	Sample media	Reference
Australia and New Zealand	New South Wales	30,000	Groundwater	Binning et al. (2001)
		300	Groundwater	Smith and Jankowski (2001)
		70	Groundwater	McLean and Jankowski (2001)
	Victoria	2830	Surface water	DMID (1991)
		5000	Surface and groundwater	Hinwood et al. (1999)
		73	Drinking water	Hinwood et al. (2003)
	Western	220,000	Groundwater	Throssell and Blessing (2001)
	Australia	7300	Groundwater	Appleyard et al. (2006)
		800	Domestic well water	
	New Zealand	47.5	Groundwater	Environment Waikato Technical Report (2006)
			Geothermal water	
Africa	Botswana	116	Groundwater	Huntsman-Mapila et al. (2006)
		3200	Groundwater	Huntsman-Mapila et al. (2011)
		180	Groundwater	Mladenov et al. (2013)
	Burkina Faso	1630	Groundwater	Smedley (1996)
	Ethiopia	96	Surface and groundwater	Reimann et al. (2003)
		566	Surface water	Rango et al. (2013)
		190	Groundwater	
	Ghana	175	Surface water	Smedley (1996)
		64	Groundwater	
		8250	Surface water	Serfor-Armah et al. (2006)
		73	Surface water	Asante et al. (2007)
		4	Groundwater	
		1760	Groundwater	Kusimi and Kusimi (2012)
	Nigeria	6.88	Groundwater	Asubiojo et al. (1997)
		28	Tap water	
	South Africa	12.3	Groundwater	Dzoma et al. (2010)
	Togo	6460	Surface water	Rezaie-Boroon et al. (2011)
Eurasia	Russian Federation	9300	Groundwater	Ilgen et al. (2011)
			Geothermal water	
		230	Groundwater	Kurbanova et al. (2013)
		59	Drinking water from well	Yurkevich et al. (2017)

(continued)

Table 2 (continued)

Region	Country/state	µg As/L	Sample media	Reference
		89	Drinking water from water-pump	Bortnikova et al. (2018)
Central Asia	Iran	1500	Drinking water	Barati et al. (2010)
		689	Groundwater	Keshavarzi et al. (2011)
		310	Drinking water	Keshavarzi et al. (2015)
		1440	Surface and ground water	Mosaferi et al. (2017)
Far East Asia	Japan	293	Well water	Kondo et al. (1999)
		17	River water	Miyashita et al. (2009)
		750	Hot spring water	
	South Korea	167	Surface and groundwater	Woo and Choi (2001)
		1.5	River water	Hong et al. (2018)

2 Europe

2.1 Balkan Countries

2.1.1 Croatia

Inorganic arsenic (iAs) in groundwater exceeding 10 µg/L (maximum contaminant level, MCL) set by the World Health Organization (WHO) is characteristic for intermediate-depth aquifers over large areas of the Pannonian Basin in Central Europe. Eastern part of Croatia belongs to the Pannonian Basin, where communities are exposed to toxic levels of As in drinking water. Groundwater, the main source of drinking water for the population in this area, contains high iron, manganese, ammonia, organic substances, and arsenic levels. Its inorganic As comes mainly from natural geological sources such as alluvial basins containing deep sediments from the Middle and Upper Pleistocene. Almost 200,000 people in eastern Croatia are daily drinking water with As concentrations ranging 10–610 µg/L. Therefore, Romić et al. (2011) sampled groundwater from 18 water wells and 12 piezometers with depth ranges 21–200 m. During the 10-year period to 2007, mean As concentration of 240 µg/L was found. Higher mean As levels (205 µg/L) were found in deeper wells (>50 m) compared to 27 µg/L in shallow groundwater (<50 m). Significant seasonal variations of total As were observed in some wells, with the highest concentrations often found during the summer. Similarly, Ujević Bošnjak et al. (2012) collected groundwater samples from 56 production wells in 2 eastern Croatian counties, Osijek-Baranja and Vukovar-Srijem. Arsenic was detected in 46 out of 56 groundwater samples, having total levels up to 491 µg/L. Also, 36 wells were found to have total As concentrations above the WHO Maximum Contaminant Level for As in drinking water, i.e. 10 µg/L. Only inorganic As species were detected, with arsenite As(III) as the predominant form. The authors interpreted As mobilization in terms of reductive dissolution of Fe oxides, desorption of As from Fe oxides and/or clay minerals, as well as competition for the sorption sites with organic matter and phosphate. Moreover, two medical studies were conducted in the same region in order to reveal some potential health issues caused by As. Ćavar et al. (2005) found the positive correlation between As in drinking water and residents hair. The mean As values in community drinking water samples were 0.14, 37.88, 171.60, and 611.89 μg/L, while the corresponding mean levels of As in hair were 0.07, 0.26, 1.74, and 4.31 μg/g. Bošnjak et al. (2008) examined prevalence and serum levels of selected markers of cardiovascular disease in 34 subjects from a rural population exposed to high drinking water As levels (611.89 ± 10.06 μg/L). The results suggest that chronic high As intake is associated with higher prevalence of obesity, hypertension, and several markers of cardiovascular disease in the exposed population.

Due to toxicity and mutagenicity, arsenic is regarded a principal pollutant in water used for drinking. Therefore, Radić et al. (2016) conducted toxicological and chemical evaluation of groundwater samples from eastern Croatia, obtained from drinking water wells enriched in As prior and following the electrochemical and ozone-UV-H2O2-based advanced oxidation processes (EAOP). They employed acute toxicity test with *Daphnia magna*, and chronic toxicity test with *Lemna minor* L., along in vitro bioassays using human peripheral blood lymphocytes (HPBLs). Several oxidative stress parameters were estimated in *L. mino*r. Untreated groundwater caused only slight toxicity to HPBLs and *D. magna* in acute experiments. However, 7-day exposure of *L. minor* to raw groundwater induced genotoxicity, a significant growth inhibition, and oxidative stress injury. EAOP treatment was highly efficient in the removal of As, ammonia, and organic compound and the complete elimination of the observed genotoxicity and toxicity of raw groundwater.

Regarding arsenic in food, Sapunar-Postružnik et al. (1996) determined total As levels in food items sold in Croatia during a 5-year period (1988–1993). Highest As mean levels were recorded in the following food groups: fish (498 μg/kg), fishery products (270 μg/kg), and cheese and dairy products (39 μg/kg). Lowest As levels were found for fruit, chocolate, and fruit products (0.2, 0.2, and 0.3 μg/kg, respectively). The authors estimated that a mean weekly dietary As intake was 81.9 μg/individual, significantly lower than in other countries, due to lower consumption of fish and fishery products in Croatia.

2.1.2 The FYR of Macedonia

The FYR of Macedonia is located in the Serbo-Macedonian Massif of the Eurasian Tethys metallogenic belt. The region contains some disused As and Sb mines (Lojane, Alchar, and Krstov Dol) which were studied by Alderton et al. (2014). They found out that soil and river sediments contained up to several hundred mg/kg of both elements, while local alkaline water contained up to hundreds of μg/L of the both. They showed how alkaline water contributes to the breakdown of As- and

Sb-sulphides and element mobility over larger areas. The Alchar locality is known as As-Sb-Tl-Au volcanogenic hydrothermal deposit, situated at the north-western margins of Kožuf mountain, close to the border between the FYR of Macedonia and Greece. There, Stevanović et al. (2010) investigated the uptake and distribution of arsenic in three *Viola* endemic species. Total As content in soil ranged from 3347 to 14,467 mg/kg, while plant available As ranged from 23 to 1589 mg/kg. The As concentration of roots ranged from 783 mg/kg in *Viola macedonica* to 2124 mg/kg in *Viola arsenica*. Only a small amount of As (<100 mg/kg) was accumulated in the aboveground parts of these species. Also, Kostik et al. (2014) determined As concentrations up to 26.4 μg/L in drinking water coming from the Kožuf mountain, as a consequence of minerals like lorandite, orpiment, realgar, arsenopyrite, etc.

2.1.3 Serbia

Central parts of the Balkan Peninsula in south-east Europe, in Serbia, and in Bosnia, mostly in the Danube River Basin, include several natural and anthropogenic sources of As, such as geological formations, ore deposits, old and active mines, and various industries. The area is also rich in mineral and thermal waters (MTWs). According to Dangić (2007), MTWs are famous for being a rich source of Fe-As medicinal water (Crni Guber in Srebrenica). Arsenic concentrations in 153 MTWs varied from <0.01 to 8 mg/L, but levels up to 30 μg/L predominate. The study showed the correlations among As levels, mineralization, Fe content, and pH in MTWs.

The first study on the distribution of As in public water supply systems in Vojvodina (the northern region of Serbia, a part of the Pannonian Basin), where aquifers contain high As values, was carried out by Jovanović et al. (2011). Around 63% of all collected waters exceeded Serbian and European standards for As in drinking water. Levels of As were much higher than in other Pannonian Basin countries, being similar to some values in Bangladesh. Large variations in As levels among water supply systems were observed (median ranged from 2 to 250 μg/L, while max values ranged from 5 to 349 μg/L). About 50.4% of them had As concentrations 11–50 μg/L, and further 38.6% systems had mean arsenic levels over 50 μg/L. The differences among the investigated municipalities were statistically significant ($p < 0.001$). Škrbić et al. (2013) examined As, Cd, and Pb in 114 samples of mostly consumed foodstuffs collected at supermarkets in Novi Sad, the capital of Vojvodina. The highest concentrations were found for Pb in candy (0.323 mg/kg), Cd in cayenne (0.118 mg/kg), and As in canned fish (0.43 mg/kg). The highest intake was estimated for Pb, 72.3 μg per day for adult population, while intakes of As and Cd were significantly lower (21.9 μg per day and 11.5 μg per day, respectively). The levels of As, Cd, and Pb in investigated foodstuffs were in compliance with the current Serbian and EC legislations.

Pontic shad (*Alosa immaculata* Bennet 1835) is an anadromous species that lives in the heavily polluted north-western part of the Black Sea and migrates into the Danube River to spawn. A total of 48 samples of Pontic shad were collected by

Višnjić-Jeftić et al. (2010) at a 863th km of the Danube River (downstream of the Djerdap II dam) to analyse content of Al, As, Cd, Cu, B, Ba, Fe, Mg, Sr, Zn, Li, Co, Cr, Mn, Mo, Ni, and Pb. Muscle samples had the lowest concentrations of most of the analysed elements, but they were characterized by the highest As levels. The study showed that As and Cd in Pontic shad muscle tissue were above maximum acceptable concentrations for human consumption, and precautions were necessary.

2.1.4 Greece

Gamaletsos et al. (2016) reviewed the existing data about the geological sources of As in Greece which include As-containing ores in active and abandoned mining areas, geothermal/hydrothermal waters, lignites in exploited and unexploited deposits, As-minerals in various rock types such as metamorphic rocks, and mineral dust originating from Sahara desert. It is considered that As release from the above sources, in conjunction with various anthropogenic As fluxes, occasionally creates distinct areas with contaminated groundwater, soils, marine, and atmospheric environment. They emphasize that the most important and persisting sources of As exposure to the Greek population are geothermal and hydrothermal fluids arising from faults as well as the volcanic activity. Eliopoulos et al. (2012) studied iron-nickel laterite deposits in the Balkan Peninsula and Turkey, located in the Mirdita-Sub-Pelagonian and Pelagonian geotectonic zones, extending into the Anatolides zone. Their arsenic contents are generally low, ranging from less than 2 to a few tens of mg/kg. However, in the Aghios Ioannis deposit (Lokris, Central Greece), As attains values up to 0.26 wt.% As. In Western Turkey, As ranges from 0.004 to 1.07 wt.% in the Gordes deposit. The authors emphasize that elevated As contents in goethite (Fe oxides) in Fe-Ni laterites of Greece and Turkey, due to its absorption capacity, are considered to be of particular significance in the remediation of aquifer and soil contamination rather than being a source of environmental risk.

Regarding groundwater, Katsoyiannis et al. (2014) summarized the arsenic contamination in Europe, where several countries are affected by elevated arsenic concentrations (i.e. Greece, Hungary, Romania, Croatia, Serbia, Turkey, and Spain). In Greece, arsenic-affected regions are classified in three categories: (1) the geothermal-affected waters, (2) the alluvial deposits of rivers and aquifers, and (3) those influenced by mineralization/mining activities. In Greece, As levels in geothermal waters vary from 30 to 4500 μg/L, in the regions close to alluvial deposits from 15 to 100 μg/L, and in areas affected by mining activities from 20 to 60 μg/L. Katsoyiannis and Katsoyiannis (2006) investigated groundwater used for drinking water supply in the greater industrial area of Thessaloniki (Northern Greece), where As levels exceeded the WHO provisional guideline value and the EU maximum contaminant level of 10 μg/L. The concentration of total arsenic was in the range 4–130 μg/L (median was 36 μg/L), while 9 out of 11 wells contained total As >10 μg/L. The examined groundwater contained elevated concentrations of manganese and phosphate. Furthermore, Kouras et al. (2007) analysed groundwater in the area of

Chalkidiki (Northern Greece) where As showed high spatial variation with range from 0.001 to 1.840 mg/L. Almost 65% of the examined groundwater samples had As >10 μg/L. Arsenic was highly correlated with potassium, boron, bicarbonate, sodium, manganese, and iron, suggesting common geogenic origin of these elements and conditions that enhance their mobility. Aloupi et al. (2009) studied the occurrence of As in water from a drainage basin of Kalloni Gulf (island of Lesvos, Greece). The aim of the study was to investigate the potential influence of the geothermal field of Polichnitos-Lisvori on the ground and surface water systems of the area. Total dissolved As varied in the range <0.7–88.3 μg/L in groundwater, 41.1–90.7 μg/L in thermal spring water, and 0.4–13.2 μg/L in stream water. Four out of 31 groundwater samples exceeded the EC standard of 10 μg/L.

Casentini et al. (2011) investigated the accumulation of As in soils and food crops due to the use of arsenic-contaminated groundwater for irrigation in the Chalkidiki prefecture. The groundwater As levels are >1000 μg/L within the Nea Triglia geothermal area. Arsenic content in sampled soils ranged from 20–513 to 5–66 mg/kg inside and outside of the geothermal area, respectively. Low As accumulation was found in collected olives (0.3–25 μg/kg in flesh and 0.3–5.6 μg/kg in pits). The authors pointed out that arsenic uptake in fast-growing plants should have been assessed as soil As values were frequently elevated far above recommended levels.

2.1.5 Cyprus

During 2007–2009, there was a national monitoring programme in Cyprus, when 84 boreholes were sampled and analysed for total arsenic by ICP-MS (Christodoulidou et al. 2012). The groundwater As concentrations ranged from <0.3 to 41 μg/L. Several boreholes were repeatedly sampled following an initial borehole washout for 5 min. Further sampling in 2010 revealed that total As concentrations ranged <0.3–64.2 μg/L, with arsenate (As^V) as the predominant As species (determined by a novel field-based methodology). The study showed that maximum total As concentration was sixfold the WHO drinking water guideline limit (10 μg/L) and approximately half the United Nations Food and Agriculture Organization irrigational limit of 100 μg/L As.

2.1.6 Romania

In Western Romania, near the border with Hungary, the Arad, Bihor, and Timis counties use drinking water coming partially or entirely from iAs-contaminated aquifers. More than 45,000 people residing in the Arad and Bihor counties are exposed to iAs above 10 μg/L via public drinking water sources. Neamtiu et al. (2015) analysed iAs in 124 public and private Timis County drinking water sources, including wells and taps, used by pregnant women participating in a case-control study of spontaneous loss. Arsenic levels in wells (median 3.1 μg/L, range

<0.5–175 μg/L) were higher than As in community taps (median 2.7 μg/L, range <0.5–36.4 μg/L). The results showed that pregnant women from the Timis County, compared to surrounding counties, were exposed to lower arsenic levels via drinking water. Butts et al. (2015) conducted a pilot study of associations between iAs in drinking water and self-reported chronic diseases in 297 pregnant women from the Timis County. Adjusted for confounding variables, they identified the positive association among iAs and heart disease, kidney disease, and high blood pressure. Also, Bloom et al. (2016) examined birth outcomes in the Timis County where they followed 122 women with singleton deliveries, for whom they constructed individual exposure indicators using self-reported water consumption weighted by arsenic measured in drinking water sources. They found out no overall confounder-adjusted effects for arsenic exposure on birth outcomes. Yet, their results suggest smoking may potentiate an otherwise benign arsenic exposure.

In the same Timis County, Susko et al. (2017) evaluated associations among low As levels in drinking water and female fecundity. Women (*n* = 94) with planned pregnancies of 5–20 weeks gestation completed a comprehensive physician-administered study questionnaire and reported the number of menstrual cycles attempting to conceive as the time to pregnancy (TTP). There was no main effect for the drinking water As exposure, yet the conditional probability for pregnancy was modestly lower among arsenic exposed women with longer TTPs, relative to women with shorter TTPs, and relative to unexposed women. Although preliminary, the results suggest that low-level As contamination in residential drinking water sources may further impair fecundity among women with longer waiting times.

2.1.7 Turkey

Turkey is characterized by complex geology with active tectonics and high geothermal potential. Particularly, its western part is a region of abundant geothermal activity, which is controlled by faults accommodating the deep circulation of hydrothermal fluids of meteoric origin. Western Anatolian young (down to about 1 my) volcanic activities and shallow intrusive emplacements resulted in the formation of considerable number of geothermal and hydrothermal systems and kept them active for long enough that gave rise not only to the formation of numerous epithermal mineralizations rich in As-Sb-Hg-bearing sulphide minerals but also to the formation of As-enriched sedimentary and magmatic rocks. Their dissolution and redistribution within the rocks and resultant soils consequently made them geogenically As-rich. According to Baba and Sözbilir (2012), the highest concentrations of naturally occurring aqueous As are found in major graben faults. Herewith, elevated As levels in geothermal resources have been detected in Western Turkey, including but not limited to Biga Peninsula, Gediz Graben, Kucuk, and Buyuk Menderes Graben, with As values ranging from 1 to 1419 μg/L. Another study related to geothermal fluids was conducted by Gunduz et al. (2010). They sampled 27 wells in the surficial aquifer and found average As concentration of 99.1 μg/L, with max value of

561.5 µg/L. There, Cu-Pb-Zn mine was in operation in the past, and arsenic-containing waste (660 mg/kg As) was deposited in an uncontrolled manner. Another potential source of As in the study area is geothermal fluid reaching As levels as high as 594 µg/L. Consequently, death statistics from the 1995 to 2005 period collected from the study area revealed increased rates of gastrointestinal cancers above Turkish average.

Ozkul et al. (2015) investigated As concentrations of soils and stream waters from an area where the world class borate deposits (Bigadiç district) were mined for about 60 years. Arsenic levels in soil and water samples ranged from 0.4 to 2488.4 mg/kg and 8–243 µg/L, respectively. Also, Gemici et al. (2008) documented the environmental impact of the borate mines, which are the largest colemanite and ulexite deposits in the world. High groundwater sulphate concentrations (up to 519 mg/L) derive from anhydrite, gypsum, and celestite minerals in the borate zone. Arsenic range (33–911 µg/L) exceeds the tolerance limit of 10 µg/L, along the suphate, Al, and Fe levels which are above the drinking water standard for groundwater samples.

Regarding medical research, Gunduz et al. (2015) compared the causes of death in five villages situated in Simav Plain, during the period 2005–2010, where groundwater was characterized by As ranges 7.1–833.9 µg/L. They formulated a two-phase research; in the first phase, public health surveys were conducted with 1003 villagers to determine the distribution of diseases, and in the second phase, verbal autopsy surveys and official death records were used to investigate the causes of death. In total, 402 death cases were found in the study area where cardiovascular system diseases (44%) and cancers (15.2%) were major causes. Cancers of lung (44.3%), prostate (9.8%), colon (9.8%), and stomach (8.2%) were comparably higher in villages with high arsenic levels in drinking water supplies. Furthermore, the majority of cases of liver, bladder, and stomach cancers were observed in villages with high arsenic levels.

2.2 Eastern Europe

2.2.1 Poland

In Poland, soil-arsenic problem is mainly confined to industrial, mining, and smelting areas. Karczewska et al. (2007) indicated a few “hot spots”, where soils are characterized by extremely high levels of As, caused by natural enrichment and long-lasting ore mining and processing activities. They presented total concentrations and speciation of As in Zloty Stok, Zelezniak, and Czarnow soils (SW Poland), where As ores were mined and processed since the thirteenth century. Maximum concentrations of As in mine spoils at the Zloty Stok, Czarnow, and Zelezniak sites were 8800, 40,600 and 18,100 mg/kg, respectively. Alluvial soils in these three regions contained up to 11,500, 4210 and 6800 mg/kg of As, respectively.

As regards the Zloty Stok mine, it is located in the southern part of a town of the same name in Lower Silesia. The exploitation of arsenic started in the eighteenth century. Arsenic occurs as loellingite (FeAs2) and arsenopyrite (FeAsS) in serpentinite and marbles. Drewniak et al. (2008) investigated whether bacteria present in ancient gold mine could transform immobilized arsenic into its mobile form and increase its dissemination in the environment. Twenty-two arsenic-hypertolerant cultivable bacterial strains were isolated. A correlation between the presence of siderophores and high resistance to arsenic was found. The results of the study showed that the detoxification processes based on arsenate reductase activity might substantially disseminate the arsenic pollution. The authors concluded that the activity of the described heterotrophic bacteria contributed to the mobilization of As in the more toxic As(III) form, and this had led to the contamination of important drinking water sources situated around the mine and mine waste deposits. There, Jedynak et al. (2012) assessed the strategy developed by terrestrial plants to avoid or minimize the toxic effects caused by As. They found out that the highest concentration of arsenic was found in herb Robert (*Geranium robertianum*) 21 mg/kg and common nettle (*Urtica dioica*) 5.3 mg/kg in the cases of Złoty Stok and Łomianki, respectively. Phytochelatins were present in all investigated plant species: PC3 was present in the highest concentration in plants from Złoty Stok (compared to other phytochelatins), while none of the phytochelatins dominated in plants from Łomianki.

In addition to natural sources and land-originated pollution, the Baltic Sea has another anthropogenic source of arsenic in bottom sediments – arsenic-based chemical warfare agents (CWA). Beldowski et al. (2015) reported elevated As levels in dumpsite areas compared to reference areas. However, very complex and variable chemical transformations of arsenic and As-containing compounds in the marine environment complicate the interpretation of sedimentary concentration data for arsenic and its compounds and hinder the establishment of any association with chemical weapons.

In terms of food research, Niedzielski et al. (2013) determined the content of As(III), As(V), and DMAA (dimethylarsinic acid) in *Xerocomus badius* fruiting bodies collected from selected Polish forests from areas subjected to very low or high anthropopressure, and some commercially available samples obtained from the Polish Sanitary Inspectorate. The analyses showed high levels (up to 27.1, 40.5, and 88.3 mg/kg for As(III), As(V), and DMAA, respectively) of arsenic, and occurrence of different species in mushrooms collected from areas subjected to high anthropopressure and two commercially available samples. Therefore, the authors suggested the need for monitoring of As in mushroom foodstuffs.

2.2.2 Czech Republic

In Central Bohemia, approximately 50 km south of Prague, there the Mokrsko-West gold deposit is situated, never mined though (Bohemian Massif). It is characterized by a low sulphide content (generally <3 vol.%), while arsenopyrite (FeAsS) is the predominant sulphide, and its weathering flux corresponds to approximately 95% of the total input of As into the soil. High concentrations of As in the groundwater (255–1690 μg/L) and surface water (50–340 μg/L) were measured in shallow wells and a stream, respectively. Drahota et al. (2009) determined the processes that caused a release of As into the water and its speciation under various redox conditions. In soils, As was found to be associated mainly with secondary arseniosiderite, pharmacosiderite, Fe oxyhydroxides, and rarely scorodite. Under oxidizing conditions, surface waters were undersaturated with respect to arsenate minerals, which promoted dissolution of secondary arsenates and increased As concentrations up to 300–450 μg/L in the stream and fishpond waters. According to the authors, microbial processes caused the transformation of aqueous As species as well as the mobility of As.

The Kutná Hora (Central Bohemia) is an area characterized by former (mediaeval) silver mining activity. Kralova et al. (2010) determined total element values in soils, i.e. 30 mg/kg As, 1.0 mg/kg Cd, 200 mg/kg Cr, 80 mg/kg Ni, 140 mg/kg Pb, and 200 mg/kg Zn, which exceeded the Czech threshold values by up to 15-, 30-, and 80-fold for zinc, cadmium, and arsenic, respectively. Diversity of vegetation cover (29 species) growing at the contaminated soil close to the former mine was ordinary, without occurrence of metallophytes. The element concentrations in aboveground biomass were low. Transfer factors (ratio of element content in plant and its "pseudo-total" content in soil) varied from 0.0003 to 0.003 for As, 0.001 to 0.174 for Cd, and 0.016 to 0.169 for Zn.

Majzlan et al. (2014) reported findings on extremely As-rich acid mine waters caused by weathering of native arsenic in the sulphide-poor environment of the Svornost mine in Jáchymov. Arsenic was rapidly oxidized to arsenolite, and droplets of liquid on the arsenolite crust had high As concentration (80,000–130,000 mg/L) and pH close to 0. The authors were able to isolate microorganisms on oligotrophic media with pH ~1.5 supplemented with up to 30 mM As(III). These microorganisms were adapted to highly oligotrophic conditions which disabled long-term culturing under laboratory conditions. The extreme conditions make this environment unfavourable for intensive microbial colonization, but the first results of this study showed that certain microorganisms could adapt even to such harsh conditions.

2.2.3 Slovak Republic

In the eastern part of the Slovak Republic, there is a significant source of contamination with As originating from the deposited coal fly ash, located near the village of Poša. The As pollution of the area has been reported since 1995, representing one of the most serious environmental risks in Slovakia (Hiller et al. 2009). There, the water of Kyjov Brook was characterized by a high content of total As ranging from >300 to 11,000 μg/L. Combined results of the column leaching, batch extraction, sequential extraction tests, and mineralogical analysis showed that As mobilization potential from sediments was likely controlled by Fe, Al, and Mn oxides and by pH. Plants overlying the impoundment had As concentrations 10–100 times above those from reference sites.

A similar study was conducted by Jurkovič et al. (2011) at the village of Zemianske Kostolany and 4 km south of a thermal power plant at Novaky, Prievidza district in central Slovakia. Soils at the study area were severely contaminated with arsenic after dam failure of the coal-ash pond. Mean As concentrations of soil samples collected from three sampling depths (0–20, 20–40, and >40 cm) were 173, 155, and 426 μg/g, respectively, exceeding greatly the Dutch intervention threshold.

Flakova et al. (2012) studied arsenic and antimony contamination at the Pezinok mining site (SW Slovak Republic). The highest dissolved As concentrations correspond to mine tailings (up to 90,000 μg/L), and arsenic was present predominately as As(V). Arsenic and antimony are transported by groundwater flow towards the Blatina Creek, where arsenic and antimony are attenuated by dilution and adsorption on ferric iron minerals in stream sediments.

Environmental contamination with As and Sb, caused by past mining activities at Sb mines, is a significant problem in Slovakia. Hiller et al. (2012) investigated environmental effects of five abandoned Sb mines on water, stream sediment, and soil close to residential areas. Mine wastes had up to 5166 mg/kg As, while water contained up to 2150 μg/L As. Leachates from mine wastes contained as much as 8400 μg/L As, suggesting that mine wastes could have a great potential to contaminate the downstream environment.

Drličkova et al. (2013) carried out a study of the growth of maize (*Zea mays* L.), hybrid Valentina, from an old Sb-Au mining area near Pernek in Male Karpaty Mountains. The below- and aboveground tissue As concentration, as well as toxic effect of As, was more prominent in plants grown in heap soil containing considerably less total As than Ochre soil. According to the authors, this paradox could be possibly explained in terms of decreased mobility of As in ochre substrates which are able to adsorb arsenate to Fe-(hydr)oxides. These compounds are able to reduce As concentration in soil solution and hence its bioavailability for plants.

Similarly, Vaculik et al. (2013) investigated selected medicinal plants (*Fragaria vesca*, *Taraxacum officinale*, *Tussilago farfara*, *Plantago major*, *Veronica officinalis*, *Plantago media*, and *Primula elatior*) naturally growing on old mining sites contaminated by As and Sb. Their levels in shoot ranged between 1 and 519 mg/kg for As and 10 and 920 mg/kg for Sb. The authors determined differences in the bioaccumulation of As and Sb as well as in their translocation from root to shoot within the same species growing on different localities. They emphasized that the increased bioaccumulation of As and Sb in biomass of investigated plants might be dangerous for humans when used for traditional medicinal purposes.

In terms of health studies, Ranft et al. (2003) assessed arsenic exposure of a population living in the vicinity of a coal-burning power plant with high arsenic emission in the Prievidza District. In total, 548 spot urine samples were speciated for inorganic As (Asinorg), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and their sum (Assum). There was a significant but weak association between As in soil and urinary Assum ($r = 0.21$, $p < 0.01$). Persons living in the vicinity of the plant had 27% higher Assum values ($p < 0.01$).

2.2.4 Hungary

Lindberg et al. (2006) published results of the study which was the part of a large case-control study of cancer risks in relation to arsenic exposure via drinking water in Central Europe: ASHRAM – Arsenic Health Risk Assessment and Molecular Epidemiology. Study areas included a few counties in Hungary (Bacs, Békés, Csongrad, and Jasz-Nagykun-Szolnok), Romania (Bihor and Arad), and Slovakia (Banska Bystrica and Nitra) with known hotspots of arsenic in drinking water. In total, 520 individuals were investigated by measuring inorganic arsenic and methylated arsenic metabolites in urine. Significantly higher concentrations of arsenic were found in both the water and the urine samples from Hungary compared to Slovakia and Romania. Significant correlation was found between water and urine As. At low water arsenic concentrations, the relative amount of dimethylarsinic acid (DMA) in urine was increased, indicating exposure via food. High body mass index was associated with higher concentrations of arsenic in urine, mostly in the form of DMA. Smokers had significantly higher urinary arsenic concentrations than nonsmokers. According to the authors, exposure to As from food, mainly as DMA, and cigarette smoke, mainly as inorganic arsenic, are major determinants of arsenic exposure at very low concentrations of arsenic in drinking water. Furthermore, Hough et al. (2010) reported their results collected under the auspices of the ASHRAM. The proportions with average lifetime exposure over 50 μg/L varied in the three countries from 1% to 16%. The proportion of population currently exposed to >50 μg/L is now between 0% and 1%, reflecting the mitigation efforts that have been made.

In terms of food safety, Soeroes et al. (2005) carried out arsenic speciation analysis on freshwater farmed fish collected from an area with elevated groundwater As concentrations as well as outside of the area. In the catfish, the accumulated total arsenic (2510–4720 μg/kg) was found mostly in the form of arsenobetaine, confirming that an uptake of As was dominated by their diet. Carp (*Cyprinus carpio*) were cultured in surface lakes with no significant arsenic pollution, containing total As concentrations 62–363 μg/kg.

Since inorganic As can get easily through the placenta, the aim of the study conducted by Rudnai et al. (2014) was to explore the associations between As content of drinking water and prevalence of some congenital anomalies. The results showed an increased risk of congenital heart anomalies among infants whose mothers were exposed to drinking water with arsenic content above 10 μg/L during pregnancy.

2.3 Scandinavia

2.3.1 Finland

In Finland, the 3-year (2004–2007) RAMAS project gathered diverse As information and identified the risk areas from the Tampere-Häme region (SW Finland), where As levels are above Finnish average As concentrations in bedrock and soil. It also provided certain risk management guidelines, mainly from groundwater and health perspectives. The subsequent ASROCKS project (2011–2014) continued the work and focused on guidelines for the rock aggregate and construction industries. Parviainen et al. (2015) published a brief review of the main results of these projects.

Abass et al. (2017) carried out a study under the auspices of the NFBC (Northern Finland Birth Cohort) programme, in order to analyse the blood levels of arsenic (B-As), cadmium (B-Cd), lead (B-Pb), total mercury (B-Hg), and selenium (B-Se) and to correlate them with calcium and haemoglobin (249 NFBC subjects). Among them, 23% of males and 17% of females had B-As levels above the ATSDR (Agency for Toxic Substances and Disease Registry) normal human levels of B-As in unexposed individuals (1.0 μg/L). Arsenic levels were elevated, statistically significantly, among those with lower reindeer, moose, and wildfowl consumptions ($p = 0.018$).

Rintala et al. (2014) reported total and inorganic As levels in long-grain rice and rice-based baby foods on Finnish market. Inorganic arsenic levels in long-grain rice varied from 0.09 to 0.28 mg/kg, and total As levels ranged from 0.11 to 0.65 mg/kg. Total As levels of rice-based baby foods ranged from 0.02 to 0.29 mg/kg. The authors estimated that inorganic arsenic intake from long-grain rice and rice-based baby food in Finland indicates that in every age group, the intake is close to the lowest $BMDL_{0.1}$ value of 0.3 μg/kg bw/day, set by the EFSA.

2.3.2 Sweden

Some 10–15 years ago, Sweden had begun remediation of its many contaminated sites, a process that would cost an estimated SEK 60,000 million (USD 9100 million). Although the risk assessment method, carried out by the Swedish EPA, was driven by health effects, it did not consider actual exposure. Instead, the sites were assessed based on divergence from guideline values. Therefore, Forslund et al. (2010) used an environmental medicine approach that took exposure into account to analyse how cancer risks on and near arsenic-contaminated sites were implicitly valued in the remediation process. The results showed that the level of ambition was high. At 23 contaminated sites, the cost per life saved varied from SEK 287 million to SEK 1,835,000 million, despite conservative calculations that in fact probably underestimated the costs. It was concluded that if environmental health risks were to be reduced, there were probably other areas where economic resources could be used more cost-effectively.

Weathering of mine tailings have resulted in high As concentrations in water (up to 2900 μg/L) and sediment (up to 900 mg/kg) samples around the Adak mine (NW Sweden). Time series-based sediment incubations were set up in the laboratory with contaminated sediments to study the microbial processes involved in transformation and remobilization of As across the sediment-water interface (Routh et al. 2007). The microcosm experiments indicated that microorganisms are capable of surviving in As-rich sediments, reducing As(V) to As(III). A decrease in total As levels in sediments is coupled with an increase in As(III) concentration in the aqueous media.

The results implied that active metabolism was necessary for As(V) reduction. According to the authors, the microorganisms possessed reduction mechanisms that were not necessarily coupled with respiration, but most likely imparted resistance to As toxicity.

Broberg et al. (2014) assessed effects of arsenic on genome-wide DNA methylation in newborns. They studied As metabolite levels in maternal urine of 127 mothers and cord blood of their infants. Urinary arsenic in early gestation was associated with cord blood DNA methylation (Kolmogorov-Smirnov test, P-value<10–15), with more pronounced effects in boys than in girls. Much weaker associations were observed with arsenic exposure in late compared with early gestation. The authors concluded that early prenatal arsenic exposure appeared to decrease DNA methylation in boys. Associations between early exposure and DNA methylation might reflected interference with de novo DNA methylation.

Jacks et al. (2013) conducted a study in northern Sweden where metasediments contain pyrite, pyrrhotite, and arsenopyrite overlain by till which has up to 100 mg/kg As, while sandy sediments may contain 100–500 mg/kg As. The cycling of As in water flora and fauna in wetlands was studied. Ferric reduction occurred in wetlands and groundwater rich in Fe, and As was found to be discharging into ditches, brooks, and streams. Wetland trees and plants showed moderately elevated As levels, and a few species had >2 mg/kg As which is the permissible level in fodder for domestic animals. The only plants with a high content of As were *Equisetum* species (up to 26 mg/kg As). Elevated As levels were found in a limited number of benthic macroinvertebrate samples (1.23–42.1 mg/kg DW). Fish species from polluted streams (pike and brown trout) had normal As levels (0.57–1.84 mg/kg DW).

Jorhem et al. (2008) carried out a survey of the levels of Cd, Pb, and As in different types of rice available on the Swedish retail market. Mean levels were the following: total As 0.20 mg/kg, inorganic As 0.11 mg/kg, Cd 0.024 mg/kg, and Pb 0.004 mg/kg. The authors concluded that in countries where rice was a staple food, it might represented a significant contribution in relation to the provisional tolerable weekly intake for Cd and inorganic As.

2.3.3 Norway

De Gieter et al. (2002) determined As levels in muscle and liver tissue of 25 sea fish and 4 shellfish species from the North Sea. Highest total As concentrations (average >20 mg/kg WW) were found in lemon sole, dogfish, ray, and witch. The same species as well as the other flatfishes contained the highest amounts of toxic As (>0.1 mg/kg WW). Toxic fractions (AsTox/AsT%) above 2% were found in the following six species: sea bass, ling, John Dory, pouting, dab, and brill. The authors pointed out that in the worst-case scenario (drying or smoking of fish when the toxic As level is high, e.g. 0.5 mg/kg WW), the As content of North Sea marine food might reach harmful levels.

Savinov et al. (2003) found highest levels of the most toxic elements Cd and Hg in birds nesting north of Spitsbergen. Extremely high levels of As were detected in tissues of all seabird species collected at colonies in Chernaya Guba (Novaya Zemlya), where nuclear tests were carried out in the 1960s. Generally, levels of all analysed trace elements in the Barents Sea seabirds were similar or lower in comparison with those reported for the same seabird species from the other Arctic areas.

Samples of complete feedingstuffs for fish, and fishmeals from the Norwegian Fish Feed Monitoring Programme in 2003 were analysed for their total arsenic and inorganic arsenic contents (Sloth et al. 2005). Levels of 3.4–8.3 and 0.010–0.061 mg/kg for complete feedingstuffs were found for total As and inorganic As, respectively. The results were in accordance with typical As levels for fish reported in the literature. The data illustrated that fish fed with high levels of total As, but low levels of inorganic As are at risk of being unnecessarily rejected from fish feed markets.

Julshamn et al. (2012) determined contents of total As and inorganic As in fillet samples of Northeast Arctic cod, herring, mackerel, Greenland halibut, tusk, saithe, and Atlantic halibut. The concentrations of total As varied greatly between fish species and ranged from 0.3 to 110 mg/kg WW, while inorganic As was very low (<0.006 mg/kg) in all cases. The authors emphasized that the obtained results questioned the assumptions made by the European Food Safety Authority (EFSA) on the inorganic As level in fish used in the EFSA opinion on arsenic in food.

The study carried out by Julshamn et al. (2013) was one of several baseline studies that would provide basic and reliable information about the contents of undesirable substances in important fish species caught in Norwegian waters. They reported levels of trace metals in muscle and liver samples of more than 800 Northeast Arctic cod caught at 32 sites in the Barents Sea. The highest total As levels were found in cod from its eastern part. Arsenic concentrations varied greatly among individual fish, ranging from 0.3 to 170 mg/kg WW in muscle. According to the authors, such high levels of total As had never been reported previously for any fish. The authors ascribed them to the shrimp in the cod's diet.

2.4 Southern Europe

2.4.1 Italy

Since the pre-Roman Age, southern Tuscany has been an important mining district in Italy. Epithermal deposits of Hg and Sb were intensely exploited until the 1970s. The intensive mining and smelting activities have resulted in huge quantities of waste which, in the absence of any reclamation, still release toxic trace elements in the local environment. Due to the fact that As is a minor but ubiquitous constituent of the epithermal mineral assemblage of those ores, arsenic also contributes to the overall pollution of the mining areas. Baroni et al. (2004) surveyed As contents of soils and higher plants at two former Sb mining areas and an old quarry once used for the ochre extraction. Total As in soil ranged from 5.3 to 2035.3 mg/kg, while soluble and extractable As ranges were 0.01–8.5 and 0.04–35.8 mg/kg, respectively. The highest As contents were found in roots and leaves of *Mentha aquatica* (540 and 216 mg/kg, respectively), and in roots of *Phragmites australis* (688 mg/kg). In general, As in plants was low, especially in crops and most common wild species.

Beni et al. (2011) investigated the effects of As-contaminated irrigation water on *Lactuca sativa* L. cropping. Two different arsenic concentrations, i.e. 25 and 85 μg/L, and two different soils, i.e. sandy and clay loam, were surveyed. They determined the As mobility in different soil fractions, its amount in groundwater, and the phytotoxicity and genotoxicity. Data indicated that at both concentrations in sandy soil, As is partly rapidly leached into the groundwater and partly absorbed by vegetables, being readily available for assimilation by consumption.

Beccaloni et al. (2013) estimated the dietary intake of arsenic, cadmium, lead, and zinc in a small town located in an industrialized area of Sardinia. Spices and herbs showed the highest element concentrations, while the highest median concentrations for other food have been found in pulses for As and Zn (0.142 and 13.03 mg/kg, respectively), in leafy vegetables for Cd (0.147 mg/kg), and in fruits for Pb (0.294 mg/kg). Human health risk assessment was evaluated for three population groups: total population, infants, and children. The authors didn't find the toxicological parameters exceeding reference values in any of the studied populations. The highest estimated intakes were found for Pb and Cd and the lowest ones for Zn and As.

Caporale et al. (2013) studied the influence of compost on the growth of bean plants irrigated with As-contaminated water and its influence on the mobility of As in the soils and the uptake of As. The bean plants exposed to As showed typical phytotoxicity symptoms, but no plants died over the study. Biomass decreased with increasing As concentrations, but the reduction in the biomass was significantly lower with the addition of compost, indicating that the As phytotoxicity was alleviated by the compost. For the same As concentration, the As content of the roots, shoots, and beans decreased with increasing compost added compared to control samples. Most of the As adsorbed by the bean plants accumulated in the roots, while a scant allocation of As occurred in the beans. Hence, the authors concluded that the addition of compost to soils could be an effective means to limit As accumulation in crops from As-contaminated waters.

Rice is comparatively efficient in terms of assimilation of inorganic arsenic (iAs) into its grain, being the dominant source of this element to mankind. Therefore, Sommella et al. (2013) investigated variation of the total arsenic (tAs) and iAs content of Italian rice grain sourced from market outlets according to geographical origin and type. Mean values of tAs concentration on a variety basis ranged from 0.18 to 0.28 mg/kg and from 0.11 to 0.28 mg/kg on the production region basis. Regarding iAs concentration, means ranged from 0.08 to 0.11 mg/kg by variety and from 0.10 to 0.06 mg/kg by region. The authors determined that there was a significant geographical variation for both tAs and iAs.

Soleo et al. (2008) characterized the different sources of exposure to arsenic. They determined urinary excretion of total As, the sum of inorganic As + MMA + DMA, As3, As5, monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and arsenobetaine in 49 workers at a steel foundry, with presumed occupational exposure to As, and 50 subjects from the general population, all males. The results pointed at no evidence of occupational exposure to As. The urinary concentrations of As3, MMA, DMA, the sum of inorganic As + MMA + DMA, and total As were not different between the two groups, while arsenobetaine was significantly higher in control participants compared to workers. The authors concluded that their research had indicated that in populations with a high consumption of seafood characterized by a significant content of As, evidence of a considerable environmental As pollution of coastal/marine aquaculture areas as well as mineral water with a relatively high content of As, minor occupational exposure to As played a negligible role in conditioning the urinary excretion of the different species of As.

2.4.2 Spain

In the area of Riaño-Valdeburón (northern Spain), there are mineral occurrences of As, Sb, Hg, Cu, and occasionally Au and Ag. A few of them have been subjected to intermittent small-scale mining since the nineteenth century. The study carried out by Alvarez et al. (2006) was focused on soil and surface water geochemistry downstream of the Santa Águeda As mine, close to the Riaño reservoir, in the Northeast of León province. There, a water reservoir (catchments of the Esla, Yuso, and Orza Rivers) was constructed for the production of hydraulic energy and drinking water purposes. It receives leachates from polluted soils and spoil heaps from a site where small-scale As mining and smelting operations were active in the first half of the twentieth century. Although total As concentrations in soils reach 23,800 mg/kg and total As values in surface waters reach 890 μg/L, the water flow from the mine catchment has a negligible contribution when compared with the total volume of water inside the dam (0.07%).

Recently, elevated As concentrations in groundwater used for drinking water supplies have been recognized in case of the Madrid Tertiary detrital aquifer. Although natural causes have been suggested as the source of As, the study by Recio-Vazquez et al. (2011) aimed to determine whether an anthropogenic contribution could have been involved too. During the sub-catchment's areas sampling, they found out that many occurrences of arsenopyrite [FeAsS] were artificially outcropped and dumped out, and mining wastes were scattered and exposed to weathering. Several mineral and ground specimens were collected, and it was determined that their content of As was very high (113,702 mg/kg). The authors concluded that the contamination of the area due to old mining activities could release arsenic to Madrid water supplies and suggested that additional decontamination studies were necessary.

Gomez-Gonzalez et al. (2014) conducted an experiment in a shrubland situated in the upper portion of a small sub-catchment of the Guadalix River (Madrid), which feeds into the Madrid Tertiary Detrital Aquifer. They point out that the formation of scorodite leads to the natural attenuation of arsenic in a wide range of environments. However, they questioned the long-term stability of scorodite-rich waste piles. Their results indicate that the deposit behaves as an acute point source of As and confirms the strong association of As(V) with Fe(III) oxide phases. Herewith, the authors emphasize that there is a need to monitor and reclamate As-rich mine deposits.

Almela et al. (2006) determined total arsenic, inorganic arsenic, lead, and cadmium levels in 112 samples of seaweed preparations sold in Spain (seaweed packed in plastic or cardboard box, seaweed in the form of tablets and concentrates, foods containing seaweed, and canned seaweed). The concentration ranges found, expressed in mg/kg, dry weight, were total As (0.031–149), inorganic As (<0.014–117), Pb (<0.050–12.1), and Cd (<0.003–3.55). All the analysed contaminants exceeded legislated values. Particularly, all the samples of *Hizikia fusiformis* exceeded the inorganic As limit established in some countries. According to the authors, the consumption of 3 g/day of the analysed samples could represent up to 15% of the respective tolerable daily intakes (TDI) established by the WHO. They specifically emphasized that the situation was especially alarming for the intake of inorganic As from *Hizikia fusiformis*, which could be three times the TDI established.

It is well-known that there is a positive correlation between rice content and As level in foods. According to Burlo et al. (2012), this is of extraordinary importance for infants below 1 year of age as their diet is very limited, especially in case of celiac disease when affected infants consume only gluten-free products, such as rice or corn. Arsenic contents were found to be significantly higher ($P < 0.001$) in gluten-free infant rice (0.057 mg/kg) than in products with gluten (0.024 mg/kg). Moreover, the authors suggested special precaution in case of preparation of rice-based products at home as arsenic content in Spanish rice was high (>0.3 mg/kg in some cases).

A similar study was conducted by Hernández-Martínez and Navarro-Blasco (2013). They determined levels of total Hg and As in 91 various infant cereals from 10 different Spanish manufacturers. In general, the content of toxic elements (median (Q1; Q3)) found in infant cereals based on conventionally obtained raw materials ($n = 74$, Hg: 2.11 (0.42; 4.58), As: 21.0 (9.4; 50.9) μg/kg) was lower than in cereals produced by organic methods ($n = 17$, Hg: 5.48 (4.54; 7.64), As: 96.3 (87.5; 152.3) μg/kg). The highest As content was found in rice-based cereals. It was calculated that 95% of the organically produced infant cereals and 70% of the conventional gluten-free infant cereals showed an inadmissible risk of arsenic intake. The authors concluded that continued efforts in standardizing routine quality control and the reduction in As levels in infant cereals are urgently needed. Also, they call for relevant legislation to be established and regulated by EC regarding As and HG.

Signes-Pastor et al. (2016a, b) investigated total arsenic and arsenic speciation in rice from the main rice-growing regions of the Iberian Peninsula. The main arsenic species found were inorganic and dimethylarsinic acid. About 26% of commercial rice samples exceeded the permissible As concentration for infant food production as governed by the European Commission.

Medrano et al. (2010) evaluated the association of municipal drinking water arsenic concentrations during the period 1998–2002 with cardiovascular mortality in the population of Spain. Mean municipal drinking water arsenic concentrations ranged from <1 to 118 μg/L. Compared to the overall Spanish population, sex- and age-adjusted mortality rates for cardiovascular (SMR 1.10), coronary (SMR 1.18), and cerebrovascular (SMR 1.04) disease were increased in municipalities with As concentrations in drinking water >10 μg/L.

2.4.3 Portugal

Lousal polymetallic massive sulphide mine is located in the SW Portugal, in the NW region of the Iberian Pyrite Belt, inside of the volcano-sedimentary complex lineament. The Lousal mine is a typical "abandoned mine" with all sorts of problems as a consequence of the cessation of the mining activity and lack of infrastructure maintenance, and heavy metal-enriched tailings have remained at the surface in oxidizing conditions. According to Luís et al. (2011), high concentrations of As occurred within the stream sediments downstream of the tailings sites, up to 817 mg/kg, and acid mine drainage water pH was 1.9–2.9.

In NE Portugal, the Santo António mine is located 3 km northwest of the Penedono village, which was a very important gold and arsenic mining centre in the 1950s. The abandoned waste dumps contain large amounts of arsenic, gold, and silver and medium to great contents of bismuth, copper, lead, manganese, and zinc, while draining waters from tailings have low pH (2.5–4.3), high electrical conductivity, and large concentrations of aluminium, arsenic, sulphate, and other trace elements. According to Madeira et al. (2012), those seepage waters along the dust transported by wind from the tailings, are responsible for the spread of hazardous trace elements, particularly As, to surrounding soils. The mean As concentration in soils in the vicinity of the mine was about 2558 mg/kg. The authors determined the influence of soil amendments (iron oxides, organic matter, and calcium phosphate) on As uptake and translocation by tomato and parsley grown in As-contaminated soil. Results showed that the health risk for adults and adolescents was within acceptable limits with an average weekly intake of 500 g of tomato and 20 g of parsley, although As levels in edible tissues were well above those at uncontaminated control sites.

In a geochemical sampling campaign undertaken by Coelho et al. (2012) in the Panasqueira Mine (Sn-W mineralization) area of central Portugal, an anomalous distribution of several metals and arsenic was identified in various biological samples (blood, urine, hair, and nails from a group of individuals living near the Panasqueira Mine). The results showed elevated levels of As, Cd, Cr, Mn, and Pb as well as elevated potential risk for the health of local residents. Since today the economic exploitation is located in Barroca Grande, Candeias et al. (2014) carried out a study at a S. Francisco de Assis village, located downstream of the Barroca Grande tailings deposit and impoundments, in order to investigate the environmental contamination impact on agricultural and residential soil. Rhizosphere samples, vegetables (*Solanum tuberosum* sava and *Brassica olerácea* L., which constitute an important part of the local human diet), irrigation waters, and road dusts were collected in private residences. The As content in rhizosphere soils exceed 20 times the reference value for agricultural soils (11 mg/kg). The results showed that some edible plants frequently used in the region could be enriched in these metals/metalloids and may represent a serious hazard if consumed. The potatoes tend to have a preferential accumulation in the leaves and roots, while in cabbages most elements had a preferential accumulation in the roots. The inhabitants of S. Francisco de Assis village are probably exposed to some potential health risks through the intake of arsenic, cadmium, and also lead via consuming their vegetables.

The old Mondego Sul uranium mine is located in the western part of the uranium-bearing Beira area, in the Ázere village, near Tábua, Coimbra district. The area belongs to the Central Iberian Zone of the Iberian Massif. The water, stream sediments, and soils in the area were found to be contaminated with U and As (Neiva et al. 2016). Arsenic concentrations were up to 158 μg/L in water, 211 mg/kg in stream sediments, and 223 mg/kg in soils. The authors stated that a restoration of the mining area was necessary to avoid a public hazard.

Marques et al. (2009) investigated the potential of *Rubus ulmifolius*, indigenous to a metal-contaminated site – “Esteiro de Estarreja” – for phytoremediation purposes. The site has a long history of metal contamination. The accumulation of lead, arsenic, and nickel in different sections (roots, stems, and leaves) of the plant was assessed and compared to the metal levels in soil and available fraction. Significant correlations were found among the total levels of Pb and As in soil and levels in plant roots.

Vieira et al. (2011) collected three commonly consumed and commercially valuable fish species (sardine, chub, and horse mackerel) from NE and eastern central Atlantic Ocean in Portuguese waters during 1 year. Maximum mean levels of mercury (0.1715 ± 0.0857 mg/kg, ww) and arsenic (1.139 ± 0.350 mg/kg, ww) were detected in horse mackerel. Based on estimates of noncarcinogenic and carcinogenic health risks, the authors suggested that the analysed species should be consumed moderately due to possible hazard and carcinogenic risks derived from arsenic (in all analysed species) and mercury ingestion (in horse and chub mackerel species).

Marquez-Garcia et al. (2012) analysed the arsenic speciation in soils from São Domingos mine area and found out that arsenate was the major species. The arsenic content and speciation analysis were carried out also in two metal-tolerant species from the area: *Erica andevalensis*, endemic heather from the mining areas of SW Iberian Peninsula, and *Erica australis*, a widely distributed species. The total soil content of As ranged from 194 to 7924 mg/kg, while levels of 1–24.4 mg/k in *E. andevalensis* and 2.7–11.6 mg/kg in *E. australis* were found.

Ereira et al. (2015) sampled sediment, suspended particulate matter (SPM), water and clam *Scrobicularia plana* from a temperate coastal lagoon with anthropogenic impact. Arsenic levels in sediments, SPM, and water presented a spatial concentration gradient. A significant linear regression between arsenic levels in *S. plana* and SPM confirmed that the SPM was the main route for As exposure. Despite the absence of regulatory guidelines, food safety assessment highlighted possible adverse effects of consuming *S. plana* in most contaminated areas.

Signes-Pastor et al. (2016) investigated total arsenic and arsenic speciation in rice over the main rice-growing regions of the Iberian Peninsula. The main arsenic species found were inorganic and dimethylarsinic acid. Samples surveyed were soil, shoots, and field-collected rice grain. Commercial polished rice had the lowest iAs content in Andalusia, Murcia, and Valencia, while Extremadura had the highest As concentrations. About 26% of commercial rice samples exceeded the permissible concentration for infant food production as governed by the European Commission.

2.5 Western Europe

2.5.1 Denmark

Larsen et al. (1998) collected samples of edible mushroom *Laccaria amethystina*, known to accumulate arsenic, from two uncontaminated beech forests, and from the As-contaminated one. Total As values were 23 and 77 µg/g DW in two uncontaminated samples and 1420 µg/g DW in a contaminated sample. The study showed that mushrooms or their associated bacteria, when grown in highly arsenate-contaminated soil (500–800 µg/g), were able to biosynthesize dimethylarsinic acid from arsenic acid in soil. The authors also detected arsenobetaine and trimethylarsine oxide for the first time in *Laccaria amethystina*. Herewith, they recommended not to consume it if collected from contaminated soil due to genotoxic effect of dimethylarsinic acid observed at high doses in animal experiments.

De Gieter et al. (2002) determined levels of As in muscle and liver tissue of 25 sea fish and 4 shellfish species from the North Sea. The highest total As concentrations were found in lemon sole, dogfish, ray, and witch. Their average total As values were above 20 mg/kg WW. The same species as well as the other flatfishes had the highest levels of toxic As (>0.1 mg/kg WW). Toxic fractions (AsTox/AsT%) above 2% were found in sea bass, ling, John Dory, pouting, dab, and brill. It was not observed any preferential concentration in the liver compared to the muscle. The authors emphasized that As content of the North Sea marine food might have reached harmful levels when fish was dried or smoked (0.5 mg/kg WW).

Arsenic occurs naturally in many types of seafood as water- and fat-soluble organoarsenic compounds. According to Taleshi et al. (2010), contrary to water-soluble compounds, the fat-soluble compounds (the so-called arsenolipids) have not been well characterized in the literature. Their paper reported that sashimi-grade tuna fish, with total arsenic content of 5.9 µg/g DW, contained approximately equal quantities of water- and fat-soluble As. The water-soluble As contained predominantly arsenobetaine (>95%) with a trace of dimethylarsinate. The authors isolated and characterized two fat-soluble compounds, which together accounted for about 40% of the lipid-arsenic. This has been the first identification of arsenolipids in commonly consumed seafood.

Epidemiological studies have proved that intake of drinking water with high As levels (>100 µg/L) is associated with risk for cardiovascular diseases. Since studies on lower levels of arsenic have showed inconsistent results, the aim of the study by Monrad et al. (2017) was to investigate the relationship between exposure to low-level As in drinking water and risk of myocardial infarction in Denmark. Arsenic levels in drinking water at baseline addresses ranged from 0.03 to 25.3 μg/L, with the highest concentrations in the Aarhus area. The authors found no overall association between 20-year average concentration of As and risk of myocardial infarction. However, in the Aarhus area, the fourth As quartile (2.21–25.34 μg/L) was associated with an IRR (incidence rate ratios) of 1.48 (95% confidence interval (CI): 1.19–1.83) when compared with the first quartile (0.05–1.83 μg/L). The value of IRR 1.26 (95% CI: 0.89–1.79) was found for ever (versus never) in case of living at an address with 10 μg/L or more arsenic in the drinking water. The authors concluded that their study provides some evidence that even low levels (2–25 μg/L) of As in drinking water might be positively associated with incident of myocardial infarction. However, they found no support for this association at As concentrations below 2 μg/L.

2.5.2 Germany

The dietary intake of arsenic, cadmium, mercury, and lead was studied among young German children with different food consumption behaviour, i.e. own grown foodstuffs vs supermarket products (Wilhelm et al. 2005). The study area comprised an industrialized and a rural area of West Germany. Geometric means of weekly intakes [$\mu g/(kg_{bw} \bullet week)$] were the following: As 1.4, Cd 2.3, Hg 0.16, and Pb 5.3. Geometric mean intake corresponded to the percentage of the provisional tolerable weekly intake (PTWI) as follows: As 9.7%, Cd 32%, Hg 3.3%, and Pb 21%. Arsenic and Hg intake were mainly influenced by fish consumption. The authors pointed out that children from an industrialized area with a substantial food consumption of homegrown vegetables or products from domestic animal products had no increased dietary intake of the analysed elements. Also, health risks due to dietary intakes of As, Cd, Hg, and Pb were low for the children studied.

Floodplain soils of the Elbe river catchment get frequently polluted with metals and arsenic. Among five common floodplain plant species, *Artemisia vulgaris* showed highest concentrations of Cd, Cu, and Hg, As was highest in *Alopecurus pratensis*, while Ni, Pb, and Zn were most elevated in *Phalaris arundinacea* (Overesch et al. 2007). In order to limit harmful transfers into the food chain, the authors suggested that low-lying terraces and flood channels containing highest contamination levels or phytoavailabilities should be excluded from mowing and grazing.

2.5.3 France

Fillol et al. (2010) carried out a cross sectional study to evaluate arsenic exposure of residents living in an area with soil naturally rich in As, through urinary measurements. It was found out that there are significant associations among urinary As concentrations and the consumption of seafood ($p = 0.03$), wine ($p = 0.03$), and beer

(p = 0.001). The paper showed that the population, living in the study area where soil is naturally enriched in As, is not dramatically overexposed to As. Urinary concentrations of As were close to those of general population and were all far below the regulation values for occupational populations.

The French Nutrition and Health Survey was conducted to determine dietary intakes, nutritional status, physical activity, and levels of various biomarkers for environmental chemicals in the French population (Saoudi et al. 2012). In total, 1500 children and 1515 adults were examined in terms of the sum of inorganic arsenic and its two metabolites, monomethylarsonic acid and dimethylarsinic acid, and for the total arsenic. Arsenic levels observed were similar to or lower than those observed in previous national studies conducted in France and other countries. The main sources of inorganic (toxic) arsenic identified were seafood and wine consumption.

Since seafood, especially fish, is considered as a major dietary source of arsenic, the aim of the study conducted by Sirot et al. (2009) was to assess As intake of frequent French seafood consumers and exposure via biomarkers. The average As dietary exposure was found to be 94.7 ± 67.5 μg/kg bw/week in case of females and 77.3 ± 54.6 μg/kg bw/week in case of males ($p < 0.001$), while the inorganic As dietary exposure was found to be 3.34 ± 2.06 μg/kg bw/week and 3.04 ± 1.86 μg/kg bw/week ($p < 0.05$), respectively. According to the authors, even among high consumers of the seafood, it is not the main source of toxic As.

2.5.4 United Kingdom

Since birds of prey forage over large areas, they might be expected to accumulate contaminants. Erry et al. (1999) tested the hypothesis that As levels in raptors from a region with naturally enhanced As levels were higher than those in birds from an uncontaminated part of Britain. Arsenic residues in kestrels were found to be significantly different between the two groups, but this was not the case for other bird species, and the authors ascribed it to both diet and arsenic metabolism.

Arsenic contamination in Cornwall is widespread due to the historic mining of polymetallic ores and the calcination of ores. In areas such as Camborne/Redruth and Hayle in West Cornwall, arsenic values typically exceed 100 mg/kg in topsoils and occasionally in the subsoil. Camm et al. (2004) investigated the dispersion of As from a calciner stack and from fugitive dusts at the New Mill site (Roseworthy, near Camborne, Cornwall) and found levels of total As above 4000 mg/kg. Agricultural disturbance by ploughing and downslope leaching has probably dispersed the As contamination in the soil. Water samples had As concentrations <50 μg/L, indicating relatively low mobility of soil arsenic. However, the authors emphasized that a large reservoir of arsenic could be remobilized if there was a change in ambient conditions.

Rieuwerts et al. (2006) sampled household dust and garden soil from 20 households in the vicinity of an ex-mining site in SW England and from 9 households in a control village. The results showed clearly elevated As levels, up to 486 μg/g in house dusts and 471 μg/g in garden soils, respectively. Arsenic concentrations in all samples from the mining area exceeded the UK Soil Guideline Value (SGV) of 20 μg/g. No significant correlation was observed between garden soil and house dust As concentrations. The most important outcome of the study is the fact that it supports the concerns expressed by previous authors about the significant As contamination in SW England and the potential implications for human health.

2.5.5 Ireland

The study by McGrory et al. (2016) amalgamates readily available national and subnational scale datasets on groundwater As in the Republic of Ireland. Several arsenic databases were integrated and the data modeled using statistical methods appropriate for non-detect data. In addition, geostatistical methods were used to assess principal risk components of elevated arsenic related to lithology, aquifer type, and groundwater vulnerability. For the majority of sampled locations in the study, the As levels in groundwater is below both the Irish GTV value of 7.5 μg/L and the WHO and USEPA value of 10 μg/L. Only a small number of locations exhibit elevated As concentrations due to Silurian and Ordovician metasedimentary formations. The study provides the preliminary steps towards the creation of a national database on Irish groundwater As levels. According to the authors, the presence of regional hotspots of contamination warrant further detailed investigations.

3 Australia

Arsenic is commonly found throughout Australia, and localized As contamination problems have been reported in many of the states and territories. The mining industry has contributed widely to the incidences of arsenic contamination throughout this continent. Not only has the mining of mainly gold deposits enhanced the release of As into the environment but the mining processes associated with gold extraction also left a lasting legacy of an As-contaminated environment.

Up to date, residual arsenic contamination from historical gold mining activity persists in the goldfields region of Victoria where elevated arsenic concentrations have been observed in mine waste and some residential soils, surface, and groundwaters. In 1991, Department of Manufacturing and Industry Development (1991) of Australia reported extremely variable As concentrations in surface and groundwater in many areas of rural Victoria, ranging from <0.001 to 2.83 mg/L. In comparison, surface water from the greater Melbourne region contained As concentrations between <1 and 52 μg/L (DMID 1991). Hinwood et al. (1999) reported a similar range of As concentrations, from 1 to 5000 μg/L, in surface and groundwater of rural Victoria.

However, most Victorian households currently depend on a reticulated water supply, whereas self-extraction from rainwater tanks or from surface or groundwater contributes less than 4%. Study of Hinwood et al. (2003) also reported high variability of arsenic concentrations in drinking water and soil in this region, ranging from below the detection limits to 73 μg/L and from 1.7 to 9900 mg/kg, respectively. Past consumption of contaminated water was possibly even greater, but their study revealed that residents living on the soil of high arsenic content (up to 9900 mg/kg) consume water with arsenic concentrations ranging from below the detection limit to 1.3 μg/L. Contrary, participants consuming drinking water with the highest concentration of arsenic were those living in the area where arsenic concentrations were lowest in the soil.

The small-area ecological study conducted by Pearce et al. (2012) on a population of residents in 61 contiguous statistical local areas in Victoria identified a small but significantly increased risk of all cancers combined, prostate and breast cancers, melanoma, and chronic myeloid leukaemia. Their study, however, revealed that arsenic-contaminated drinking water is unlikely to be the major contributor to arsenic exposures for studied population.

Although mining activities have contributed to the contamination of soil and water primarily in the Western Australia and Victoria, the same can be found in other parts of the Australian territory as well. For instance, in the upper part of the Macleay River catchment, northern New South Wales (NSW), historic mine waste disposal practices of the Hillgrove mineral field, a major producer of gold (Au) and antimony (Sb), have resulted in an As- and Sb-contaminated sediment dispersion plume. This contamination extends few hundred kilometres eastwards to the coastal floodplain at Kempsey, where population density is higher and land use more intense. Due to the production and subsequent redistribution of sediment from the upper catchment, the surface soils of the Macleay River floodplain are enriched with both arsenic (As) and antimony (Sb) (up to 40 mg/kg of both metalloids).

Other mining processes associated with the recovery of rare metals such as titanium also result in the arsenic contamination of groundwater systems. Binning et al. (2001) reported that mining of titanium from sand beds near Newcastle, New South Wales, led to oxidation of arsenopyrite material in the sand beds which subsequently led to an increase in As concentrations up to 30 mg/L in the unconfined aquifer.

Other anthropogenic activities such as agriculture, forestry, and industry have also contaminated soil and water at a localized scale in Australia. Namely, arsenic has been widely used in the agricultural industry, as both a pesticide and herbicide. Industrial activities, such as timber treatment plants and ammonia production processes, also led to occurrences of elevated As levels in surface and groundwater. Throssell and Blessing (2001) reported As concentrations in the range from 0.005 to 220 mg/L in groundwater accidentally contaminated by As solution used in the production of ammonia at Kwinana, Western Australia.

The geological setting combined with an increase in population density and consequently increased water requirements is becoming one of the main reasons for occurrences of elevated arsenic concentrations in groundwater in Australia. Smith and Jankowski (2001) identified elevated concentrations of As (up to 300 μg/L) in groundwater used as a source of drinking water in the small coastal community of Stuarts Point, New South Wales. According to these authors, the source of As contamination of the groundwater from Stuarts Point was due to a number of processes controlling the release of arsenic into the groundwater environment, with the desorption of As from Al hydroxides and As-enriched Fe oxyhydroxides and the oxidation of arsenical pyrites as the dominant one. Similarly, McLean and Jankowski (2001) attributed elevated As concentrations (up to 70 μg/L) in groundwater collected from the lower Namoi River catchment, New South Wales, to natural mobilization of As from within the groundwater environment.

The combination of increasing population density in urban areas and low rainfall increased groundwater abstraction and contributed to the emergence of As enrichment within the Gwelup groundwater management area, several kilometres north of the Perth city centre. Namely, a prolonged drought in Perth is causing the water table to fall in some parts of the metropolitan area to the point where substantial changes in the chemistry of groundwater are taking place, including acidification and the release of As and metals from aquifer sediments. According to study of Appelyard et al. in 2006, groundwater in the Gwelup groundwater management area in Perth has been enriched in As (up to 7000 μg/L) due to the exposure of pyritic sediments caused by reduced rainfall, increased groundwater abstraction for irrigation and water supply, and prolonged dewatering carried out during urban construction activities. Arsenic was initially released into groundwater through the oxidation of arsenian pyrite when sulfidic peaty sediments were dewatered and excavated for the construction of housing estates. These activities caused the pH of shallow groundwater to decline from 6–7 to as low as 2.5 and produced arsenic concentrations of up to 22,000 μg/L in groundwater. Although the pH of groundwater was subsequently moderated (up to 5.5), arsenic concentrations remain high in many areas (up to 800 μg/L), posing an ongoing health risk to residents who use domestic bores for garden watering and other household uses.

According to Appleyard et al. (2006), decline in the water table due to prolonged period of low rainfall, and the disturbance of sulfidic peat soils by dewatering and excavation in the Perth suburb of Stirling, led to widespread acidification of groundwater at the water table in the residential area and contamination of groundwater by arsenic and other metals. The dewatering and peat excavation caused pH values to drop as low as 1.9, resulting in a high concentration of arsenic (up to 7 mg/L), aluminium (up to 290 mg/kg), and iron (up to 1300 mg/kg) in the groundwater. Although acidic water extends 5–10 m below the water table and the deeper groundwater remains unaffected by contamination, the fact that groundwater forms 70% of Perth's total water usage and sulphide-rich peat soils are common in the region brings many people at risk of consuming water contaminated with arsenic.

Historically, much of this arsenic contamination has been isolated due to the small population base of Australia, but the current changing demographics of Australia and an increased concern about the environment put forefront As contamination as an important public issue in this country. Recently, a lot of attention was given to elevated levels of arsenic in food, primarily in rice and rice-related products.

Williams et al. (2006) reported total As (tAs) concentrations in Australian rice in the range from 20 to 40 μg/kg, with a mean of 30 μg/kg (n = 5), whereas Juhasz et al. (2006) reported 189 ± 18 μg/kg of As in Australian long-grain white rice. Rahman et al. (2014) studied total and speciated As in Australian-grown and imported rice on sale in Australia. According to their study, the mean and range of tAs concentrations in Australian-grown rice were 270 μg/kg and 188–438 μg/kg, respectively. The highest tAs was found in organic brown rice (438 ± 23 μg/kg) followed by medium-grain brown rice (287 ± 03 μg/kg) and organic white rice (283 ± 18 μg/kg). It is notable that tAs concentration in the organic brown rice exceeds the FAO/WHO (1985) recommended maximum permissible limit of 300 μg/kg. In general, total As concentrations in Australian-grown rice were higher than in imported rice on sale in Australia, with the exception of Italian Arborio rice. While Asian rice contained mainly inorganic As (iAs; 86–99%), 18–26% of the tAs in Australian-grown rice was dimethylarsinic acid (DMA). Among the Australian-grown rice varieties, the highest concentration of organic arsenic, in the form of dimethylarsinic acid (DMA), was found in organic brown rice (115 ± 02 μg/kg), which was ~26% of the tAs. Since inorganic arsenic presents a significant fraction (about 63%) of tAs in this rice type, Australian organic brown rice may be a matter of human health concern, especially for infants who eat cereals and formulas manufactured from organic brown rice and rice bran and for adults who regularly eat organic brown rice.

Islam et al. (2017) investigated total and inorganic arsenic (As) content in rice and rice-based diets obtained from supermarkets in Adelaide, South Australia, in 2015. Results of their research show that of the 59 rice-based products, 31 (53%) had As higher than the maximum level of 100 μg/kg recommended by European Union (EU) for young children and 13 (22%) samples had As higher than maximum level of 200 μg/kg recommended for adults (EFSA 2014). Arsenic content varied in order rice crackers > baby rice > rice cakes > puffed rice > other rice-based snacks > ready-to-eat rice. Of the six studied categories of rice-based products, except ready-to-eat rice, all others exceeded the value recommended by EU for young children. Even manufacturers recommended servings deliver significant amounts (0.56–6.87 μg) of inorganic As.

4 New Zealand

Similarly to Australia, arsenic presents one of the major national groundwater quality issues in New Zealand. While nitrate contamination is a major issue in shallow groundwater due to numerous anthropogenic sources, naturally elevated concentrations of arsenic, iron, and manganese are found in deeper groundwater. In Canterbury, on the other hand, high arsenic, iron, and manganese concentrations are often encountered in areas of reduced groundwater. In this region, the elevated As, Fe, and Mn levels in groundwater originate from minerals in the aquifer sediments, which are mostly derived from the weathering of greywacke rock. Furthermore, weathering of arsenic-bearing source rocks in the mountains leads to accumulation of arsenic in fine-grained estuarine deposits near the coast. Reduced groundwater conditions make the arsenic more mobile and limit arsenic being adsorbed by iron oxides, which are also soluble in such conditions. Occasionally, high arsenic may originate from old sheep dips or wood treatment plants. Consequently, at a number of sites, mostly in the Woodend and Sefton areas, groundwater exceeds the Provisional Maximum Acceptable Value (PMAV) for arsenic (10 μg/L).

In a review of contaminants in New Zealand drinking water, Davies et al. (2001) identified arsenic concentrations exceeding half-PMAV (5 μg/L) in 70 distribution zones serving a population of approximately 285,000 and those exceeding the PMAV (10 μg/L) in 28 distribution zones serving a population of approximately 21,000. According to these authors, higher-than-average arsenic occurs in greywackes (old ocean sediments), schists (the same sediments transformed with heat and pressure and chemically similar to greywackes), Tertiary volcanics, and some coals and peats. Geochemical interactions between the water and mentioned geological units, i.e. mineral dissolution and weathering, sorption/desorption processes, and leaching, cause an increase in arsenic concentrations in associated groundwater. Rates of weathering, dissolution, and leaching of various major and trace elements are further increased by geothermal heating in this region.

In most of the previous work on arsenic in the Waikato region's water supplies, the focus was on arsenic in surface waters and, in particular, the Waikato River. The Waikato River currently receives a significant load of geothermal arsenic and its concentrations equal twice the drinking water standard before treatment. According to the Environment Waikato Technical Report (2006), arsenic concentrations in the Waikato River decreased over the years due to reducing inputs from the Wairakei Geothermal Power Station. Removal of arsenic during water treatment at Hamilton has also improved, with the efficiency of 90% of arsenic removal attained in 2002, resulting in the average arsenic concentration of Hamilton drinking water in 2002 of about 2.3 μg/L.

5 Africa

High concentrations of arsenic have been recorded in both surface and groundwater in different parts of Africa, including Botswana, Burkina Faso, Ethiopia, Ghana, Morocco, Nigeria, South Africa, Tanzania, Togo, and Zimbabwe. Although the elevated level of arsenic in groundwater has been documented only sporadically across the continent, it represents a serious health threat in many African countries that are already facing multiple challenges related to water quality and shortages.

Ahoulé et al. (2015) summarized findings regarding arsenic distribution and sources in African waters and probable extent of As contamination in Africa. The values quoted in their work show a very large range of values, from 0.02 to 1760 μg/L for groundwater and up to 10,000 μg/L for surface water. According to the African literature, high level of arsenic in surface water is generally related to mining operations, agricultural drains, local sediments, disposal, and incineration of municipal and industrial wastes, whereby mining activities remain the main source of surface water pollution. As for groundwater, arsenic occurrences are generally related to local geology, mineralization, geothermal waters, etc. Since African people rely mainly on local groundwater sources for their water needs, either deep boreholes or shallow wells, the use of such water over a long period of time can lead to fatal consequences.

Botswana is presently one of only a few well-studied cases of geogenic arsenic contamination on the African continent. Huntsman-Mapila et al. (2006) reported elevated levels of arsenic (up to 116 μg/L) in deep groundwater (>70 m) southeast of the Okavango Delta, near the town of Maun, while later study of Huntsman-Mapila et al. in 2011 recorded even higher arsenic concentrations in shallow groundwater underlying the Camp Island (up to 3.2 mg/L). Mladenov et al. (2013) also determined elevated levels of arsenic (up to 180 μg/L) in the groundwater of the Okavango Delta. According to these authors, high arsenic zones in this large arid zone wetland are probably controlled by evapotranspiration and throughflow conditions of the aquifers. High evapotranspiration rates possibly concentrate As and other solutes, while alkaline pH leads to desorption of arsenic or dissolution of arsenic sulphides and formation of thioarsenic complexes which keep arsenic in solution.

In Central Burkina Faso, where surface water availability is limited, groundwater is the main source of water supply for the local communities. In contrast to groundwater availability, groundwater quality has received little attention in Burkina Faso, and the available data indicate that groundwater resources are frequently exposed to various sources of contamination. Few studies, including the one from Smedley et al. in 2007, have reported the occurrence of high arsenic concentrations (>10 μg/L) in groundwater around gold mineralized zones in the north-central region of Burkina Faso. In places, Smedley et al. (2007) found extremely high arsenic concentrations in the groundwater in Burkina Faso (up to 1630 μg/L), while Kusimi and Kusimi (2012) reported a similar range of concentrations (up to 1760 μg/L) in groundwater in Ghana. In both countries, occurrences of high arsenic levels in groundwater were attributed to the underlying geology. According to Bretzler et al. (2017), 14.6% of Burkina Faso rural population uses drinking water from boreholes containing arsenic concentrations higher than the maximum permissible levels (>10 μg/L). The arsenic in this region derives from zones of gold mineralization in Birimian (Lower Proterozoic) volcano-sedimentary rocks and altered sulphide minerals (pyrite, chalcopyrite, arsenopyrite).

Nonetheless, mining activities in Ghana seem to affect more surface waters than the groundwater. Namely, study of Asante et al. (2007) conducted in Tarkwa, capital of Tarkwa-Nsuaem Municipal district (South Ghana) and the centre of gold mining, revealed much higher arsenic concentrations in surface waters (0.5–73 μg/L) compared to the groundwater (<0.1–4 μg/L). A similar observation was reported by Smedley (1996) for Obuasi, another gold mining area in Ghana, where As concentrations ranged from <2 to 175 μg/L and from <2 to 64 μg/L in surface waters and groundwater, respectively. Serfor-Armah et al. (2006) measured even higher arsenic concentrations in the surface waters in Prestea in Ghana, ranging from 150 to 8250 μg/L, whose origin was also linked to mining activities in the area.

Hadzi et al. (2018) assessed the contamination and health risk of heavy metal(loid)s, including arsenic, in selected waterbodies around gold mining areas in Ghana. They found maximum As concentrations (0.23 ± 0.03 mg/L) during a dry season. Compared to the pristine areas encompassed by their study, arsenic concentrations in rivers of the mining areas were two to three orders of magnitude higher. Although there could be other sources accounting for heavy metal(loid) presence in these rivers, anthropogenic activities, primarily mining, are suspected to be the major contributor.

Despite the apparent differences in the concentration of arsenic between surface and groundwater in Ghana, the same high concentrations of arsenic in urine samples among residents of both the mining town of Tarkwa and the town of Accra (devoid of any mining activities) have been reported, suggesting that arsenic contamination has another source, probably food. However, drinking water is still considered a significant pathway of human exposure to arsenic.

In Ethiopia, in the East African Rift Valley, Reimann et al. (2003) found arsenic in the concentration higher than 10 μg/L in 9 out of 138 wells (i.e. 6.5%). For comparison, in Botswana, 6 out of the 20 wells used for the analysis of arsenic showed concentration exceeding the WHO recommended limit (10 μg/L). Studies of Rango et al. (2013) reported high arsenic concentrations in groundwater of the main Ethiopian Rift aquifers, up to 278 μg/L, while surface water of the region exhibited even higher arsenic concentrations (up to 566 μg/L). While elevated levels of arsenic in surface water in Ghana are generally attributed to mining activities, local sediments are considered the main source of arsenic in water in the Rift Valley, Ethiopia.

In Southern Nigeria, study of Asubiojo et al. (1997) reported arsenic levels in the groundwater ranging from 0.4 to 6.88 μg/L, whereas sporadic occurrences of elevated As concentrations (up to 28 μg/L) were reported sporadically near mechanic and panel beaters workshops.

Rezaie-Boroon et al. (2011) have also highlighted high concentrations (6460 μg/L) of arsenic in the surface water in the vicinity of Lomé, Togo, and other big cities. High concentration of arsenic in surface waters near abovementioned cities was attributed to the impact of the effluents from the industrial activity as well as hazardous waste dumping.

Nonetheless, borehole water is a primary source of drinking water supply in many rural parts of Africa, including South Africa. In the Limpopo Province, groundwater accounts for about two-thirds of the total water supply. The elevated arsenic concentrations have been primarily related to bedrock geology and Au mineralization. In places, where As concentrations reach 1000 μg/L in groundwater, cases of severe arsenic poisoning have been reported. Another source of arsenic to groundwater and soil in South Africa is the use of chromated copper arsenate in the preservation of timber. Although arsenic protects the timber from wood-destroying insects, improper disposal of waste from timber plants contaminates the soil and water systems around the plants. Kootbodien et al. (2012) detected high levels of arsenic in school vegetable garden soils as well as in vegetables grown in these gardens in Johannesburg area of South Africa, whereas George and Gqaza (2015) reported elevated arsenic levels (1.5–1.9 mg/kg) in leafy vegetables collected from home gardens in the Eastern Cape Province of South Africa.

6 Russian Federation

About 70% of the population of the Russian Federation receives drinking water from surface water sources, 40% of which do not comply with hygienic standards, of sanitary or aesthetic nature. Permafrost which occupies about 65% of Russian territory (including the whole Arctic and the bulk of Siberia and the Far East) is the main cause of the rare use of groundwater sources in the northern regions of Russia.

In general, the quality of drinking water in Russia was reported to be low due to poor aquifer protection from surface contamination, lack of sanitary protection, and delayed repair, cleaning, and disinfecting of wells and interception ditches. The lack of municipal financing led to serious deterioration of water distribution and sewerage networks, as well as numerous accidents on those networks that led to secondary pollution of drinking water; and instead of systematic preventive maintenance and repair of water supply facilities and networks, problems are usually addressed after the accidents. According to the study of Dudarev et al. (2013), about 28% of the Russian population currently consumes highly mineralized drinking water (1.610 g/L), and about 50 million people in the country (one-third of the population) consume drinking water with enhanced iron content.

The literature on arsenic occurrences in the ground- and drinking water in the territory of Russian Federation is scarce and related to sporadic occurrences of elevated levels of As, associated with both the geogenic and anthropogenic sources. The arsenic limit in drinking water and reservoirs for domestic use recommended by Russian Ministry of Health is 10 μg/L, same as the limit recommended by the World Health Organization.

Among some of the main causes of high arsenic in groundwater in Russia, arsenic-containing ore tailings represent a powerful source of technogenic arsenic. Yurkevich et al. (2012) reported arsenic concentrations substantially greater than the maximum permissible water-use standards (10 μg/L) in drainage waters from tailings at the Belovo (Kemerovo region, Russia) and Karabash (Chelyabinsk region, Russia) ore processing facilities. These drainages enter the Bachat and Sak-Elga Rivers elevating levels of dissolved arsenic up to 21 μg/L and 12 μg/L, respectively, i.e. above values considered safe for use. Further studies identified zones of geochemical anomalies near the Belovo Zn-processing and the Karabash mineral-processing plants where the concentrations of As, Fe, Cu, Zn, Cd, and Pb were two to three orders of magnitude higher compared to the drinking water standards (for rivers) and background levels (for snow).

Chelyabinsk and its region are nowadays one of the most polluted subjects of the Russian Federation, whereas Karabash is considered as one of the most polluted cities in the world. The high rate of pollution in this city occurs due to the presence of the copper smelter, contributing also to an increased As emissions into the environment. As previously mentioned, toxic elements migrate out of numerous tailing dumps with drainage streams that discharge into the nearest rivers and also seep into groundwater. Concentrations of dissolved metals, As and Sb, in drainage waters and influenced rivers often exceed drinking water standards and background levels by one to four orders of magnitude.

In turn, as confirmed by studies of Gilmundinov et al. (2014), people living in Chelyabinsk area were characterized by different health problems like impaired nervous and haematopoietic systems functioning in children and a high number of pregnancy complications, premature births, and neonatal morbidity. Study of Skalny et al. (2016) has shown that whole blood As level in children living in Karabash significantly exceeds that in two other cities of Chelyabinsk region, Varna and Tomino by 69% and 57%, respectively. In particular, hair As in children living in As-polluted region was nearly 34-fold higher as compared to the respective values from Varna and Tomino.

High levels of arsenic in groundwater associated with mine tailings were also registered by Bortnikova et al. (2018) in the vicinity of the Komsomolsk and Berikul gold deposit, located in the Kemerovo region. While most of the element (Fe, Pb, Cd, Cu, Zn, Se, As, Sb, etc.) concentrations in the Komsomolsk tailings pond (pH ~8) do not exceed the maximum permissible concentrations (MPC), the latter does not apply to arsenic and antimony, whose concentrations exceed the MPC by factors of 21 and 170 on average, respectively. The element concentrations in the Berikul ponds are even higher than those at the Komsomolsk tailings pond. The ponds that formed on the Berikul mine tailings have acidic (pH ~2) and extra-mineralized solutions (up to 100 g/L) with extremely high As concentrations for any type of water worldwide influenced by the mining industry, from 10^4 to 10^7 μg/L. Surface drainage from the tailings enters the Voskresenka River and the concentrations of As (~8 μg/L) in the river water approach the MPCs established by the Russian Ministry of Health (10 μg/L). According to Bortnikova et al. (2018), the uncontrolled leakage of acidic and highly mineralized solutions through a natural geological fault into groundwater horizons causes groundwater contamination. The latter was confirmed by increased arsenic concentrations in the water from a well located near the fault (up to 89 μg/L).

For the European part of Russia, on the other hand, there are no reports of groundwater contamination with arsenic. Salminen et al. (2004) observed elevated concentrations of arsenic in surface waters of the Barents region. However, the risk of geogenic groundwater contamination to human health in the Barents region is probably very small since people do not depend on groundwater as a source of drinking water.

Similarly to the Barents region, the geological setting is responsible for elevated levels of arsenic in groundwater in Dagestan. Namely, regional pollution of fresh groundwater with arsenic was attributed by Kurbanova et al. (2013) to assemblages of arsenic minerals in some sandy-clayey beds in contact with productive horizons. Intensive exploitation of artesian waters and related activation of the groundwater movement have led to an increase in heat and mass exchange between fluids and mineral particles of rocks, which also facilitated the increase in arsenic concentration in associate groundwater. In places, arsenic in the groundwater exceeds 40 times the WHO limit. Moreover, unlike the Barents region, 65% of the need for public water supply in Dagestan is provided by artesian groundwater.

Elevated levels of arsenic are also found in river waters nearby geothermal fields. One such occurrence was described by Ilgen et al. (2011) for Falshivaia River, situated within the Mutnovsky geothermal region on the Kamchatka peninsula. This high-temperature field is used for electricity production, whereby the spent fluids, containing elevated concentrations of arsenic (up to 9.3 mg/L), are discharged into near-surface environments. Fortunately, the extent of elevated arsenic concentrations in surface water is limited by adsorption to the bottom sediment and dilution, and geothermal waste fluids released in the river create only a localized area of arsenic contamination. However, one of the wells was the subject of hydrothermal explosions in 2003–2004 and, as reported by Melnikov (2004), has been freely discharging hot fluid (that enters the Falshivaia River) since then.

According to Zakharova et al. (2002), fertilizer industry plants, and particularly the resulting solid waste storage areas, represent one of the main potential sources of environmental contamination in Russia with regard to arsenic. Built in the 1950–1960s, without necessary technical measures for prevention of environmental pollution, solid waste from fertilizer plants is neither processed nor treated in Russia but dumped for storage. Consequently, soils in areas near fertilizer industry plants often contain elevated levels of arsenic, which is unfortunately reflected further in elevated arsenic levels in cultures grown on these soils, as well as in the groundwater of that area. Total arsenic content in soils around the Voskresensky phosphorus fertilizer plant in the Moscow Region ranged from 0.51 to 1.65 mg/kg, while plants grown on these soils (fruits, vegetables, grains) contained from 0.41 to 1.32 mg/kg of total arsenic. The health risk assessment study conducted by Zakharova et al. (2002) revealed that the arsenic exposure pathways through "ingestion of meat" and "inhalation (indoor/outdoor)" pose a negligible health risk, while arsenic exposure pathways through "ingestion of agricultural products", "groundwater uptake", and a minor extent "dermal contact" and "direct soil ingestion" appeared significant.

7 Central, Western, and Far East Asia

The water system of the Aral Sea Drainage Basin covers the main part of Central Asia. Spreading of persistent pollutants in this spatially extensive water system was investigated by Törnqvist et al. (2011). Overexploitation of water caused a significant lowering of the river discharge into the Aral Sea, making groundwater flows increasingly important for the overall water budget. Agricultural and industrial sources distributed throughout the water system area are considered as the main sources of pollutants, including arsenic, producing a cumulative health hazard in the downstream surface waters. The high spatial variability of concentrations of As in the river water is considered to result from its local presence in the top soil of the agricultural fields.

7.1 Iran

The arsenic-related groundwater problems in Iran are mostly from naturally occurring sources. Barati et al. (2010) found that in drinking water sources of 21 out of the 530 studied villages from cities Qorveh and Bijar, the level of As (and Cd and Se) exceeded the WHO or the National Standard limits. The concentration of arsenic in the drinking water ranged from 42 to 1500 μg/L, and signs of chronic arsenical poisoning were found in 180 of 587 investigated participants from the affected areas (Mee's line, keratosis, and pigment disorders). A strong linear relationship between arsenic exposure and occurrence of multi-chronic arsenical poisoning was established.

Keshavarzi et al. (2011) investigated the elevated As content in the groundwater of the Kurdistan and West Azerbaijan provinces in the western Iran, the main sources of drinking water. The travertine springs, used for bathing, were also studied as a possible source of arsenic in groundwater. The total arsenic in travertine springs ranged from 212 to 987 μg/L and in the groundwater from 0.4 to 689 μg/L. Arsenite was the dominant arsenic species in the travertine spring (68.2–98.9%). The geochemical investigation confirmed that the travertine springs, belonging to a hydrothermal system related to volcanic setting of the investigated area, was the main source controlling arsenic concentration in the groundwater. Further investigation focused on the occurrence and distribution of As in other environmental samples from this area. Specifically, in addition to drinking water, the agricultural soil, the alfalfa hay used for sheep and blood and wool samples from sheep were investigated by Keshavarzi et al. (2015). Sampling was performed in the Ebrahim-abad and Babanazar villages in the Kurdistan province (western Iran). Increased levels of As were found in all investigated samples. The total As concentrations ranged from 119 to 310 μg/L in the drinking water, 46.7–819 mg/kg in soil, 1.90–6.90 mg/kg in vegetation, 1.56–10.8 mg/kg in the sheep's wool, and 86.3–656 μg/L in the blood samples. The most probable source of As in the sheep samples were the drinking water and plants used for their feeding. The signs of long-term exposure to inorganic As, liver damage and anaemia, were observed in sheep. The obtained results raise concern about possible human exposure to increased arsenic levels through the food chain.

The Sahand region reservoir in the north-western Iran (East Azerbaijan province) is an important reservoir of drinking water for the region, as well as water used for industrial and agricultural purposes. Mosaferi et al. (2017) found elevated concentrations of arsenic (up to 1440 μg/L and a mean concentration 172 μg/L) in the water basin and dam. The contamination is especially significant in the Almalu River and inside the Sahand reservoir. Regional geological formations and volcanic activities are considered as the main sources of the natural genesis of arsenic in the study area.

The canned tuna fish in Iran as a possible source of human exposure to arsenic was studied by Rahmani et al. (2018). A review and a meta-analysis of metal concentrations were performed and carcinogenic risks were evaluated. While concentrations of As were below the recommended limits, according to the Incremental

Lifetime Cancer Risk (ILCR) for As (3.21E-5 in adults and 4.18E-5 in children), it was concluded that adults and children, consuming canned tuna fish in Iran, have a carcinogenic risk due to As.

As a main pistachio producing country, water and five commercial pistachio cultivars from four geographical regions of Iran were analysed with respect to arsenic and other heavy metals by Taghizadeh et al. (2017). The infield metal content in soil showed good correlation with that of pistachio. The highest level of arsenic was determined in the Kaleghoochi cultivar (mean concentration 1.963 ± 0.005 mg/kg) and Sarakhs region. However, the pistachio samples were found to be safe for consumption.

Additional information on arsenic concentration in various food products was provided by Hashemi et al. (2017) in a review of 40 studies investigating level of heavy metals contamination in food in Iran. Kelishadi et al. (2018) conducted a randomized 8-week clinical trial with the aim to analyse human milk with respect to several metals, including arsenic, and investigated influence of the jujube fruit consumption in reducing the concentration of the investigated metals. The study included 40 postpartum mothers in Isfahan, which is the second largest and polluted city in Iran. The mean (standard deviation) concentrations of arsenic were 1.23 (0.63) μg/L, while its concentration declined in both groups, as for other metals. The consumption of jujube fruit exhibited no significant change on the arsenic level.

7.2 Kuwait

Seafood is an important part of diet in the Arabian Gulf countries. Husain et al. (2017) studied the speciation of As in fish, shrimp, and crab in 578 samples of commonly consumed seafood, of 15 different species, from the main fish markets in Kuwait. The mean daily intake of inorganic As through fish consumption was 0.058 μg/kg/day, and the 95th percentile was 0.15 μg/kg/day. While the mean intake level did not exceed the incremental lifetime cancer risk (ILCR) at 1 × 10–4, the 95th percentile of inorganic As intake showed an ILCR of 2.7 × 10–4. A higher mean intake of inorganic As was estimated for the Kuwaiti children (aged 6–12 years), 0.10 μg/kg/day with an ILCR of 1 × 10–4. The hamour fish (*Epinephelus coioides*) was found to be the main source of inorganic As intake. Arsenobetaine was the dominant As species in the tissues of all seafood samples.

7.3 Oman

The concentrations of arsenic in the marine biota (fish and various bivalves) and coastal sediment from the Gulf and Gulf of Oman (Bahrain, Oman, Qatar, and the United Arab Emirates (UAE)) were investigated by deMora et al. (2004). In the investigated sediment samples concentrations of As were low (0.7–9.6 μg/g).

However, high concentrations of As were measured in clams and pen shells, 156 µg/g and 153 µg/g, respectively. The As concentrations in the muscle of the orange spotted grouper *(Epinephelus coioides*, hamour) and the spangled emperor (*Lethrinus nebulosus*, sheiry) varied between 0.83–14.4 and 2.5–10 µg/g, respectively.

7.4 Arabian Gulf

Kosanovic et al. (2007) analysed life essential and toxic elements, including As, in liver and muscle samples of red spot emperor (*Lethrinus lentjan*) from three different locations of the Arabian Gulf Coast. Despite the determined increased content of metals in highly industrial areas, the values did not exceed permitted levels, and fish was considered safe for human consumption.

Levels of total arsenic and arsenic species in marine biota (clams, pearl oyster, cuttlefish, shrimp, and seven commercially important finfish species) in the western Arabian Gulf were analysed by Krishnakumar et al. (2016). The total As concentrations in bivalves ranged from 16 to 118 mg/kg, dry weight, but the inorganic As contributed on average less than 0.8% of the total As, while arsenobetaine formed around 58%. In the remaining seafood (cuttlefish, shrimp, and finfish), the total As concentrations ranged from 11 to 134 mg/kg, dry weight, and the inorganic As and arsenobetaine contributed on average 0.03% and 81% of the total As, respectively. No significant relationship was found between tissue concentrations of the total and the inorganic As in the investigated samples.

7.5 South Korea

The Gubong mine, once among the largest Au-Ag mines in Korea, was the source of arsenic contamination for the surrounding area. Woo and Choi (2001) analysed surface water from the nearby Guryong-chun stream, groundwater from domestic wells tapped into the floodplain deposits along the stream and seepage from the mining wastes. In said waters, the levels of As, Cd, and Mn exceeded the drinking water guidelines of WHO, and the highest concentration of As, 0.167 mg/L, was determined in the floodplain area. The source of arsenic in the water was arsenopyrite, and its concentration was controlled through adsorption-desorption processes with iron oxyhydroxides and solubility of carbonate minerals and is strongly pH dependant. The arsenic level in surface water reflected its concentration in the stream sediments.

Hong et al. (2018) studied the speciation of arsenic in water, suspended particles, zooplankton, sediments, and sediment porewater from the freshwater and saltwater region of the Youngsan River Estuary, in South Korea. The freshwater samples showed significantly lower values of arsenic (mean concentration 1.5 µg/L) compared to the saltwater (mean concentration 5.2 μg/L), but the contrary was found for suspended particles. The major form in water and particle samples was As(V). The results suggested that direct consumption through the food web plays a considerable role in the bioaccumulation of As in the zooplankton, with As(V) and As(III) as the dominant forms. However, the levels of As in the Youngsan River Estuary did not exceed the tolerable levels of ecotoxicological risk.

Hong et al. (2014) investigated water, sediment, and biota in the Pohang City area significantly influenced by the surrounding industry. Arsenic was found in all investigated aquatic organisms, with largest mean concentration determined in crab, than bivalves, shrimps, and gastropods, while fishes exhibited the lowest concentrations. It was found that the concentrations of As in the investigated biota, especially in fishes, and filter-feeders, were dependent on its concentration in the water. The bioaccumulation factors suggested, however, that As does not biomagnify in either freshwater or marine food webs. Arsenobetaine was the dominant form in fishes, bivalves, crabs, and shrimps and As(III) in the freshwater snails.

Jung et al. (2018) investigated arsenic contents in different types of rice commonly consumed in Korea (white, brown, black, and waxy rice) and microwavable ready-to-eat rice products. Mean content of inorganic As in the ready-to-eat rice products was 59 μg/kg (dry weight basis), with the range of 20–131 μg/kg. While in the investigated ready-to-eat rice products inorganic As was below the legal maximum level (200 μg/kg) for adults, 17% of products was not appropriate for the infant and young children foods (the inorganic As maximum level 100 μg/kg set by European Union). In the white (polished) rice, the determined mean value of inorganic As was 65 μg/kg, with the range 33–120 μg/kg, and among 51 different samples, two contained inorganic As over 100 μg/kg. The mean inorganic As content in the brown rice was 109 μg/kg, with the range 67–156 μg/kg, and 70% of samples were found not suitable for production of foods for infants and young children. The non-polished brown rice contained significantly higher content of inorganic As than the polished rice. The mean inorganic As content in the unpolished black rice was 91 μg/kg, with the range of 22–148 μg/kg, and 5 out of 14 tested black rice samples had inorganic As level over 100 μg/kg. Brown and black rice showed significantly higher quantity of inorganic As compared to the polished non-waxy white rice and polished waxy rice. The mean inorganic As content in the polished waxy rice was 66 μg/kg, with the range 46–85 μg/kg. None of the waxy rice samples contained over 100 μg/kg of inorganic As. On the other hand, brown and black rice contained significantly higher content of inorganic As than white rice and waxy rice.

7.6 Japan

Sources of arsenic in rivers of Japan are mostly natural, resulting from geothermal activities and dissolution from soil and sediment. Miyashita et al. (2009) investigated levels of arsenic in water and biological samples of the Hayakawa River (Kanagawa, Japan), where it is delivered from hot springs at Mt. Hakone. Arsenate prevailed in the hot spring water, river water, and the water bug from the river, while oxo-arsenosugar-glycerol and/or oxo-arsenosugar-phosphate were determined in the green macroalgae, crustaceans, and several fish samples. Arsenobetaine was the dominant form in the crustaceans and fish. The concentration of arsenic in the hot spring water was 750 μg/L and in the river water 17 μg/L. The highest level of arsenic in the biological samples was determined in the water bug and the green macroalga, 18,000 μg/kg and 18,000 μg/kg, dry weight, respectively. In the crustacean and fish muscle tissues, concentrations were 2600 ± 90 μg/kg and 150–2100 μg/kg, dry weight, respectively.

Naturally occurring dissolution from soil caused elevated levels of arsenic in the groundwater in the southern Fukuoka Prefecture, as reported by Kondo et al. (1999). Of the investigated 67 samples, in 29 the arsenic levels exceeded the established standard for drinking water, e.g. 0.01 mg/L, with the maximum determined concentration of 0.293 mg/L.

Seafood and rice are among the most investigated dietary products for their arsenic content. Hirata et al. (2011) analysed fish and prawn from Lake Biwa, a source of drinking water for the Kinki area in central Japan. In 2007 a mass mortality event of the endemic fish Isaza (*Gymnogobius isaza*) and the lake prawn (*Palaemon paucidens*) occurred in the lake. The authors found higher mean levels of arsenic and manganese, in the affected biological samples compared to fresh samples from the lake.

Rice, an important part of daily diet in Japan, is especially efficient in assimilation of arsenic. Signes-Pastor et al. (2009) studied total arsenic and arsenic speciation in rice and rice products (misos, syrups, amazake, barley, rice, and millet). The results showed higher content of inorganic arsenic in the investigated rice products, compared to barley and millet. Most of the total arsenic in rice products was inorganic (63–83%). The authors calculated that consumption of these products on regular basis could reach up to 23% of the provisional tolerable daily intake of arsenic, set by the WHO. Sun et al. (2009) reported concentrations of arsenic in the range from 0.14 to 0.28 mg/kg in 40 of the investigated rice products. Liquid rice products (oil, vinegar) and rice milk had the lowest concentration of As, even though higher than the water standard of 0.01 mg/L. However, the authors highlight that while the vinegar and oil contribute small part of the dietary intake, rice milk, as a beverage, could have a more significant contribution to the dietary intake of arsenic. Solid rice products contained higher levels of arsenic, and the highest were determined in the soil rice crackers. Oguri et al. (2014) found inorganic arsenic in 9 out of 19 food composites, prepared from products from the Shizuoka city in Japan. Source of the highest daily intake were cereals (13 μg/person/day) and algae (5.7 μg/person/day). Rice and hijiki were found to contribute most to the total daily inorganic arsenic intake by Japanese population, which is estimated to be 21 μg/person/day.

A group of arsenolipids was also found to exhibit negative effects on the human health. Their level in 17 food composites prepared from 152 food items from the Shizuoka city marketplace was investigated by Amin et al. (2018). The study confirmed marine food (algae, fish, and shellfish) as a predominant source of arsenolipids. Yorifuji et al. (2017) investigated health issues of survivors of arsenic poisoning by contaminated milk powder in infancy. The authors found decreased height in the exposed individuals as well as higher mean serum concentration of alkaline phosphatase (ALP).

7.7 Polynesia

Speciation of arsenic compounds in marine fish and shellfish from the two islands of the US territory of American Samoa, Tutuila and Ofu (South Pacific), showed only a minor fraction of inorganic arsenic, as found by Peshut et al. (2008). The concentrations of the total arsenic ranged from 0.235 to 98.2 μg/g, while the inorganic As was below detection limit in majority of samples and, if detectable, ranged from 0.0096 to 0.244 μg/g. The inorganic arsenic comprised less than 0.5% of the total arsenic, except for the few samples of molluscs in which inorganic arsenic ranged from 1% to 5%. In addition, Peshut et al. (2008) found no indications of biomagnification or bioaccumulation trends of arsenic in the investigated biota samples. The authors concluded that total arsenic is not a good indication of the possible arsenic toxicity for humans, highlighting the necessity of speciation analysis in these assessments.

8 Conclusion

Local geology and decades of mining activity, combined with increasing population density and increased water requirements, are the main reasons for the rise in arsenic concentration in surface water as well as groundwater, not only in Australia but also in Russian Federation and some African countries. Regardless of the origin of arsenic in drinking water, arsenic-contaminated water is usually the biggest contributor to total arsenic exposure in population of these regions. Additionally, rice as an agricultural crop that may contain elevated arsenic concentrations when grown on soils enriched with this element presents a staple food for a large part of the population in most of the developing countries in sub-Saharan Africa as well as in many Asian countries. Although the scarcity of data precludes a broader image on As contamination of drinking water and food products in the mentioned regions, reported figures emphasize the necessity of further research. In European countries, several regional hotspots of As contamination are mostly related to geogenic sources associated with bedrock lithology. Most notable is the case of the Pannonian Basin (Hungary, Serbia, and Romania), where more than 600,000 residents are at risk of drinking water containing high As concentrations. Other regions threatened by waterborne As include Czech Republic, Croatia, Finland, Greece, Italy, Spain, and Turkey. European research has indicated that there are large natural variations in As distribution in the environment and that geochemical maps at a variety of scales should be provided in the near future.

References

Abass K, Koiranen M, Mazej D et al (2017) Arsenic, cadmium, lead and mercury levels in blood of Finnish adults and their relation to diet, lifestyle habits and sociodemographic variables. Environ Sci Pollut Res 24:1347–1362

Ahoulé DG, Lalanne F, Mendret J, Brosillon S, Maïga AH (2015) Arsenic in African waters: a review. Water Air Soil Pollut 226:302. https://doi.org/10.1007/s11270-015-2558-4

Alderton D, Serafimovski T, Burnset L et al (2014) Distribution and mobility of arsenic and antimony at mine sites in FYR Macedonia. Carpath J Earth Environ 9:43–56

Almela C, Clemente J, Velez D et al (2006) Total arsenic, inorganic arsenic, lead and cadmium contents in edible seaweed sold in Spain. Food Chem Toxicol 44:1901–1908

Aloupi M, Angelidis MO, Gavriil AM et al (2009) Influence of geology on arsenic concentrations in ground and surface water in central Lesvos, Greece. Environ Monit Assess 151:383–396

Alvarez R, Ordonez A, Loredo J (2006) Geochemical assessment of an arsenic mine adjacent to a water reservoir (Leon, Spain). Environ Geol 50:873–884

Amin MHA, Xiong C, Glabonjat RA, Francesconi KA, Oguri T, Yoshinaga J (2018) Estimation of daily intake of arsenolipids in Japan based on a market basket survey. Food Chem Toxicol 118:245–225

Appleyard SJ, Angeloni J, Watkins R (2006) Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia. Appl Geochem 21:83–97

Asante KA, Agusa T, Subramanian A, Ansa-Asare OD, Biney CA, Tanabe S (2007) Contamination status of arsenic and other trace elements in drinking water and residents from Tarkwa, a historic mining township in Ghana. Chemosphere 66(8):1513–1522

Asubiojo OI, Nkono NA, Ogunsua AO, Oluwole AF, Ward NI, Akanle OA, Spyrou NM (1997) Trace elements in drinking and groundwater samples in Southern Nigeria. Sci Total Environ 208:1–8

Baba A, Sözbilir H (2012) Source of arsenic based on geological and hydrogeochemical properties of geothermal systems in Western Turkey. Chem Geol 334:364–377

Barati AH, Maleki A, Alasvand M (2010) Multi-trace elements level in drinking water and the prevalence of multi-chronic arsenical poisoning in residents in the west area of Iran. Sci Total Environ 408:1523–1529

Baroni F, Boscagli A, Di Lella LA et al (2004) Arsenic in soil and vegetation of contaminated areas in southern Tuscany (Italy). J Geochem Explor 81:1–14

Beccaloni E, Vanni F, Beccaloni M et al (2013) Concentrations of arsenic, cadmium, lead and zinc in homegrown vegetables and fruits: estimated intake by population in an industrialized area of Sardinia, Italy. Microchem J 107:190–195

Bełdowski J, Szubska M, Emelyanov E et al (2015) Arsenic concentrations in Baltic Sea sediments close to chemical munitions dumpsites. Deep-Sea Res II 128:114–122

Beni C, Marconi S, Boccia P (2011) Use of arsenic contaminated irrigation water for lettuce cropping: effects on soil, groundwater, and vegetal. Biol Trace Elem Res 143:518–529

Binning P, Naidu R, Hettipathirana T (2001) Determining the impact of high iron and arsenic concentrations caused by mining induced oxidation of an unconfined aquifer. In: Arsenic in the Asia-Pacific Region Abstracts; Adelaide, South Australia, November 2001, CSIRO Land and Water, pp 34–36

Bloom MS, Neamtiu IA, Surdu S et al (2016) Low level arsenic contaminated water consumption and birth outcomes in Romania—an exploratory study. Reprod Toxicol 59:8–16

Bortnikova S, Olenchenko V, Gaskova O, Yurkevicha N, Abrosimova N, Shevko E, Edelev A, Korneeva T, Provornaya I, Eder L (2018) Characterization of a gold extraction plant environment in assessing the hazardous nature of accumulated wastes (Kemerovo region, Russia). Appl Geochem 93:145–157. https://doi.org/10.1016/j.apgeochem.2018.04.009

Bošnjak Z, Ćavar S, Klapec T et al (2008) Selected markers of cardiovascular disease in a population exposed to arsenic from drinking water. Environ Toxicol Pharmacol 26:181–186

Bretzler A, Lalanne F, Nikiema J, Podgorski J, Pfenninger N, Berg M, Schirmer M (2017) Groundwater arsenic contamination in Burkina Faso, West Africa: predicting and verifying regions at risk. Sci Total Environ 584–585:958–970

Broberg K, Ahmed S, Engström K et al (2014) Arsenic exposure in early pregnancy alters genome-wide DNA methylation in cord blood, particularly in boys. J Dev Orig Health Dis 5:288–298

Burlo F, Ramırez-Gandolfo A, Signes-Pastor AJ et al (2012) Arsenic contents in Spanish infant rice, pureed infant foods, and rice. J Food Sci 77:T15–T19

Butts CD, Bloom MS, Neamtiu IA et al (2015) A pilot study of low-moderate drinking water arsenic contamination and chronic diseases among reproductive age women in Timiş County, Romania. Environ Toxicol Pharmacol 40:1001–1004

Camm GS, Glass HJ, Bryce DW et al (2004) Characterisation of a mining-related arsenic-contaminated site, Cornwall, UK. J Geochem Explor 82:1–15

Candeias C, Melo R, Ávila PF et al (2014) Heavy metal pollution in mine–soil–plant system in S. Francisco de Assis – Panasqueira mine (Portugal). Appl Geochem 44:12–26

Caporale AG, Pigna M, Sommella A et al (2013) Influence of compost on the mobility of arsenic in soil and its uptake by bean plants (*Phaseolus vulgaris* L.) irrigated with arsenite contaminated water. J Environ Manag 128:837–843

Casentini B, Hug SJ, Nikolaidis NP (2011) Arsenic accumulation in irrigated agricultural soils in Northern Greece. Sci Total Environ 409:4802–4810

Ćavar S, Klapec T, Jurišić Grubešić R et al (2005) High exposure to arsenic from drinking water at several localities in eastern Croatia. Sci Total Environ 339:277–282

Christodoulidou M, Charalambous C, Aletrari M et al (2012) Arsenic concentrations in groundwaters of Cyprus. J Hydrol 468–469:94–100

Coelho P, Costa S, Silva S et al (2012) Metal(loid) levels in biological matrices from human populations exposed to mining contamination – Panasqueira Mine (Portugal). J Toxicol Environ Health A 75:893–908

Dangić A (2007) Arsenic in surface- and groundwater in central parts of the Balkan Peninsula (SE Europe). In: Bhattacharya P, Mukherjee AB, Bundschuh J et al (eds) Arsenic in soil and groundwater environment, Trace metals and other contaminants in the environment, vol 9. Elsevier, Amsterdam, pp 127–156

Davies H, Nokes C, Ritchie J (2001) A report on the chemical quality of New Zealand's community drinking water supplies, Report for the Ministry of Health. Institute of Environmental Science and Research Ltd, Christchurch

De Gieter M, Leermakers M, Van Ryssen R et al (2002) Total and toxic arsenic levels in north sea fish. Arch Environ Contam Toxicol 43:406–417

de Mora S, Fowler SW, Wyse E, Azemard S (2004) Distribution of heavy metals in marine bivalves, fish and coastal sediments in the Gulf and Gulf of Oman. Mar Pollut Bull 49:410–424

DMID (Department of Manufacturing and Industry Development) (1991) Arsenic in the environment. Stage 1 Report Natural Systems Research Environmental Consultants for Department of Manufacturing and Industry Development, Victoria: Australia, February 1991

Drahota P, Rohovec J, Filippi M et al (2009) Mineralogical and geochemical controls of arsenic speciation and mobility under different redox conditions in soil, sediment and water at the Mokrsko-West gold deposit, Czech Republic. Sci Total Environ 407:3372–3384

Drewniak L, Styczek A, Majder-Lopatka M et al (2008) Bacteria, hypertolerant to arsenic in the rocks of an ancient gold mine, and their potential role in dissemination of arsenic pollution. Environ Pollut 156:1069–1074

Drličkova G, Vaculık M, Matejkovic P et al (2013) Bioavailability and toxicity of arsenic in maize (*Zea mays* L.) grown in contaminated soils. Bull Environ Contam Toxicol 91:235–239

Dudarev AA, Dushkina EV, Sladkova YN, Alloyarov PR, Chupakhin VS, Dorofeyev VM, Kolesnikova TA, Fridman KB, Evengard B, Nilsson LM (2013) Food and water security issues in Russia II: water security in general population of Russian Arctic, Siberia and Far East, 2000–2011. Int J Circumpolar Health 72:22646. https://doi.org/10.3402/ijch.v72i0.22646

Dzoma BM, Moralo RA, Motsei LE, Ndou RV, Bakunzi FR (2010) Preliminary findings on the levels of five heavy metals in water, sediments, grass and various specimens from cattle grazing and watering in potentially heavy metal polluted areas of the north west province of South Africa. J Anim Vet Adv 9(24):3026–3033

EFSA (European Food Safety Authority) (2014) Panel on contaminants in the food chain. Scientific opinion on arsenic in food. EFSA J

Eliopoulos DG, Economou-Eliopoulos M, Apostolikas A et al (2012) Geochemical features of nickel-laterite deposits from the Balkan Peninsula and Gordes, Turkey: the genetic and environmental significance of arsenic. Ore Geol Rev 48:413–427

Environment Waikato Technical Report 2006/14 (2006) Arsenic in Groundwater of the Waikato Region, Hamilton East, New Zealand

Ereira T, Coelho JP, Duarte AC et al (2015) Size-dependent arsenic accumulation in *Scrobicularia Plana* in a temperate coastal lagoon (Ria de Aveiro, Portugal). Water Air Soil Pollut 226:213

Erry BV, Macnair MR, Meharg AA et al (1999) Arsenic residues in predatory birds from an area of Britain with naturally and anthropogenically elevated arsenic levels. Environ Pollut 106:91–95

FAO/WHO (1985) Guidelines for the study of dietary intakes of chemical contaminants. World Health Organization, Geneva, p 104

Fillol C, Dor F, Labat L et al (2010) Urinary arsenic concentrations and speciation in residents living in an area with naturally contaminated soils. Sci Total Environ 408:1190–1194

Flakova R, Zenisova Z, Sracek O et al (2012) The behavior of arsenic and antimony at Pezinok mining site, southwestern part of the Slovak Republic. Environ Earth Sci 66:1043–1057

Forslund J, Samakovlis E, Vredin Johansson M et al (2010) Does remediation save lives? – On the cost of cleaning up arsenic-contaminated sites in Sweden. Sci Total Environ 408:3085–3091

Gamaletsos P, Godelitsas A, Dotsika E et al (2016) Geological sources of As in the environment of Greece: a review. In: Scozzari A, Dotsika E (eds) Threats to the Quality of Groundwater Resources: Prevention and Control, Hdb Env Chem, vol 40. Springer, Berlin, pp 77–114

Gemici U, Tarcan G, Helvacı C et al (2008) High arsenic and boron concentrations in groundwaters related to mining activity in the Bigadiç borate deposits (Western Turkey). Appl Geochem 23:2462–2476

George G, Gqaza B (2015) Arsenic contamination of selected indigenous and exotic leafy vegetables in the Eastern Cape Province of South Africa. J Adv Agric Technol. https://doi.org/10.12720/joaat.2.1.29-33

Gilmundinov VM, Kazantseva LK, Tagaeva TO (2014) Pollution and its influence on health of population in Russia. Reg Res Russ 4(1):1–9

Gomez-Gonzalez MA, Serrano S, Laborda S et al (2014) Spread and partitioning of arsenic in soils from a mine waste site in Madrid province (Spain). Sci Total Environ 500–501:23–33

Gunduz O, Simsek C, Hasozbek A (2010) Arsenic pollution in the groundwater of Simav Plain, Turkey: its impact on water quality and human health. Water Air Soil Pollut 205:43–62

Gunduz O, Bakar C, Simsek C et al (2015) Statistical analysis of causes of death (2005–2010) in villages of Simav Plain, Turkey, with high arsenic levels in drinking water supplies. Arch Environ Occup Health 70:35–46

Hadzi GY, Kofi D, Godwin E, Ayoko A (2018) Assessment of contamination and health risk of heavy metals in selected water bodies around gold mining areas in Ghana. Environ Monit Assess 190(7):406

Hashemi M, Salehi T, Aminzare M, Raeisi M, Afshari A (2017) Contamination of toxic heavy metals in various foods in Iran: a review. J Pharm Sci Res 9(10):1692–1697

Hernández-Martínez R, Navarro-Blasco I (2013) Survey of total mercury and arsenic content in infant cereals marketed in Spain and estimated dietary intake. Food Control 30:423–432

Hiller E, Jurkovič L, Kordík J et al (2009) Arsenic mobility from anthropogenic impoundment sediments – consequences of contamination to biota, water and sediments, Poša, Eastern Slovakia. Appl Geochem 24:2175–2185

Hiller E, Lalinská B, Chovan M et al (2012) Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia. Appl Geochem 27:598–614

Hinwood AL, Jolley DJ, Sim MR (1999) Cancer incidence and high environmental arsenic concentrations in rural populations: results of an ecological study. Int J Environ Health Res 9:131–141

Hinwood AL, Sim MR, Jolley D, de Klerk N, Bastone EB, Gerostamoulos J, Drummer OH (2003) Hair and toenail arsenic concentrations of residents living in areas with high environmental arsenic concentrations. Environ Health Perspect 111(2):187–193

Hirata SH, Hayase D, Eguchi A, Itai T, Nomiyama K, Isobe T, Agusa T, Ishikawa T, Kumagai M, Tanabe S (2011) Arsenic and Mn levels in Isaza (*Gymnogobius isaza*) during the mass mortality event in Lake Biwa, Japan. Environ Pollut 159:2789–2796

Hong S, Khim JS, Park J, Son HS, Choi SD, Choi K, Ryu J, Kim CY, Chang GS, Giesy JP (2014) Species- and tissue-specific bioaccumulation of arsenicals in various aquatic organisms from a highly industrialized area in the Pohang City, Korea. Environ Pollut 192:27–35

Hong S, Choi SD, Khim JS (2018) Arsenic speciation in environmental multimedia samples from the Youngsan River Estuary, Korea: a comparison between freshwater and saltwater. Environ Pollut 237:842–850

Hough RL, Fletcher T, Leonardi GS et al (2010) Lifetime exposure to arsenic in residential drinking water in Central Europe. Int Arch Occup Environ Health 83:471–481

Huntsman-Mapila P, Mapila T, Letshwenyo M, Wolski P, Hemond C (2006) Characterization of arsenic occurrence in the water and sediments of the Okavango Delta, NW Botswana. Appl Geochem 21(8):1376–1391

Huntsman-Mapila P, Nsengimana H, Torto N, Diskin S (2011) Arsenic distribution and geochemistry in island groundwater of the Okavango Delta in Botswana. In: Jones JAA (ed) Sustaining groundwater resources. Springer, Dordrecht, pp 55–67

Husain A, Kannan K, Chan HM, Laird B, Al-Amiri H, Dashti B, Sultan A, Al-Othman A, Mandekar B (2017) A comparative assessment of arsenic risks and the nutritional benefits of fish consumption in Kuwait: arsenic versus omega 3-fatty acids. Arch Environ Contam Toxicol 72:108–118

Ilgen AG, Rychagov SN, Trainor TP (2011) Arsenic speciation and transport associated with the release of spent geothermal fluids in Mutnovsky field (Kamchatka, Russia). Chem Geol 288:115–132

Islam S, Rahman MM, Rahman MA, Naidu R (2017) Inorganic arsenic in rice and rice-based diets: health risk assessment. Food Control. https://doi.org/10.1016/j.foodcont.2017.06.030

Jacks G, Šlejkovec Z, Mörth M et al (2013) Redox-cycling of arsenic along the water pathways in sulfidic metasediment areas in northern Sweden. Appl Geochem 35:35–43

Jedynak Ł, Kowalska J, Leporowska A (2012) Arsenic uptake and phytochelatin synthesis by plants from two arsenic-contaminated sites in Poland. Pol J Environ Stud 21:1629–1633

Jorhem L, Strand CA, Sundstrom B et al (2008) Elements in rice from the Swedish market: 1. Cadmium, lead and arsenic (total and inorganic). Food Addit Contam 25:284–292

Jovanović D, Jakovljević B, Rašić-Milutinović Z et al (2011) Arsenic occurrence in drinking water supply systems in ten municipalities in Vojvodina Region, Serbia. Environ Res 111:315–318

Juhasz AL, Smith E, Weber J, Rees M, Rofe A, Kuchel T, Sansom L, Naidu R (2006) In vivo assessment of arsenic bioavailability in rice and its significance for human health risk assessment. Environ Health Perspect 114(12):1826–1831

Julshamn K, Nilsen BM, Frantzen S et al (2012) Total and inorganic arsenic in fish samples from Norwegian waters. Food Addit Contam B 5:229–235

Julshamn K, Duinker A, Nilsen BM et al (2013) A baseline study of levels of mercury, arsenic, cadmium and lead in Northeast Arctic cod (*Gadus morhua*) from different parts of the Barents Sea. Mar Pollut Bull 67:187–195

Jung MY, Kanga JH, Jungb HJ, Ma SY (2018) Inorganic arsenic contents in ready-to-eat rice products and various Korean rice determined by a highly sensitive gas chromatography-tandem mass spectrometry. Food Chem 240:1179–1183

Jurkovič L, Hiller E, Veselska V et al (2011) Arsenic concentrations in soils impacted by dam failure of coal-ash pond in Zemianske Kostolany, Slovakia. Bull Environ Contam Toxicol 86:433–437

Karczewska A, Bogda A, Krysiak A (2007) Arsenic in soils in the areas of former mining and mineral processing in Lower Silesia, Southwestern Poland. Arsenic in soil and groundwater environment. In: Bhattacharya P, Mukherjee AB, Bundschuh J, Zevenhoven R, Loeppert RH (eds) Trace metals and other contaminants in the environment vol 9. Elsevier, Amsterdam, pp 411–440

Katsoyiannis IA, Katsoyiannis AA (2006) Arsenic and other metal contamination of groundwaters in the industrial area of Thessaloniki, northern Greece. Environ Monit Assess 123:393–406

Katsoyiannis IA, Mitrakas M, Zouboulis AI (2014) Arsenic occurrence in Europe: emphasis in Greece and description of the applied full-scale treatment plants. Desalin Water Treat 1–8. https://doi.org/10.1080/19443994.2014.933630

Kelishadi R, Hasanghaliaei N, Poursafa P, Keikha M, Ghannadi A, Yazdi M, Rahimi E (2018) Randomized controlled trial on the effects of jujube fruit on the concentrations of some toxic trace elements in human milk. J Res Med Sci 21:108

Keshavarzi B, Moore F, Mosaferi M, Rahmani F (2011) The source of natural arsenic contamination in groundwater, West of Iran. Water Qual Expo Health 3(1):135–147

Keshavarzi B, Seradj A, Akbari Z, Moore F, Shahraki AR, Pourjafar M (2015) Chronic arsenic toxicity in sheep of Kurdistan Province, Western Iran. Arch Environ Contam Toxicol 69:44–53

Kondo H, Ishiguro Y, Ohno K, Nagase M, Toba M, Takagi M (1999) Naturally occurring arsenic in the groundwaters in the southern region of Fukuoka prefecture, Japan. Water Res 33:1967–1972

Kootbodien T, Mathee A, Naicker N, Moodley N (2012) Heavy metal contamination in a school vegetable garden in Johannesburg. S Afr Med J 102(4):226–227

Kosanovic M, Hasan MY, Subramanian D, Al Ahbabi AA, Al Kathiri OA, Aleassa EM, Adem A (2007) Influence of urbanization of the western coast of the United Arab Emirates on trace metal content in muscle and liver of wild Red-spot emperor (*Lethrinus lentjan*). Food Chem Toxicol 45:2261–2266

Kostik V, Gjorgeska B, Angelovska B et al (2014) Distribution of the total arsenic content in drinking water obtained from different water sources in the Republic of Macedonia. J Food Nutr Sci 2(4):146–155

Kouras A, Katsoyiannis I, Voutsa D (2007) Distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece. J Hazard Mater 147:890–899

Králová L, Száková J, Kubík Š et al (2010) The variability of arsenic and other risk element uptake by individual plant species growing on contaminated soil. Soil Sediment Contam 19:617–634

Krishnakumar PK, Qurban MA, Stiboller M, Nachman KE, Joydas TV, Manikandan KP, Mushir SA, Francesconi KA (2016) Arsenic and arsenic species in shellfish and finfish from the western Arabian Gulf and consumer health risk assessment. Sci Total Environ 566–567:1235–1244

Kurbanova LM, Samedov SG, Gazaliev IM, Abdulmutalimova TO (2013) Arsenic in the groundwaters of the North Dagestan Artesian Basin. Geochem Int 51(3):237–239

Kusimi JM, Kusimi BA (2012) The hydrochemistry of water resources in selected mining communities in Tarkwa. J Geochem Explor 112:252–261

Larsen EH, Hansen M, Gössler W (1998) Speciation and health risk considerations of arsenic in the edible mushroom *Laccaria amethystina* collected from contaminated and uncontaminated locations. Appl Organomet Chem 12:285–291

Lindberg AL, Goessler W, Gurzau E et al (2006) Arsenic exposure in Hungary, Romania and Slovakia. J Environ Monit 8:203–208

Luís AT, Teixeira P, Almeida SFP et al (2011) Environmental impact of mining activities in the Lousal area (Portugal): chemical and diatom characterization of metal-contaminated stream sediments and surface water of Corona stream. Sci Total Environ 409:4312–4325

Madeira AC, de Varennes A, Abreu MM et al (2012) Tomato and parsley growth, arsenic uptake and translocation in a contaminated amended soil. J Geochem Explor 123:114–121

Majzlan J, Plášil J, Škoda R et al (2014) Arsenic-rich acid mine water with extreme arsenic concentration: mineralogy, geochemistry, microbiology, and environmental implications. Environ Sci Technol 48:13685–13693

Marques APGC, Moreira H, Rangel AOSS et al (2009) Arsenic, lead and nickel accumulation in *Rubus ulmifolius* growing in contaminated soil in Portugal. J Hazard Mater 165:174–179

Márquez-García B, Pérez-López R, Ruíz-Chancho J et al (2012) Arsenic speciation in soils and Erica andevalensis Cabezudo & Rivera and Erica australis L. from São Domingos Mine area, Portugal. J Geochem Explor 119–120:51–59

McGrory ER, Brown C, Bargary N et al (2016) Arsenic contamination of drinking water in Ireland: a spatial analysis of occurrence and potential risk. Sci Total Environ 579:1863–1875

McLean W, Jankowski J (2001) The occurrence of arsenic in an alluvial aquifer system, northern New South Wales. In: Arsenic in the Asia-Pacific Region Abstracts; Adelaide, South Australia, November 2001, CSIRO Land and Water, pp 21–23

Medrano J, Boix R, Pastor-Barriuso R et al (2010) Arsenic in public water supplies and cardiovascular mortality in Spain. Environ Res 110:448–454

Melnikov DV (2004) Some features of morphology of hydrothermal explosions in area Mutnovsky of hydrothermal power plant. Vestnik KRAUNTS 4:120–124

Miyashita S, Shimoya M, Kamidate Y, Kuroiwa T, Shikino O, Fujiwara S, Francesconi KA, Kaise T (2009) Rapid determination of arsenic species in freshwater organisms from the arsenic-rich Hayakawa River in Japan using HPLC-ICP-MS. Chemosphere 75:1065–1073

Mladenov N, Wolski P, Hettiarachchi GM, Murray-Hudson M, Enriquez H, Damaraju S, Galkaduwa MB, McKnight DM, Masamba W (2013) Abiotic and biotic factors influencing the mobility of arsenic in groundwater of a through-flow island in the Okavango Delta, Botswana. J Hydrol 518:326–341

Monrad M, Ersbøll AK, Sørensen M et al (2017) Low-level arsenic in drinking water and risk of incident myocardial infarction: a cohort study. Environ Res 154:318–324

Mosaferi M, Nemati S, Armanfar F, Nadiri A, Mohammadi A (2017) Geogenic arsenic contamination in northwest of Iran; role of water basin hydrochemistry. J Environ Health Sustain Dev 2(1):209–220

Neamtiu I, Bloom MS, Gati G et al (2015) Pregnant women in Timis County, Romania are exposed primarily to low-level (<10 μg/L) arsenic through residential drinking water consumption. Int J Hyg Environ Health 218:371–379

Neiva AMR, Antunes IMHR, Carvalhoa PCS et al (2016) Uranium and arsenic contamination in the former Mondego Sul uranium mine area, Central Portugal. J Geochem Explor 162:1–15

Niedzielski P, Mleczek M, Magdziak Z et al (2013) Selected arsenic species: As(III), As(V) and dimethylarsenic acid (DMAA) in Xerocomus badius fruiting bodies. Food Chem 141:3571–3577

Nordstrom DK (2002) Worldwide occurrences of arsenic in ground water. Science 296:2143–2145

Oguri T, Yoshinaga J, Tao H, Nakazato T (2014) Inorganic arsenic in the Japanese diet: daily intake and source. Arch Environ Contam Toxicol 66:100–112

Overesch M, Rinklebe J, Broll G et al (2007) Metals and arsenic in soils and corresponding vegetation at Central Elbe river floodplains (Germany). Environ Pollut 145:800–812

Ozkul C, Iftci EC, Koprubası N et al (2015) Geogenic arsenic anomalies in soils and stream waters of Neogene Emet basin (Kutahya-Western Turkey). Environ Earth Sci 73:6117–6130

Parviainen A, Loukola-Ruskeeniemi K, Tarvainen T et al (2015) Arsenic in bedrock, soil and groundwater—the first arsenic guidelines for aggregate production established in Finland. Earth Sci Rev 150:709–723

Pearce DC, Dowling K, Sim MR (2012) Cancer incidence and soil arsenic exposure in a historical gold mining area in Victoria, Australia: a geospatial analysis. J Expo Sci Environ Epidemiol 22:248–257

Peshut PJ, Morrison RJ, Brooks BA (2008) Arsenic speciation in marine fish and shellfish from American Samoa. Chemosphere 71:484–492

Radić S, Crnojević H, Vujčić V et al (2016) Toxicological and chemical assessment of arsenic-contaminated groundwater after electrochemical and advanced oxidation treatments. Sci Total Environ 543:147–154

Rahman MA, Rahman MM, Reichman SM, Lim RP, Naidu R (2014) Arsenic speciation in Australian-grown and imported rice on sale in Australia: implications for human health risk. J Agric Food Chem 62:6016–6024. https://doi.org/10.1021/jf501077w

Rahmani J, Fakhri Y, Shahsavani A, Bahmani Z, Urbina MA, Chirumbolo S, Keramati H, Moradi B, Bay A, Bjørklund G (2018) A systematic review and meta-analysis of metal concentrations in canned tuna fish in Iran and human health risk assessment. Food Chem Toxicol 118:753–765

Ranft U, Miskovic P, Pesch B et al (2003) Association between arsenic exposure from a coal-burning power plant and urinary arsenic concentrations in Prievidza District, Slovakia. Environ Health Perspect 111:889–894

Rango T, Vengosh A, Dwyer G, Bianchini G (2013) Mobilization of arsenic and other naturally occurring contaminants in groundwater of the Main Ethiopian Rift aquifers. Water Res 47(15):5801–5818

Recio-Vazquez L, Garcia-Guinea J, Carral P et al (2011) Arsenic mining waste in the catchment area of the Madrid detrital aquifer (Spain). Water Air Soil Pollut 214:307–320

Reimann C, Bjorvatn K, Frengstad B, Melaku Z, Tekle-Haimanot R, Siewers U (2003) Drinking water quality in the Ethiopian section of the East African Rift Valley I—data and health aspects. Sci Total Environ 311(1):65–80

Reimann C, Matschullat J, Birke M et al (2009) Arsenic distribution in the environment: the effects of scale. Appl Geochem 24:1147–1167

Rezaie-Boroon MH, Gnandi K, Folly K-M (2011) Presence and distribution of toxic trace elements in water and sediments of the southern Togo rivers watershed, West Africa. Fresenius Environ Bull 20(7):1853–1865

Rieuwerts JS, Searle P, Buck R (2006) Bioaccessible arsenic in the home environment in southwest England. Sci Total Environ 371:89–98

Rintala EM, Ekholm P, Koivisto P et al (2014) The intake of inorganic arsenic from long grain rice and rice-based baby food in Finland – low safety margin warrants follow up. Food Chem 150:199–205

Romić Ž, Habuda-Stanić M, Kalajdžić B et al (2011) Arsenic distribution, concentration and speciation in groundwater of the Osijek area, eastern Croatia. Appl Geochem 26:37–44

Routh J, Bhattacharya A, Saraswathy A et al (2007) Arsenic remobilization from sediments contaminated with mine tailings near the Adak mine in Västerbotten district (Northern Sweden). J Geochem Explor 92:43–54

Rudnai T, Sándor J, Kádár M et al (2014) Arsenic in drinking water and congenital heart anomalies in Hungary. Int J Hyg Environ Health 217:813–818

Salminen R, Chekushin V, Tenhola M et al (2004) Geochemical atlas of eastern Barents region. J Geochem Explor 83:1–530

Saoudi A, Zeghnoun A, Bidondo ML et al (2012) Urinary arsenic levels in the French adult population: the French National Nutrition and Health Study, 2006–2007. Sci Total Environ 433:206–215

Sapunar-Postružnik J, Bažulić D, Kubala H (1996) Estimation of dietary intake of arsenic in the general population of the Republic of Croatia. Sci Total Environ 191:119–123

Savinov VM, Gabrielsen GW, Savinova TN (2003) Cadmium, zinc, copper, arsenic, selenium and mercury in seabirds from the Barents Sea: levels, inter-specific and geographical differences. Sci Total Environ 306:133–158

Serfor-Armah Y, Nyarko BJB, Dampare SB, Adomako D (2006) Levels of arsenic and antimony in water and sediment from Prestea, a gold mining town in Ghana and its environs. Water Air Soil Pollut 175(1):181–192

Sharma N, Bhatnagar P, Chatterjee S et al (2017) Waste water microbes and environmental ‘clean up’: roadmap to environmental sustainability. Int J Adv Res Sci Eng Tech 4:3341–3350

Signes-Pastor AJ, Deacon C, Jenkins RO, Haris PI, Carbonell-Barrachina AA, Meharg AA (2009) Arsenic speciation in Japanese rice drinks and condiments. J Environ Monit 11:1930–1934

Signes-Pastor AJ, Carey M, Carbonell-Barrachina AA (2016a) Geographical variation in inorganic arsenic in paddy field samples and commercial rice from the Iberian Peninsula. Food Chem 202:356–363

Signes-Pastor AJ, Carey M, Carbonell-Barrachina AA et al (2016b) Geographical variation in inorganic arsenic in paddy field samples and commercial rice from the Iberian Peninsula. Food Chem 202:356–363

Sirot V, Guérin T, Volatier J-L et al (2009) Dietary exposure and biomarkers of arsenic in consumers of fish and shellfish from France. Sci Total Environ 407:1875–1885

Skalny AV, Zhukovskaya EV, Kireeva GN, Skalnaya MG, Grabeklis AR, Radysh IV, Shakieva RA, Nikonorov AA, Tinkov AA (2016) Whole blood and hair trace elements and minerals in children living in metal-polluted area near copper smelter in Karabash, Chelyabinsk region, Russia. Environ Sci Pollut Res Int 25(3):2014–2020. https://doi.org/10.1007/s11356-016-7876-6

Sloth JJ, Julshamn K, Lundebye A-K (2005) Total arsenic and inorganic arsenic content in Norwegian fish feed products. Aquac Nutr 11:61–66

Smedley PL (1996) Arsenic in rural groundwater in Ghana: part special issue: hydrogeochemical studies in sub-Saharan Africa. J Afr Earth Sci 22(4):459–470

Smedley PL, Knudsen J, Maiga D (2007) Arsenic in groundwater from mineralised Proterozoic basement rocks of Burkina Faso. Appl Geochem 22(5):1074–1092

Smith JVS, Jankowski J (2001) Natural occurrences of inorganic arsenic in the Australian coastal groundwater. Implications for water quality in Australian coastal communities. In Arsenic in the Asia-Pacific Region Abstracts; Adelaide, South Australia, November 20–23, CSIRO Land and Water, pp 14–17

Soeroes C, Goessler W, Francesconi KA et al (2005) Arsenic speciation in farmed Hungarian freshwater fish. J Agric Food Chem 53:9238–9243

Soleo L, Lovreglio P, Iavicoli S et al (2008) Significance of urinary arsenic speciation in assessment of seafood ingestion as the main source of organic and inorganic arsenic in a population resident near a coastal area. Chemosphere 73:291–299

Sommella A, Deacon C, Norton G et al (2013) Total arsenic, inorganic arsenic, and other elements concentrations in Italian rice grain varies with origin and type. Environ Pollut 181:38–43

Srivastava S, Tripathi RD, Dhankher OP et al (2016) Arsenic transport, metabolism and toxicity in plants. Int J Plant Environ 2:17–28

Stevanović B, Dražić G, Tomović G et al (2010) Accumulation of arsenic and heavy metals in some Viola species from an abandoned mine, Alchar, Republic of Macedonia (FYROM). Plant Biosyst 144:644–655

Sun X-G, Williams PN, Zhu Y-G, Deacon C, Carey A-M, Raab A, Feldmann J, Meharg AA (2009) Survey of arsenic and its speciation in rice products such as breakfast cereals, rice crackers and Japanese rice condiments. Environ Int 35:473–475

Susko ML, Bloom MS, Neamtiu IA et al (2017) Low-level arsenic exposure via drinking water consumption and female fecundity – a preliminary investigation. Environ Res 154:120–125

Škrbić B, Živančev J, Mrmoš N (2013) Concentrations of arsenic, cadmium and lead in selected foodstuffs from Serbian market basket: estimated intake by the population from the Serbia. Food Chem Toxicol 58:440–448

Taghizadeh SF, Davarynejad G, Asili J, Nemati SH, Rezaee R, Goumenou M, Tsatsakis AM, Karimi G (2017) Health risk assessment of heavy metals via dietary intake of five pistachio (*Pistacia vera* L.) cultivars collected from different geographical sites of Iran. Food Chem Toxicol 107:99–107

Taleshi M, Edmonds J, Goessler W et al (2010) Arsenic-containing lipids are natural constituents of sashimi tuna. Environ Sci Technol 44:1478–1483

Throssell JS, Blessing NV (2001) The mobility of arsenic in a shallow sandy aquifer and the implications for ecological risks and remediation targets. In: Arsenic in the Asia-Pacific Region Abstracts; Adelaide, South Australia, November 2001, CSIRO Land and Water, pp 34–36

Törnqvist R, Jarsjö J, Karimov B (2011) Health risks from large-scale water pollution: trends in Central Asia. Environ Int 37:435–442

Ujević Bošnjak M, Capak K, Jazbec A et al (2012) Hydrochemical characterization of arsenic contaminated alluvial aquifers in Eastern Croatia using multivariate statistical techniques and arsenic risk assessment. Sci Total Environ 420:100–110

Upadhyay MK, Yadav P, Shukla A et al (2018) Utilizing the potential of microorganisms for managing arsenic contamination: a feasible and sustainable approach. Front Environ Sci 6:1–11

Vaculík M, Jurkovič L, Matejkovič P et al (2013) Potential risk of arsenic and antimony accumulation by medicinal plants naturally growing on old mining sites. Water Air Soil Pollut 224:1546

Vieira C, Morais S, Ramos S et al (2011) Mercury, cadmium, lead and arsenic levels in three pelagic fish species from the Atlantic Ocean: intra- and inter-specific variability and human health risks for consumption. Food Chem Toxicol 49:923–932

Višnjić-Jeftić Ž, Jarić I, Jovanović L et al (2010) Heavy metal and trace element accumulation in muscle, liver and gills of the Pontic shad (*Alosa immaculata* Bennet 1835) from the Danube River (Serbia). Microchem J 95:341–344

Wilhelm M, Wittsiepe J, Schrey P et al (2005) Consumption of homegrown products does not increase dietary intake of arsenic, cadmium, lead, and mercury by young children living in an industrialized area of Germany. Sci Total Environ 343:61–70

Williams PN, Islam MR, Adomako EE, Raab A, Hossain SA, Zhu YG, Feldmann J, Meharg AA (2006) Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. Environ Sci Technol 40:4903–4908

Woo NC, Choi MJ (2001) Arsenic and metal contamination of water resources from mining wastes in Korea. Environ Geol 40:305–311

Yorifuji T, Matsuoka K, Grandjean P (2017) Height and blood chemistry in adults with a history of developmental arsenic poisoning from contaminated milk powder. Environ Res 155:86–91

Yurkevich NV, Saeva OP, Pal'chik NA (2012) Arsenic mobility in two mine tailings drainage systems and its removal from solution by natural geochemical barriers. Appl Geochem 27:2260–2270. https://doi.org/10.1016/j.apgeochem.2012.05.012

Yurkevich NV, Abrosimova NA, Bortnikova SB, Karin YG, Saeva OP (2017) Geophysical investigations for evaluation of environmental pollution in a mine tailings area. Toxicol Environ Chem 99(9–10):1328–1345

Zakharova T, Tatàno F, Menshikov V (2002) Health cancer risk assessment for arsenic exposure in potentially contaminated areas by fertilizer plants: a possible regulatory approach applied to a case study in Moscow Region–Russia. Regul Toxicol Pharmacol 36:22–33. https://doi.org/10.1006/rtph.2002.1561

Global Market and Field Studies of Arsenic Accumulation in Rice

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Abstract Arsenic (As) is a ubiquitous and naturally occurring metalloid that poses significant carcinogenic and noncarcinogenic health risks to human. Apart from drinking water, food is the other major source of As exposure for humans. A principal source of As in diet for the general population living in the non-As endemic areas is rice. Rice is a staple food for the global population. The annual rice consumption per capita has been increasing over time. The issue of As accumulation in rice and its potential health impacts have become a global public health concern for several decades, as the rice consumption per capita is normally high and As is classified as group 1 carcinogen. Therefore, the Codex Alimentarius Commission, the Joint Food and Agriculture Organization (FAO) of the United Nations, and the World Health Organization (WHO) food standards program have established the maximum allowance level of As, especially inorganic As, in rice grain. This chapter draws attention to the most updated data on the total and inorganic As concentrations in the most popular types of rice sold in the markets of all the world regions. The bioaccessible As concentrations were also reported in this chapter, as this fraction is believed to represent the amount of As that is actually taken up by the human body. Furthermore, considerable attention is given to the field studies of As in rice grain which were cultivated in the As-contaminated areas.

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Keywords Raw rice · Polished rice · White rice · Brown rice · Inorganic arsenic · Bioaccessibility

1 Introduction

Arsenic (As), the 52nd most abundant element in the earth's crust, is a naturally occurring metalloid with a wide range of concentrations in different environmental media. It generally mobilizes in the environment through both natural processes and anthropogenic activities (Adriano 2001). Elevated As concentrations in the environment, especially in the air, soil, groundwater, and food, have become a global issue with respect to environmental and public health concerns (Chung et al. 2014; Flora 2015) due to their high toxicity and lethal effects. Acute exposure of As is quite rare and mainly occurs from the accidental ingestion of insecticides or pesticides and even less commonly from suicidal or homicidal ingestion (Ratnaike 2003; ASTDR 2014). Acute As poisoning depends on the dose of exposure, and its symptoms include nausea, vomiting, abdominal pain, gastrointestinal hemorrhage, and severe diarrhea (ASTDR 2014). Meanwhile, chronic As exposure has caused evident negative effects on health to a broad range of internal organs and systems in a human body, such as the skin, lungs, liver, kidney, bladder, and prostate, as well as the nervous, cardiovascular, respiratory, gastrointestinal, immune, and endocrine systems (Kapaj et al. 2006; Naujokas et al. 2013; Sohn 2014). The negative health outcomes of chronic As exposure can include noncarcinogenic and carcinogenic effects. The toxicity of As in terms of noncarcinogenic and carcinogenic health effects is well studied and extensively reported by many studies (Tchounwou et al. 2003; Kapaj et al. 2006; Hughes et al. 2011; Naujokas et al. 2013; Hong et al. 2014; Mazumder 2015).

Among the three environmental exposure pathways, a main route of chronic As exposure is ingestion. There is a strong relationship between chronic As ingestion and negative effects on health (Naujokas et al. 2013). Apart from drinking water, food is the other major source of As for human exposure (IARC 2012; Chung et al. 2014; Flora 2015). Approximately 40% of As in the human body comes from the food chain (Flora 2015). It was also reported that rice is a principal source of As, especially inorganic As exposure, in the general population living in the non-As endemic regions (Sohn 2014; Flora 2015; Lai et al. 2015).

As a source of dietary carbohydrates, micronutrients, vitamins, and amino acids, rice has become one of the world's most popular foods (Food and Agriculture Organization of the United Nations 2004; Rohman et al. 2004). The theme "rice is life" launched by the Food and Agriculture Organization (FAO) of the United Nations in 2004 has, to date, truly confirmed the importance of rice as a basic food commodity for more than half of the world's population (Food and Agriculture Organization of the United Nations 2004; OECD-FAO 2008; Jeong et al. 2017). Unfortunately, rice generally takes up and accumulates As concentrations approximately ten times higher than those in other food grains such as maize and barley

(Williams et al. 2007; Sohn 2014). Thus, risks of As exposure and its poisoning through rice consumption have been a public health concern for several decades. To ensure the safe exposure of As from rice consumption, many scientific studies were conducted to determine the levels of As in rice grains collected from both local markets and paddy fields worldwide. This chapter, therefore, deals with the occurrence of As in rice grains from the perspectives of market basket and field studies.

2 Total Global Rice Consumption

Besides wheat, rice is another one of the world's most important cereal grains. It is a staple food for more than half of the world's population (IRIN 2010; Jeong et al. 2017). The global rice production has been annually increased by approximately 1.61% during the last 20 years (OECD-FAO 2008). In addition, it is expected that the total global rice consumption will increase from 439 million tons in 2010 to 555 million tons by 2035 (Jeong et al. 2017). In terms of consumption, the current percentage of global rice consumption to the major cereal grains is approximately 35% (Fig. 1a). Meanwhile, approximately 49% of the cereal grains consumed in Asia are rice. Figure 1b clearly confirms that rice is the most important staple food for the Asian population.

Figure 2 shows the average annual rice consumption in the world and Asia. It is projected that the global and Asian rice consumption per capita from 2017 to 2026 will increase by approximately 0.10–0.24% and 0.28–0.43%, respectively. The average annual rice consumption per capita in the Asian population is approximately 1.5 times higher than the global rice consumption. This high amount of rice consumption has caused a significant concern, especially when the rice is contaminated with highly toxic elements such as As. Therefore, several international and

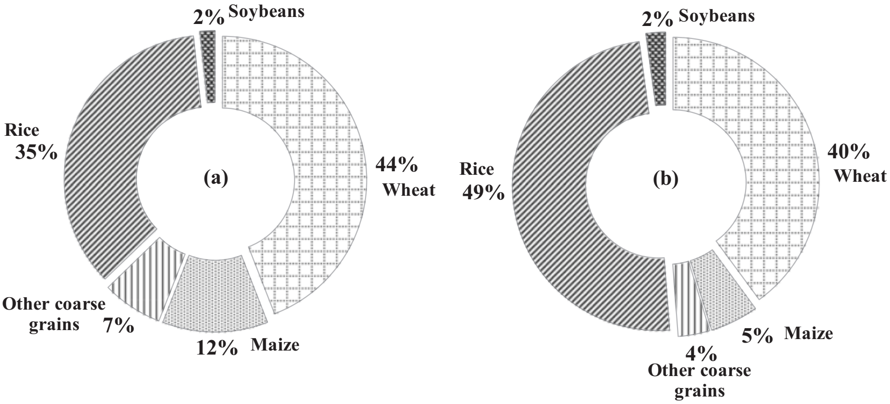

Fig. 1 Percentages of major cereal grain consumption in the (**a**) world and (**b**) Asia. (Note: raw data on the amount of consumption was obtained from OECD-FAO (2017))

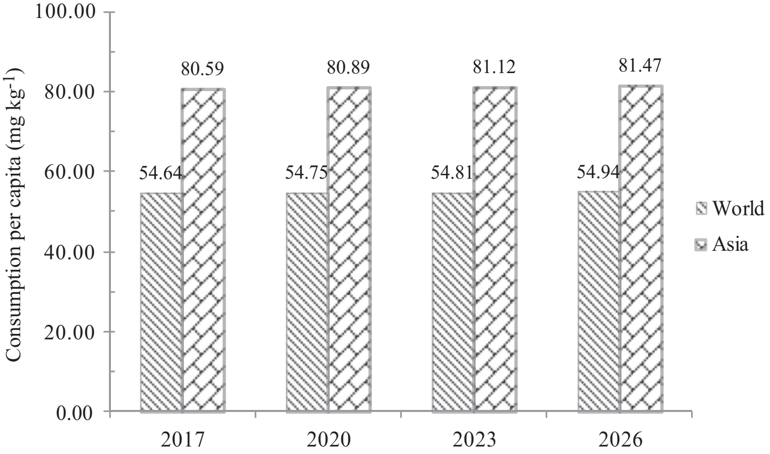

Fig. 2 Projections of the global and Asian rice consumption per capita. (Note: Raw data on the consumption per capita was obtained from OECD-FAO (2017))

national organizations have established the maximum levels of As in rice and rice commodities to protect the population from the potential adverse consequences on public health.

3 International and National Standards of As in Rice

The toxicity of As in humans is a high concern of many international and national organizations that perform work related to food safety. The maximum levels of As in rice and some rice commodities were set to ensure the safe exposure level and reduce the potential negative health outcomes in the general population and some susceptible population such as infants, toddlers, and young children. The standard levels of As in rice and commodities are summarized in Table 1. Even though both organic (monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)) and inorganic (arsenite (As(III)) and arsenate (As(V))) As species are commonly present in rice, most of the standards generally regulate only the level of inorganic As in rice because inorganic As species are more toxic than the organic As species. In principle, the inorganic As is the summation of As(III) and As(V).

As seen from Table 1, those countries such as European countries, China, and South Korea where the analysis of inorganic As is reliable, the inorganic As level has been adopted into the regulation. In the case of countries with limitations to inorganic As analysis, the Codex Alimentarius Commission has agreed that they may use the total As concentration as a screening level for the inorganic As in rice. If the total As concentration is below the regulated maximum level for inorganic As, no further testing is required, and the sample is determined to be compliant with the Codex Alimentarius Commission regulation. If the total As concentration is above

Table 1 Standard levels of As in rice and its commodities

Regulated organization	Type of rice/rice commodities	Regulation		References
		Species	Concentration (mg kg^{-1})	
Codex Alimentarius Commission (the Joint FAO/World Health Organization (WHO) food standards program	Raw polished rice[a]	Inorganic As	0.20	Codex Alimentarius Commission (2014)
	Raw husked rice[b]	Inorganic As	0.35	Codex Alimentarius Commission (2016)
European Commission	Nonparboiled milled rice[a] (polished or white rice)	Inorganic As	0.20	EU Commission Regulation (2015)
	Parboiled rice[c] and husked rice	Inorganic As	0.25	
	Rice waffles, rice wafers, rice crackers, and rice cakes	Inorganic As	0.30	
	Rice destined for the production of food for infants and young children	Inorganic As	0.10	
Food Standards Australia New Zealand	Rice	NI[d]	1.0	Food Standards Australia New Zealand (2017)
China	Raw rice, brown rice, rice	Inorganic As	0.2	United States Department of Agriculture (2014)
Iran	NI[d]	NI[d]	0.15	Chaleshtori et al. (2016)
Israel	Rice	Total As[e]	1.0	United States Department of Agriculture (2011)
		Inorganic As	1.0	
South Korea	Rice	Inorganic As	0.2	Yim et al. (2017)

[a] Polished rice (milled rice or white rice) is husked rice from which all or part of the bran and germ has been removed by milling (Codex Alimentarius Commission 1995, 2017)

[b] Husked rice (brown rice or cargo rice) is paddy rice from which only the husk has been removed. The process of husking and handling may result in some loss of bran (Codex Alimentarius Commission 1995, 2017)

[c] Parboiled rice may be husked or milled rice that is processed from paddy or husked rice that has been soaked in water and subjected to a heat treatment so that the starch is fully gelatinized. It is followed by a drying process (Codex Alimentarius Commission 1995)

[d] Not identified

[e] If the total As (organic and inorganic As) exceeds the value listed, the maximum concentration of the inorganic As should be checked

the regulated maximum level for inorganic As, follow-up testing should be conducted to determine if the inorganic As is above the maximum level.

4 Market Basket Studies of Total As in Rice

The total concentration of As that is equal to the concentrations of both organic and inorganic As in rice is more frequently reported and widely available, especially in less developed countries, since the determination of the total As concentration requires more simple digestion and extraction methods, a less advanced analytical technique, less time consumption, and more affordable costs of analysis. It is worth noting that this chapter mainly concentrates on the most updated official reports and scientific publications on the total As concentration in raw rice during the last decade (2009–2018), as shown in Table 2, to comply with the Codex standards for early public health protection. In addition, the concentration of As can be changed after various methods of cooking (Kollander and Sundstrom 2015); therefore, this part of the study is only focused on the total As content in raw rice prior to any preparation and cooking processes.

The significant number of official reports and scientific publications on the total As concentration in rice grain published in the last 10 years has strongly confirmed the importance of the As contamination in rice issue. It is getting more attention from the developed countries, and more efforts on the monitoring of As contamination in rice have been continuously raised in developing and less developed countries. Table 2 summarizes the results of the market basket surveys on the total As concentrations in rice without taking into account the variation in the crop production year, countries of production, collection, and distribution. All reported values are the levels of total As in the raw rice sold in grocery stores, local markets, supermarkets, commercial food stores, and online shopping stores in 36 countries covering all of the world regions. Two main types of rice for direct human consumption, namely, polished (white) rice and husked (brown) rice, were reported.

4.1 *Total As Concentration in Polished Rice*

The total As concentrations in the commercial polished (white) rice from different countries as shown in Table 2 varied greatly (nondetectable to 1.170 mg kg^{-1}). The highest total As concentration was found in rice collected from Pakistan. Since the Codex Alimentarius Commission has agreed to the use of the total As concentration as a screening level of inorganic As in rice, the maximum and mean As concentrations in rice reported in Table 2 were compared to the Codex maximum standard of the As in polished rice (0.2 mg kg^{-1}). Considering the maximum total As concentration, the As concentrations in the rice from most countries (30/36 countries) were higher than that of the Codex standard.

Table 2 Summary of the worldwide market basket studies of total As concentrations (mg kg^{-1}) in raw polished and husked rice

Country	Polished/white rice		Husked/brown rice		References
	Range	Mean	Range	Mean	
Africa region					
Eastern Africa					
Malawi	<0.003–0.036	0.010	<0.003–0.100	0.040	Joy et al. (2017)
Western Africa					
Nigeria	0.030–0.078	0.059			Adeyemi et al. (2017)
Ghana	0.010–0.500	0.125	0.002–0.330	0.110	Adomako et al. (2011)
America region					
Northern America					
United States of America	0.081–0.313	0.181	0.107–0.282	0.217	Trenary et al. (2012)
South America					
Argentina	0.087–0.316	0.180			Sirgist et al. (2016)
Brazil	0.005–0.376	0.173	0.138–0.428	0.275	Batista et al. (2011) and Segura et al. (2016)
Caribbean					
Jamaica	0.110–0.487	0.200	0.082–0.250	0.165	Antoine et al. (2012)
Asia region					
Central Asia					
Kazakhstan	0.030–1.160	0.266	0.040–0.360	0.240	Tattibayeva et al. (2016)
Eastern Asia					
China	ND[a]–0.437	0.129	0.083–0.739	0.267	Liang et al. (2010), Fang et al. (2014), Li et al. (2015, 2018), Ma et al. (2016, 2017), and Zhuang et al. (2016)
Japan	0.025–0.296		0.040–0.487		Naito et al. (2015)
South Korea	0.031–0.195	0.088	0.084–0.282	0.161	Yim et al. (2017) and Lee et al. (2018)
Southeastern Asia					
Cambodia	0.008–0.771	0.157			Wang et al. (2013) and Gilbert et al. (2015)
Malaysia	0.088–0.123	0.103			Nookabkaew et al. (2013a)
Myanmar	0.010–0.400	0.250			Mwale et al. (2018)

(continued)

Table 2 (continued)

Country	Polished/white rice		Husked/brown rice		References
	Range	Mean	Range	Mean	
Thailand	0.053–0.304	0.147	0.077–0.489	0.223	Ruangwises et al. (2012), Nookabkaew et al. (2013a, b), and Hensawang and Chanpiwat (2017, 2018)
Vietnam	0.093–0.204	0.136	0.254–0.345	0.299	Nookabkaew et al. (2013a)
Southern Asia					
Bangladesh	0.003–0.680	0.197			Islam et al. (2015), Ahmed et al. (2016), and Islam et al. (2017a, b)
India	0.028–0.961	0.283			Halder et al. (2014)
Iran	ND[a]–0.314	0.109			Ghazanfarirad et al. (2014), Nemati et al. (2014), Cano-Lamadrid et al. (2015), Roya and Ali (2017), and Jafari et al. (2018)
Pakistan	0.160–1.170	0.430			Nawab et al. (2018)
Sri Lanka	ND[a]–0.716	0.051			Magamage et al. (2017)
Western Asia					
Iraq	0.054–0.161	0.095			Sadee et al. (2016)
Qatar	0.041–0.169	0.111			Rowell et al. (2014)
Saudi Arabia	0.020–0.304	0.163			Mohamed et al. (2017) and Shraim (2017)
Turkey	0.145–0.823	0.323			Sadee et al. (2016)
United Arab Emirates	0.098–0.945	0.726			Shirwaikar et al. (2013)
Europe region					
Northern EU					
Finland	0.110–0.650	0.250			Rintala et al. (2014)
Scotland	0.084–0.392	0.165			Petursdottir et al. (2014)
United Kingdom	0.062–0.249	0.095			Sadee et al. (2016)
Southern EU					
Greece	0.042–0.271	0.167			Pasias et al. (2013)
Italy	0.070–0.460	0.210			Sommella et al. (2013)
Spain	0.037–0.433	0.143	0.083–0.619	0.302	Signes-Pastor et al. (2016)

(continued)

Table 2 (continued)

Country	Polished/white rice		Husked/brown rice		References
	Range	Mean	Range	Mean	
Western EU					
Belgium	0.061–0.216	0.133		0.200	Ruttens et al. (2018)
France	0.048–0.213	0.126		0.079	Jitaru et al. (2016)
Switzerland	0.007–0.281	0.143	0.147–0.238	0.205	Guillod-Magnin et al. (2018)
Oceania					
Australia	ND[a]–0.547	0.146	0.198–0.438	0.308	Rahman et al. (2014) and Fransisca et al. (2015)

The summary is based on the world regions by the United Nations Country Grouping (United Nations 2018)

[a]ND means the nondetectable concentration

The range of the mean total As concentrations in the raw polished rice collected from all 36 countries around the globe ranged from 0.010 to 0.726 mg kg^{-1}. The mean total As concentrations in the rice from Kazakhstan (0.266 mg kg^{-1}), Myanmar (0.250 mg kg^{-1}), India (0.283 mg kg^{-1}), Pakistan (0.430 mg kg^{-1}), Turkey (0.323 mg kg^{-1}), the United Arab Emirates (0.726 mg kg^{-1}), Finland (0.250 mg kg^{-1}), and Italy (0.210 mg kg^{-1}) were higher than the Codex standard. With the exception of the United Arab Emirates, the levels of As in rice from these countries fall within the category of high As concentration in rice (>0.202–0.357 mg kg^{-1}) as prescribed in the study on global normal levels of total As in rice grain (>0.082–0.202 mg kg^{-1}) by Zavala and Duxbury (2008). According to this previous study, rice collected in the United Arab Emirates contained unusually high As content (>0.357 mg kg^{-1}). Zavala and Duxbury (2008) concluded that the levels of high (>0.202–0.357 mg kg^{-1}) and unusually high (>0.357 mg kg^{-1}) As in rice are indications of rice production in an As-contaminated environment. Similarly, to the sources of As contamination in the environment, As accumulation in rice can be caused by natural and anthropogenic sources. The natural sources of As in the rice production system are the levels of As in paddy soil and irrigation water (Sahoo and Kim 2013; Ruangwises et al. 2014), the addition of As through flooding and the wet and dry atmospheric deposition (Meharg and Zhao 2012). Meanwhile, the anthropogenic sources of As in paddy rice are point and nonpoint sources of industrial and urban pollution and the usage of As-bearing fertilizers and arsenical pesticides (Meharg and Zhao 2012). In the case of the United Arab Emirates (Shirwaikar et al. 2013) (Table 2), rice that contained unusually high As concentrations were imported from the United States (0.925 ± 0.017 mg kg^{-1}), Egypt (0.786 ± 0.065 mg kg^{-1}), and India (Kolkata, 0.808 ± 0.018 mg kg^{-1}, and South India, 0.721 ± 0.056 mg kg^{-1}). This finding is in accordance with Meharg and Zhao (2012), who stated that the higher mean total As concentration was generally found in rice cultivated from the more industrialized countries such as the United States. Meanwhile, the mean total As concentrations in rice from Egypt and India as shown in Table 2 were in contrast to the mean total As concentrations in rice from India (0.07 mg kg^{-1}) and Egypt (0.05 mg kg^{-1}) that were reported by Meharg et al. (2009). This outcome might be due to the significantly smaller number of rice samples collected from the United Arab Emirates ($n = 3$ for rice imported from each country) and those reported by Meharg et al. (2009) ($n > 100$), as well as the influence of samples with high As levels.

Apart from those eight countries (Kazakhstan, Myanmar, India, Pakistan, Turkey, the United Arab Emirates, Finland, and Italy) in which rice sold in the country contained higher total As concentrations than the global normal level, rice available in the markets of most remaining countries in Table 2 contained typical concentrations of As in rice grain (>0.082–0.202 mg kg^{-1}). Zavala and Duxbury (2008) have compiled the total As concentrations in rice from different world regions and considered the level of As in rice of >0.082–0.202 mg kg^{-1} as the global normal As content in rice produced from the environment without As contamination. The levels of total As in rice in these particular countries (Table 2) are also in good agreement with those total As concentrations in the rice of the same countries reported during the last two decades (1990s–2009) (Rahman et al. 2014).

As clearly shown in Table 2, the total As in rice from the countries with less industrialization and urbanization processes such as Malawi, Nigeria, and Sri Lanka was relatively low (ranging from 0.01 to 0.059 mg kg^{-1}). Zavala and Duxbury (2008) have classified the level of As in rice less than 0.082 mg kg^{1} as an unusually low As content in the grain.

4.2 Total As Concentration in Husked Rice

Total As concentrations ranging from <0.003 to 0.739 mg kg^{-1} were found in the commercial husked (brown) rice (Table 2). The maximum total As concentration in the rice collected from half of the countries that were surveyed exceeded the Codex maximum standard of the As in husked rice (0.35 mg kg^{-1}). The mean total As concentrations in rice from most of the countries are in the category of high As in rice grain (>0.202–0.357 mg kg^{-1}), as determined by Zavala and Duxbury (2008).

Comparing the total As concentration in polished and husked rice from the same country of study (Table 2), the concentrations of the total As in husked rice were approximately, on average, 1.7-fold higher than its total concentration in polished rice. The level of As in the husked rice collected in Malawi was even up to four times higher than that of polished rice. The localization of As, which is mainly distributed between the husk and the endosperm (starchy grain), is the main reason for the significantly higher As concentration in husked (brown) rice than the polished (white) rice. Meharg et al. (2008) and Lombi et al. (2009) found that the As in the rice grain usually localizes within the pericarp and aleurone layers, which are the layers that give the rice grain its brown color. Meharg et al. (2008) further concluded that As, especially As(III), in rice basically has a high affinity for the protein and nonprotein with the thiol (–SH) functional group, such as phytochelatin and glutathione. Thus, the higher content of As was found in the husked rice which normally contains approximately 14.5–24.1% higher protein than the polished rice (Juliano 1993). The examples of the thiol-containing protein in husked rice are cysteine and methionine, which account for up to 9.1% and 10.2%, respectively, of the amino acids content in rice. Thiamine is an example of a thiol-containing vitamin in husked rice grain (Juliano 1993).

5 Market Basket Studies of Inorganic As in Rice

Regarding its high and lethal toxicity, As is one of the WHO's ten chemicals of major public health concern. It is well known that inorganic As (As(III) and As(V)) is more toxic than organic As (MMA and DMA). The International Agency for Research on Cancer (IARC) has classified As and its inorganic compounds as Group 1 human carcinogens. Although low levels of inorganic and organic As (generally less than 0.25 mg kg^{-1}) have been found in most foodstuffs, one's daily intake can be influenced by not only the level of As in food but also the quantity of the food consumed. The IARC (2012) has estimated that approximately 25% of daily dietary As intake is inorganic As. In addition, the ingestion of 70–180 mg of inorganic As could result in human death (Ruangwises et al. 2014). Since the daily rice consumption per capita is even as high as 422 g day^{-1} (OECD-FAO 2018), a concern regarding the exposure of As (especially inorganic As) to the level that may cause detrimental effects to an individual has been raised. This concern resulted in the establishment of the maximum level of inorganic As in rice, as summarized in Table 1.

5.1 Inorganic As Concentration in Polished Rice

Levels of inorganic As in the commercial polished rice grain (Table 3) from various countries were highly variable in the range of 0.002–0.699 mg kg^{-1}. The highest inorganic As, which was approximately 3.5-folds higher than the Codex maximum standard of inorganic As in polished rice (0.2 mg kg^{-1}), was detected in the Turkish polished rice grain. Apart from Turkish rice, the maximum inorganic As in rice from Canada (0.343 mg kg^{-1}), Argentina (0.221 mg kg^{-1}), Brazil (0.218 mg kg^{-1}), Kazakhstan (0.550 mg kg^{-1}), China (0.211 mg kg^{-1}), Japan (0.221 mg kg^{-1}), India (0.576 mg kg^{-1}), and Finland (0.280 mg kg^{-1}) was higher than the Codex standard. Interestingly, rice from those abovementioned countries from America and Asian regions that contained a maximum total As concentration (Table 2) higher than the Codex standard also contained inorganic As exceeding the Codex standard (Table 3). Nonetheless, the total As concentration in rice from all European countries was lower than the Codex standard, and only the maximum inorganic As in rice from

Table 3 Inorganic As concentrations (mg kg^{-1}) in raw polished and husked rice from various countries

Country	Polished/white rice		Husked/brown rice		References
	Range	Mean	Range	Mean	
Africa region					
Northern Africa					
Egypt	0.044–0.075	0.060			Raab and Ducos (2016)
Libya	0.098[a]				Raab and Ducos (2016)
Eastern Africa					
Malawi	NA[a]	NA[a]	0.015–0.093	0.060	Joy et al. (2017)
Western Africa					
Nigeria	0.025–0.066	0.047			Adeyemi et al. (2017)
America region					
Northern America					
Canada	0.002–0.343	0.217			Canadian Food Inspection Agency (2014)
United States of America	0.020–0.196	0.068	0.034–0.249	0.118	Trenary et al. (2012) and U.S. Food and Drug Administration (2016)
South America					
Argentina[b]	0.061–0.221	0.126			Sirgist et al. (2016)
Brazil	0.004–0.218	0.081	0.031–0.233	0.136	Batista et al. (2011)
Asia region					
Central Asia					
Kazakhstan	0.100–0.550	0.215	0.250–0.450	0.360	Tattibayeva et al. (2016)
Eastern Asia					
China	0.049–0.211		0.120–0.288		Liang et al. (2010), Fang et al. (2014), Li et al. (2015, 2018), Ma et al. (2016, 2017), and Zhuang et al. (2016)
Hong Kong	0.016–0.026	0.022	0.037–0.046	0.043	Wong et al. (2013)
Japan	0.031–0.221		0.044–0.431		Naito et al. (2015)
South Korea		0.060		0.138	Yim et al. (2017) and Lee et al. (2018)
Southeastern Asia					
Cambodia[c]	0.126–0.176	0.148			Wang et al. (2013) and Gilbert et al. (2015)
Malaysia	0.061–0.085	0.071			Nookabkaew et al. (2013a)
Thailand	0.016–0.162	0.074	0.073–0.207	0.123	Ruangwises et al. (2012) and Nookabkaew et al. (2013a)

(continued)

Table 3 (continued)

Country	Polished/white rice		Husked/brown rice		References
	Range	Mean	Range	Mean	
Vietnam	0.046–0.156	0.091	0.196–0.235	0.212	Nookabkaew et al. (2013a)
Southern Asia					
India	0.025–0.576	0.194			Halder et al. (2014)
Iran	0.040–0.135	0.082			Cano-Lamadrid et al. (2015)
Western Asia					
Iraq	0.040–0.098	0.065			Sadee et al. (2016)
Turkey	0.083–0.699	0.165			Raab and Ducos (2016) and Sadee et al. (2016)
Europe region					
Northern EU					
Finland	0.090–0.280	0.160			Rintala et al. (2014)
Scotland	0.029–0.149	0.087			Petursdottir et al. (2014)
United Kingdom	0.045–0.162	0.115			Sadee et al. (2016)
Southern EU					
Greece	0.030–0.147	0.093			Pasias et al. (2013)
Italy	0.001–0.200	0.100			Sommella et al. (2013)
Spain	0.027–0.175	0.071	0.053–0.247	0.157	Signes-Pastor et al. (2016)
Western EU					
Belgium	0.030–0.172	0.090			Ruttens et al. (2018)
France	0.034–0.160	0.093		0.079	Jitaru et al. (2016)
Switzerland	0.006–0.188	0.094	0.117–0.172	0.152	Guillod-Magnin et al. (2018)
Oceania					
Australia	0.016–0.296	0.124	0.178–0.276	0.227	Rahman et al. (2014)

The summary is based on the world regions by the United Nations Country Grouping (United Nations 2018)

[a] NA means that the inorganic As concentration was not analyzed because of the low total As concentration

[b] Inorganic As was estimated as 70% of the total As concentration

[c] Inorganic As was estimated as 80% of the total As concentration

Finland was found to be higher than the Codex standard. In general, Meharg and Zhao (2012) found a highly significant relationship between the total and inorganic As concentrations in rice ($r^2 = 0.768$, $p < 0.001$). Therefore, it is possible to estimate the inorganic As concentration in grain as 0.01 + 0.54 times the total As concentration.

The mean concentrations of inorganic As in the polished rice grain ranged from 0.022 to 0.217 mg kg^{-1} (Table 3). Only the rice from Canada and Kazakhstan were found to have mean inorganic As concentrations higher than the Codex standard (0.2 mg kg^{-1}). Table 3 shows that the inorganic As in rice grain varies between countries and regions. The rice grain from African countries such as Egypt and Nigeria had the lowest mean inorganic As concentrations. This outcome is in accordance with the low level of total As concentrations in rice from those countries, as reported in Table 2. By comparing the concentrations of inorganic As in rice from this study (Table 3) to those same countries reported during the last two decades (1990s–2009) (Rahman et al. 2014), similar ranges of inorganic As in rice from Italy, Spain, Thailand, and the United States were found. However, rice grain from China and India in this study contained 1.3- to 2.6-fold higher and 4.9- to 6.5-fold lower inorganic As concentrations than those reported by Rahman et al. (2014).

Regarding the percentage of inorganic As concentration (Table 3) to its total concentration (Table 2) in commercial rice, the percentages of inorganic As to total As varied from 0.4% to 100%. The lowest percentage of inorganic As to total As was found in Italian rice. This outcome was in good agreement with Williams et al. (2005) and Meharg et al. (2009), who reported great differences in the As speciation in the rice produced from different parts of the world. On average, 63.3% of the total As in rice grain in this study (Tables 2 and 3) is inorganic As. Meanwhile, organic As generally represents approximately 15.1–62.4% (mean: 36.7%) of the total concentration. Since it was reported by several researchers that DMA is the dominant organic As species in rice grain (Zavala et al. 2008; Meharg et al. 2009; Meharg and Zhao 2012; Rahman et al. 2014), rice can then be classified into two types: the DMA type and the inorganic As type. Rice with a concentration of inorganic As higher than DMA can be classified as the inorganic As type and vice versa.

It is clearly shown in Fig. 3 that rice from most countries comprise the inorganic As type with the average percentages of inorganic As to total As ranging from 50.3% to 84.9%. The percentages of inorganic As in rice grains were inconsistent with the countries and regions of this study. For example, rice from Kazakhstan, Japan, and Thailand contain 43.9–45.5% (Tattibayeva et al. 2016), 75–100% (Naito et al. 2015), and 42.5–96.1% (Ruangwises et al. 2012; Nookabkaew et al. 2013a), respectively, of inorganic As to total As. This outcome means that even though the rice is produced within one particular country, it is possible to find both types (DMA and inorganic As) in the study.

Regarding Fig. 3, rice from the United States, Brazil, China, and a few European countries including Italy and Spain can be classified as DMA rice type. Williams et al. (2005) and Meharg and Zhao (2012) found that the rice produced in the United States and European countries had high percentages of DMA. In contrast, Rahman et al. (2014) found that Australian and American rice mostly contained DMA, while

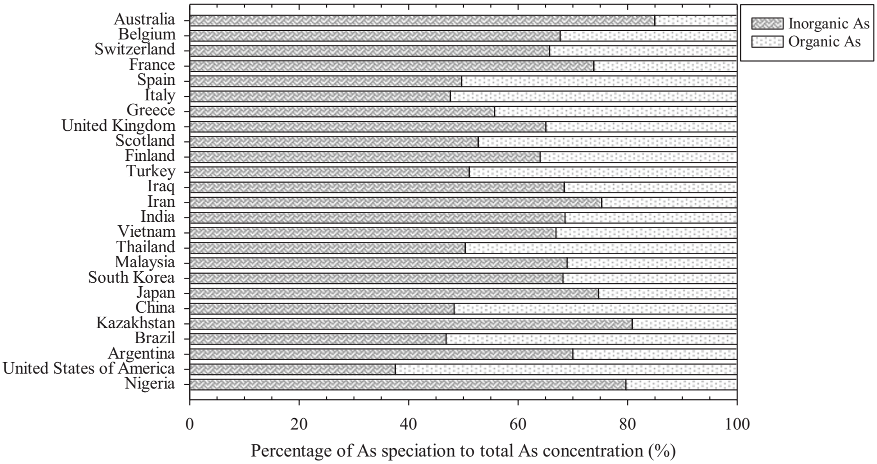

Fig. 3 The percentages of inorganic and organic As concentrations to the total As concentration in polished rice from different countries. The plots are made regarding the mean total and inorganic As concentrations shown in Tables 2 and 3

European and Asian rice mainly contained inorganic As. Figure 3 accords with those previous studies in that the rice from the United States is predominant with DMA, while the rice from Asian and European countries and Australia are dominated by inorganic As. Zavala et al. (2008) concluded that the accumulation of different As species in rice grain is mainly controlled by the genetic features of rice rather than the environmental conditions, such as climate conditions, the water management regime, and the As speciation in the soil and soil solution.

5.2 *Inorganic As Concentration in Husked Rice*

The concentrations of inorganic As in commercial husked rice varied from 0.015 to 0.450 mg kg^{-1} (Table 3). The maximum inorganic As concentrations in Kazakh and Japanese rice were approximately 1.2 times higher than the Codex standard of inorganic As in husked rice of 0.35 mg kg^{-1}. The mean inorganic As concentrations in rice from most of the countries surveyed except for the Kazakh rice were lower than the Codex standard. The concentrations of inorganic As in husked rice were higher than the corresponding inorganic As concentrations in the polished rice by approximately 1.8 times. This comparison has a similar magnitude to the total As concentration in the husked rice compared to that of the polished rice.

The ratios of inorganic As to total As in rice also varied widely. The highest ratio of inorganic total As in rice was found in Malawian rice (95%) (Adeyemi et al. 2017). The ratios of inorganic As in Asian rice were 90% for Kazakhstan (Tattibayeva et al. 2016), 68–88% for China (Liang et al. 2010; Li et al. 2015; Ma et al. 2017), 55.1–91.3% for South Korea (Yim et al. 2017; Lee et al. 2018), 40.5–83.7% for

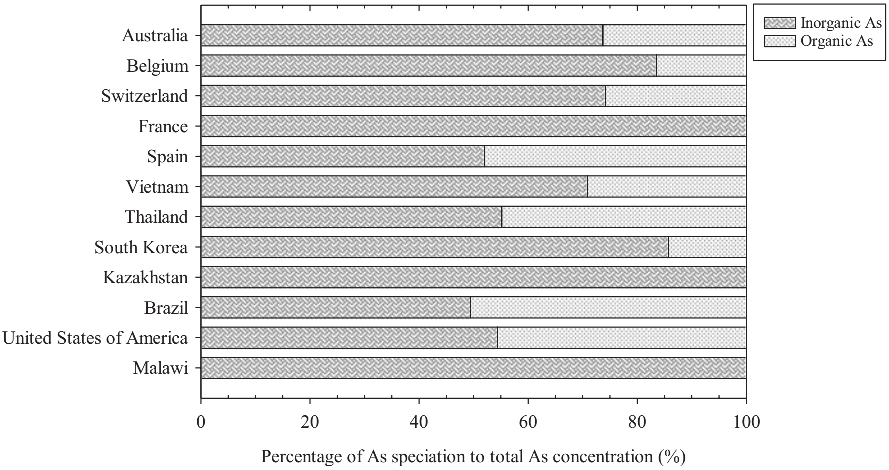

Fig. 4 The percentages of inorganic and organic As concentrations to the total As concentration in the husked rice from different countries. The plots are made regarding the mean total and inorganic As concentrations shown in Tables 2 and 3

Thailand (Nookabkaew et al. 2013a), and 67.5–77.9% for Vietnam (Nookabkaew et al. 2013a). Asian rice usually contained higher inorganic As than American and European rice. By comparing it to the total As concentration, commercial husked rice from Belgium, Spain, France, and Switzerland had approximately 62.5%, 52.0%, 62%, and 75.6%, respectively, of inorganic As in its grain (Jitaru et al. 2016; Signes-Pastor et al. 2016; Ruttens et al. 2018). Meanwhile, the lowest percentages of inorganic As to total As were generally found in the rice from the American region including the United States (53.2–67.2%) (Trenary et al. 2012; U.S. Food and Drug Administration 2016) and Brazil (53.9–54%) (Batista et al. 2011).

The classification of husked rice regarding the presence of inorganic and organic As in rice is shown in Fig. 4. This result is in good agreement with the polished rice in that rice from the American region is generally the DMA type while Asian and European rice are considered as the inorganic rice type. A comparison between Fig. 4 and Fig. 3 agrees well with the results reported by Meharg et al. (2008) in which the higher inorganic As proportion is generally present in husked rice rather than polished rice. Carey et al. (2010) studied the spatial unloading of As species in the grain and found the dispersion of As(III), which is one of the inorganic As species, in the external parts of the grain (rice bran). Conversely, the DMA was generally dispersed in the endosperm (the starchy part of the grain) (Carey et al. 2012). Approximately 70–80% of As(III) was found in the pericarp and aleurone layer, which is called rice bran after polishing (Meharg et al. 2008). In contrast, about half of the total As in the polished rice was As(III) (Meharg et al. 2008).

6 Bioaccessible As in the Commercial Rice

The determination of total and inorganic As is of significant interest in terms of the food safety for countries around the world for several decades. However, during the past few years, the study of the bioaccessibility of As in rice grain has been under the spotlight because it is believed that both the total and inorganic As concentrations in rice grain could not represent the actual amount of As that is readily absorbed by the human body after passing through the digestive system. Therefore, the determination of the bioaccessible As using the in vitro digestion model has been introduced. This in vitro digestion, which is a simplified version of the digestive system of the human body, principally includes the sequential steps of food digestion in the oral cavity by saliva, the stomach by gastric juice, and the small intestine by intestinal fluid. The bioaccessibility refers to the maximum concentration of the contaminant that is released from the food into the gastrointestinal media and readily available for absorption into the bloodstream (Ruangwises et al. 2014).

The bioaccessibility of As in the certified reference material of rice (CRM-T07151QC) was studied by Chavez-Capilla et al. (2016). Approximately 80 ± 1% of the bioaccessible As to the total As in the rice after passing through the simulated gastrointestinal digestion was found. Regarding the total As concentration, approximately 50.0% and 35.7% of bioaccessible As were released from rice in the stomach and small intestine, respectively.

In comparison to the bioaccessibility of As in the reference material, He et al. (2012) purchased locally grown polished ($n = 8$) and husked ($n = 9$) rice samples from food stores in New York City and analyzed the bioaccessible As, and its speciation in those samples had a total As concentration higher than the Codex standard (0.2 mg kg^{-1}). The in vitro digestion system in this study mimics the stomach and small intestine human digestion. The concentrations of bioaccessible As were 0.27–0.32 mg kg^{-1} in polished rice ($n = 5$; mean, 0.29 ± 0.05 mg kg^{-1}) and 0.13–0.62 mg kg^{-1} in husked rice ($n = 6$; mean, 0.32 ± 0.05 mg kg^{-1}). They found higher As bioaccessibility in the polished rice (92.6%) than in the reference material (80.0%) reported by Chavez-Capilla et al. (2016). The DMA was the predominant As species in the polished rice. Meanwhile, 66.2%, on average, of the total As in husked rice was bioaccessible As. The higher bioaccessible inorganic As was found in four husked rice samples. The ratios of bioaccessible inorganic As to total As in both types of rice (40.2 ± 7.4% for polished rice and 57.0 ± 15.7% for husked rice) were in the same magnitude of those ratios of inorganic As to total As in raw rice, as shown in Figs. 3 and 4.

On a contrary, Althobiti et al. (2018) studied the bioaccessible As in the polished and husked rice sold in Canada and found a lower mean level of bioaccessible As in polished ($n = 7$, 60.5 ± 25.6%) and husked ($n = 3$, 61.9 ± 21.8%) rice. Wide ranges of bioaccessible As to total As in both types of rice (16.0–93% in polished rice and 43.4–86.0% in husked rice) were reported. Compared to the stomach digestion, higher bioaccessible As species including As(III), As(V), and DMA were released into the saliva than the gastric juice. Interestingly, the most prevalent species was As(V).

In the case of the bioaccessible As in rice sold in Asia, Zhuang et al. (2016) analyzed the bioaccessible As in commercial and greenhouse-grown polished rice following two steps of gastric and small intestine digestion. High As bioaccessibilities were found in all rice samples with the highest bioaccessibility found in the greenhouse-grown rice (94.5%). The commercial rice sold in the local markets around the mining area contained higher bioaccessible As (88%) than that of the rice sold in the supermarket in South China (68.5%). An increase in bioaccessible As was found when comparing the bioaccessible As concentration between the gastric and gastrointestinal digestion steps. In contrast to Althobiti et al. (2018), this study concluded that the gastrointestinal phase plays an important role in the solubilization of As during the digestion process.

Meanwhile, Li et al. (2018) determined the As bioaccessibility in 70 Eastern Chinese rice samples after three digestive steps (oral, stomach, and intestine) and reported lower levels of bioaccessibility (n = 70, 37.9 ± 7.9%) than those levels in the rice collected in the United States (He et al. 2012) and Canada (Althobiti et al. 2018).

For Southeast Asian countries, Hensawang and Chanpiwat (2018) determined the bioaccessible As concentration in polished and husked rice sold in the local markets in Bangkok. Three simultaneous simulated human digestive steps (oral, stomach, and small intestine) were applied to dissolve the bioaccessible As from the rice grain. The concentrations of bioaccessible As in polished (n = 32, 0.026–0.134 mg kg^{-1}) and husked (n = 17, 0.099–0.196 mg kg^{-1}) rice were well below the Codex standards for both types of rice. Approximately 2.2–3.4 times and 1.8–2.5 times of the bioaccessible As concentrations were lower than the total As in polished and husked rice, respectively. In addition, 1.5- to 3.8-fold significantly higher concentrations of bioaccessible As were determined in the husked rice than the polished rice. Even though wide variations in the bioaccessibility of As in both types of rice were found (8.7–76.3% for polished rice and 29.4–74.0% for husked rice), a significant difference in the mean As bioaccessibilities in both types of rice could not be observed.

7 Field Studies of Arsenic in Rice Grain

In contrast to the market basket studies in which most of the studies are usually focused on the levels of total, inorganic, and bioaccessible As in the rice grain that was sold and consumed by the general population, the field studies of As in rice grain were mainly conducted in the As-contaminated areas to (i) investigate the levels of As in rice grain, (ii) determine the relationship between the As concentrations in soils and rice grains, and (iii) determine the soil factors that could affect the level of As in rice grain. Most of the study areas can be classified into two different types according to the sources of As contamination based on whether it is a natural or anthropogenic source. As clearly shown in the following summary, different levels of total As in rice grain according to the category of normal (>0.082–0.202 mg kg^{-1}), high (>0.357 mg kg^{-1}), and unusually high (>0.202–0.357 mg kg^{-1}) As as classified by Zavala and Duxbury (2008) were found from different studies.

The paddy soil and rice grain grown in the geogenic or mining-derived As origin in the Iberian Peninsula were collected by Signes-Pastor et al. (2016). The range and mean total As concentrations were 2.3–17 mg kg^{-1} and 8.7 mg kg^{-1}, respectively. The highest mean total As was found in the Portuguese soil (15 mg kg^{-1}). However, the inorganic As concentrations in dehusked rice (0.052–0.161 mg kg^{-1}) were lower than the Codex standard. The rice grown in this region was the inorganic As rice type. The range and mean percentage of inorganic As to total As were 41–97% and 85%, respectively. The relationship between the total As in soil and the inorganic As in rice followed a hyperbolic pattern and approached a maximum level of more than 0.100 mg kg^{-1}. In other words, a moderate level of inorganic As in rice was found when rice was cultivated in the soil with a high total As. In addition, this study found positive correlations between the total and inorganic As concentrations in locally grown and commercial rice with the levels of 0.98 and 0.76, respectively.

Another study was conducted in the paddy fields located near the industrial zone comprised of printing, dyeing, electroplating, electronics, metallurgy, chemicals, pesticides, and livestock and poultry breeding farms in the Yangtze River Delta (Hang et al. 2009). A total of 155 samples of each paddy soil and the corresponding rice grains were collected. The total As concentrations in the soil ranged from 4.46 to 16.10 mg kg^{-1} (mean: 8.60 mg kg^{-1}). The highest level of As in the soil was higher than the background value of As in soil (15 mg kg^{-1}) that was regulated by the National Environmental Protection Agency. A wide variation in the total As in polished rice grain within the range of nondetectable to 0.587 mg kg^{-1} was observed. However, the mean total As concentration in rice (0.199 mg kg^{-1}) was lower than the Codex standard. A bioaccumulation factor or a ratio between the total concentrations of As in rice grain and the corresponding soil in this study was approximately 0.025. A spatial distribution analysis of the As concentration in soil indicated that a high As concentration in soil was well matched to the locations of the industrial zone and agricultural area with pesticide applications. In contrast, high concentrations of As in the rice grain were distributed around the city. The different spatial distribution patterns of As in the soil and rice indicated that the As accumulation in rice was not only affected by concentration of As in the soil but also by the soluble concentration fraction in the deposited air pollutant.

In Brazil, rice samples were collected from the fields with high application rates of phosphate fertilizers for at least 8 years (Corguinha et al. 2015). The levels of As in the agricultural soils (11 ± 0.5 mg kg^{-1}) were not significantly different from the noncultivated soils (12 ± 2.0 mg kg^{-1}) and were lower than the Brazilian maximum allowable concentration in agricultural soils. Even though rice has a high potential to accumulate greater amounts of As than other crops, this study found a nondetectable level of total As (<0.015 mg kg^{-1}) in all rice samples ($n = 60$).

For those natural sources of As contamination in the paddy fields, the As accumulation in rice grains as a result of cultivation with As-contaminated irrigation water and soil was reported. The total As concentrations in the rice grain cultivated in the western part of Bangladesh varied from 0.03 to 1.84 mg kg^{-1} (Rajmohan and Prathapar 2014). High As in the rice was generally correlated with high As in the soil. The levels of As concentrations in rice were in the order of husk>bran>husked rice>polished rice. Approximately 44–86% of the total As in Bangladeshi rice was inorganic As.

Phan et al. (2013) investigated the total As concentration in the paddy rice irrigated with groundwater from the As-contaminated areas in the Kandal and Kampong Cham provinces in Cambodia. There were significantly higher total As concentrations in both paddy soil and rice collected from Kandal (soil, 12.858 ± 10.430 mg kg^{-1}, rice, 0.247 ± 0.187 mg kg^{-1}) than those from Kampong Cham (soil, 0.794 ± 0.088 mg kg^{-1}, rice, 0.029 ± 0.024 mg kg^{-1}). The mean total As concentration in rice from Kandal ($n = 8$, 0.247 ± 0.187 mg kg^{-1}) was greater than the Codex standard of 0.2 mg kg^{-1} because rice in Kandal was irrigated by As-contaminated groundwater ($n = 46$, 846 ± 298 μg L^{-1}). Meanwhile, the groundwater ($n = 18$) in Kampong Cham contained only 1.28 ± 0.58 μg L^{-1} of total As. A high significant relationship between levels of As in the soil and rice grain was observed ($r^2 = 0.826$, $p < 0.01$). In 2014, Seyfferth et al. (2014) investigated the As concentrations in paddy soil and rice in the major rice-growing regions of Cambodia (Kandal, Prey Veng, Battambang, Banteay Meanchey, and Kampong Thom). The total As concentrations in husked rice ranged from 0.10 to 0.37 mg kg^{-1}, which exceeded the Codex maximum level of As in husked rice of 0.35 mg kg^{-1}. However, the average As concentration (0.20 ± 0.06 mg kg^{-1}) in rice grain was within the Codex standard. The rice produced from Banteay Meanchey contained significant higher As concentrations than those rice that were grown in the other areas. It was interesting to see that the total As in rice grain grown in Kandal, which is one of the most severely As-impacted areas in Cambodia, was not significantly higher than the rice grown in other areas, even though total As concentrations in the soil from Kandal and Prey Veng were significantly higher than the soil collected from Banteay Meanchey and Battambang. The total As concentration in the soil ranged from 0.8 to 18 mg kg^{-1}. In contrast to a significant relationship between the As in the soil and rice grain reported by Phan et al. (2013), Seyfferth et al. (2014) could not observe significant relationships between either the total or $CaCl_2$ extractable As concentrations, which are readily available concentrations for plants, to the As level in rice grain. However, they found that the As concentrations in husk and straw were important predictors of the As in rice grain.

In the case of Bolan et al. (2017), a study was conducted under either the greenhouse or field conditions to study the As accumulation in rice. Rice was irrigated with water containing various As (supplied as $Na_2HAsO_4{\cdot}7H_2O$) levels. The total As contents in rice ranged from 0.456 to 1.095 mg kg^{-1}. Rice cultivation with As-contaminated water was a reason for the total As in rice exceeding the Codex standard. The total As concentrations in rice grains were significantly correlated with its concentrations in both irrigation water and soil. This study further determined the levels of gastric bioaccessible As in rice grain. The percentage of As bioaccessibility ranged from 23.2% to 32.3%.

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References

Adeyemi JA, Adedire CO, Martins-Junior AC, Paulelli AC, Awopetu AF, Segura FR, de Oliveira-Souza VC, Batista BL, Barbosa F (2017) Arsenic speciation in rice consumed in south-western Nigeria, and estimation of dietary intake of arsenic species through rice consumption. Toxicol Environ Chem 99(5–6):999–1006

Adomako EE, Williams PN, Deacon C, Meharg AA (2011) Inorganic arsenic and trace elements in Ghanaian grain staples. Environ Pollut 159:2435–2442

Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risk of metals, 2nd edn. Springer-Verlag, New York, p 867

Agency for Toxic Substances & Disease Registry (ASTDR) (2014) Toxic substances portal: arsenic trioxide. https://www.atsdr.cdc.gov/MMG/MMG.asp?id=1200&tid=279. Accessed 20 Jul 2018

Ahmed MK, Shaheen N, Islam MS, Habibullah-Al-Mamun M, Islam S, Islam MM, Kundu GK, Bhattacharjee L (2016) A comprehensive assessment of arsenic in commonly consumed foodstuffs to evaluate the potential health risk in Bangladesh. Sci Total Environ 544:125–133

Althobiti RA, Sadiq NW, Beauchemin D (2018) Realistic risk assessment of arsenic in rice. Food Chem 257:230–236

Antoine JMR, Fung LAH, Grant CN, Dennis HT, Lalor GC (2012) Dietary intake of minerals and trace elements in rice on the Jamaican market. J Food Compos Anal 26:111–121

Batista BL, Souza JMO, Souza SSD, Barbosa FJ (2011) Speciation of arsenic in rice and estimation of daily intake of different arsenic species by Brazilians through rice consumption. J Hazard Mater 191(1–3):342–348

Bolan S, Kunhikrishnan A, Chowdhury S, Seshaadri B, Naidu R, Ok YS (2017) Comparative analysis of speciation and bioaccessibility of arsenic in rice grains and complementary medicines. Chemosphere 182:433–440

Canadian Food Inspection Agency (2014) Food safety action plan report (2011–2013 Targeted surveys – chemistry): arsenic speciation in selected foods. Food Safety Division, Canadian Food Inspection Agency, Ottawa

Cano-Lamadrid M, Munera-Pizaco S, Burlo F, Hojjati M, Carbonell-Barrachina AAC (2015) Total and inorganic arsenic in Iranian rice. J Food Sci 80(5):T1129–T1135

Carey AM, Scheckel KG, Lombi E, Newville M, Choi Y, Norton NJ, Charnock JM, Feldmann J, Price AH, Meharg AA (2010) Grain unloading of arsenic species in rice. Plant Physiol 152:309–319

Carey AM, Lombi E, Donner E, de Jonge MD, Punshon T, Jackson BP, Guerinot ML, Price AH, Meharg AA (2012) A review of recent developments in the speciation and location of arsenic and selenium in rice grain. Anal Bioanal Chem 402:3275–3286

Chaleshtori FS, Kopaei MR, Chaleshtori RS (2016) A review of heavy metals in rice (*Oryza sativa*) in Iran. Toxin Rev 36(2):147–153

Chavez-Capilla T, Beshai M, Maher W, Kelly T, Foster S (2016) Bioaccessibility and degradation of naturally occurring arsenic species from food in the human gastrointestinal tract. Food Chem 212:189–197

Chung JY, Yu SD, Hong YS (2014) Environmental source of arsenic exposure. J Prev Med Public Health 47:253–257

Codex Alimentarius Commission (1995) Codex standard 198–1995L standard for rice. http://www.fao.org/fao-who-codexalimentarius/sh-proxy/ru/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FStandards%252FCODEX%2BSTAN%2B198-1995%252FCXS_198e.pdf. Accessed 2 May 2018

Codex Alimentarius Commission (2014) Joint FAO/WHO food standards programme (Codex Alimentarius Commission) 37th session Geneva, Switzerland, 14–18 July 2014 and report of the eighth session of the Codex committee on contaminants in foods, The Hague, The Netherlands, 31 March-4 April 2014. http://www.codexalimentarius.org/download/report/906/REP14_CFe.pdf. Accessed 2 May 2018

Codex Alimentarius Commission (2016) Joint FAO/WHO food standards programme (Codex Alimentarius Commission) 39th session Rome, Italy, 27 June–1 July 2016 and report of the 10th session of the Codex committee on contaminants in foods, Rotterdam, The Netherlands, 4–8 April 2016. http://www.fao.org/fao-who-codexalimentarius/sh-proxy/zh/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FMeetings%252FCX-735-10%252FReport%252FREP16_CFe.pdf. Accessed 2 May 2017

Codex Alimentarius Commission (2017) Joint FAO/WHO food standards programme (Codex Alimentarius Commission) 40th session ICCG, Geneva, Switzerland, 17–22 July 2017 and report of the 11th session of the Codex committee on contaminants in foods, Rio de Janeiro, Brazil, 3–7 April 2017. https://www.livsmedelsverket.se/globalassets/om-oss/samarbeten/codex-alimentarius/rapport-fran-cccf-mote-april-2017-.pdf. Accessed 3 May 2017

Corguinha APB, de Souza GA, Goncalves VC, Carvalho CA, de Lima WEA, Martins FAD, Yamanaka CH, Francisso EAB, Chulherme LRG (2015) Assessing arsenic, cadmium, and lead contents in major crops in Brazil for food safety exposure. J Food Compos Anal 37:143–150

EU Commission Regulation (2015) Commission regulation (EU) 2015/1006 of 25 June 2015 amending regulation (EC) No. 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32015R1006. Accessed 2 May 2018

Fang Y, Sun X, Yang W, Ma N, Xin Z, Fu J, Liu X, Liu M, Mariga AM, Zhu X, Hu Q (2014) Concentrations and health risks of lead, cadmium, arsenic, and mercury in rice and edible mushrooms in China. Food Chem 147:147–151

Flora SJS (2015) Arsenic: chemistry, occurrence, and exposure. In: SJS F (ed) Handbook of arsenic toxicology, 1st edn. Academic, San Diego, pp 1–49

Food and Agriculture Organization of the United Nations (2004) Rice is life. http://www.fao.org/newsroom/en/focus/2004/36887/index.html. Accessed 2 Apr 2018

Food Standards Australia New Zealand (2017) Arsenic. http://www.foodstandards.gov.au/consumer/chemicals/arsenic/Pages/default.aspx. Accessed 2 May 2018

Fransisca Y, Small DM, Morrison PD, Spencer MJS, Ball AS, Jones OAH (2015) Assessment of arsenic in Australian grown and imported rice varieties on sale in Australia and potential links with irrigation practices and soil geochemistry. Food Chem 147:147–151

Ghazanfarirad N, Dehghan K, Fakhernia M, Rahmanpour F, Bolouki M, Zeynali F, Asadzadeh J, Bahmani M (2014) Determination of lead, cadmium and arsenic metals in imported rice into the west Azerbaijan province, northwest of Iran. J Nov Appl Sci 3(5):452–456

Gilbert PJ, Polya DA, Cooke DA (2015) Arsenic hazard in Cambodian rice from a market-based survey with a case study of Preak Russey village, Kandal Province. Environ Geochem Health 37(4):757–766

Guillod-Magnin R, Bruschweiler BJ, Aubert R, Haldimann M (2018) Arsenic species in rice and rice-based products consumed by toddlers in Switzerland. Food Addit Contam Part A 35(6):1164–1178

Halder D, Biswas A, Slejkovec Z, Chatterjee D, Nriagu J, Jacks G, Bhattacharya P (2014) Arsenic species in raw and cooked rice: implications for human health in rural Bengal. Sci Total Environ 497–498:200–208

Hang Z, Wang H, Zhou J, Ma C, Du C, Chen X (2009) Risk assessment of potentially toxic element pollution in soils and rice (*Oryza sativa*) in a typical area of the Yangtze river delta. Environ Pollut 157:2542–2549

He Y, Pedigo CE, Lam B, Cheng Z, Zheng Y (2012) Bioaccessibility of arsenic in various types of rice in an in vitro gastrointestinal fluid system. J Environ Sci Health B 47:74–80

Hensawang S, Chanpiwat P (2017) Health impact assessment of arsenic and cadmium intake via rice consumption in Bangkok, Thailand. Environ Monit Assess 189(11):599

Hensawang S, Chanpiwat P (2018) Analysis and probabilistic risk assessment of bioaccessible arsenic in polished and husked jasmine rice sold in Bangkok. Chemosphere 207:637–648

Hong YS, Song KH, Chung JY (2014) Health effects of chronic arsenic exposure. J Prev Med Public Health 47(5):245–252

Hughes MF, Beck BD, Chen Y, Lewis AS, Thomas DJ (2011) Arsenic exposure and toxicology: a historical perspective. Toxicol Sci 123(2):305–332

IARC (2012) IARC monographs on the evaluation of carcinogenic risks to humans: volume 100C (arsenic and arsenic compounds). http://monographs.iarc.fr/ENG/Monographs/vol100C/mono100C-6.pdf. Accessed 9 Jan 2018

IRIN (2010) Key facts about rice. http://www.irinnews.org/report/91012/asia-key-facts-about-rice. Accessed 2 May 2018

Islam MS, Ahmed MK, Habibullah-Al-Mamun M, Raknuzzaman M (2015) The concentration, source and potential human health risk of heavy metals in the commonly consumed foods in Bangladesh. Ecotoxicol Environ Saf 122:462–469

Islam MS, Ahmed MK, Habibullah-Al-Mamun A, Eaton DW (2017a) Arsenic in the food chain and assessment of population health risks in Bangladesh. Environ Syst Decis 37(3):344–352

Islam MS, Ahmed MK, Habibullah-Al-Mamun M, Eaton DW (2017b) Geographical variation and age-related dietary exposure to arsenic in rice from Bangladesh. Sci Total Environ 601–602:122–131

Jafari A, Kamrehie B, Ghaderpoori M, Khoshnamvand N, Birjandi M (2018) The concentration data of heavy metals in Iranian grown and imported rice and human health hazard assessment. Data Brief 16:453–459

Jeong JM, Kim EC, Venkatanagappa S, Lee JS (2017) Review of rice: production, trade, consumption and future demand in Korea and worldwide. Kor J Crop Sci 62(3):157–165

Jitaru P, Millour S, Roman M, Koulali KE, Noel L, Guerin T (2016) Exposure assessment of arsenic speciation in different rice types depending on the cooking mode. J Food Compos Anal 54:37–47

Joy EJM, Ander EL, Broadley MR, Young SD, Chilimba ADC, Hamilton EM, Watts MJ (2017) Elemental composition of Malawian rice. Environ Geochem Health 39:835–845

Juliano BO (1993) Rice in human nutrition. The International Rice Research Institute and Food and Agriculture Organizations of the United States, Rome. http://www.fao.org/docrep/t0567e/T0567E00.htm#Contents. Accessed 2 May 2018

Kapaj S, Peterson H, Liber K, Bhattacharya P (2006) Human health effects from chronic arsenic poisoning–a review. J Environ Sci Health A 41:2399–2428

Kollander B, Sundstrom B (2015) Inorganic arsenic in rice and rice products on the Swedish market 2015. Part I –a survey of inorganic arsenic (Rapport 16–205). Livsmedelsverket National Food Agency https://www.livsmedelsverket.se/globalassets/publikationsdatabas/rapporter/2015/a-survey-of-inorganic-arsenic-in-rice-and-rice-products-on-the-swedish-market-2015%2D%2D-part-1.pdf. Accessed 19 Jul 2018

Lai PY, Cottingham KL, Steinmaus C, Karaga MR, Miller MD (2015) Arsenic and rice: translating research to address health care providers' needs. J Pediatr 167(4):797–803

Lee SG, Kim DH, Lee YS, Cho SY, Chung MS, Cho MJ, Kang YW, Kim HJ, Kim DS, Lee KW (2018) Monitoring of arsenic contents in domestic rice and human risk assessment for daily intake of inorganic arsenic in Korea. J Food Compos Anal 69:25–32

Li X, Xie K, Yue B, Gong Y, Shao Y, Shang X, Wu Y (2015) Inorganic arsenic contamination of rice from Chinese major rice-producing areas and exposure assessment in Chinese population. Science China Chem 58(12):1898–1905

Li T, Song Y, Yuan X, Li J, Ji J, Fu X, Zhang Q, Guo S (2018) Incorporating bioaccessibility into human health risk assessment of heavy metals in rice (*Oryza sativa* L.): a probabilistic-based analysis. J Agric Food Chem 66(2):5683–5690

Liang F, Li Y, Zhang G, Tan M, Lin J, Liu W (2010) Total and speciated arsenic levels in rice from China. Food Addit Contam Part A 27(6):810–816

Lombi E, Scheckel KG, Pallon J, Carey AM, Zhu YG, Meharg AA (2009) Speciation and distribution of arsenic and localization of nutrients in rice grains. New Phytol 184:193–201

Ma L, Wang L, Jia Y, Yang Z (2016) Arsenic speciation in locally grown rice grains from Hunan Province, China: spatial distribution and potential health risk. Sci Total Environ 557–558:438–444

Ma L, Wang L, Tang J, Yang Z (2017) Arsenic speciation and heavy metal distribution in polished rice grown in Guangdong Province, Southern China. Food Chem 233:110–116

Magamage C, Waidyaratna WHMCU, Dhanapala WPAP (2017) Determination of heavy metals in rice available in Kandy district, Sri Lanka. Ann Sri Lanka Dep Agric 19:351–368

Mazumder DNG (2015) Health effects chronic arsenic toxicity. In: SJS F (ed) Handbook of arsenic toxicology, 1st edn. Academic, San Diego, pp 137–177

Meharg AA, Zhao FJ (2012) Arsenic & rice, 1st edn. Springer, New York

Meharg AA, Lombi E, Williams PN, Scheckel KG, Feldmann J, Raab A, Zhu Y, Islam R (2008) Speciation and localization of arsenic in white and brown rice grains. Environ Sci Technol 42:1051–1057

Meharg AA, Williams PN, Adomako E, Lawgali YY, Deacon C, Villada A, Cambell RCJ, Sun G, Zhu YG, Feldmann J, Raab A, Zhao FJ, Islam R, Hossain S, Yanai J (2009) Geographical variation in total and inorganic arsenic content of polished (white) rice. Environ Sci Technol 43:1612–1617

Mohamed H, Haris PI, Brima EI (2017) Estimated dietary intakes of toxic elements from four staple foods in Najran city, Saudi Arabia. Int J Environ Res Public Health 14:1575

Mwale T, Rahman MM, Mondal D (2018) Risk and benefit of different cooking methods on essential elements and arsenic in rice. Int J Environ Res Public Health 15:1056

Naito S, Matsumoto E, Shinhdoh K, Nishimura T (2015) Effects of polishing, cooking, and storing on total arsenic and arsenic species concentrations in rice cultivated in Japan. Food Chem 168:294–301

Naujokas MF, Anderson B, Ahsan H, Aposhian HV, Graziano JH, Thompson C, Suk WA (2013) The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem. Environ Health Perspect 121(3):295–302

Nawab J, Farooqi S, Xiaoping W, Khan S, Khan A (2018) Levels, dietary intake, and health risk of potentially toxic metals in vegetables, fruits, and cereal crops in Pakistan. Environ Sci Pollut Res 25(6):5558–5571

Nemati S, Mosaferi M, Ostadrahimi A, Mohammadi A (2014) Arsenic intake through consumed rice in Iran: markets role or government responsibility. Health Promot Perspect 4(2):180–186

Nookabkaew S, Rangkadilok N, Mahidol C, Promsuk G, Satayavivad S (2013a) Determination of arsenic species in rice from Thailand and other Asian countries using simple extraction and HPLC-ICP-MS analysis. J Agric Food Chem 61:6991–6998

Nookabkaew S, Rangkadilok N, Akib CA, Tuntiwigit N, Saehun J, Satayavivad J (2013b) Evaluation of trace elements in selected foods and dietary intake by young children in Thailand. Food Addit Contam Part B 6(1):55–67

OECD-FAO (2008) OECD-FAO agricultural outlook 2008–2017. http://argus.iica.ac.cr/Esp/organizacion/LTGC/Documentacion/BibliotecaVenezuela/Boletines/2008/n11/OECD-FAO-Agricultural%20Outlook.pdf. Accessed 2 Apr 2018

OECD-FAO (2017) OECD-FAO agricultural outlook 2017–2026, by commodity. http://stats.oecd.org/Index.aspx?datasetcode=HIGH_AGLINK_2017. Accessed 1 Apr 2018

OECD-FAO (2018) OECD-FAO agricultural outlook 2018–2027. https://stats.oecd.org/Index.aspx?datasetcode=HIGH_AGLINK_2018 Accessed 30 Jul 2018

Pasias IN, Thomaidis NS, Piperaki EA (2013) Determination of total arsenic, total inorganic arsenic and inorganic arsenic species in rice and rice flour by electrothermal atomic absorption spectrometry. Microchem J 108:1–6

Petursdottir AH, Friedrich N, Musil S, Raab A, Gunnlaugsdottir H, Krupp EM, Feldman J (2014) Hydride generation ICP-MS as a simple method for determination of inorganic arsenic in rice for routine biomonitoring. Anal Methods 6:5392–5396

Phan K, Sthiannopkao S, Heng S, Huoy L, Wong MH, Kim KW (2013) Arsenic contamination in the food chain and its risk assessment of populations residing in the Mekong river basin of Cambodia. J Hazard Mater 262:1064–1071

Raab A, Ducos SM (2016) Determination of inorganic arsenic in rice using IC-ICP-MS (application note 43255). Thermo Scientific. https://pdfs.semanticscholar.org/160a/0c72f5f2f308f8865808354143e020eff6cd.pdf. Accessed 20 Jul 2018

Rahman MA, Rahman MM, Naidu R (2014) Arsenic in rice: sources and human health risk. In: Watson RR, Preedy VR, Zibadi S (eds) Wheat and rice in disease prevention and health, 1st edn. Academic, San Diego, pp 365–375

Rajmohan N, Prathapar SA (2014) Extent of arsenic contamination and its impacts on the food chain and human health in the eastern Ganges Basin: a review. International Water Management Institute (IWMI)., 47 p. (IWMI Working Paper 161), Colombo. https://doi.org/10.5337/2014.224. Accessed 20 Jul 2018

Ratnaike RN (2003) Acute and chronic arsenic toxicity. Postgrad Med J 79(933):391–396

Rintala EM, Ekholm P, Koivisto P, Peltonen K, Venalainen ER (2014) The intake of inorganic arsenic from long grain rice and rice-based baby food in Finland – low safety margin warrants follow up. Food Chem 150:199–205

Rohman A, Helmiyati S, Hapsari M, Setyaningrum DL (2004) Rice in health and nutrition. Int Food Res J 21(1):13–24

Rowell C, Kuiper N, Al-Saad K, Nriagu J, Shomar B (2014) A market basket survey of As, Zn and Se in rice imports in Qatar: health implications. Food Chem Toxicol 70:33–39

Roya AQ, Ali MS (2017) Heavy metals in rice samples on the Torbat-Heidarieh market, Iran. Food Addit Contam Part B 10(1):59–63

Ruangwises S, Saipan P, Tengjaroenkul B, Ruangwises N (2012) Total and inorganic arsenic in rice and rice bran purchased in Thailand. J Food Prot 75(4):771–774

Ruangwises S, Saipan P, Ruangwises N (2014) Inorganic arsenic in rice and rice bran: health implications. In: Watson RR, Preedy VR, Zibadi S (eds) Wheat and rice in disease prevention and health, 1st edn. Academic, Cambridge, MA, pp 393–399

Ruttens A, Cheyns K, Blanpain AC, Temmerman LD, Waegeneers N (2018) Arsenic speciation in food in Belgium. Part 2: cereals and cereal products. Food Chem Toxicol 118:32–41

Sadee BA, Foulkes ME, Hill SJ (2016) An evaluation of extraction techniques for arsenic in staple diets (fish and rice) utilizing both classical and enzymatic extraction methods. Food Addit Contam Part A 33(3):433–441

Sahoo PK, Kim K (2013) A review of the arsenic concentration in paddy rice from the perspective of geoscience. Geosci J 17(1):107–122

Segura FR, Souza JMO, Paula ESD, Martin ACJ, Paulelli ACCP, Barbosa FJ, Babista BL (2016) Arsenic speciation in Brazilian rice grains organically and traditionally cultivated: is there any difference in arsenic content? Food Res Int 89(1):169–176

Seyfferth AL, McCurdy S, Schaefer MV, Fendorf S (2014) Arsenic concentrations in paddy soil and rice and health implications for major rice-growing regions of Cambodia. Environ Sci Technol 48:4699–4706

Shirwaikar A, Jacob S, Salman YG, Hamoudi NM, Chandrasekharan VR (2013) Preliminary investigation of arsenic in rice consumed in United Arab Emirates. Gulf Med J 2(S1):S146–S153

Shraim AM (2017) Rice is a potential dietary source of not only arsenic but also other elements like lead and chromium. Arab J Chem 10(S2):S3434–S3443

Signes-Pastor AJ, Carey M, Carbonell-Barrachina AA, Moreno-Jimenez E, Green AJ, Meharg AA (2016) Geographical variation in inorganic arsenic in paddy field samples and commercial rice from the Iberian Peninsula. Food Chem 202:356–363

Sirgist M, Hilbe N, Brusa L, Campagnoli D, Beldomenico H (2016) Total arsenic in selected food samples from Argentina: estimation of their contribution to inorganic arsenic dietary intake. Food Chem 210(1):96–101

Sohn A (2014) Contamination: the toxic side of arsenic. Nature 514:S62–S63

Sommella A, Deacon C, Norton G, Pigna M, Violante A, Meharg AA (2013) Total arsenic, inorganic arsenic, and other elements concentrations in Italian rice grain varies with origin and type. Environ Pollut 181:38–43

Tattibayeva D, Nebot C, Miranda JM, Cepeda A, Mateyev E, Erkebaev M, Franco CM (2016) A study on toxic and essential elements in rice from the Republic of Kazakhstan: comparing the level of contamination in rice from the European community. Environ Geochem Health 38(1):85–98

Tchounwou PB, Patlolla AK, Centeno JA (2003) Carcinogenic and systematic health effects associate with arsenic exposure – a critical review. Toxicol Pathol 31:575–588

Trenary HR, Creed PA, Young AR, Mantha M, Schwegel CA, Xue J, Kohan MJ, Herbin-Davis K, Thomas DJ, Caruso JA, Creed JT (2012) An in vitro assessment of bioaccessibility of arsenicals in rice and the use of this estimate within a probabilistic exposure model. J Expo Environ Epidemiol 22:369–375

U.S. Food and Drug Administration (FDA) (2016) Arsenic in rice and rice products risk assessment report. Center for Food Safety and Applied Nutrition, Food and Drug Administration, U.S. Department of Health and Human Services. https://www.fda.gov/downloads/food/foodscienceresearch/risksafetyassessment/ucm486543.pdf. Accessed 23 Jul 2018

United Nations (2018) Methodology: standard country or area codes for statistical use (M49). https://unstats.un.org/unsd/methodology/m49/. Accessed 20 Jul 2018

United States Department of Agriculture (2011) USDA foreign agricultural service (global agricultural information network: Israel food safety–heavy metals in foodstuffs. https://gain.fas.usda.gov/Recent%20GAIN%20Publications/Food%20Safety%20%E2%80%93%20Heavy%20Metals%20in%20Foodstuffs_Tel%20Aviv_Israel_1-18-2011.pdf. Accessed 3 May 2018

United States Department of Agriculture (2014) USDA foreign agricultural service (global agricultural information network: Peoples Republic of China's maximum levels for contaminants in foods. https://gain.fas.usda.gov/Recent%20GAIN%20Publications/Maximum%20Levels%20of%20Contaminants%20in%20Foods%20_Beijing_China%20-%20Peoples%20Republic%20of_12-11-2014.pdf. Accessed 3 May 2018

Wang HS, Sthiannopkao S, Chen ZJ, Man YB, Du J, Xing GH, Kim KW, Mohamed Yasin M, Hashim JH, Wong MH (2013) Arsenic concentration in rice, fish, meat and vegetables in Cambodia: a preliminary risk assessment. Environ Geochem Health 35(6):745–755

Williams PN, Price AH, Raab A, Hossain SA, Feldmann J, Meharg AA (2005) Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. Environ Sci Technol 39:5531–5540

Williams PN, Villada A, Deacon C, Raab A, Figuerola J, Green AJ, Feldmann J, Meharg AA (2007) Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. Environ Sci Technol 41:6854–6859

Wong WWK, Chung SWC, Chan BTP, Ho YY, Xiao Y (2013) Dietary exposure to inorganic arsenic of the Hong Kong population: results of the first Hong Kong total diet study. Food Chem Toxicol 51:379–385

Yim SR, Park GY, Lee KW, Chung MS, Shim SM (2017) Determination of total arsenic content and arsenic speciation in different types of rice. Food Sci Biotechnol 26(1):293–298

Zavala YJ, Duxbury JM (2008) Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain. Environ Sci Technol 42:3856–3860

Zavala YJ, Gerards R, Gurleyuk H, Duxbury JM (2008) Arsenic in rice: II. Arsenic speciation in USA grain and implications for human health. Environ Sci Technol 42:3861–3866

Zhuang P, Zhang C, Li Y, Zou B, Mo H, Wu K, Wu J, Li Z (2016) Assessment of influences of cooking on cadmium and arsenic bioaccessibility in rice, using an in vitro physiologically-based extraction test. Food Chem 213:206–214

Arsenic in Rice-Based Food Products for Adults and Children

Tatiana Pedron, Bruna Moreira Freire, Fernanda Pollo Paniz, and Bruno Lemos Batista

Abstract Currently, there is a range of rice-based foods such as baby foods, crackers, porridge, and milk, among others. Children and celiac population highly consume these foods. Rice and rice-based food are essential for society due to their health benefits and historical cultivation. However, nowadays, rice is the focus of several studies not only for the benefits but also because it is a plant able to absorb about tenfold more arsenic (As) than other cereals. Arsenic is known by its genotoxic and carcinogenic capacity, mainly concerning inorganic As (i-As), about 100-fold more toxic than organic As. Several rice-based foods were above 200 μg kg^{-1}, the maximum limit recommended by Codex for i-As, such as husked rice flour with a concentration of 528 μg kg^{-1}. Other rice-based foods with lower concentrations of i-As, such as milk with 4.3 μg kg^{-1}, are also relevant to mention since there is no safe daily intake for As. In this regard, values for confidence limit lower than the reference dose (BMDL 0.1) of 0.3 to 8 μg kg^{-1} body weight per day are used for assessment and characterization of the related health risks, such as bladder cancer. Thus, the determination of As concentrations in these foods is fundamental for a better risk assessment, especially concerning children, due to their physical and physiological condition, in which they may be more exposed to the damages caused by As when compared to adults in general.

Keywords Arsenic exposure · Rice derivatives · Baby food · Arsenic species · Inorganic As · Risk assessment

1 Introduction

With an important role in societies and especially in food security, rice is the predominant source of carbohydrates for more than 50% of the world's population. Rice is the third largest cereal culture in the world, after corn and wheat (Gomez and

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Magalhães 2004; Nunes 2016), being related to nutrition and food safety, mainly in Asia, Caribbean, Latin America, and Africa. Rice is also a cultural commodity in many developed and developing countries, such as China and Brazil (Muthayya et al. 2014; Calpe 2006). This grain is a valuable cereal because, once polished, their grains can be stored for thereabout 1 year and it needs just cooking to eat.

World rice utilization in 2017–2018 is estimated at 503.9 million tons of polished grains (FAO 2018). The primary use, 85% of the annual production, is intended for human consumption (Maclean 2002). However, there are other uses, such as seeds and animal feed. China and India are the largest producers and consumers of rice in the world. However, in countries from Africa and Latin America, the consumption of rice has increased considerably in the last decades. (Muthayya et al. 2014; Calpe 2006; FAO 2018).

Even though the most popular form of consumption of rice is as kernels, there are other possibilities. After the cultivation, harvesting, and polishing, rice may either be consumed as grains or be processed to produce rice-based food. In the last case, rice is used in different amounts to produce baby meals, pasta, flour, noodles, milk, cereals, cakes, flakes, snacks, and crackers. These products are consumed by populations who have some dietary restrictions, including babies, celiac, and lactose intolerant (De Los Santos et al. 2012).

Because of its insipidity, high energy value, and low allergic potential, its derivatives are one of the first foods to be consumed by children (Meharg et al. 2008a, b). Figure 1 illustrates the processes of some examples of foods that may be produced from rice. The production of rice-based value-added food has increased in response to new consumer needs, such as the need for gluten-free products mostly for people suffering from the celiac disease (Muthayya et al. 2014; Calpe 2006; Niewinski 2008).

Celiac disease is caused by gluten intolerance, a protein found in wheat, rye, and barley. This protein causes toxic effects in intestinal cells, characterized as a genetic digestive disease that damages the small intestine membrane and interferes with the absorption (decreases) of nutrients in food (De Los Santos et al. 2012; Husby et al. 2012; NIDDKD 2008).

Essential elements to human physiology such as zinc, copper, and magnesium are present in rice and its derivatives (Parsons and Barbosa 2007; Valko et al. 2005). About 20% of the world's daily caloric intake is provided by rice. This value can reach more than 50% in developing countries. Although providing proper amounts of energy, protein, and zinc, rice is not a good source of vitamins and minerals such as iron and vitamin A. The polishing process is responsible to increase the removal of these nutrients (Muthayya et al. 2014; Calpe 2006; FAO 2018; Pedron et al. 2019) and nonessential elements like arsenic (As) and cadmium (Batista et al. 2011, Pedron et al. 2016). Even at low concentrations, exposure to potentially toxic elements in rice may pose a risk to human health once it is a highly consumed food. Studies indicate tumorigenicity (>50%) and metastasis (>40%) of cells exposed to As in rats. Cells were treated with As 0, 0.125, 0.250, and 0.500 μM for 18 weeks and inoculated subcutaneously in nude mice (Zhao et al. 1997).

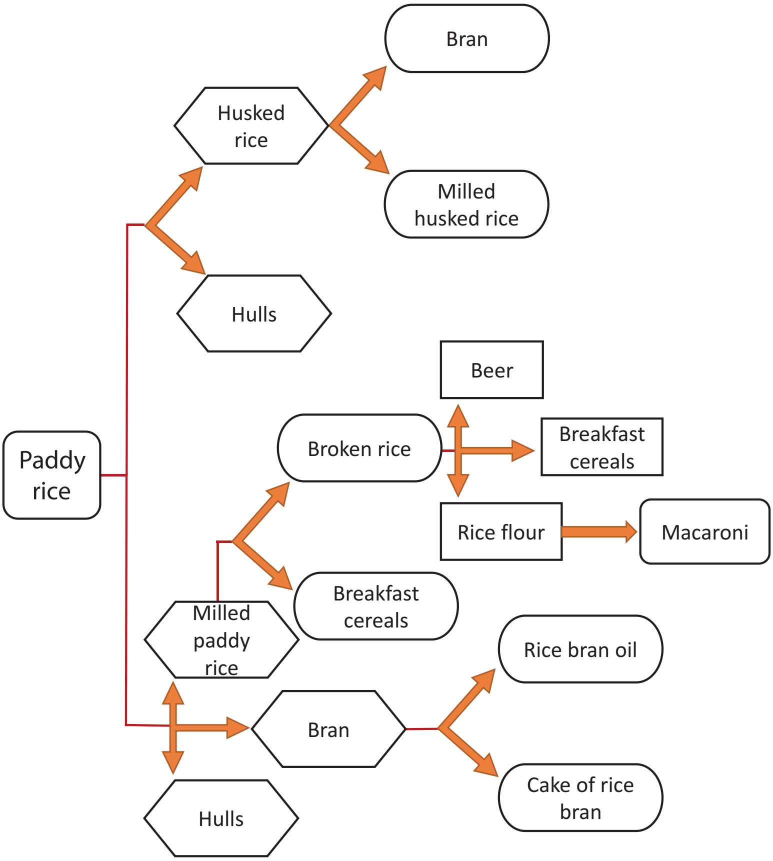

Fig. 1 Production of rice-based foods. Two main products are produced from paddy rice. Husked (brown) rice and polished (milled, white) rice. The bran generated by rice polishing can be used to produce a cake of rice bran and rice bran oil. From the polished grains, many derivatives may be produced, namely, breakfast cereals, rice flour, beer, and macaroni

1.1 Arsenic in Food

Arsenic is a ubiquitous element, being present in the form of more than 200 species. Classified as metalloid, As can occur in the environment in various states of oxidation (−3, 0, +3, and +5) and forms, such as organic (o-As) (monomethylarsonic, MMA, and dimethylarsinic, DMA) and inorganic forms (i-As) as arsenite (As^{3+}) and arsenate (As^{5+}) (Das et al. 1995; Smedley and Kinniburgh 2001).

Arsenic is mainly found as a mineral in the environment, usually bound to other elements such as iron, copper, nickel, and gold. When these minerals are exposed to the atmospheric surface, reactions of oxide reduction, complexation, and adsorption take place, forming other species of As with higher solubility in water and mobility in the atmospheric compartments (Vaughan 2006).

Islam et al. (2017) investigated total i-As in 59 samples from supermarkets in South Australia. The i-As content at six categories of rice-based products demonstrated the following order of concentration: rice crackers > baby rice > rice cakes > puffed rice > other rice-based snacks > ready-to-eat rice. This study shows that 53% of rice products had As greater than 100 μg kg^{-1} for young children (EU recommended value) and 22% of samples was higher than 200 μg kg^{-1} (Islam et al. 2017).

Food contamination by As occurs naturally; however the anthropogenic action contributes by the use of pesticides (cacodylic acid), wood preservatives, led (gallium arsenide), parasitic medications and rapid development facilitator of poultry and horse roxarsone ((4-hydroxy-3-nitrophenyl)arsonic acid) and nitarsone ((4-nitrophenyl)arsonic acid), and other applications (Butcher 2007; GPO 2012a, b; Navas-Acien and Nachman 2013). Compounds such as roxarsone are considered to be nontoxic. However, this compound can be converted into As^{3+} and As^{5+}. Microorganisms can convert the roxarsone present in animal manure in As^{5+} in less than 10 days. About 70–90% of As present in poultry manure is soluble in water, thus contaminating soils and groundwater (Dionísio et al. 2011).

Arsenic is transported in the environment mainly through water (WHO 2000). It is estimated that more than 200 million people in the world are exposed to As through drinking water (WHO 2008). In non-endemic regions, exposure to As occurs mainly through food and water (Meacher et al. 2002; Meliker et al. 2006; Tsuji et al. 2007; Meharg et al. 2008b; Sun et al. 2008).

The presence of As in food and water is a public health problem. Cardiac, lung, and bladder diseases and diabetes are related to exposure to As and its compounds. These diseases are not only related to the time and dosage of exposure but also the methylation of As in the human organism, nutritional status of the individual, sex, pregnancy, and others (IARC 2012). According to the International Agency for Research on Cancer (IARC), the daily intake of As through food and drink is generally 20–300 μg day^{-1}. In this concern is rice. This cereal accumulates tenfold higher As compared to other cereals such as wheat or barley (Meharg and Zhao 2012). Generally, about 50% of the total As in the rice grain is inorganic (As^{3+} + As^{5+}), the most toxic species of As (Heikens 2006).

Given its ubiquity and risk, FAO has discussed the provisional tolerable intake for several contaminants, including As (FAO 2010). Currently, there is no safe limit for As ingestion. According to the European Food Safety Authority, values for confidence limit lower than the reference dose (BMDL 0.1) of 0.3–8 μg As kg^{-1} body weight per day should be used for the assessment and characterization of exposure-related risks (EFSA 2009).

1.2 Arsenic and Rice: Relation, Species, and Monitoring

The rice specie *Oryza rufipogon* began to be cultivated and consumed about 10,000 years ago in the subtropical and tropical areas of Asia. Since then, it has undergone a continuous selection until reaching the species *Oryza sativa* L., considered a monocotyledon of the Poaceae family. This specie is considered the most cultivated (Gomez and Magalhães Junior 2004; Khush 1997).

The rice grain consists of the husk, pericarp, integument, nucleus, aleurone, endosperm, and embryo. During processing, three kinds of grains can be obtained: husked, polished, and parboiled. The husked rice is due to the removal of the husk. The polished rice is due to the removal of the husk and other outer layers of the grain (pericarp, integument, and aleurone) by polishing. The parboiled rice is the whole grain (with husk) partially cooked for internalization in the grain of the nutrients present in the husk and outer layers (Gomez and Magalhães Junior 2004).

The plant of rice tends to absorb easily As, more than other plants. Generally, rice is cultivated in flooded soils. This condition promotes an anoxic environment, where As^{3+} is released from minerals by microbial activity. The As^{3+}, the predominant form, have high solubility in water, being readily absorbed by the roots, reaching the grains (FDA 2016a, b; Ma et al. 2008; Xu et al. 2008).

Compared to inorganic forms, the organic forms of As (mainly MMA and MDA) are absorbed by the roots more slowly and transported efficiently to the grains. Different rice cultivars with high As concentration present higher concentrations of organic As relatively to inorganic As (Abedin et al. 2002; Carey et al. 2018; Meharg and Zhao 2012; Batista et al. 2014; Segura et al. 2018).

In the root, plants efficiently capture and transport employing silicate carriers the MMA and DMA forms, which are analogous forms of silicic acid. In the plant, the silicate is related to the increase of the resistance to the attack of pests, nematodes, and diseases and decrease of the transpiration rate and greater photosynthetic efficiency. Concerning inorganic forms such as As^{3+} and As^{5+}, these are structurally similar to silicic acid and phosphate, respectively. Phosphate is indispensable for plant growth and production since it is linked to several processes, such as energy storage and transfer, cell division, and photosynthesis (Karimi et al. 2009; Meharg and Zhao 2012; Korndörfer 2015). Once absorbed by the roots, As^{5+} is reduced to As^{3+} by arsenate reductase (AR). Through the xylem and the phloem, As arrives to the leaves and the grains. Arsenite and DMA are the main As species found in the grains (Smith et al. 2008; Ali 2012).

Several studies relate As/rice through research on contaminated soils, irrigated with contaminated water and also by the risk of their consumption (Williams et al. 2007; Batista et al. 2010, 2011). After fish and seafood, rice is the third food that contributes to As intake (Tao and Bolger 1999).

The necessity to determine the total concentration of an element is fundamental to evaluate its presence in a specific sample matrix. In this sense, several studies have determined the concentrations of As in foods (Tao and Bolger 1999; Williams et al. 2007; FDA 2016a, b).

There is increasing concern about the toxic effects that chemical substances can cause to the human body; however, information about total concentration is limited when analyzed alone as they do not indicate the real health risk. Biochemical and toxicological effects are related to chemical species, as well as their amounts (Kot and Namiesnik 2000).

Table 1 Maximum limits (mg kg^{-1}) of As (total) and i-As (As^{3+} + As^{5+}) in different processed grains of rice and baby foods

	Rice											
	Polished			Husked			Parboiled			Baby food		
Analyte	CAC	CE	MS	CAC	CE	MS	CAC	CE	MS	CAC	CE	MS
As	–	–	0.3	–	–	0.3	–	–	0.3	–	–	–
i-As[Θ]	0.2	0.2	–	0.35	0.25	–	–	0.25	–	–	0.1	–

CAC Codex Alimentarius Commission (Program of the Food and Agriculture Organization of the United Nations (FAO) and United Nations World Health Organization (WHO)), *EC* European Community, *MS* MERCOSUL, *As* arsenic (total), *i-As* inorganic arsenic (sum of As^{3+} + As^{5+}), [Θ] i-As determination is only performed when As (total) value exceeds the maximum threshold for i-As. Sources: EU 2015/1006 (i-As); CXS 193–1995 Revised 2017 (i-As); MERCOSUR Resolution RDC No. 42 of August 29, 2013 (Annex GMC/RES.No12/11)

Chemical species are dependent on various conditions, such as concentration, mobility, pH, redox conditions, temperature, and microbiological activity (Robertson 1989; Kot and Namiesnik 2000). These conditions differentiate the element not only by its chemical and physical form but also by its toxicity.

Inorganic species are 100 times more toxic than organic ones (MMA and DMA) (Das et al. 1995; Smedley and Kinniburgh 2001). Among the inorganics, As^{3+} is about 60 times more toxic than arsenate As^{5+} (Aposhian and Aposhian 2006).

Generally, methylation in humans is considered a detoxification process and is related to several factors such as age, dose of exposure, susceptibility, and nutritional factors (Faraj 2011).

Currently, the maximum allowed value of As for polished rice is 200 μg kg^{-1} inorganic As (i-As), and for husked rice, values have been discussed in the range of 300–400 μg kg^{-1} of i-As (CAC 2014) (Table 1).

1.3 Fetal Exposure

There are no direct studies regarding fetal As exposure through rice consumption. Most of the studies focus on direct exposure to pregnant women, especially in relation to consumption through ingestion of water, and some are related to rice cultivated at contaminated areas with consequent ingestion and exposure of population (Hopenhayn-Rich et al. 2000; Smith et al. 2000; Abedin et al. 2002; Meharg and Rahman 2003). These studies focus on the determination of the urine of pregnant women in which is a bioindicator of exposure to the pregnant women's As and indirectly of the fetus (Farzan et al. 2013; Nadeau et al. 2014; Davis et al. 2015; Liu et al. 2018)

Firstly, it is important to understand the As-metabolism. The As^{3+} enters in the body through mechanisms of simple diffusion. Arsenite is methylated to MMA^{5+} and DMA^{5+} by the enzyme methyltransferase. About As^{5+}, its cellular permeability is probably lower due to the energy-dependent transport system. Once in the bloodstream, As^{5+} is reduced to As^{3+}, which allows the entry into the cells for methylation

(Huang and Lee 1996; Aposhian and Aposhian 2006; Klaassen and Watkins 2008, Vahter 2002).

Some studies have shown that rice is an important source of As exposure for infants, adolescents, adults, and particularly for fetuses (Davis et al. 2017; Carey et al. 2018). For instance, As inhibits several processes concerning the metabolism of iodine by the interaction with biomolecules or competition for absorption (Klaassen and Watkins 2008).

Sanders et al. (2014) observed an interactive potential between As and manganese in pregnant women. This association can cause cardiac malformations, cleft lip, and bifida spine in the fetus. Raqib et al. (2009) evaluated 140 pregnant in Bangladesh. Urinary As during pregnancy was positively associated with fever and diarrhea in mothers and acute respiratory infections in the infants. Male children were especially affected, leading to believe that it could be partially gender dependent.

A study was carried out analyzing chemical elements in urine samples from US 229 pregnant women (Gilbert-Diamond et al. 2011). In the sixth month of pregnancy, a sample of urine was collected with a dietary record from 3 days for water, fish, seafood, and rice. The authors also analyzed the home tap water from participants and estimated that women consumed a median of 0.27 μg day^{-1} of As through home tap water. From the 229 voluntaries, only 73 consumed rice 2 days before urine collection. The rice intake ranged from 0 to 112.5 g day^{-1} (measured as a dry mass) with a mean of 28.3 g day^{-1}. The median of total As in urine was 3.78 μg L^{-1} (total women, $n = 229$) and 5.27 μg L^{-1} (rice eaters $n = 73$). Analysis by HLPC-ICP-MS found that the concentrations of inorganic As (As^{3+} + As^{5+}) were 0.24 μg L^{-1} ($n = 229$) and 0.28 μg L^{-1} ($n = 73$) and DMA were 3.25 μg L^{-1} ($n = 229$) and 4.09 μg L^{-1} ($n = 73$). The increased concentrations of DMA and other methylated forms in urine are due mainly to the individual methylation efficiency (Vahter 2002). Nowadays, the DMA is an emergent concern. Some studies showed the ability of DMA causes bladder carcinogen in rats and mice (Wei et al. 2004). However, studies involving humans indicate that there is a negative relationship between DMA and the development of cancer, despite its genotoxicity. Concerning MMA, the relationship is positive for the development of several types of cancer (Gamboa-Loira et al. 2017).

Rice consumption in the United States is about 32 g of cooked rice a day (USDA 2008); however, it's worthy of investigation to mention that the fetal development represents a highly vulnerable phase for As exposure with both immediate and long-term health risks (Concha et al. 1998; Vahter 2008; Gilbert-Diamond et al. 2011).

1.4 Child Exposure

The period of prenatal and weaning may give rise to adverse effects on child health and development. The brain is particularly vulnerable during development (gestation and early childhood), and often the damage induced by neurotoxic agents is permanent (Vahter 2008). Experimental studies in rats have shown associations between fetal exposure and neurotoxicity and behavioral changes (Wang et al. 2006).

Evaluation of breast milk is critical once infants below 6 months of age are fed exclusively with breast milk. A study evaluated samples of breast milk from 36 women living in an area of chemical weapon disposal after the World War II. They found that the As concentration was below 0.3 $\mu g\ L^{-1}$ (Sternowsky et al. 2002). Fängström et al. (2008) analyzed metabolites of As in breast milk and infant urine of 3 months of age. Results showed the prevalence of i-As in milk in very low concentration (1 $\mu g\ kg^{-1}$). The urine analysis showed that the infants had a higher fraction of DMA. Arsenic in breast milk was associated with its value in maternal blood, urine, and saliva. Other studies have shown that rice-based infant foods have higher amounts of As than those non-rice based (Pedron et al. 2016). Rice derivatives such as cakes, waffles, crackers, and wafers can contribute to i-As exposure of infants and young children since these products have high amounts of that As specie (EU 2015).

Figure 2 presents the most studied rice-based food products considering a group of 22 papers published from 2008 to 2018. Pastries and infant food are the most representative. The group "pastries" includes sweets, biscuits, cookies, crackers, cereal bars, cupcakes and cakes, wafers, and other snacks, and it is cited in 20.97% of the literature analyzed. The category "baby/infant food" includes food specially

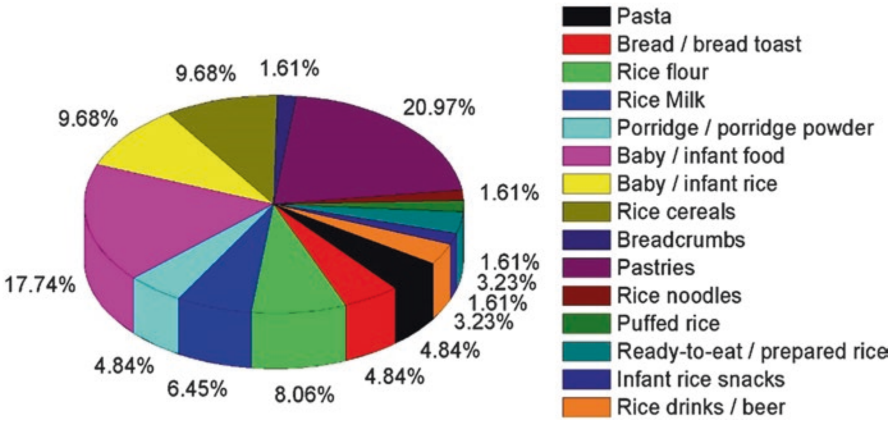

Fig. 2 The most frequently studied rice-based food products, considering a total of 22 papers published from 2008 to 2018 that analyzed samples from Australia, Austria, Belgium, Brazil, Canada, China, Croatia, the Czech Republic, England, the European Union, Finland, France, Germany, Greece, India, Italy, Japan, Korea, Mexico, the Netherlands, New Zealand, Northern Ireland, Poland, Spain, Switzerland, the United Kingdom, the United States, and Thailand. (Cano-Lamadrid et al. 2016; Carbonell-Barrachina et al. 2012; Carey et al. 2018; Guillod-Magnin et al. 2018; Hernández-Martínez and Navarro-Blasco 2013; Huber et al. 2017; Islam et al. 2017; Jung 2018; Llorente-Mirandes et al. 2014; Mania et al. 2015; Meharg et al. 2008a, b; Munera-Picazo et al. 2014a, b; Narukawa et al. 2012, 2014; Orecchio et al. 2014; Pasias et al. 2013; Pedron et al. 2016; Rintala et al. 2014; Ruiz-de-Cenzano et al. 2017; Signes-Pastor et al. 2016, 2017)

developed for children, such as infant rice powders, baby muesli, infant cereal, and rice gruel for infants. These products are cited in 17.74% of the literature.

Children are a group of particular concern due to their vulnerability and the wide variety of rice-based products consumed by them such as pastries and baby/infant food (Table 2). Moreover, children consume more food in relation to their body weight compared to adults. Therefore they may be two- to threefold more exposed than adults. Another group which is particularly exposed is the population suffering from celiac disease. This population ingests higher amounts of rice-based products because they are gluten-free. Both susceptible populations, children under 3 years old and with celiac, are highly exposed to i-As mainly through rice and rice-based products (Pedron et al. 2016; EFSA 2009; Carey et al. 2018; EU 2015).

The graph illustrated in Fig. 3 shows the number of rice-based samples as a function of the mean As concentration. The majority of the sample ($n = 580$) presented levels of As from 0 to 100 μg kg^{-1}, considered a safe concentration. On the other hand, 31 samples presented As in the range from 250 to 300 μg kg^{-1}, which can be considered a concerning level. Eight products, four samples of rice flour and four of baby rice, presented more than 300 μg kg^{-1} of As. These foods are consumed particularly for the most susceptible populations: celiac and children. Rice flour is an alternative to wheat flour for the celiac population, while baby rice is a food intended for children.

Table 2 Concentration of total and inorganic arsenic in rice-based food products from different countries analyzed from 2008 to 2018

Sample	Country	*N*	Total As (μg.kg^{-1}) Mean (Min.–Max.)	i-As (μg.kg^{-1}) Mean (Min.–Max.)
Pasta (Munera-Picazo et al. 2014a)	Spain	4	158.1 (46.3–256)	92.3 (30.9–135)
Bread (Munera-Picazo et al. 2014a)	Spain	2	66.8 (62–71.6)	34.2 (34.1–34.4)
B. cereals (Munera-Picazo et al. 2014a)	Spain	1	136	124
Biscuits (Munera-Picazo et al. 2014a)	Spain	3	25.6 (16.8–31.8)	20.7 (12–35.3)
I. rice (Carbonell-Barrachina et al. 2012)	China	14	135 (70–353)	114 (52–247)
I. rice (Carbonell-Barrachina et al. 2012)	USA	5	253 (164–496)	125 (93–159)
I. rice (Carbonell-Barrachina et al. 2012)	UK	5	237 (137–394)	162 (107–267)
I. rice (Carbonell-Barrachina et al. 2012)	Spain	7	181 (36–315)	85 (10–111)
Rice flour (Pasias et al. 2013)	Greece	3	102.3 (<22.1–170)	107 (<30.1–107)
Porridge (Pedron et al. 2016)	Brazil	1	102.4	34.3
Rice flour (Pedron et al. 2016)	Brazil	2	75.3 (39.1–111.6)	55.4 (47.4–63.4)
Pasta (Pedron et al. 2016)	Brazil	3	119.4 (70.6–202.3)	69.3 (63.2–79.7)
Milk (Pedron et al. 2016)	Italy	3	30.7 (16.4–57)	22.3 (16.8–26.6)
Baby food (Pedron et al. 2016)	Brazil	2	15.6 (12.6–18.7)	20.1 (17.5–22.8)
White rice flour (Narukawa et al. 2012)	Japan	20	148.7 (83–322)	102.3 (56–197)
Baby rice (Signes-pastor et al. 2016)	UK	29	180.2 (63–334)	119.6 (56–268)

(continued)

Table 2 (continued)

Sample	Country	*N*	Total As (μg.kg^{-1}) Mean (Min.–Max.)	i-As (μg.kg^{-1}) Mean (Min.–Max.)
Rice cereals (Signes-pastor et al. 2016)	UK	53	149 (42–396)	112.7 (8–323)
Rice crackers (Signes-pastor et al. 2016)	UK	97	132.7 (19–328)	108.2 (19–212)
Baby food (Rintala et al. 2014)	Finland	10	89 (20–290)	112.5 (<LOD-210)
Baking flour (Munera-Picazo et al. 2014b)	Spain	4	52.4 (14–107)	42 (11–85.8)
Breadcrumbs (Munera-Picazo et al. 2014b)	Spain	2	64.1 (49.8–78.4)	50.1 (38.5–61.7)
Pasta (Munera-Picazo et al. 2014b)	Spain	2	114.5 (109–120)	78.6 (73–84.2)
Bread toast (Munera-Picazo et al. 2014b)	Spain	3	51 (33.9–80.2)	37.9 (21.8–60.6)
Pastries (Munera-Picazo et al. 2014b)	Spain	8	21.5 (6.2–46.9)	18.9 (<LOQ-36.9)
Beer (Munera-Picazo et al. 2014b)	Spain	2	15.7 (15.7–15.7)	16.5 (<LOQ-16.5)
Milk (Munera-Picazo et al. 2014b)	Spain	4	14.3 (8.4–18.9)	11.5 (7.3–17.2)
Rice cakes (Cano-Lamadrid et al. 2016)	Spain	12	149 (42.6–278)	112.1 (30.2–178)
B. cereals (Cano-Lamadrid et al. 2016)	Spain	5	72.9 (37.8–112)	49 (18.2–104)
Cereal bars (Cano-Lamadrid et al. 2016)	Spain	9	17.6 (7.9–28.1)	12.4 (6.9–16.1)
Prepared rice (Cano-Lamadrid et al. 2016)	Spain	5	65.8 (12.1–190)	41.34 (8.4–140)
Milk (Cano-Lamadrid et al. 2016)	Spain	6	10.9 (4.3–20.3)	9.8 (4.3–15.6)
Husked rice flour (Narukawa et al. 2014)	Japan	2	467 (316–618)	413 (297.8–528.3)
I. cereal (Llorente-Mirandes et al. 2014)	Spain	1	267.4	74.3
Baby rice (Meharg et al. 2008b)	UK	17	232.9 (120–470)	117.1 (60–160)
Rice crackers (Islam et al. 2017)	Divers	10	209.7 (171–239)	88 (61–126)
Puffed rice (Islam et al. 2017)	Divers	6	145 (77–213)	49.5 (45–54)
Rice cakes (Islam et al. 2017)	Divers	11	175.3 (152–204)	98.3 (94–105)
Baby rice (Islam et al. 2017)	Divers	4	204 (140–268)	75 (73–77)
Ready-to-eat rice (Islam et al. 2017)	Divers	22	38.7 (30–54)	33.7 (13–45)
Rice-based snacks (Islam et al. 2017)	Divers	6	183 (93–273)	60.5 (33–88)
Porridge powders (Huber et al. 2017)	Divers	5	144.2 (120–190)	83.6 (65–99)
Baby meals (Huber et al. 2017)	Divers	6	81.3 (5.8–152)	39.3 (4.2–68)
Baby food – D (Guillod-Magnin et al. 2018)	CH	12	83.2 (13–138)	67.5 (9.5–119)
Baby food – R (Guillod-Magnin et al. 2018)	CH	9	14.2 (5.2–33.1)	8.6 (3.4–12.9)
Milk (Guillod-Magnin et al. 2018)	CH	6	14.9 (10.9–24.9	9 (6.5–13.2)
Rice cereals (Guillod-Magnin et al. 2018)	CH	7	278 (65.4–630)	204 (45.9–331)
Rice crackers (Guillod-Magnin et al. 2018)	CH	25	168 (46.6–361)	134 (40–279)
Rice drinks (Guillod-Magnin et al. 2018)	CH	15	19.4 (5.2–28)	16.9 (4.8–34)

N number of samples, *Min* minimum, *Max* maximum, *D* dry form, *R* ready-to-eat form, *B* breakfast, *I* infant, *CH* Switzerland, *UK* United Kingdom

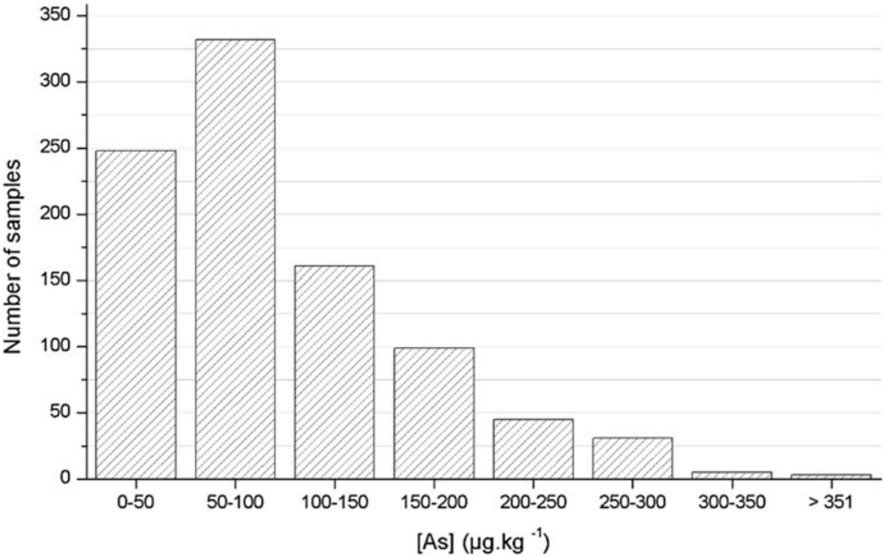

Fig. 3 Mean concentration of As in rice-based food products, considering 924 samples that had been analyzed in 19 papers published from 2008 to 2018. (Cano-Lamadrid et al. 2016; Carbonell-Barrachina et al. 2012; Guillod-Magnin et al. 2018; Hernández-Martínez and Navarro-Blasco 2013; Huber et al. 2017; Islam et al. 2017; Llorente-Mirandes et al. 2014; Mania et al. 2015; Meharg et al. 2008a, b; Munera-Picazo et al. 2014a, b; Narukawa et al. 2012, 2014; Orecchio et al. 2014; Pasias et al. 2013; Pedron et al. 2016; Rintala et al. 2014; Ruiz-de-Cenzano et al. 2017; Signes-pastor et al. 2016)

The concentration of (total) As does not provide accurate information about the risks associated with the ingestion of these products. The investigation of As species, especially i-As, is important for better risk evaluation. Figure 4 illustrates the percentages of organic and i-As in different categories of rice-based foods. As observed, i-As is the main specie in most of the rice-based foods. Beverages such as drinks and milk are the categories with the highest fractions of i-As (94% and 83%, respectively). Pastries, rice crackers, and rice flour present 76%, 75%, and 73% of i-As, respectively. Products specially developed for children (grouped in baby food) and puffed rice presented the lowest percentages of i-As (45% and 42%, respectively).

Figure 5 shows the i-As concentration in the rice-based food categories. Although it is observed in Fig. 4 that rice milk contains a higher fraction of i-As, this product presented the lowest levels of i-As (mean 11.8 µg kg^{-1}). This fact indicates that, although as i-As, the concentration of (total) As in milk is low. Products that presented the highest levels of i-As were rice cereals (mean 96.1 µg kg^{-1}), baby rice (mean 113.5 µg kg^{-1}), rice flour (mean 114.9 µg kg^{-1}), and rice crackers (mean 106.4 µg kg^{-1}). Figure 5 also shows discrepancies in the As concentration for some categories. For example, rice flour, despite the mean of 114.9 µg kg^{-1}, one sample

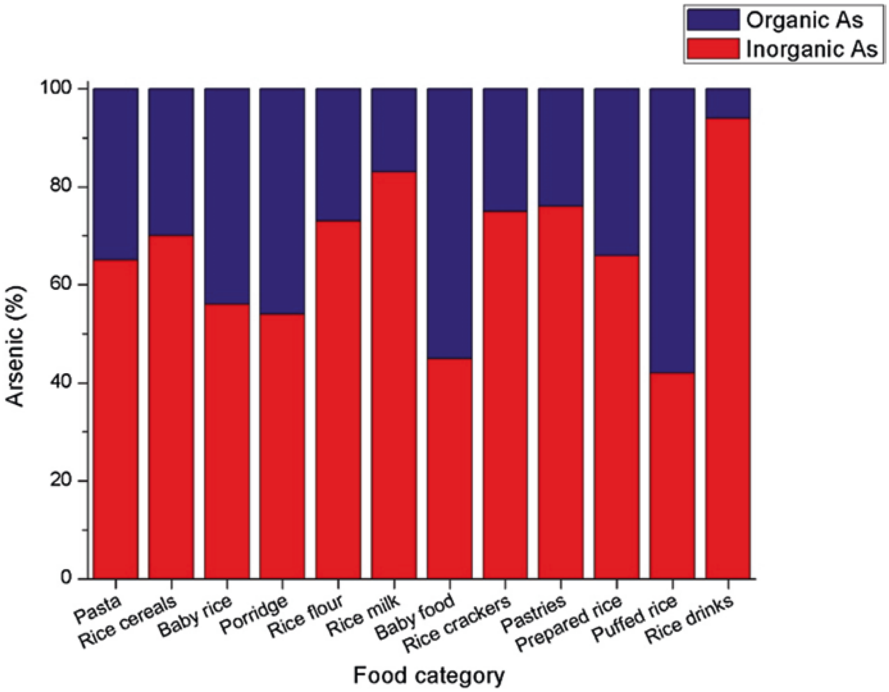

Fig. 4 Percentages of organic and inorganic As in 12 categories of rice-based food products from Australia, Belgium, Brazil, China, Finland, India, Italy, Japan, the Netherlands, New Zealand, Spain, Switzerland, Thailand, the United Kingdom, and the United States. (Cano-Lamadrid et al. 2016; Carbonell-Barrachina et al. 2012; Guillod-Magnin et al. 2018; Huber et al. 2017; Islam et al. 2017; Llorente-Mirandes et al. 2014; Meharg et al. 2008a, b; Munera-Picazo et al. 2014a, b; Narukawa et al. 2012, 2014; Pasias et al. 2013; Pedron et al. 2016; Rintala et al. 2014; Ruiz-de-Cenzano et al. 2017; Signes-pastor et al. 2016)

presented 528 μg kg^{-1} of i-As. Therefore, constant monitoring must be conducted by industry and government for rice safety.

The European Community has established since 2016 maximum levels of i-As for polished rice (200 μg kg^{-1}), parboiled and husked rice (250 μg kg^{-1}), rice-based foods (waffles, wafers, crackers, and cakes, 300 μg kg^{-1}), and rice-based products for young children (100 μg kg^{-1}) (EU 2015). The reported values show that most of the products are below the maximum limit. Regarding the infant foods, only one baby food sample presented 210 μg kg^{-1} of i-As, twofold higher than the limit. Other samples in this category were all below 100 μg kg^{-1}. Baby rice samples also presented levels above the limits, with a mean of 113.5 μg kg^{-1} and maximum of 190 μg kg^{-1}. Other food groups, although not exclusively for children, are high consumed by them, such as rice cereals and pastries. These products presented maximum levels of 234 and 178 μg kg^{-1}, respectively, which are below the limit for global rice-based food and above the limit for children. These observations show the

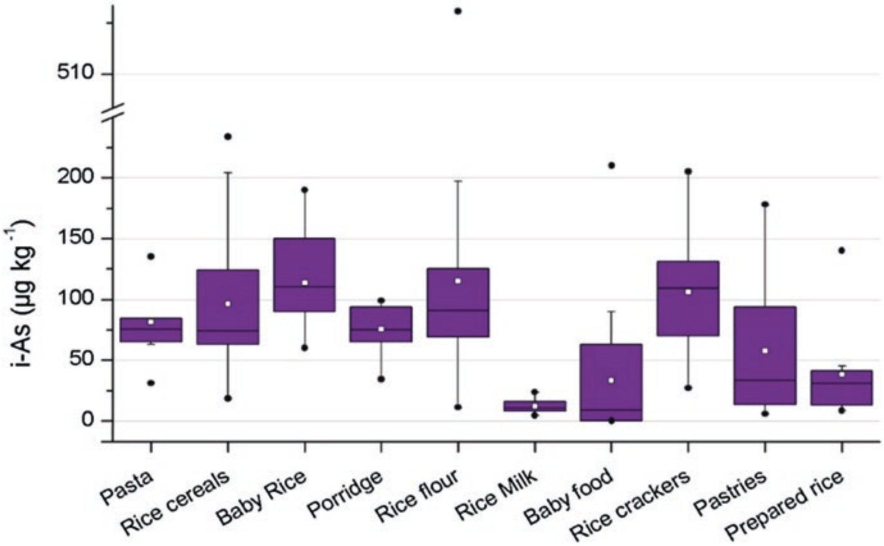

Fig. 5 Box plot with median (*central lines*), first and third quartiles (*box*), mean (*white squares*), lower and higher boundaries (*whiskers*), and outliers (*dots*) for i-As levels in 10 categories of rice-based food products analyzed for 19 papers published from 2008 to 2018. (Cano-Lamadrid et al. 2016; Carbonell-Barrachina et al. 2012; Carey et al. 2018; Guillod-Magnin et al. 2018; Huber et al. 2017; Islam et al. 2017; Jung 2018; Llorente-Mirandes et al. 2014; Meharg et al. 2008a, b; Munera-Picazo et al. 2014a, b; Narukawa et al. 2012, 2014; Pasias et al. 2013; Pedron et al. 2016; Rintala et al. 2014; Ruiz-de-Cenzano et al. 2017; Signes-Pastor et al. 2016, 2017)

need for the development of measures aiming to reduce the concentration of i-As in foods for adults and especially for children.

Arsenic is associated with both cancer and noncancer effects. There is sufficient evidence to conclude that As is carcinogenic. The NRC (2001) summarizes epidemiological studies based on dose-response relationships in drinking water. However, there are uncertainties in the dose-response relationship for nonmalignant conditions such as ischemic heart disease and diabetes mellitus, frequently associated with As exposure (Mondal and Polya 2008).

Exposure of As from rice is an important route for many people, especially at low chronic As exposures. A positive relationship between rice consumption and urinary As excretion is reported (Lai et al. 2015; Mondal et al. 2008). Li et al. (2011) analyzed i-As in Chinese food and estimated that daily intake is around 42 μg day^{-1} and rice is the most significant contributor to total i-As intake accounting for about 60%. In rice-based infant foods where i-As was determined, the mean intake for a 4-, 6-, 8-, or 12-month infant are 0.05, 0.16, 0.25, and 0.26 μg d^{-1} kg^{-1}. In the group of infants that has celiac disease, the daily intakes increased up to 0.26, 0.27, 0.41, and 0.40 μg d^{-1} kg^{-1} for the same ages (Carbonell-Barrachina et al. 2012).

Analysis of As species in rice and rice-based products for infants and children demonstrated that about 60–80% of total As content is As^{3+} followed by DMA and

As^{5+}. Health risk regarding ingestion of As is associated to specific groups with higher consumption of rice grains and rice-based products (persons with celiac disease, vegans, cow-milk allergic, and Asians) (Guillod-Magnin et al. 2018).

Quantitative analyses are essential in the determination of As and its species since they allow to assess toxicological implications and to estimate the daily intake of nonessential and potentially toxic elements and thus to obtain parameters to reach acceptable safe intake levels.

References

Abedin MJ, Cotter-Howells J, Meharg AA (2002) Arsenic uptake and accumulation in rice (*Oryza sativa* L.) irrigated with contaminated water. Plant Soil 240(2):311–319

Ali W (2012) Arsenic transport in plants. Thesis. University of York

Aposhian HV, Aposhian MM (2006) Arsenic toxicology: five questions. Chem Res Toxicol 19(1):1–15

Batista BL, De Oliveira Souza VC, Da Silva FG et al (2010) Survey of 13 trace elements of toxic and nutritional significance in rice from Brazil and exposure assessment. Food Addit Contam 3(4):253–262

Batista BL, Souza JM, De Souza SS et al (2011) Speciation of arsenic in rice and estimation of daily intake of different arsenic species by Brazilians through rice consumption. J Hazard Mater 191(1):342–348

Batista BL, Nigar M, Mestrot A et al (2014) Identification and quantification of phytochelatins in roots of rice to long-term exposure: evidence of individual role on arsenic accumulation and translocation. J Exp Bot 65(6):1467–1479

Butcher DJ (2007) Environmental applications of arsenic speciation using atomic spectrometry detection. Appl Spectrosc Rev 42:1–22

CAC: CODEX ALIMENTARIUS COMMISSION (2014) Report of the Eighth Session of the Codex Committee on Contaminants in Food, The Hague, The Netherlands, 31 March–4 April 2014

Calpe C (2006) Rice international commodity profile. Food and Agricultural Organization of the United Nations (FAO), Rome

Cano-Lamadrid M, Munera-Picazo S, Burgos-Hernández A et al (2016) Inorganic and total arsenic contents in rice and rice-based foods consumed by a potential risk subpopulation: sportspeople. J Food Sci 81(4):T1031–T1037

Carbonell-Barrachina ÁA, Wu X, Ramírez-Gandolfo A et al (2012) Inorganic arsenic contents in rice-based infant foods from Spain, UK, China and USA. Environ Pollut 163:77–83

Carey M, Donaldson E, Signes-Pastor AJ et al (2018) Dilution of rice with other gluten free grains to lower inorganic arsenic in foods for young children in response to European Union regulations provides impetus to setting stricter standards. PLoS One 13(3):1–9

Concha G, Vogler G, Lezcano D et al (1998) Exposure to inorganic arsenic metabolites during early human development. Toxicol Sci 44(2):185–190

Das D, Chatterjee A, Mandal BK et al (1995) Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 2. Arsenic concentration in drinking water, hair, nails, urine, skin-scale and liver tissue (biopsy) of the affected people. Analyst 120(3):917–924

Davis MA, Higgins J, Li Z et al (2015) Preliminary analysis of in utero low-level arsenic exposure and fetal growth using biometric measurements extracted from fetal ultrasound reports. Environ Health 14(1):12

Davis MA, Signes-Pastor AJ, Argos M et al (2017) Assessment of human dietary exposure to arsenic through rice. Sci Total Environ 586:1237–1244

De Los Santos AM, Cores PR, Navarro F et al (2012) Síndrome de malabsorción (II). Enfermedad celiaca. Intolerancia a la lactosa. Sobrecrecimiento bacteriano. Med-Programa Formación Médica Contin Acreditado 11(4):206–213

Dionísio AG, Gonzalez MH, Nóbrega JA (2011) Determinação de arsênio em amostras da cadeia produtiva de frangos de corte por espectrometria de absorção atômica com forno de grafite. Quim Nova 34(1):49–52

EFSA: European Food Safety Authority (2009) Panel on contaminants in the food chain (CONTAM); Scientific opinion on arsenic in food. EFSA J 7(10):1351

EU (2015) Commission Regulation 2015/1006 of 25 June 2015 amending Regulation (EC) No 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs. http://eur-lex.europa.eu/legalcontent/EN/TXT/?uri=OJ:JOL_2015_161_R_0006. Accessed 10 Oct 2018

Fängström B, Moore S, Nermell B et al (2008) Breast-feeding protects against arsenic exposure in Bangladeshi infants. Environ Health Perspect 116(7):963–969

FAO: Food and Agriculture Organization (2010) Joint FAO/WHO Expert Committee on Food Additives. Seventy-second meeting Rome, 16–25 February 2010

FAO: Food and Agriculture Organization (2018) Rice Market Monitor. http://www.fao.org/economic/est/publications/rice-publications/rice-market-monitor-rmm/en/. Accessed 20 Oct 2018

Faraj JM (2011) Iron status, inflammation and anemia in Bangladeshi women exposed to arsenic. Dissertation. University of Massachusetts

Farzan SF, Korrick S, Li Z et al (2013) In utero arsenic exposure and infant infection in a United States cohort: a prospective study. Environ Res 126:24–30

FDA: Food And Drug Administration (2016a) Total arsenic in Mott's and Nestle/Gerber Apple Juice. http://www.fda.gov/food/foodborneillnesscontaminants/metals/ucm280223.htm. Accessed 3 Oct 2018

FDA: Food And Drug Administration (2016b) FDA statement on proposed action level for inorganic arsenic in infant rice cereal. http://www.fda.gov/Food/FoodborneIllnessContaminants/Metals/ucm367263.htm. Accessed 3 Oct 2018

Gamboa-Loira B, Cebrián ME, Franco-Marina F et al (2017) Arsenic metabolism and cancer risk: A meta-analysis. Environ Res 156:551–558

Gilbert-Diamond D, Cottingham KL, Gruber JF et al (2011) Rice consumption contributes to arsenic exposure in US women. Proc Natl Acad Sci 108(51):20656–20660

Gomes AS, Magalhães Jr AM (2004) Arroz irrigado no Sul do Brasil. Embrapa Clima Temperado. Embrapa Informação Tecnológica, Brasília

GPO: Government Publishing Office (2012a) Roxarsone (21CFR558.530), pp 500–503

GPO: Government Publishing Office (2012b) Arsanilic acid (21CFR558.62), pp 413–414

Guillod-Magnin R, Brüschweiler BJ, Aubert R et al (2018) Arsenic species in rice and rice-based products consumed by toddlers in Switzerland. Food Addit Contam Part A 35(6):1164–1178

Heikens A (2006) Arsenic contamination of irrigation water, soil and crops in Bangladesh: risk implications for sustainable agriculture and food safety in Asia. RAP Publication (FAO)

Hernández-Martínez R, Navarro-Blasco I (2013) Survey of total mercury and arsenic content in infant cereals marketed in Spain and estimated dietary intake. Food Control 30(2):423–432

Hopenhayn-Rich C, Browning SR, Hertz-Picciotto I et al (2000) Chronic arsenic exposure and risk of infant mortality in two areas of Chile. Environ Health Perspect 108(7):667–673

Huang RN, Lee TC (1996) Cellular uptake of trivalent arsenite and pentavalent arsenate in KB cells cultured in phosphate-free medium. Toxicol Appl Pharmacol 136(2):243–249

Huber CS, Vale MGR, Dessuy MB et al (2017) Sample preparation for arsenic speciation analysis in baby food by generation of substituted arsines with atomic absorption spectrometry detection. Talanta 175:406–412

Husby S, Koletzko S, Korponay-Szabo IR et al (2012) European Society for Pediatric Gastroenterology, Hepatology, and Nutrition guidelines for the diagnosis of coeliac disease. J Pediatr Gastroenterol Nutr 54(1):136–160

IARC: International Agency For Research On Cancer (2012) Arsenic, metals, fibres, and dusts. IARC monographs on the evaluation of carcinogenic risks to humans, vol 100 C Paris

Islam S, Rahman MM, Rahman MA et al (2017) Inorganic arsenic in rice and rice-based diets: health risk assessment. Food Control 82:196–202

Jung MY (2018) Inorganic arsenic contents in infant rice powders and infant rice snacks marketed in Korea determined by a highly sensitive gas chromatography-tandem mass spectrometry following derivatization with British Anti-Lewisite. Food Sci Biotechnol 27(2):617–622

Karimi N, Ghaderian SM, Raab A et al (2009) An arsenic-accumulating, hypertolerant brassica, Isatis capadocica. New Phytol 184(1):41–47

Khush GS (1997) Origin, dispersal, cultivation and variation of rice. Plant Mol Biol 35(1–2):25–34

Klaassen CD, Watkins JB (eds) (2008) Casarett and Doull's toxicology: the basic science of poisons. McGraw-Hill, New York

Korndörfer GH (2015) Uso do silício na agricultura. Grupo de Pesquisa "Silicio na Agricultura". http://www.dpv24.iciag.ufu.br/Silicio/Efeitos/Efeitos.htm. Accessed 13 Apr 2016

Kot A, Namieśnik J (2000) The role of speciation in analytical chemistry. Trends Analyt Chem 19(2):69–79

Lai PY, Cottingham KL, Steinmaus C et al (2015) Arsenic and rice: translating research to address health care providers' needs. J Pediatr 167(4):797–803

Li G, Sun GX, Williams PN et al (2011) Inorganic arsenic in Chinese food and its cancer risk. Environ Int 37(7):1219–1225

Liu H, Lu S, Zhang B et al (2018) Maternal arsenic exposure and birth outcomes: A birth cohort study in Wuhan, China. Environ Pollut 236:817–823

Llorente-Mirandes T, Calderón J, Centrich F et al (2014) A need for determination of arsenic species at low levels in cereal-based food and infant cereals. Validation of a method by IC–ICPMS. Food Chem 147:377–385

Ma JF, Yamaji N, Mitani N et al (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proc Natl Acad Sci 105(29):9931–9935

Maclean JL (2002) Rice almanac: source book for the most important economic activity on earth. Int Rice Res Inst

Mania M, Wojciechowska-Mazurek M, Starska K et al (2015) Toxic elements in commercial infant food, estimated dietary intake, and risk assessment in Poland. Pol J Environ Stud 24(6):2525–2536

Meacher DM, Menzel DB, Dillencourt MD et al (2002) Estimation of multimedia inorganic arsenic intake in the US population. Hum Ecol Risk Assess 8(7):1697–1721

Meharg AA, Rahman MM (2003) Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption. Environ Sci Technol 37(2):229–234

Meharg AA, Zhao FJ (2012) Arsenic & rice. Springer Science & Business Media, Dordrecht

Meharg AA, Lombi E, Williams PN et al (2008a) Speciation and localization of arsenic in white and brown rice grains. Environ Sci Technol 42(4):1051–1057

Meharg AA, Sun G, Williams PN et al (2008b) Inorganic arsenic levels in baby rice are of concern. Environ Pollut 152(3):746–749

Meliker JR, Franzblau A, Slotnick MJ et al (2006) Major contributors to inorganic arsenic intake in southeastern Michigan. Int J Hyg Environ Health 209(5):399–411

Mondal D, Polya DA (2008) Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: a probabilistic risk assessment. Appl Geochem 23(11):2987–2998

Mondal D, Adamson GC, Nickson R et al (2008) A comparison of two techniques for calculating groundwater arsenic-related lung, bladder and liver cancer disease burden using data from Chakdha block, West Bengal. Appl Geochem 23(11):2999–3009

Munera-Picazo S, Ramírez-Gandolfo A, Burló F et al (2014a) Inorganic and total arsenic contents in rice-based foods for children with celiac disease. J Food Sci 79(1):T122–T128

Munera-Picazo S, Burló F, Carbonell-Barrachina ÁA (2014b) Arsenic speciation in rice-based food for adults with celiac disease. Food Addit Contam Part A 31(8):1358–1366

Muthayya S, Sugimoto JD, Montgomery S et al (2014) An overview of global rice production, supply, trade, and consumption. Ann N Y Acad Sci 1324(1):7–14

Nadeau KC, Li Z, Farzan S et al (2014) In utero arsenic exposure and fetal immune repertoire in a US pregnancy cohort. Clin Immunol 155(2):188–197

Narukawa T, Hioki A, Chiba K (2012) Speciation and monitoring test for inorganic arsenic in white rice flour. J Agric Food Chem 60(4):1122–1127

Narukawa T, Suzuki T, Inagaki K et al (2014) Extraction techniques for arsenic species in rice flour and their speciation by HPLC–ICP-MS. Talanta 130:213–220

National Research Council (2001) Arsenic in drinking water. National Academies Press, Washington, DC

Navas-Acien A, Nachman KE (2013) Public health responses to arsenic in rice and other foods. JAMA Intern Med 173:1395–1396

NIDDKD: National Institute of Diabetes and Digestive and Kidney Diseases-USA (2008) Celiac disease. http://digestive.niddk.nih.gov/ddiseases/pubs/celiac/celiac.pdf. Accessed 2 Sept 2018

Niewinski MM (2008) Advances in celiac disease and gluten-free diet. J Am Diet Assoc 108:661–672

Nunes JLS (2016) Características do Arroz (*Oryza sativa*). http://www.agrolink.com.br/culturas/arroz/caracteristicas.aspx. Accessed 10 Sept 2018

Orecchio S, Amorello D, Raso M et al (2014) Determination of trace elements in gluten-free food for celiac people by ICP-MS. Microchem J 116:163–172

Parsons PJ, Barbosa F (2007) Atomic spectrometry and trends in clinical laboratory medicine. Spectrochim Acta B 62(9):992–1003

Pasias IN, Thomaidis NS, Piperaki EA (2013) Determination of total arsenic, total inorganic arsenic and inorganic arsenic species in rice and rice flour by electrothermal atomic absorption spectrometry. Microchem J 108:1–6

Pedron T, Segura FR, da Silva FF et al (2016) Essential and non-essential elements in Brazilian infant food and other rice-based products frequently consumed by children and celiac population. J Food Compos Anal 49:78–86

Pedron T, Segura FR, Paniz FP, de Moura Souza F, dos Santos MC, de Magalhães Júnior AM, Batista BL (2019) Mitigation of arsenic in rice grains by polishing and washing: evidencing the benefit and the cost. J Cereal Sci 87:52–58

Raqib R, Ahmed S, Sultana R et al (2009) Effects of in utero arsenic exposure on child immunity and morbidity in rural Bangladesh. Toxicol Lett 185(3):197–202

Rintala EM, Ekholm P, Koivisto P et al (2014) The intake of inorganic arsenic from long grain rice and rice-based baby food in Finland–Low safety margin warrants follow up. Food Chem 150:199–205

Robertson FN (1989) Arsenic in ground-water under oxidizing conditions, south-west United States. Environ Geochem Health 11:171–185

Ruiz-de-Cenzano M, Rochina-Marco A, Cervera ML et al (2017) Evaluation of the content of antimony, arsenic, bismuth, selenium, tellurium and their inorganic forms in commercially baby foods. Biol Trace Elem Res 180(2):355–365

Sanders AP, Desrosiers TA, Warren JL et al (2014) Association between arsenic, cadmium, manganese, and lead levels in private wells and birth defects prevalence in North Carolina: a semi-ecologic study. BMC Public Health 14(1):955

Segura FR, Paulelli ACC, Braga GÚL, dos Reis Pedreira Filho W, Silva FF, Batista BL (2018) Promising filamentous native fungi isolated from paddy soils for arsenic mitigation in rice grains cultivated under flooded conditions. J Environ Chem Eng 6:3926–3932

Signes-Pastor AJ, Carey M, Meharg AA (2016) Inorganic arsenic in rice-based products for infants and young children. Food Chem 191:128–134

Signes-Pastor AJ, Woodside JV, McMullan P et al (2017) Levels of infants' urinary arsenic metabolites related to formula feeding and weaning with rice products exceeding the EU inorganic arsenic standard. PLoS One 12(5):e0176923

Smedley PL, Kinniburgh DG (2001) Source and behavior of arsenic in natural waters. United Nations synthesis report on arsenic in drinking water. World Health Organization, Geneva. http://www.who.int/water_sanitation_health/dwq/arsenicun1.pdf. Accessed 7 Sept 2018

Smith AH, Lingas EO, Rahman M (2000) Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull World Health Organ 78:1093–1103

Smith E, Juhasz AL, Weber J et al (2008) Arsenic uptake and speciation in rice plants grown under greenhouse conditions with arsenic contaminated irrigation water. Sci Total Environ 392(2):277–283

Sternowsky HJ, Moser B, Szadkowsky D (2002) Arsenic in breast milk during the first 3 months of lactation. Int J Hyg Environ Health 205(5):405–409

Sun GX, Williams PN, Carey AM et al (2008) Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain. Environ Sci Technol 42(19):7542–7546

Tao SSH, Michael Bolger P (1999) Dietary arsenic intakes in the United States: FDA total diet study, September 1991-December 1996. Food Addit Contam 16(11):465–472

Tsuji JS, Yost LJ, Barraj LM et al (2007) Use of background inorganic arsenic exposures to provide perspective on risk assessment results. Regul Toxicol Pharmacol 48(1):59–68

US Department of Agriculture (2008) Food availability (per capita) data system/food availability. Econ Res Serv, Washington, DC

Vahter M (2002) Mechanisms of arsenic biotransformation. Toxicology 181:211–217

Vahter M (2008) Health effects of early life exposure to arsenic. Basic Clin Pharmacol Toxicol 102(2):204–211

Valko M, Morris H, Cronin MTD (2005) Metals, toxicity and oxidative stress. Curr Med Chem 12(10):1161–1208

Vaughan DJ (2006) Arsenic. Elements 2(2):71–75

Wang A, Holladay SD, Wolf DC et al (2006) Reproductive and developmental toxicity of arsenic in rodents: a review. Int J Toxicol 25(5):319–331

Wei M, Arnold L, Cano M et al (2004) Effects of co-administration of antioxidants and arsenicals on the rat urinary bladder epithelium. Toxicol Sci 83(2):237–245

WHO: World Health Organization (2000) Air quality guidelines for Europe, 2nd edn

WHO: World Health Organization (2008) Guidelines for drinking-water quality: incorporating first and second addenda to third edition. Recommendations

Williams PN, Raab A, Feldmann J et al (2007) Market basket survey shows elevated levels of As in South Central US processed rice compared to California: consequences for human dietary exposure. Environ Sci Technol 41(7):2178–2183

Xu XY, McGrath SP, Meharg AA et al (2008) Growing rice aerobically markedly decreases arsenic accumulation. Environ Sci Technol 42(15):5574–5579

Zhao CQ, Young MR, Diwan BA et al (1997) Association of arsenic-induced malignant transformation with DNA hypomethylation and aberrant gene expression. Proc Natl Acad Sci U S A 94(20):10907–10912

Arsenic in Wheat, Maize, and Other Crops

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Abstract Arsenic (As) is a harmful metalloid that can be naturally found in soils and water. Consumption of contaminated groundwater is the most common source of human poisoning; furthermore, the ingestion of contaminated food is currently getting much attention. The main problem arises when crops incorporate the metalloid by direct absorption of groundwater or artificial irrigation containing high levels of the toxic element, or through contaminated soils, being the first stage of As distribution in the trophic chain. This issue constitutes not only an agronomic problem, due to the effect in grain quality and yield, but also a serious risk for human health. In this chapter, we aim to summarize the effect of As on growth and metalloid accumulation and distribution on cereal and legume crops used for human consumption. The comprehension of the responses evoked by plants under As exposure could contribute to a better understanding of metalloid toxicity and the possible risks of grain contamination as well to as assess mitigation strategies to prevent human poisoning.

Keywords Arsenic · Legumes · Maize · Peanut · Soybean · Wheat

1 Introduction

Arsenic (As) is a well-known metalloid, naturally found in soil and water due to geological activities. Nonetheless, anthropogenic activities such as mining, use of fertilizers, and agrochemicals have an additional impact on metalloid levels in the environment (Trueb 1996; Reimann and De Caritat 1998). The As concentration varies considerably among geographic regions being groundwater the principal

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source of human contamination (Smedley and Kinniburgh 2002). Additionally, human poisoning could also be achieved by ingestion of contaminated food. The problem arises when crop plants directly absorb the metalloid from groundwater (due to a phreatic level near the soil) or incorporate it by artificial irrigation and accumulate in edible parts, acting as the first stage of As distribution in the trophic chain (Smedley and Kinniburgh 2002; Bustingorri and Lavado 2014). Moreover, studies have revealed that human contamination from As contained in polluted-food is higher than in drinking water (Diaz et al. 2004). Thus, crop contamination constitutes not only an agronomic problem due to yield losses but also a risk for human health.

Inorganic and organic species of As can be found in water and soil. Arsenate ($H_2AsO_4^-$, As(V)) and arsenite ($H_2AsO_3^-$, As(III)) are the inorganic chemical species of As and prevails in reduced or oxidized conditions, respectively. Monomethylarsonic acid (MMAV), dimethylarsinic acid (DMAV), and trimethylarsine oxide (TMAOV) are the methylated organic species of arsenate. The methylated derivatives of As(III) (MMAIII, DMAIII, TMAIII) are volatile (Finnegan and Chen 2012). In general, arsenic methylated species production in soils are limited by microbial transformation of As(V) and As(III) (Finnegan and Chen 2012; Lomax et al. 2012). Although arsenical inorganic species are more toxic than the organic ones, methylated species such as MMA and DMA are known to be highly phytotoxic (Raab et al. 2005; Xu et al. 2007; Zhao et al. 2010a).

Arsenic concentration in water and soil is variable. It is known that total As concentration in non-contaminated soil can be found in an average of 10 mg Kg^{-1} soil (Adriano 2001), but this value can reach hundreds and even thousands of mg Kg^{-1} in contaminated environments (Kabata-Pendias and Pendias 1992; Vaughan 1993; IARC 2004). The permissible limit of arsenic in agricultural soils is 20 mg Kg^{-1}, and this value has been accepted by numerous countries (Rahaman et al. 2013); however, the presence of even 5 mg Kg^{-1} in soils is toxic to several crops (Garg and Singla 2011).

The availability of As for plants is related to edaphic properties, the environmental conditions, and the modification of the physical-chemical properties of the soil at the rhizosphere level (soil-root interface). Generally in plants, the metalloid enters as an inorganic form. Arsenate uses phosphate (Pht) transporters due to its chemical analogy and arsenite enters through aquaporins (Tripathi et al. 2007; Verbruggen et al. 2009). Once As(V) is inside the cell, several modifications can disrupt normal cellular processes such as photosynthesis and mitochondrial respiration, by alteration of ATP synthesis and phosphate-mediated cellular metabolism regulation (Tripathi et al. 2007). However, under reducing condition, most As(V) could be rapidly reduced to As(III) by arsenate reductase enzymes, constituting the first step of As detoxification in cells (Dhankher et al. 2006; Duan et al. 2007; Sánchez-Bermejo et al. 2014). Besides the already known As transporters, it was reported that there are transporters which allow As(III) passage into the xylem (OsLsi2 and OsLsi1) (Ma et al. 2008; Mitani et al. 2009). However, the transport of As(III) from the xylem to the shoot is less well characterized. Su et al. (2009) revealed that As(III) was the As form mainly found in the xylem (86–97% of the total As content) of cereals, such as rice, wheat, and barley. Additionally, As is transported to the grain mainly via the phloem (Carey et al. 2010, 2011) (Fig. 1). It is known that As(III) is more toxic than As(V) since it can bind to sulfhydryl groups of thiol-rich peptides such as glutathione (GSH) and phytochelatins (PCs), reducing the antioxidant defense system (Pickering et al. 2000). Therefore, inorganic forms of As generate a redox imbalance in the cell, due to an accumulation of reactive oxygen species (ROS) (Requejo and Tena 2005; Talukdar 2013) and changes in

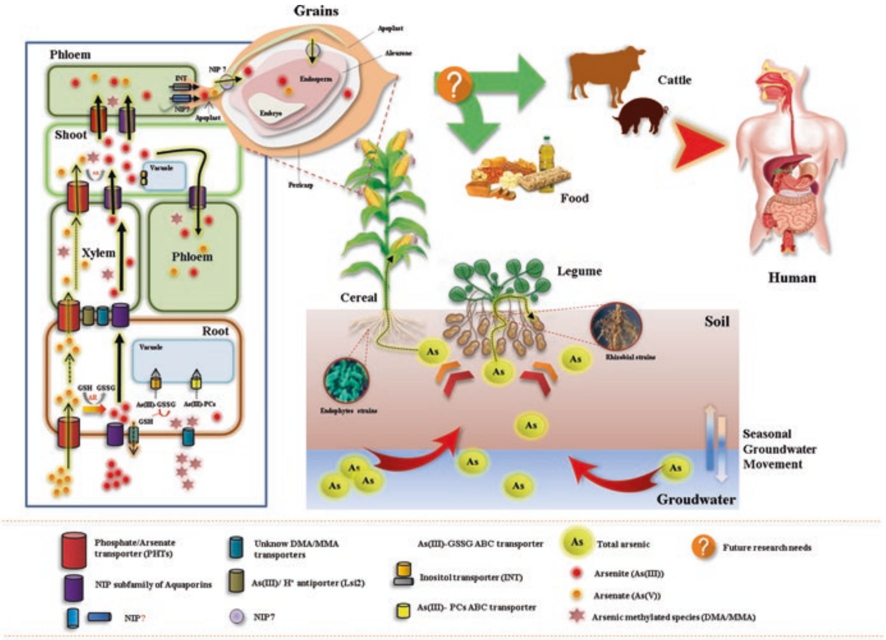

Fig. 1 Overview of arsenic in agroecosystems. A schematic representation of known and putative proteins and processes involved in arsenic uptake, efflux, distribution, and detoxification in plants. In plant roots, arsenate (As(V)) and arsenite (As(III)) are taken up by phosphate transporters (PHTs) and aquaporins (nodulin 26-like intrinsic protein (NIP)), respectively. Arsenic methylated species (DMA/MMA) uptake is carried out by unknown transporters or by NIP. As(V) is reduced to As(III) by arsenate reductases (AR) using glutathione (GSH) as a reducing agent. As(III) is coordinated with phytochelatins (PCs) and GSH before sequestration in the vacuole via ATP-binding cassette (ABC) transporters. Long-distance transport of arsenic species through the xylem/phloem to the shoot and seed is at least partially mediated by NIP aquaporins and inositol transporters (INTs). Although the details are largely unknown, there is now evidence that NIP-type aquaporins and INT-type sugar symporters significantly impact on arsenic deposition in seeds. The current data suggest that INTs may be involved in the mobilization of arsenic from source tissues, for example, by pumping apoplastic arsenic into the phloem for subsequent transport to seed tissues. Grains and their post-processing waste can be used to feed livestock and/or produce edible products. Thus, arsenic can enter the food chain, and finally human health can be affected. To mitigate the impact of arsenic on agrifood systems, the use of beneficial microorganisms that interact with plants (not only to improve growth but also to reduce As accumulation in shoots and therefore in the harvest product), could be a promising biotechnological tool to be used in contaminated field

the antioxidant response (Mylona et al. 1998) leading to an oxidative stress (Hernández et al. 2015; Bianucci et al. 2017a).

The negative impact of As on rice crop production and food safety has been well-documented (Heikens et al. 2007; Brammer and Ravenscroft 2008; Zhao et al. 2010a; Li et al. 2016). Nevertheless, As toxicity, uptake, translocation, and accumulation in other food crops have not been widely studied at field trials yet. In order to understand the impact of As on food crops, it is important to consider several factors which are involved in plant response such as concentration and chemical form of the metalloid, the substrate, period of growth, and time of exposure. All these variables are specific to each area/region; therefore, local studies should be done in order to prevent human poisoning. Most of the researches related to As toxicity in plants are performed in hydroponic system (Cho and Park 2000; Gothberg et al. 2004; Cargnelutti et al. 2006; Moreno-Jiménez et al. 2007, 2008; Sobrino-Plata et al. 2009, 2013; Bianucci et al. 2017a, 2018a, b) since the root is completely immersed on the growth culture media and directly exposed to the contaminant. Besides, it eliminates the problems of substrate interaction, such as As forming complexes with particles, allowing to have the clearest result regarding As effect on the whole plant (Finnegan and Chen 2012). Although the results obtained in this system generally cannot be directly comparable to field conditions, it gives valuable information about the mechanism evoked by plants.

Depending on the ability of plants to accumulate As and to translocate it from root to shoot, they can be classified into three categories: (a) *excluders* that have a low translocation factor, <0.1, (TF = As concentration of shoots/As concentration of roots) since they restrict As uptake and translocation from roots to shoots; (b) *hyperaccumulators* that show a translocation factor higher than 1, able to accumulate high As concentrations in shoots and widely used for bioremediation purposes; and (c) *non-hyperaccumulators* that have an intermediate translocation factor, whose roots accumulate the major metalloid concentration. Non-hyperaccumulators have been used for remediation of soil, sediment, and sludge since they have the ability to accumulate metal(loid)s in roots avoiding its translocation to shoots, process known as phytostabilization (Ghosh and Singh 2005; Angle and Linacre 2005). However, it is known that a slightly translocation of As via xylem or its recirculation by phloem to shoots can be achieved. This could represent a problem since, depending on several factors (i.e., plant, microbe interactions, concentration, and chemical form of As), unknown concentrations of metalloid could be accumulated into edible crop tissues, constituting a serious risk to human health (Zhao et al. 2010a; Li et al. 2016).

Food crops such as peanut and soybean are non-hyperaccumulator and non-tolerant to As. Generally, they are able to develop up to 6 mg L^{-1} As without showing strong deleterious effects on growth. They are widely used for human consumption therefore, they are not advised to be used for bioremediation processes (Bianucci et al. 2017a, 2018a, b). On the other hand, cereals such as maize or wheat are also non-hyperaccumulator plants, and they are able to develop up to 30 and 50 mg L^{-1} As. Moreover, maize was classified as an As-tolerant crop (Requejo and Tena 2014). Thus, considering that As is taken up by crops exposed to natural sources of metalloid and, food crops cultivation cannot be avoided, mitigation strategies must be taken into consideration in order to develop safe crops that can grow in the presence of contaminants as arsenic.

Microbial interaction with plants has gained much attention in the past few years, since some microorganisms are able not only to enhance plant growth but also to contribute to bioremediation processes. Soil microorganisms interact with plants in the rhizosphere, in the interphase soil-root, constituting a dynamic environment in which several microbes can develop (Pedraza et al. 2010). Microorganisms that generate a beneficial effect to plants are commonly known as plant growth-promoting bacteria (PGPB) (Glick 2012). The mechanisms triggered by PGPB in plants are related to an induction of secondary metabolites as flavonoids and phytohormones; regulation of ethylene levels through amino-cyclopropane-1-carboxylic (ACC)-deaminase enzyme activity; solubilization of phosphorus (P) and potassium (K); siderophore production involved in the solubilization of minerals and organic compounds; and contribution to biological nitrogen fixation (BNF). Particularly, the BNF is one of the most studied mechanisms since it is the principal source of N in the biosphere and contributes with a 65% of the global N supply. This process is done by a scarce group of microorganism named diazotrophs, in free-living or symbiotic interactions (commonly known as rhizobia). It has been demonstrated that under stressful growth conditions, as metal(loid)s soil contamination, inoculation of food crops with PGPB not only increased the BNF but also phosphate solubilization and siderophores production, protecting plant development (Reichman 2007; Wani et al. 2008; Dary et al. 2010).

Concerning As concentration in food crops, it is important to point out that there is no threshold level proposed by the Codex Alimentarius Commission, the European Union, nor the Argentinian or Brazilian legislations for crop grains. There is a maximum level proposed by the Codex Alimentarius Commission for vegetable oils, including soybean oil (0.1 mg Kg^{-1}) (FAO 2017). In the UK, the maximum recommended As concentration for food crops is 1 mg Kg^{-1} (Arsenic in Food Regulations 1959). In South America, the technical regulation of MERCOSUR (ANMAT, 2012) that regulates food quality in Argentina, Brazil, Uruguay, Paraguay, Bolivia, and Venezuela allows a maximum As level of 1 mg Kg^{-1} in legumes, except soybean.

Considering all these information, in this chapter we will focus on As effects on cereal and legume plants used as food, at the cellular level and at field conditions. The knowledge of the integrated data exposed here will contribute to understand the toxicity of the metalloid on plant and the risk that could have on human poisoning by the ingestion of contaminated grains.

2 Arsenic in Cereals

Cereals are plants belonging to the *Poaceae* or *Gramineae* family, with five subfamilies and approximately 10,000 species (Chapman 1996). Most common cereals are rice, wheat, and maize that are members of the grass family, and they are particularly important to humans due to their role as food crops in many areas of the world. Cereal grains are produced worldwide and provide more food energy than any other types of crop; they are, therefore, staple food crops. In their natural form (whole grain), they are a rich source of vitamins, minerals, carbohydrates, fats, oils, and proteins (Sarwar et al. 2013). Cereals are also used to produce animal feed, oils, starch, flour, sugar, syrup, processed foods, malt, alcoholic beverages, gluten, and renewable energy (Pomeranz and Muck 1981; Chopra and Prakash 2002). Chemical fertilization is a widely used practice on cereals, generating environmental disturbances. To avoid or reduce their uses, researches have been focused in identifying bacteria able to fix N_2 in association with these crops (Beatty and Good 2001; Roesch et al. 2008).

2.1 Wheat

Wheat (*Triticum aestivum*) is the first food grain crop in terms of global consumption and production (Costa et al. 2013). Consumption rate of wheat is rising because of its low production cost, good market price, and nutritional value.

The level of metalloid uptake by plants varies with crops and cultivars (Kundu et al. 2012). It was observed that irrigation with As-rich water affected plant height, crop yield, and development of root growth (Hossain 2006). In wheat kernels, arsenic accumulation was lesser than any other tissues being root> stem> leaf>kernel, across varieties (Kamrozzaman et al. 2016). In a similar study, Pigna et al. (2010) reported that uptake and translocation of this toxic metalloid in the wheat kernel is less compared with the wheat root and shoot. In general, distribution of As in plants was in the order: below ground parts>aerial parts (Sanyal 2005). On the other hand, Bhattacharya et al. (2010) carried out a study in Ganga-Meghna-Brahmaputra, one of the major As-contaminated hotspot in the world. Arsenic concentration in soil was lower than the reported global average of 10 mg Kg^{-1}, but the irrigation water presented a metalloid concentration many folds higher than that recommended as permissible limit for drinking and irrigation water by FAO. This study showed that rice, wheat, vegetables, and pulses, grown in this area were safe for consumption. However, metalloid accumulation must be monitored periodically in crops, specially in edible parts, due to daily increasing level of arsenic in the study area.

Zhang et al. (2009) reported that wheat varieties (Jimai, Gaoyou, Weimai, and Wennong) growing in soil supplemented with As (50 or 100 mg Kg^{-1}) showed a reduced root, stem, and spike dry weight and yield components, which resulted in the decrease of grain yield per plant. Arsenic concentrations in plant tissues increased significantly with treatments, and its uptake varied considerably among wheat varieties, plant tissues, and As treatments. It was found that As concentration in root was about ten times higher than in straw. These results suggested that As distribution in the upper plant parts was lower than in the below ground parts, which might be due to its lower mobility. Upon the exposition to As, its concentration in bran was about two to three times higher than in flour. Most of the As-contaminated flour exceeded the Chinese tolerance limit. Arsenic contents of grain parts were dependent on wheat variety and treatment level in polluted soils. Weimai and Wennong varieties revealed the highest amounts of As in flour at 50 or 100 mg Kg^{-1} soil treatment, respectively. Weimai variety possessed significantly lower amount of As in bran than any other wheat variety. Thus, these results showed significant differences in response to the plant variety and the arsenic concentration tested.

Scarce information is available on As accumulation, distribution, and speciation in wheat. Zhao et al. (2010b) analyzed the arsenic concentration and speciation in grain samples of 26 wheat cultivars grown in five field trials located in farming regions in Europe. Grain from four trials contained low concentrations of total As reflecting low levels of As in the soils. In contrast, at one trial site, the As level in the soil was greater (29 mg Kg^{-1}), and much higher As concentrations were present in the wheat grain. Two methods (a phosphate buffer solution and 1% HNO_3) were used to extract As species from whole meal, bran, and white flour of wheat, with average extraction efficiencies of 65% and 88%, respectively. Only inorganic As was found in the extracts, with no methylated As being detected. The contribution of wheat to human intake of inorganic As is small for wheat crops grown in uncontaminated soils but becomes significant for those grown in soils with elevated As concentration. In the latter case, milling can be used to reduce As levels in the white flour. The findings showed no evidence of methylated As species in wheat whole meal flour, bran, or white flour. Other study was conducted in four wheat flour samples collected in Texas, USA, which revealed that mean values for total As and inorganic As were of 39 and 11 μg Kg^{-1}, respectively. However, it was not clear whether the difference between the amounts of total and inorganic As was due to incomplete extraction of the As species for analysis or the presence of organic As (Schoof et al. 1999).

In arsenic-contaminated soils at Faridpur (Bangladesh), an experiment was carried out to evaluate five wheat varieties (BARI Gom-21, BARI Gom-23, BARI Gom-24, BARI Gom-25, and BARI Gom-26) in order to determine arsenic accumulation in grain and straw. The results revealed that wheat varieties differed in their grain arsenic concentration (0.49–1.15 mg Kg^{-1}). BARI Gom-26 was found to accumulate least arsenic in grains followed by BARI Gom-25 and BARI Gom-24 varieties. Maximum grain yield (4.36 t ha^{-1}) was obtained from BARI Gom-26 variety followed by BARI Gom-25 variety, and the lowest yield (3.43 t ha^{-1}) was recorded from BARI Gom-23 variety. Therefore, BARI Gom-26 and BARI Gom-25 varieties could be grown for higher yield in arsenic-contaminated soils and water of Faridpur (Kamrozzaman et al. 2016).

2.2 *Maize*

Maize (*Zea mays* L.) is the main cereal cultivated in the world. The global production of maize according to the Food and Agriculture Organization of the United Nations (FAOSTAT) exceeded 883 million tons per year in 2011, a production greater than the corresponding production for wheat (704 million tons) and rice (723 million tons) (FAOSTAT 2004). It is a staple food for more than 200 million people in Latin America, sub-Saharan Africa, and Southeast Asia. Maize contains approximately 72% starch, 10% protein, and 4% lipid, with an approximately 365 kcal 100 g^{-1}. For this reason, maize has become highly integrated into the global agriculture, human diet, and cultural traditions (Nuss and Tanumihardjo 2010). Thus, the possibility that maize contributes to arsenic transfer to humans via consumption of contaminated food cannot be discarded. The mechanism of As uptake in maize is subject to metalloid forms in the soil. Generally, maize crop is grown in an aerobic environment in which As is primarily present in the oxidized As(V) form.

So far, As accumulation, distribution, and speciation in maize have not been taken into consideration. There are studies that described a significant relationship between As concentration in irrigation water or in agricultural soils and the metalloid level accumulated by maize crops. In this regards, Gulz et al. (2005) found a linear relationship between the As concentration in the soil and the As uptake by the maize root in calcareous and sandy loam soils contaminated with the metalloid. In the same study, a high correlation coefficient was obtained for soluble As in soil and metalloid uptake by roots. Similarly, Prabpai et al. (2009) revealed that the concentration of As accumulated in maize plant was significantly correlated with the As concentration in the agricultural soil of Thailand (0.144 mg Kg^{-1}) amended with different ratios of residues from municipal solid waste landfills (2 mg Kg^{-1}). *Zea mays* presents lower translocation capacities compared to other cereal crops and behaves like a non-hyperaccumulator plant. Metalloid concentrations of different maize organs decrease in the following order: root ˃ stem ˃ leaf ˃ grain. A recent research on As impact on soil-plant system indicated that metalloid translocation to plants varies with its speciation (Abbas et al. 2018). In this sense, Raab et al. (2007) conducted a study with 46 corn species grown under hydroponic conditions and demonstrated that DMA(V) was more effectively translocated from root to shoot than As(V) and MMA(V). They concluded that plants exposed to methylated As species have higher metalloid content in shoots than inorganic As form; therefore, an important As translocation to edible part could be achieved. Gulz et al. (2005) demonstrated that the characteristics of the soil in which maize is grown have an important impact on As uptake. In this regard, a lower As translocation were found when maize grew in silty loam soil (0.4%) compared to sandy loam soil (4.7%), having both soils an As concentration of 2.8 mg Kg^{-1}. Thus, the higher translocation efficiency that presents sandy loam soil could have a critical effect on the final concentration in the kernel. This was demonstrated by the high As concentration found in corn seeds compared to plants grown in the silty loam soil. Surprisingly, the As concentration in maize roots cultivated in this soil was 1.7 times higher than in sandy loam soil, suggesting that this type of soil contributes to the phytostabilization of the metalloid in maize root. Requejo and Tena (2014) revealed that maize has a low translocation factor from roots to shoots being a safe crop food. Additionally, they proposed maize crop to be used in agricultural useless land contaminated with As.

Until now, genetic mechanisms underlying As accumulation in maize is unclear. The use of marker-assisted selection results in a very useful tool to accelerate genetic improvement in crops. Ding et al. (2011) and Fu et al. (2016) revealed that the quantitative trait locus (QTL) mapping gives valuable information regarding As accumulation in different tissues and that they are controlled by diverse molecular mechanisms.

Biochemical and metabolic pathways show several disturbances when plants are exposed to As. In this regard, limitation of nutrients uptake, alteration on photosynthetic process, disruption on plant water status, interaction with enzymes functional groups, and replacement of essential ions are the most common responses evoked by plants exposed to the metalloid (Khalid et al. 2017; Rafiq et al. 2017). Evans et al. (2005) revealed that in the absence of phosphorus (P), As induced length and biomass of maize roots compared to phosphate treatment. In a similar revision, Srivastava (2014) showed that phosphate addition ameliorated the detrimental effects caused by arsenic in maize plants. Stoeva et al. (2003) studied the effect of metalloid addition (2 and 5 mg L^{-1}) on maize seedlings for 5 days. They revealed a significant growth decrease, changes in the gases exchange, and a reduction on chlorophyll and carotene content and chlorophyll fluorescence levels. These results indicate a deficiency on photosynthetic process by metalloid. Additionally, high peroxidase activity and a malondialdehyde (MDA) accumulation in roots were detected demonstrating a severe oxidative stress. In a proteomic study, Requejo and Tena (2005, 2006) revealed the impact of 90 mg L^{-1} As(V) and 75 mg L^{-1} As(III) on corn seedlings. From the total of proteins, 10% were up- or downregulated by metalloid addition, 20% were selected as being quite reproducibly affected by the metalloid, and 7% were related to cellular homeostasis (superoxide dismutase, glutathione/peroxiredoxin peroxidase) and others presenting heterogeneous functions. Mallick et al. (2011) obtained similar results where a plethora of enzymatic activities was modified by As addition on maize plants. Additionally, in an integrative study, Ghosh et al. (2016) evaluated the effect of 15 and 30 mg L^{-1} As(V) on corn seedlings. They found a significant biomass decrease, yellowing and drying of the leaves accompanied by loss of root cell viability. In addition, evidence of oxidative stress damage and an exacerbated phytochelatins (PCs) synthesis in the roots was detected. However, glutathione (GSH)/oxidized glutathione (GSSG) rate and glutathione S-transferase (GST) enzyme activity were enhanced but was not enough to prevent metalloid damage. All these findings are in agreement with those obtained by Hernández et al. (2015) and Bianucci et al. (2017b) that demonstrated that oxidative stress is the main process involved in metalloid toxicity.

The knowledge of the differential tolerance to As of different cultivars gives valuable information regarding crop protection in a contaminated environment. In this sense, Mallick et al. (2011) revealed that in the As-tolerant maize cultivar, the translocation factor from roots to shoots was lower than in the sensitive one. Moreover, total chlorophyll and protein levels as well as induction of superoxide dismutase (SOD) and glutathione reductase (GR) enzymes activities were observed in tolerant plants. These results suggest that As tolerance could be mediated by different detoxification mechanism among cultivars. Thus, the selection of a cultivar able to tolerate high As concentration and able to maintain its productivity in contaminated environments results in a promising ecological tool to be used.

Information regarding PGPB uses on maize exposed to arsenic, in order to prevent metalloid toxicity and induce growth, is scarce. In a recent study performed by Peralta et al. (2018) in a controlled environment, the impact of a realistic As(V) dose (1 mg L^{-1}) in maize plants and the contribution of *Azospirillum* strains to metalloid translocation were evaluated. They found that inoculation of maize with either *Azospirillum* strain reduced metalloid translocation to shoots compared to non-inoculated plants. Although inoculation restricted As translocation, *Azospirillum brasilense* Az39 strain was able to promote plant growth under As toxicity suggesting that the selection of the best PGPB-plant interaction is necessary to prevent metalloid translocation and avoid As distribution in the trophic chain.

Regarding As accumulation in maize grain, an experiment carried out at agricultural fields of the Ropar Wetland (India) demonstrated that the daily dietary intake of corn grains and groundwater both contaminated with inorganic As resulted in a health risk (Sharma et al. 2018). Although maize bioaccumulation factor was low, it was enough to contaminate grain constituting a serious risk of cancer in human. Additionally, cereal-based products constitute an important dietary source of arsenic, especially in geographical locations with naturally high concentration of the element or in polluted areas (EFSA 2014). In this aspect, Esperanza et al. (2017) evaluated As concentration and speciation in Mexican maize tortillas. They found that in seven products from local markets, total As was found in the range of 0.02 and 0.2 mg Kg^{-1}. The analysis of metalloid species showed that 72–98.0% was found in arsenate form.

3 Arsenic in Legumes

Legumes are plants that belong to Leguminosae family, also called as Fabaceae, that produce seeds within a pod. They play central roles in nature; however, the most relevant are (**a**) food source of protein to human and animals; (**b**) enhancement of humus and nitrogen content and phosphorus availability in soil (Jensen et al. 2012); and (**c**) mitigation of greenhouse gases emissions (Lemke et al. 2007).

Leguminosae family comprises 800 genera and 20,000 species (Lewis et al. 2005) representing the third largest family of flowering plants (Stagnari et al. 2017). Although legumes represent an important crop in the world, food legumes (legumes used for human consumption such as peas, broad beans, lentils, soybeans, lupins, lotus, sprouts, mung bean, green beans, and peanuts) occupy a minimal part of the arable land compared with cereal crops (Siddique et al. 2012). Thus, studies aiming to increase yields in the current used areas are of significant relevance to contribute to food provision to an increasing human population.

3.1 Peanut

Peanut, also known as groundnut, is a self-pollinating, indeterminate, annual, herbaceous legume plant originally from South America. Genus *Arachis* involves 22 species from which 9 are nodulated by rhizobia and only one (*Arachis hypogaea* L.) is currently cultivated. The fruit is a pod with one to five seeds that develop underground being in contact with soil particles. Generally, all peanut parts are used for some purposes such as human and animal feed or industrial raw material. In terms of nutrition, peanut seeds are rich in oils and contain 50% fat, 20–50% protein, 10–20% carbohydrate, vitamins, amino acids, calcium, phosphorus, magnesium, zinc, and iron (Fabra et al. 2010).

Peanuts are considered the 13th most important food crop in the world and the 4th most important source of edible oil. The global peanut production has increased by an average 20% in the last 10 years (Worldatlas 2018). The top peanut exporting countries of groundnuts are led by Argentina followed by India and the USA (Agriexchange 2017).

Studies on the As impact on peanut development and yield are currently being undertaken, due to the negative effect that metalloid could have on human dietary. It is known that As has potent genotoxic effects that causes aberrant chromosomal arrangement and cell cycle arrest, resulting in a low root meristematic activity (Wu et al. 2010). Thus, Bianucci et al. (2017a) studied the impact of As on peanut plants observing that metalloid addition induced a significant reduction of plant growth accompanied by a diminution of root volume, architecture, and lateral roots development, being these responses exacerbated at the increasing As concentrations (2–30 mg L^{-1}). One of the most interesting root modification was the deposit of unknown material over the epidermis and cortex cells that could be limiting the natural lateral root development as observed in the same crop but exposed to the heavy metal Cd (Bianucci et al. 2012). Conversely, addition of a low arsenic concentration (1 mg L^{-1}), an average concentration found in groundwater of Córdoba province (Argentina), did not induce growth reduction, deposit accumulations in epidermal cells, nor exomorphological changes (Peralta et al. 2018). Since roots are the first organ in contact with the contaminant, another symptom of As exposure is a darkening of root system (Bianucci et al. 2017a; Peralta et al. 2018). Shri et al. (2009) and Bianucci et al. (2017a) explained that this darkening is related to a cellular redox imbalance that oxidize roots surface components. In some cases, this oxidative burst induced by an enhancement of NADPH oxidase and ROS production can lead to an oxidative stress as observed by the peroxidation of membrane lipids of peanut plants exposed to 6 and 30 mg L^{-1} As (Bianucci et al. 2017a).

Although it is known that metalloid addition causes oxidative stress, cells have an integral antioxidant mechanism system to counteract ROS and ROS-oxidative product damage. In this sense, the antioxidant response to As is generally mediated by GSH due to the high affinity of As(III) to sulfhydryl groups (Li et al. 2006; Sobrino-Plata et al. 2013; Bianucci et al. 2017a). GSH is a well-known thiol present in all eukaryotic cells and in most of prokaryotes. It is the most abundant intracellular tripeptide and plays fundamental roles such as protein and DNA synthesis, cell transport, enzyme activity modulation, and cellular metabolism as well as defense against ROS (Foyer and Noctor 2011). The balance between GSH and its oxidized form (GSSG) keeps a strong reducing environment in the cell (Bianucci et al. 2017b). Different antioxidant enzymes related to the thiol metabolism (GSH and thioredoxins) such as GR, GSTs, and glutathione peroxidase/peroxiredoxin (GPX/PRX) are also involved in the detoxification of free radicals (Foyer and Noctor 2011). In this regard, the antioxidant response of peanut plants exposed to As showed that a high metalloid concentration (30 mg L^{-1}), enhanced GSH content. Contrarily, enzymes related to its metabolism, such as GR and GPX/PRX, were severely reduced since high ROS accumulation can decrease antioxidant enzymes activities, due to direct interactions (Gratão et al. 2005; Sharma and Dietz 2009). Conversely, the activity of GST enzyme, induced by As, is fundamental, due to its ability of detoxify organic peroxides, radicals, and xenobiotics (Schröder et al. 2009). In peanut plants exposed to As, GST activity rose remarkably at increasing metalloid concentrations (Bianucci et al. 2017a). Thus, the comprehension of the oxidative and antioxidant response of peanut plants exposed to As contributes to understand how low metalloid concentrations could generate a reduction of peanut growth variables, affecting peanut production.

Regarding As accumulation, most of the As absorbed is present in roots, as expected for a non-hyperaccumulator plants as peanut (Bianucci et al. 2018a; Peralta et al. 2018). The retention of As in this organ occurs mainly at the cell walls of epidermal cells by the formation of an iron plaque that could acts as a barrier to the uptake of potentially harmful elements (Hansel et al. 2002; Liu et al. 2004). This plaque is precipitated onto the root surface as iron (Fe), as a product of the oxidation of the ferrous to ferric (Armstrong 1967). Although As translocation rate is low in legumes, metalloid can be found in leaves, and therefore it is deducted that it can be translocated via phloem to the grain. However, As concentration found in edible parts of peanuts is subjected to the edaphic condition in which the legume is developed. In this regard, researches showing As concentration in food grains, in particular peanut, are scarce. In a study performed in Ohio (USA), the As concentration was analyzed in different types of nuts, randomly purchased from local market. The results revealed that peanut oil contained approximately 2.2 ng total As g^{-1}, distributed in three different As species, 0.7 ng As(III) g^{-1}, 0.3 ng DMA(V) g^{-1}, and 1.2 ng As(V) g^{-1} (Kannamkumarath et al. 2004).

In another revision, As concentration was measured in peanut grain, grown in a chamber pot experiment, using a lead arsenate-contaminated soil from Michigan (USA) with a total As concentration of 90 mg Kg^{-1}. Results showed that As concentration in peanut kernel and pods was significantly high in the contaminated soil compared to control condition. Moreover, As concentration found in kernel and pods were 3 and 22 mg Kg^{-1}, respectively (Codding 2018). The high As concentration found in pod suggests that during grain filling, a significant amount of As from xylem and phloem are loaded into the grain, together with photoassimilated products, as it was observed in peanut plants exposed to Cd (Bianucci et al. 2018b). Another explanation is that a small amount of the metalloid could be directly absorbed through the pod from contaminated soil, although conclusive evidences are required (McLaughlin et al. 2000). The addition of a P source is an alternative to reduce As uptake by peanut plants (Gunes et al. 2009; Srivastava 2014); however, Codding (2018) demonstrated that the addition of neither superphosphate nor broiler litter ash, modified As content in by peanut kernel or pods at field condition.

These results show that even a small amount of As can be translocated to edible parts of peanut plants constituting a possible risk to human health. Thus, it is of an extreme importance to study the chemical composition of soils before planting food legumes as peanuts, in order to avoid grain contamination.

In Argentina, the main source of possible peanut contamination is groundwater. Approximately 90% of the Argentinean production of peanut is located in Córdoba province, positioning the country as one of the major producer in the world (Ministry of Production and Work, Argentina 2006; Agriexchange 2017). Two factors converge in the same region; one is the presence of a high As concentration in groundwater and the other is an elevated phreatic level that, due to increasing rainfalls, easily reaches soil surface. Interestingly, in these cropping areas, where groundwater is near the rhizosphere, crop yield is significantly increased due to water availability (Scilingo et al. 2011). The problem arises since local studies showed that 90% of this region is affected by groundwater As concentrations that exceed the maximum allowed level of the metalloid in drinking water (0.01 mg L^{-1}) (FAO, OMS 2006), reaching in some areas up to 1.7 mg L^{-1} (Cabrera et al. 2005; Francisca et al. 2006) (Fig. 2). Although, no information of As speciation in Córdoba groundwater is available, it is known that under oxidant condition and in the range of pH of Córdoba's groundwater, the predominant As form would be As(V). Moreover, the dissolved levels of oxygen, nitrate, and sulfate contribute to maintain the arsenate form, as it was observed by Smedley et al. (2000). Another study, performed by the national Institute of Agricultural Technology (INTA), did not detect arsenic in peanut kernels (Badini et al. 2012). However, these studies were performed in areas where the phreatic level was deep.

Researches are currently being made in order to determine the influence of the phreatic level, in which groundwater has As, on peanut kernel. Preliminary results showed that the metalloid was absorbed by peanut roots in areas with groundwater (containing As) near to soil surface. The analysis of metalloid presence in peanut kernels revealed in some cases up to tenfold the reference level imposed in the technical regulation MERCOSUR (ANMAT 2012) (Bianucci et al. unpublished). It is important to highlight that contrasting results were obtained in different lots that belongs to the same field. This could be explained since the depth of the phreatic level can vary in the same land used for peanut cultivation due to different slopes of the land, so that groundwater containing As can affect in a different manner the same crop in a lot destined to peanut production.

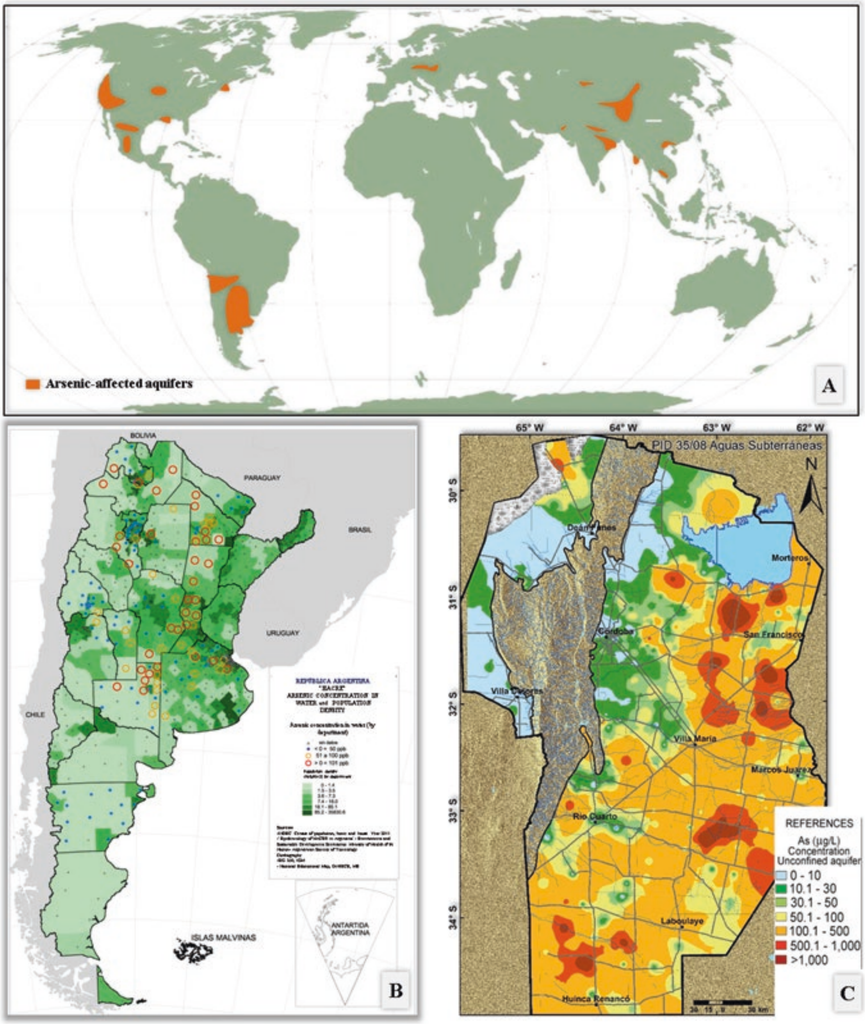

Fig. 2 Distribution of groundwater with arsenic concentrations in a global perspective (**A**), in the República Argentina (**B**) and in the free aquifer waters of the Córdoba's province (**C**) (Figures extracted and adapted from Federal Council of Health Services Entities of Argentina (2018) and Bécher Quiñodóz et al. (2019))

3.2 *Soybean*

Soybean (*Glycine max* L.) is an annual, herbaceous legume plant originally from Asia; however, its cultivation was worldwide dispersed, being cultivated in the five continents (López et al. 2013). The fruits are pods of up to 7 cm long with one to four seed inside (Bianco et al. 2007). Nitrogen constitutes a limiting nutrient to achieve good yields in this crop, and can be satisfied by the BNF process.

Soybean has a high level of protein content and high nutritional quality, and the seeds are considered one of the major food sources for human and livestock due to its nutritional composition; containing high concentration of protein (40%), oil t (25%), and carbohydrates (35%) (Sharma et al. 2014). In terms of world economy, soybean is considered a very important crop being mainly produced in Argentina, Brazil, and the USA (SOPA 2018).

Effects of As on soybean plants have been widely studied at controlled environmental chambers wherein different As concentrations were used and added to hydroponics or solid substrates (Reichman 2007; Sobrino-Plata et al. 2013; Panigrahi and Randhawa 2010; Panigrahi et al. 2013; Talano et al. 2013; Bustingorri and Lavado 2014; Bianucci et al. 2018a). Regarding As impact on growth variables, all these researchers found significant decreases in biomass production, being exacerbated as metalloid concentrations increased. Growing disturbances were associated to modifications in the cortex cell of roots accompanied with broken cells and the observation of deposits of unknown composition in the epidermis and vascular cylinder of soybean roots exposed to the toxic element. Metalloid addition also induced reduction of chlorophyll content and stomata closure in order to reduce transpiration (Armendariz et al. 2016a, b). Besides, other toxicity effects mainly related to the generation of ROS and oxidative stress have been observed. An increase of lipid peroxidation in soybean leaves and roots, at different stages of growth, was detected and consistent with As increasing concentration (Bianucci et al. 2018a; Bustingorri et al. 2015). Moreover, metalloid addition induced an activation of the antioxidant system in leaves and roots. In this sense, at 35 mg Kg^{-1} As, catalase (CAT) and guaiacol peroxidase (GPOX) activities were significantly increased; however, it was not high enough to cope with the oxidative damage imposed by the metalloid (Bustingorri et al. 2015).

A major antioxidant compound in soybean, besides GSH, is homo-GSH, a tripeptide containing β-Ala instead of Gly and precursor of hPCs. It was observed that hPC synthesis was associated with soybean growth maintenance under metalloid toxicity, constituting an effective defense mechanism under As exposure (Oven et al. 2001; Vázquez et al. 2005, 2009).

In regard to metalloid concentration in grains, published data is scarce. Bustingorri et al. (2015) showed that soybean plants exposed to 35 mg Kg^{-1} of As significantly reduced crop yield but most importantly did not accumulate the metalloid in the grain. Besides, these researchers showed that higher metalloid concentration induced soybean death before harvesting. Thus, according to this data the exposition of soybean plant to these As concentrations and under the mentioned conditions does not constitute a human health concern.

3.3 Other Legume Crops

Studies of the impact of As in other legume crops such as peas, broad beans, lentils, lupins, lotus, sprouts, mung bean, and green beans are scarce. Mung bean (*Vigna radiata*) is extensively grown in tropical and subtropical Asia and, like all legumes, is a rich source of seed proteins. It is easily adapted to several environments, fitting well in multi-cropping systems (Singh et al. 2013). Van den Broeck et al. (1998) suggests the use of mung bean seedlings as bioindicators to determine the degree of As contamination in water and soil. This plant is very sensitive to different sources of pollution showing modifications of its metabolic system, accompanied with visual changes when exposed to contaminants as arsenic. However, this study was performed under hydroponics, and direct extrapolation to field is not advised since different results could be achieved. In another study, it was demonstrated that As caused severe toxicity symptoms being the loss of crop productivity one of the most alarming in terms of economy (Singh et al. 2007). Similar results were observed in mung bean plants exposed to As, accompanied with an alteration of the antioxidant system such as reduction in GSH redox state, ascorbate peroxidase, dehydroascorbate reductase, and glutathione reductase activities. Moreover, significant ROS production was also observed leading to an oxidative stress (Talukdar 2014). In a recent work, Das and Sarkar (2018) showed that inoculation of mung bean, exposed to As (22.5 mg Kg^{-1}) in a controlled environment, with a tolerant strain, limited metalloid adsorption from soil and improved plant growth, representing a biotechnological tool to be used in contaminated sites avoiding possible grain contamination.

Phaseolus is a large genus of annual vegetables in the pea family that are primarily native to Central America and South America, with a few species native to North America, and commonly known as bean. Carbonell-Barrachina et al. (1997) studied the effects of As on bean plants exposed to different metalloid concentrations (2–10 mg L^{-1}) on hydroponics. They found that metalloid is highly phytotoxic causing plant death. In another study, Talukdar (2013) showed that addition of 15 mg L^{-1} reduced bean growth and modified anatomical features. Also, a reduction in pigment composition, an increase on ROS production, and modifications of the antioxidant system activity were detected. All these disturbances ended in an oxidative damage being roots severely affected.

Lupine is a legume widely used for stockfeed and in some extent (less than 4% of global production) as human food (Lawrence et al. 2007). Interestingly, researches on *Lupinus albus* L. (an annual legume) at field conditions allowed to classify white lupine as a good candidate for phytoremediation process, due to the high tolerance to pollutant. Also, lupine has also been involved in revegetation of degraded landfill with polluted soils (Ximénez-Embún et al. 2002; Zornoza et al. 2002; Tassi et al. 2004; Vázquez et al. 2006, 2008; Dary et al. 2010). However, its use as legume food in contaminated environments has not been well addressed; the only available information regarding to As concentration in lupine grains comes from the work performed by Vázquez et al. (2008) who found 9 mg Kg^{-1} fresh weight when exposed to 30 mg Kg^{-1}.

3.4 Use of Legume-Rhizobia Symbiotic Interaction as a Biotechnological Tool to Avoid Grain Contamination

Nitrogen constitutes a limiting nutrient in crop yield, and the BFN established between legumes with members of rhizobia or bradyrhizobia family results in the main source of N in the biosphere. Besides, it is an economically and ecologically sustainable alternative against the use of nitrogen fertilizers (Wang and Li 2003).

Originally, the inoculation of symbiotic microorganisms had a sole and important function: to serve as a nitrogen source for legumes in order to improve growth and increase yield. Nowadays, it has an additional function: improving phytoremediation process and/or protecting plant development in contaminated sites. In a transcriptomic research performed by Lafuente et al. (2015) with *Medicago* plants, it was revealed that the inoculation of an As-tolerant rhizobia alleviated the toxicity imposed by the metalloid and enhanced the activity of an enzyme involved in the first step of the symbiosis (chalcone synthase) suggesting that plants exposed to As prefer to establish a symbiotic interaction rather than not.

In the past few years, the usages of symbiotic microorganisms for bioremediation processes have been widely taken into consideration (Reichman 2007; Mandal et al. 2011; Safronova et al. 2011; Gómez-Sagasti and Marino 2015). Interestingly, the symbiotic interaction that legumes establish with rhizobia allows to enhance phytostabilization processes serving as a promising biotechnological tool to reduce metal(loid)s content in plants. Nevertheless, special care must be taken in remediation processes using food legumes due to the possible metal(loid)s translocation to edible plant organs (Gómez-Sagasti and Marino 2015).

An important aspect to consider is the knowledge of the metabolic response of microsymbionts to metal(oid)s exposure, since the capability to establish a symbiotic interaction with a legume exposed to arsenic will determine its growth. It is known that rhizospheric bacteria induce changes in metal(loid)s speciation and mobility of metals, being able to control the biogeochemical cycle of metals in the environment (Finnegan and Chen 2012; Lomax et al. 2012). However, heavy metals and metalloids, like As, negatively impact in the growth of prokaryotic cells, being its toxicity related to ROS accumulation inducing oxidative stress (Hughes 2002; Mandal et al. 2008; Verbruggen et al. 2009; Panigrahi et al. 2013; Sharma 2012; Talano et al. 2013; Bianucci et al. 2016, 2018a, b). In these conditions, bacteria can respond through their antioxidant defense system activation. Some of the most studied defense system are: (a) the tripeptide GSH, that plays a fundamental role binding to As(III) reducing its toxicity in cells; (b) antioxidant enzymes related to GSH metabolism that eliminate ROS from affected biomolecules such as lipids, proteins, and DNA and superoxide dismutase (SOD) and CAT, which decrease radicals accumulation; (c) activation of a specific efflux system that allows to expulse the metalloid outside the cell; and (d) an enzymatic detoxification process carried out by arsenate reductases and methyltransferases that transform As into non- or less toxic forms (Bhattacharjee and Rosen 2007; Bianucci et al. 2016). Regarding these two last points, *ars* genes that code for As(III)-responsive repressors, efflux permease, and/or ATPase to extrude As(III) have been widely studied in a wide range of bacterial species (Bhattacharjee and Rosen 2007; Yang and Rosen 2016). However, less it is known regarding symbiotic bacteria responses under metalloid exposure. In a study performed with commercial and native bradyrhizobial strains (soybean symbionts) exposed to As, remarkable differences were observed among them (Bianucci et al. 2018a). In this research, *Bradyrhizobium diazoefficiens* USDA110, a reference strain widely used as soybean inoculant, and the native isolate *Bradyrhizobium* sp. Per 3.64, were able to grow up to 4000 mg L^{-1}; however, the native isolate *Bradyrhizobium* sp. Per 3.61, grew up to 3000 mg L^{-1}. The native isolates were obtained from soils cultivated with soybean plants in Pergamino (Buenos Aires, Argentina) by Fernández et al. (2008). In a different study, *Bradyrhizobium japonicum* E109, another reference strain also used in Argentina as a soybean inoculant, was able to grow up to 30 mg L^{-1}, without showing differences with control condition (Armendariz et al. 2015). Nonetheless, these researchers observed that the strain accumulated a significant amount of As, and it was able to reduced it to As(III). Moreover, a significant production of exopolysaccharides and biofilm was observed compared to control condition. Peanut microsymbionts were classified regarding As tolerance, and the reference strain *Bradyrhizobium* sp. SEMIA6144 that grew up to 3000 mg L^{-1} was classified as sensitive. On the other hand, the reference strain *Bradyrhizobium* sp. C-145 and the native strains *Bradyrhizobium* sp. NOD31 and *Bradyrhizobium* sp. NLH25, able to grow up to 6000 mg L^{-1}, were classified as tolerant (Bianucci et al. 2016). All these findings showed that each strain responded in a specific manner when exposed to the same contaminant.

Considering symbiotic variables, it is known that metal(loid)s exposure can induce changes in the microbial population, reduces nodule formation, and impairs the efficiency of nitrogen fixation (Alexander et al. 1999; Broos et al. 2004; Abou-Shanab et al. 2005; Liao et al. 2005; Younis 2007; Paudyal et al. 2007; Akerblom et al. 2007; Sobolev and Begonia 2008; Bamborough and Cummings 2008). Particularly, As presence in the environment negatively impacts in nitrogen-fixing bacteria viability and plant growth (Pajuelo et al. 2008; Talano et al. 2013; Armendariz et al. 2015; Nocelli et al. 2016; Bianucci et al. 2018a). In the symbiotic interaction established between *Medicago sativa* and *Rhizobium* sp., As induced a significant reduction of nodule number (Neumann et al. 1998). Similar results were observed in the symbiotic association between soybean and bradyrhizobia members exposed to different As concentrations (Reichman 2007; Vázquez et al. 2008; Talano et al. 2013; Bianucci et al. 2018a, b). In peanut, a significant reduction of nodulation variables was also observed, accompanied by a reduction in the total nitrogen content (Peralta et al. 2018). Additionally, Reichman (2007) observed a retarding nodule formation in soybean. The reduction in the number of formed nodules in legumes could be attributed to an alteration in the formation of root hair. Furthermore, it could be suggest that a reduction of the infection zone contributes to a less nodule number. Lafuente et al. (2015) showed that the negatively impact of As was mainly due to an alteration of genes involved in the early stages of symbiosis, since the metalloid reduced the expression of early nodulins (*nork*, *NIN*, *N6*, *Enod2*). Also, they demonstrated that no differences were observed regarding the expression of initiation and differentiation markers of the primordium (*Enod40* and *ccs52*, respectively). In this sense, Pajuelo et al. (2008) showed that once the interaction between the plant and the rhizobia is established, the nodule development contuse as normally. In a similar way, Bianucci et al. (2018a, b) demonstrated that although nodule formation was decreased in soybean plant due to As addition, inside the nodules a red color characteristic from active nodules given by leghemoglobin activity was detected demonstrating their ability to continue fixing nitrogen. Thus, in soybean plants, As caused a reduction in the number of nodules but not in terms of nitrogen fixation. Nonetheless, it impacted on the total nitrogen content in plants (Bianucci et al. 2018a) and, therefore, it could reduce crop yield.

An important issue to consider is the selection of the best symbiotic partnership to the legume, since not all rhizobia acts in a same manner when inoculated to plants exposed to different As concentrations. It is known that the microbial tolerance to different metal(loid)s is important to achieve an effective symbiotic interaction in contaminated sites (Reichman 2007); however, it is important to point out that each field constitutes a singular experience, and most of the times, extrapolation should not be advised since different responses could be achieved. Studies performed by Bianucci et al. (2018a) and Peralta et al. (2018) showed that soybean inoculation, exposed to a low As concentration (2 mg L^{-1}), with a native strain (*Bradyrhizobium japonicum* PER 3.61), reduced metalloid translocation to the shoot. However, when the plant was subjected to middle As concentration (6 mg L^{-1}), the only strain able to establish a symbiosis with the legume and induced plant development was the reference strain *Bradyrhizobium diazoefficiens* USDA110. In peanut, the inoculation of a tolerant As strain (*Bradyrhizobium* sp. C-145) increased growth variables compared to non-inoculated plants and to plants inoculated with a sensitive strain. Moreover, the comparison of the symbiotic properties among these strains showed that although As reduced nodule number, the inoculation of peanut with the tolerant strain did not modified BNF since total N content was unchanged compared to control condition. Although legume inoculation with a sensitive strain reduced significantly peanut growth and nitrogen content, translocation of As to aerial part of the plant was highly reduced compared with plants inoculated with the tolerant rhizobia. A future alternative to be investigated is the co-inoculation of rhizobia with other PGPB that enhance rhizobia activity and therefore plant growth.

Generally, As concentration in natural soils used for food legumes is above 1000 mg Kg^{-1}; hence, most of the mentioned rhizobia strains can grow in such conditions. However, the host plant experiments several cellular changes that could interfere with the normal development of the symbiotic interaction (Bianucci et al. 2016). Thus, studies of specific plant-microorganism interactions, for each legume and metalloid concentrations, are fundamental to reach substantial conclusions in order to prevent or avoid grain contamination.

The evidence strongly suggests that food legumes are not advisable for phytoremediation processes in highly contaminated sites since the metalloid could reach grains and enter the food chain. Nevertheless, inoculation of specific symbiotic partners into legumes could be proposed in order to improve the phytostabilization process reducing metalloid translocation to edible parts of the plant and avoid human health problems.

4 Conclusions and Future Perspectives

This chapter summarized the As effects on cereal and legume crops used as food. Crop contamination is mainly achieved by groundwater containing As, constituting a serious human health risk. The overview included metalloid impacts at cellular level, describing plant responses at biochemical, anatomical, and genetic levels, and the mechanisms evoked by crops in contaminated environments. Thus, the knowledge of the integrated data exposed here could contribute to understand the metalloid toxicity on plant and the risk that could have on human poisoning by the ingestion of contaminated grains.

Although cereals and legumes could be used for phytoremediation processes, food crops are not advisable in highly contaminated sites, since the metalloid could reach grains and enter the food chain. One of the biotechnological approaches that is currently being studied is the use of PGPB in order to increase yield and limit As translocation to aerial parts of the plant, preventing grain contamination. Considering that metalloid concentration varies among geographic regions and that each field constitutes a singular experience, it is important to study the specific plant-microorganism interactions, for each cereal or legume crop and the metalloid concentrations present in the environment, in order to choose the best partnership for the plant and, therefore, prevent or avoid grain contamination.

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References

Abbas G, Murtaza B, Bibi I, Shahid M, Niazi NK, Khan MI, Hussain M (2018) Arsenic uptake, toxicity, detoxification, and speciation in plants: physiological, biochemical, and molecular aspects. Int J Environ Res Public Health 15(1):59

Abou-Shanab RA, Ghozlan H, Ghanem K, Moawad H (2005) Behaviour of bacterial populations isolated from rhizosphere of *Diplachne fusca* dominant in industrial sites. World J Microbiol Biotechnol 21:1095–1101

Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals: Chapter 7: arsenic, 2nd edn. Springer, Berlin, pp 220–256

Agriexchange (2017). http://agriexchange.apeda.gov.in/ Accessed Sept 2018

Akerblom S, Baath E, Bringmark L, Bringmark E (2007) Experimentally induced effects of heavy metal on microbial activity and community structure of forest more layers. Biol Fert Soils Journal 44:79–91

Alexander E, Pham D, Steck TR (1999) The viable but non-culturable condition is induced by copper on *Agrobacterium tumefaciens* and *Rhizobium leguminosarum*. Appl Environ Microbiol 65:3754–3756

Angle JS, Linacre NA (2005) Metal phytoextraction: a survey of potential risks. Int J Phytoremediation 7:241–254

ANMAT Administración Nacional de Medicamentos, Alimentos y Tecnología Médica (2012). http://www.anmat.gov.ar/alimentos/normativas_alimentos_caa.asp. Accessed Sept 2018

Armendariz AL, Talano MA, Wevar Oller AL, Medina MI, Agostini E (2015) Effect of arsenic on tolerance mechanisms of two plant growth-promoting bacteria used as biological inoculants. J Environ Sci 33:203–210

Armendariz AL, Talano MA, Travaglia C, Reinoso H, Wevar Oller AL, Agostini E (2016a) Arsenic toxicity in soybean seedlings and their attenuation mechanisms. Plant Physiol Biochem 98:119–127

Armendariz AL, Talano MA, Villasuso AL, Travaglia C, Racagni GE, Reinoso H, Agostini E (2016b) Arsenic stress induces changes in lipid signalling and evokes the stomata closure in soybean. Plant Physiol Biochem 103:45–52

Armstrong W (1967) Oxidising activity of roots in waterlogged soils. Physiol Plant 20:920–926

Arsenic in Food Regulations (1959) Statutory Instrument 1959 No 831, as amended in 1960 (S.I. 1960 No. 2261) and 1973 (S.I. 1973 No. 1052). HMSO, London

Badini RG, Inga CM, Aguilar RC, Silva MC, Martinez MJ (2012) Analisis elemental comparativo en mani confiteria de cordoba por técnicas de espectroscopía atómica. Reuniones y Congresos INTA ISSN On line 1851–4987

Bamborough L, Cummings SP (2008) The impact of increasing heavy metal stress on the diversity and structure of the bacterial and actinobacterial communities of metallophytic grassland soil. Biol Fertil Soils J 45:273–280

Beatty P, Good A (2001) Future prospects for cereals that fix nitrogen. Science 333:416–417

Bécher Quinodóz F, Maldonado L, Blarasin M, Matteoda E, Lutri V, Cabrera A, Giacobone D (2019) The development of a conceptual model for arsenic mobilization in a fluvio-eolian aquifer using geochemical and statistical methods. Environ Earth Sci 78:206

Bhattacharjee H, Rosen BP (2007) Arsenic metabolism in prokaryotic and eukaryotic microbes. In: Nies DH, Silver S (eds) Molecular microbiology of heavy metals, pp 372–405

Bhattacharya P, Samal AC, Majumder J, Santra SC (2010) Arsenic concentration in rice, wheat pulses and vegetables: a study in an arsenic affected area of West Bengal, India. Water Air Soil Pollut 213:3–13

Bianco C, Kraus T, Núñez C (2007) Botánica Agrícola. 2nd ed. Ed. Universidad Nacional de Río Cuarto.zhao Río Cuarto, Argentina

Bianucci E, Sobrino-Plata J, Carpena-Ruiz RO, Tordable MC, Fabra A, Hernández LE, Castro S (2012) Contribution of phytochelatins to cadmium tolerance in peanut plants. Metallomics 4:1119–1124

Bianucci E, Furlan A, Isaia A, Peralta JM, Hernández LH, Castro S. (2016) Impact of arsenic in Bradyrhizobia strains and in the symbiotic interaction with peanut plant. 52th annual meeting Argentine Society for Biochemistry and Molecular Biology. Córdoba; Biocell 40. 113

Bianucci E, Furlan A, Tordable MC, Hernández LE, Carpena-Ruiz RO, Castro S (2017a) Antioxidant responses of peanut roots exposed to realistic groundwater doses of arsenate: identification of glutathione S-transferase as a suitable biomarker for metalloid toxicity. Chemosphere 181:551–561

Bianucci E, Furlan A, Castro S (2017b) Importance of glutathione in the legume-rhizobia symbiosis. In: Hossain M, Mostofa M, Diaz-Vivancos P, Burritt D, Fujita M, Tran LS (eds) Glutathione in plant growth, development, and stress tolerance. Springer, Cham, pp 373–396

Bianucci E, Godoy A, Furlan A, Peralta JM, Hernández LE, Carpena-Ruiz RO, Castro S (2018a) Arsenic toxicity in soybean alleviated by a symbiotic species of *Bradyrhizobium*. Symbiosis 74(3):167–176

Bianucci E, Furlan A, Tordable MC, Fabra A, Hernández LE, Carpena-Ruiz R, Castro S (2018b) Impacto del cadmio sobre la acumulación y la producción de granos en cultivos de maní. In the book: Biorremediación de los recursos naturales. Ed. INTA, pp 367–385. ISBN: 978-987-521-911-3

Blarasin M, Cabrera A, Matteoda E, Aguirre M, Giuliano Albo J, Becher Quinodoz F, Maldonado L, Felizzia J, Palacio D, Echevarría K, Frontera H (2014) Aspectos geoquímicos, isotópicos, contaminación y aptitudes de uso In: Aguas Subterráneas De La Provincia De Córdoba. Ed: UniRío, pp 83–148

Brammer H, Ravenscroft P (2008) Arsenic in groundwater: a threat to sustainable agriculture in South and South-east Asia. Environ Int 35:647–654

Broos K, Uyttebroek M, Mertens J, Smolders E (2004) A survey of symbiotic nitrogen fixation by white clover grown on metal contaminated soils. Soil Biol Biochem 36:633–640

Bustingorri C, Lavado RS (2014) Soybean as affected by high concentrations of arsenic and fluoride in irrigation water in controlled conditions. Agric Water Manag 144:134–139

Bustingorri C, Balestrasse K, Lavado RS (2015) Effects of high arsenic and fluoride soil concentrations on soybean plants. Phyton Intern J Exp Bot 84:407–416

Cabrera A, Blarasin M, Matteoda E, Villalba G, Gomez ML (2005) Composición química del agua subterránea en el sur de córdoba: línea de base hidroquímica o fondo natural en referencia a arsénico y flúor. http://www.produccion-animal.com.ar. Accessed Aug 2018

Carbonell-Barrachina AA, Burlo F, Burgos-Hernandez A, Lopez E, Mataix J (1997) The influence of arsenite concentration on arsenic accumulation in tomato and bean plants. Sci Hort 71(3–4):167–176

Carey AM, Scheckel KG, Lombi E, Newville M, Choi Y, Norton GJ, Charnock JM, Feldmann J, Price AH, Meharg AA (2010) Grain unloading of arsenic species in rice (*Oryza sativa* L.). Plant Physiol 152:309–319

Carey AM, Norton GJ, Deacon C, Scheckel KG, Lombi E, Punshon T, Guerinot ML, Lanzirotti A, Newville M, Choi Y, Price AH, Meharg AA (2011) Phloem transport of arsenic species from flag leaf to grain during grain filling. New Phytol 192:87–98

Cargnelutti D, Tabaldi LA, Spanevello RM, Jucoski GO, Battisti V, Redin M, Linares CEB, Dressler VL, Flores MM, Nicoloso FT, Morsch VM, Schetinger MRC (2006) Mercury toxicity induces oxidative stress in growing cucumber seedlings. Chemosphere 65:999–1006

Chapman GP (1996) The biology of grasses. CAB International, Wallingford. (Gramene Reference ID 8384)

Chen TB, Fan ZI, Lei MEI (2002) Effect of phosphorus on arsenic accumulation in As-hyperaccumulator: *Pteris vittata* L. and its implication. Chin Sci Bull 499:15–16

Cho UH, Park JO (2000) Mercury-induced oxidative stress in tomato seedlings. Plant Sci 156:1–9

Chopra VL, Prakash S (2002) Evolution and adaptation of cereal crops. Science Publishers, Enfield

Codding EE (2018) Accumulation of lead and arsenic by peanut grown on lead and arsenic contaminated soils amended with broiler litter ash or superphosphate. J Plant Nutr 41:1615–1623

Costa R, Pinheiro N, Ameida AS, Gomes C, Coutinho J, Coco J, Costa A, Nacas B (2013) Effect of sowing date and seeding ratio on bread wheat yield and test weight under Mediterranean conditions. Emir J Food Agric 25:951–961

Dary M, Chamber-Pérez MA, Palomares AJ, Pajuelo E (2010) "In situ" phytostabilisation of heavy metal polluted soils using *Lupinus luteus* inoculated with metal resistant plant-growth promoting rhizobacteria. J Hazard Mater 177:323–330

Das J, Sarkar P (2018) Remediation of arsenic in mung bean (*Vigna radiata*) with growth enhancement by unique arsenic-resistant bacterium Acinetobacter lwoffii. Sci Total Environ 624:1106–1118

Dhankher OP, Rosen BP, McKinney EC, Meagher RB (2006) Hyperaccumulation of arsenic in the shoots of *Arabidopsis* silenced for arsenate reductase (ACR2). Proc Natl Acad Sci U S A 103:5413–5418

Diaz OP, Leyton I, Munoz O, Nunez N, Devesa V, Suner MA, Velez D, Montoro R (2004) Contribution of water, bread and vegetables (raw and cooked) to dietary intake of inorganic arsenic in a rural village of Northern Chile. J Agric Food Chem 52:1773–1779

Ding JQ, Ma JL, Zhang CR, Dong HF, Xi ZY, Xia ZL, Wu JY (2011) QTL mapping for test weight by using F 2: 3 population in maize. J Genet 90(1):75–80

Duan GL, Zhou Y, Tong YP, Mukhopadhyay R, Rosen BP, Zhu YG (2007) A CDC25 homologue from rice functions as an arsenate reductase. New Phytol 174:311–321

EFSA. European Food Safety Authority (2014) EFSA J 12:1–68

Esperanza MG, Barrientos EY, Wrobel K, Aguilar FJA, Escobosa ARC, Wrobel K (2017) Determination of total arsenic and speciation analysis in Mexican maize tortillas by hydride generation–microwave plasma atomic emission spectrometry and high performance liquid chromatography–inductively coupled plasma–mass spectrometry. Anal Methods 9(13):2059–2068

Evans G, Evans J, Redman A, Johnson N, Foust RD (2005) Unexpected beneficial effects of arsenic on corn roots grown in culture. Environ Chem 2(3):167–170

Fabra A, Castro S, Taurian T, Angelini J, Ibañez F, Dardanelli M, Tonelli M, Bianucci E, Valetti L (2010) Interaction among *Arachis hypogaea* L. (peanut) and beneficial soil microorganisms: how much is it known? Crit Rev Microbiol 36:179–194

FAOSTAT. Food and Agriculture Organization of the United Nations (2004). http://faostat.fao.org/site/613/DesktopDefault.aspx?PageID=613#ancor. Accessed July 2018

FAO/OMS (2006) Qué es el Codex Alimentarius. [ed.] Organización Mundial de la Salud. Organización de las Naciones Unidas para la Agricultura y la Alimentación. 3ra. Edición. Roma: Secretaría del Programa Conjunto FAO/OMS sobre Normas Alimentarias, p 51

Fernández LA, Perotti EB, Sagardoy MA, Gómez MA (2008) Denitrification activity of Bradyrhizobium sp. isolated from argentine soybean cultivated soils. World J Microbiol Biotechnol 24:2577–2585

Finnegan P, Chen W (2012) Arsenic effects on plant metabolism. Front Plant Physiol 3:1–18

Food and Agricultural Organization of the United Nations (FAO) (2017) http://faostat.fao.org. Accessed July 2017

Foyer CH, Noctor G (2011) Ascorbate and glutathione: the heart of the redox hub. Plant Physiol 155:2–18

Francisca FM, Celollada-Verdaguer MP, Carro-Pérez ME (2006) Presented in part at Conference VIII Congreso Latinoamericano de hidrología subterránea. Distribución espacial del arsénico en las aguas subterráneas de la provincia de Córdoba, Argentina. Asunción

Fu Z, Li W, Xing X, Xu M, Liu X, Li H, Tang J (2016) Genetic analysis of arsenic accumulation in maize using QTL mapping. Sci Rep 6:21292

Garg N, Singla P (2011) Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms. Environ Chem Lett 9:303–321

Ghosh M, Singh SP (2005) A review on phytoremediation of heavy metals and utilization of its byproducts. Appl Ecol Environ Res 3:1–18

Ghosh S, Shaw AK, Azahar I, Adhikari S, Jana S, Roy S, Hossain Z (2016) Arsenate (AsV) stress response in maize (*Zea mays* L.). EEB 130:53–67

Glick BR (2012) Plant growth-promoting bacteria: mechanisms and applications. Scientifica. Article ID 963401

Gómez-Sagasti MT, Marino D (2015) PGPRs and nitrogen-fixing legumes: a perfect team for efficient Cd phytoremediation? Front Plant Sci 81:1–9

Gothberg A, Greger M, Holm K, Bengtson BE (2004) Influence level on uptake and effects of mercury, cadmium and lead in water spinach. J Environ Qual 33:1247–1255

Gratão PL, Polle A, Lea PJ, Azevedo RA (2005) Making the life of heavy metal stressed plants a little easier. Funct Plant Biol 32:481–494

Gulz PA, Gupta SK, Schulin R (2005) Arsenic accumulation of common plants from contaminated soils. Plant Soil 272(1–2):337–347

Gunes A, Pilbeam D, Inal A (2009) Effect of arsenic-phosphorus interaction on arsenic-induced oxidative stress in chickpea plants. Plant Soil 314(1–2):211–220

Hansel CM, La Force MJ, Fendorf S, Sutton S (2002) Spatial and temporal association of as and Fe species on aquatic plant roots. Environ Sci Technol 36:1988–1994

Heikens A, Panaullah GM, Meharg AA (2007) Arsenic behaviour from groundwater and soil to crops: impacts on agriculture and food safety. Rev Environ Contam Toxicol 197:43–87

Hernández LE, Sobrino-Plata J, Montero-Palmero MB, Carrasco-Gil S, Flores-Cáceres ML, Ortega-Villasante C, Escobar C (2015) Contribution of glutathione to the control of cellular redox homeostasis under toxic metal and metalloid stress. J Exp Bot 66:2901–2911

Hossain F (2006) Arsenic contamination in Bangladesh – an overview. Agric Ecosyst Environ 113(1–4):1–16

Hughes MF (2002) Arsenic toxicity and potential mechanisms of action. Toxicol Lett 133:1–16

IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, World Health Organization, & International Agency for Research on Cancer (2004). Some drinking-water disinfectants and contaminants, including arsenic, vol 84

Jensen ES, Peoples MB, Boddey RM, Gresshoff PM, Hauggaard-Nielsen H, Alves BJ, Morrison MJ (2012) Legumes for mitigation of climate changeand the provision of feedstock for biofuels and biorefineries: a review. Agron Sustain Dev 32:329–364

Kabata-Pendias A, Pendias H (1992) Trace element in soil and plants, 2nd edn. CRC, London, pp 239–244

Kamrozzaman M, Khan M, Ahmed S, Sultana N, Ruhul Quddus A (2016) Evaluation of five wheat varieties on arsenic contaminated soils of Bangladesh. Int J Appl Sci Biotechnol 4(3):330–337

Kannamkumarath SS, Wrobel K, Wrobel K, Caruso JA (2004) Speciation of arsenic in different types of nuts by ion chromatography-inductively coupled plasma mass spectrometry. J Agric Food Chem 52:1458–1463

Khalid S, Shahid M, Niazi NK, Rafiq M, Bakhat HF, Imran M, Dumat C (2017) Arsenic behaviour in soil-plant system: biogeochemical reactions and chemical speciation influences. In: Enhancing cleanup of environmental pollutants. Springer, Cham, pp 97–140

Kundu R, Majumder A, Pal S (2012) Arsenic accumulation pattern of different potato cultivars under arsenic contaminated zone of India. Agric Sci Res J 3:135–137

Lafuente A, Pérez-Palacios P, Doukkali B, Molina-Sánchez M, Jiménez-Zurdo JI, Caviedes MA, Rodríguez-Llorente ID, Pajuelo E (2015) Unraveling the effect of arsenic on the model *Medicago–Ensifer* interaction: a transcriptomic meta-analysis. New Phytol 205:255–272

Lawrence D, D'odorico P, Diekmann L, Delonge M, Das R, Eaton J (2007) Ecological feedbacks following deforestation create the potential for a catastrophic ecosystem shift in tropical dry forest. Proc Natl Acad Sci 104:20696–20701

Lemke RL, Zhong Z, Campbell CA, Zentner RP (2007) Can pulse crops play a role in mitigating greenhouse gases from North American agriculture? Agron J 99:1719–1725

Lewis G, Schrire B, Mackinder B, Lock M (2005) Legumes of the world. Royal Botanic Gardens, Kew

Li Y, Dankher OP, Carreira L, Smith AP, Meagher RB (2006) The shoot-specific expression of gamma-glutamylcysteine synthetase directs the long-distance transport of thiol-peptides to roots conferring tolerance to mercury and arsenic. Plant Physiol 141:288–298

Li N, Wang J, Song WY (2016) Arsenic uptake and translocation in plants. Plant Cell Physiol 57(1):4–13

Liao M, Luo YK, Zhao X, Huang CY (2005) Toxicity of cadmium to soil microbial biomass and its activity: effect of incubation time on Cd ecological dose in a paddy soil. J Zhejiang Univ Sci 6:324–330

Liu WJ, Zhu YG, Smith FA, Smith SE (2004) Do iron plaque and genotypes affect arsenate uptake and translocation by rice seedlings (*Oryza sativa* L.) grown in solution culture? J Exp Bot 55:1707–1713

Lomax C, Liu WJ, Wu L, Xue K, Xiong J, Zhou J, McGrath SP, Meharg AA, Miller AJ, Zhao FJ (2012) Methylated arsenic species in plants originate from soil microorganisms. New Phytol 193:665–672

López S, Pastorino G, Martínez-Alcántara V, Salvucci D, Balatti P (2013) Microbiología Agrícola: un aporte de la investigación en Argentina. Los rizobios que nodulan soja en sitios con ambientes nativos y cultivados de la Argentina, Segunda edición. Magna Publicaciones, Tucumán. ISBN: 978-987-1726-17-2

Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. PNAS 105:9931–9935

Mallick S, Sinam G, Sinha S (2011) Study on arsenate tolerant and sensitive cultivars of *Zea mays* L.: differential detoxification mechanism and effect on nutrients status. Ecotoxicol Environ Saf 74(5):1316–1324

Mandal SM, Pati B, Das R, Amit K, Ghosh KA (2008) Characterization of a symbiotically effective *Rhizobium* resistant to arsenic: isolated from root nodules of *Vigna mungo* (L.) Hepper grown in arsenic-contaminated field. J Gen Appl 54:93–99

Mandal SM, Gouri SS, De D, Das BK, Mondal KC, Pati BR (2011) Effect of arsenic on nodulation and nitrogen fixation of Blackgram (*Vigna mungo*). Indian J Microbiol 51:44–47

McLaughlin MJ, Bell M, Wright G, Cozens G (2000) Uptake and partitioning of cadmium by cultivars of peanut (*Arachis hypogaea* L.). Plant Soil 222:51–58

Ministry of production and work, Argentina (2006) https://datos.magyp.gob.ar/. Accessed July 2016

Mitani N, Chiba Y, Yamaji N, Ma JF (2009) Identification and characterization of maize and barley Lsi2-like silicon efflux transporters reveals a distinct silicon uptake system from that in rice. Plant Cell 21(7):2133–2142

Moreno-Jiménez E, Peñalosa JM, Esteban E, Carpena RO (2007) Mercury accumulation and resistance to mercury stress in Rumex induratus and *Marrubium vulgare* grown on perlite. J Plant Nutr Soil Sci 170:485–494

Moreno-Jiménez E, Peñalosa JM, Carpena-Ruiz RO, Esteban E (2008) Comparison of arsenic resistance in Mediterranean woody shrubs used in restoration activities. Chem 71:466–473

Mylona PV, Polidoros AN, Scandalios JG (1998) Modulation of antioxidant responses by arsenic in maize. Free Radic Biol Med 25:576–585

Neumann H, Bode-Kirchhoff A, Madeheim A, Wetzel A (1998) Toxicity testing of heavy metals with the rhizobium-legume symbiosis: high sensitivity to cadmium and arsenic compounds. Environ Sci Pollut Res Int 5:28–36

Nocelli N, Bogino PC, Banchio E, Giordano W (2016) Roles of extracellular polysaccharides and biofilm formation in heavy metal resistance of rhizobia. Materials 9:418

Nuss ET, Tanumihardjo SA (2010) Maize: a paramount staple crop in the context of global nutrition. Compr Rev Food Sci Food Saf 9:417–436

Oven M, Raith K, Neubert RHH, Kutchan TM, Zenk MH (2001) Homo-phytochelatins are synthesized in response to cadmium in azuki beans. Plant Physiol 126:1275–1280

Pajuelo E, Rodríguez-Llorente ID, Dary M, Palomares AJ (2008) Toxic effects of arsenic on *Sinorhizobium-Medicago sativa* symbiotic interaction. Environ Pollut 154:203–211

Panigrahi DP, Randhawa GS (2010) A novel method to alleviate arsenic toxicity in alfalfa plants using a deletion mutant strain of *Sinorhizobium meliloti*. Plant Soil 336:459–467

Panigrahi DP, Sagar A, Dalal S, Randhawa GS (2013) Arsenic resistance and symbiotic efficiencies of alfalfa and cowpea rhizobial strain isolated from arsenic agricultural fields. J Exp Biol 3:322–333

Paudyal SP, Aryal RR, Chauhan SVS, Maheshwari DK (2007) Effect of heavy metals on growth of *Rhizobium* strains and symbiotic efficiency of two species of tropical legumes. Sci World 5:27–32

Pedraza RO, Motok J, Salazar SM, Ragout A, Mentel MI, Tortora ML, Guerrero Molina MF, Winik BC, Díaz Ricci JC (2010) Growth-promotion of strawberry plants inoculated with *Azospirillum brasilense*. World J Microbiol Biotechnol 26:265–272

Peralta JM, Travaglia CN, Gil RA, Furlan A, Castro S, Bianucci EC (2018) An effective rhizoinoculation restraints arsenic translocation in peanut and maize plants exposed to a realistic groundwater metalloid dose. International congress and exhibition: Arsenic in the environment, Beijing, P.R.. Environmental Arsenic in a Changing World As2018, China 2018

Pickering IJ, Prince RC, George MJ, Smith RD, George GN, Salt DE (2000) Reduction and coordination of arsenic in Indian mustard. Plant Physiol 122:1171–1177

Pigna M, Cozzolino V, Caporale AG, Mora ML, Di-Meo V, Jara AA, Violante A (2010) Effects of phosphorus fertilization on arsenic uptake by wheat grown in polluted soils. J Soil Sci Plant Nutr 10:428–442

Pomeranz Y, Munck L (1981) Cereals: a renewable resource. American Association of Cereal Chemists, St. Paul. (Gramene Reference ID 8387)

Prabpai S, Charerntanyarak L, Siri B, Moore MR, Noller BN (2009) Effects of residues from municipal solid waste landfill on corn yield and heavy metal content. Waste Manag 29:2316–2320

Raab A, Schat H, Meharg AA, Feldmann J (2005) Uptake, translocation and transformation of arsenate and arsenite in sunflower (*Helianthus annuus*): formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations. New Phytol 168:551–558

Raab A, Williams PN, Meharg A, Feldmann J (2007) Uptake and translocation of inorganic and methylated arsenic species by plants. Environ Chem 4:197–203

Rafiq M, Shahid M, Abbas G, Shamshad S, Khalid S, Niazi NK, Dumat C (2017) Comparative effect of calcium and EDTA on arsenic uptake and physiological attributes of *Pisum sativum*. Int J Phytoremediation 19(7):662–669

Rahaman S, Sinha AC, Pati R, Mukhopadhyay D (2013) Arsenic contamination: a potential hazard to the affected areas of West Bengal,India. Environ Geochem Health 35:119–132

Reichman SM (2007) The potential use of the legume–rhizobium symbiosis for the remediation of arsenic contaminated sites. Soil Biol Biochem 39:2587–2593

Reimann C, De Caritat P (1998) Chemical elements in the environment: factsheets for the geochemist and environmental scientist. Springer, Berlin, pp 92–229

Requejo R, Tena M (2005) Proteome analysis of maize roots reveals that oxidative stress is a main contributing factor to plant arsenic toxicity. Phytochemistry 66:1519–1528

Requejo R, Tena M (2006) Maize response to acute arsenic toxicity as revealed by proteome analysis of plant shoots. Proteomics 6(S1):S156–S162

Requejo R, Tena M (2014) Intra-specific variability in the response of maize to arsenic exposure. Environ Sci Pollut Res 21(18):10574–10582

Roesch LFW, Camargo FAO, Bento FM, Triplett EW (2008) Biodiversity of diazotrophic bacteria within the soil, root and stem of field-grown maize. Plant Soil 302(1–2):91–104

Safronova VI, Piluzza G, Bullitta S, Belimov AA (2011) Use of legume-microbe symbioses for phytoremediation of heavymetal polluted soils: advantages and potential problems. In: Handbook for phytoremediation. Nova Publishers, New York, pp 443–470

Sánchez-Bermejo E, Castrillo G, del Llano B, Navarro C, Zarco-Fernáandez S et al (2014) Natural variation in arsenate tolerance identifies an arsenate reductase in *Arabidopsis thaliana*. Nat Commun 5:4617

Sanyal SK (2005) Arsenic contamination in agriculture: a threat to water-soil-crop-animal-human continuum. Presidential address. Section of Agriculture and Forestry Sciences. Paper presented at the 2th Session of the Indian Science Congress Association. Ahmadabad, Gujarat, India, pp 1–26

Sarwar MH, Sarwar MF, Sarwar M, Qadri NA, Moghal S (2013) The importance of cereals (Poaceae: Gramineae) nutrition in human health: a review. J Cereals Oilseeds 4:32–35

Schoof RA, Yost LJ, Eickhoff J, Crecelius EA, Cragin DW, Meacher DM, Menzel DB (1999) A market basket survey of inorganic arsenic in food. Food Chem Toxicol 37:839–846

Schröder P, Lyubenova L, Huber C (2009) Do heavy metals and metalloids influence the detoxification of organic xenobiotics in plants? Environ Sci Pollut Res 16:795–804

Scilingo JM, Cisneros JM, Giayetto O, Jobbágy EG (2011) Paper presented at 26° Jornada Nacional de Maní. General Cabrera, Córdoba (AR): CIA – INTA. pp 53–54

Sharma I (2012) Arsenic induced oxidative stress in plants. Biologia (Bratisl) 67:447–453

Sharma SS, Dietz KJ (2009) The relationship between metal toxicity and cellular redox imbalance. Trends Plant Sci 14:43–50

Sharma S, Kaur M, Goyal R, Gill BS (2014) Physical characteristics and nutritional composition of some new soybean (*Glycine max* (L.) Merrill) genotypes. J Food Sci Technol 51:551–557

Sharma S, Kaur I, Nagpal AK (2018) Estimation of arsenic, manganese and iron in mustard seeds, maize grains, groundwater and associated human health risks in Ropar wetland, Punjab, India, and its adjoining areas. Environ Monit Assess 190(7):385

Shri M, Kumar S, Chakrabarty D, Trivedi PK, Mallick S, Misra P, Shukla D, Mishra S, Srivastava S, Tripathi RD, Tuli R (2009) Effect of arsenic on growth, oxidative stress, and antioxidant system in rice seedlings. Ecotoxicol Environ Saf 72:1102–1110

Siddique KH, Johansen C, Turner NC, Jeuffroy MH, Hashem A, Sakar D, Gan Y, Alghamdi SS (2012) Innovations in agronomy for food legumes: a review. Agron Sustain Dev 32:45–64

Singh HP, Batish DR, Kohli RK, Arora K (2007) Arsenic-induced root growth inhibition in mung bean (*Phaseolus aureus* Roxb.) is due to oxidative stress resulting from enhanced lipid peroxidation. Plant Growth Regul 53(1):65–73

Singh AK, Kumar P, Chandra N (2013) Studies on yield production of mung bean (*Vigna radiata*) sown at different dates. J Environ Biol 34:1007–1011

Smedley PL, Kinniburgh DG (2002) A review of the source, behaviour and distribution of arsenic in natural waters. Appl Geochem 17:517–568

Sobolev D, Begonia M (2008) Effects of heavy metal contamination upon soil microbes: lead induced changes in general and denitrifying microbial communities as evidenced by molecular markers. Int J Environ Res Publ Health 5:450–456

Sobrino-Plata J, Ortega-Villasante C, Flores-Cáceres ML, Escobar C, Del Campo FF, Hernández LE (2009) Differential alterations of antioxidant defenses as bioindicators of mercury and cadmium toxicity in alfalfa. Chemosphere 77:946–954

Sobrino-Plata J, Herrero J, Carrasco-Gil S, Pérez-Sanz A, Lobo C, Escobar C, Millán R, Hernández LE (2013) Specific stress responses to cadmium, arsenic and mercury appear in the metallophyte *Silene vulgaris* when grown hydroponically. RSC Adv 3:4736–4744

SOPA The Soybean Processors Association of India (2018). http://www.sopa.org/statistics/world-soybean-production/. Accessed Sept 2018

Srivastava J (2014) Arsenic induced changes in growth and physiology of maize (*Zea mays* L.) seedlings and its possible amelioration using phosphate. Plant Physiol Pathol 2:3

Stagnari F, Maggio A, Galieni A, Pisante M (2017) Multiple benefits of legumes for agriculture sustainability: an overview. Chem Biol Technol Agric 4:2

Stoeva N, Berova M, Zlatev Z (2003) Physiological response of maize to arsenic contamination. Biol Plantarum 47(3):449–452

Su YH, McGrath SP, Zhao FJ (2009) Rice is more efficient in arsenite uptake and translocation than wheat and barley. Plant Soil 328:27–34

Talano M, Cejas RB, González PS, Agostini E (2013) Arsenic effect on the model crop symbiosis *Bradyrhizobium*-soybean. Plant Physiol Biochem 63:8–14

Talukdar D (2013) Arsenic-induced oxidative stress in the common bean legume, *Phaseolus vulgaris* L. seedlings and its amelioration by exogenous nitric oxide. Physiol Mol Biol Plants 19:69–79

Talukdar D (2014) Arsenic-induced oxidative stress and its reversal by thiourea in mung bean (*Vigna radiata* (L.) Wilczek.) genotype. Cent Euro J Exp Biol 2:13–18

Tassi E, Pedron F, Barbafieri M, Petruzzelli G (2004) Phosphate-assisted phytoextraction in As-contaminated soil. Eng Life Sci 4:341–346

Tripathi RD, Srivastava S, Mishra S, Singh N, Tuli R, Gupta DK, Maathuis FJ (2007) Arsenic hazards: strategies for tolerance and remediation by plants. Trends Biotech 25:158–165

Trueb LF (1996) Die chemischen elemente ein streifzug durch das periodensystem. Hiirzel, Stuttgart, pp 300–305

Van den Broeck K, Vendecasteele C, Geuns JMC (1998) Speciation by liquid chromatography-inductively coupled plasma-mass spectrometry of arsenic in mung bean seedlings used as a bio-indicator for the arsenic contamination. Anal Chim Acta 361:101–111

Vaughan GT (1993) The environmental chemistry and fate of arsenical pesticides in cattle tick dip sites and banana land plantations. CSIRO Division of Coal Industry, Centre for Advanced Analytical Chemistry, NSW, Melboune

Vázquez S, Esteban E, Goldsbrough P (2005) Arsenate-induced phytochelatins in white lupin: influence of phosphate status. Physiol Plant 124:42–50

Vázquez S, Agha R, Granado A, Sarro MJ, Esteban E, Peñalosa JM, Carpena RO (2006) Use of white lupine plant for phytostabilization of Cd and As polluted acid soil. Water Air Soil Pollut 177:349–365

Vázquez S, Esteban E, Carpena RO (2008) Evolution of arsenate toxicity in nodulated white lupine in a long-term culture. J Agric Food Chem 56:8580–8587

Vázquez S, Goldsbrough P, Carpena RO (2009) Comparative analysis of the contribution of phytochelatins to cadmium and arsenic tolerance in soybean and white lupin. Plant Physiol Biochem 47:63–67

Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or cadmium excess in plants. Curr Opin Plant Bio 12:1–9

Wang ZH, Li SX (2003) Effects of N forms and rates on vegetable growth and nitrate accumulation. Pedosphere 13:309–316

Wani PA, Khan MS, Zaidi A (2008) Effect of metal-tolerant plant growthpromoting rhizobium on the performance of pea grown in metalamended soil. Arch Environ Contam Toxicol 55:33–42

Worldatlas (2018). https://www.worldatlas.com/. Accessed Sept 2018

Wu L, Yi H, Yi M (2010) Assessment of arsenic toxicity using *Allium/Vicia* root tip micronucleus assays. J Hazard Mat 176:952–956

Ximénez-Embún P, Rodríguez-Sanz B, Madrid-Albarrán Y, Cámara C (2002) Uptake of heavy metals by Lupin plants in artificially contaminated sand: preliminary results. Int J Environ An Ch 82(11/12):805–814

Xu XY, McGrath SP, Zhao FJ (2007) Rapid reduction of arsenate in the medium mediated by plant roots. New Phytol 176:590–599

Yang HC, Rosen BP (2016) New mechanisms of bacterial arsenic resistance. Biom J 39:5–13

Younis M (2007) Response of *Lablab purpureus–Rhizobium* symbiosis to heavy metals in pot and field experiments. World J Agric Sci 3:111–122

Zhang WD, Liu DS, Tian JC, He FL (2009) Toxicity and accumulation of arsenic in wheat. Phyton Int J Exp Bot 78:147–154

Zhao FJ, McGrath SP, Meharg AA (2010a) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559

Zhao F, Stroud J, Eagling T, Dunham S, Mc Grath S, Shewry P (2010b) Accumulation, distribution, and speciation of arsenic in wheat grain. Environ Sci Technol 44:5464–5468

Zornoza P, Vázquez S, Esteban E, Fernández-Pascual M, Carpena RO (2002) Cadmium- stress in nodulated white lupin: strategies to avoid toxicity. Plant Physiol Bioch 4:1003–1009

Arsenic in Mushrooms, Fish, and Animal Products

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Abstract Arsenic is a ubiquitous metalloid that occurs in all kinds of soils. The International Agency for Research on Cancer (IARC) has documented As and As complexes as group 1 carcinogens. Millions of people around the world are suffering from the toxic effects of arsenicals in many countries because of natural groundwater contamination as well as arsenic in food. This has stimulated a lot of efforts from researchers, NGOs, and government to understand the extent of As contamination in different types of food items. The continuous research is revealing the story of arsenic contamination, infiltration, and its effect on several crops, food, mushrooms, fruits, vegetables, sea animals, and fish and animal products. The commercial foodstuffs formulated from As-tainted raw material were also contaminated by As. Thus, the hazard of As exposure becomes relevant not only to people living in As-contaminated regions but also to other parts of the world. This chapter deals with As contamination issue in fish, mushrooms, and other animal products.

Keywords Arsenic · Egg · Fish · Milk · Mushrooms

1 Introduction

Arsenic (As) a ubiquitous metalloid occurs inherently in all kinds of soils. Arsenic is found in numerous minerals, frequently in amalgamation with sulfur and metals States et al. (2011). The International Agency for Research on Cancer (IARC) has documented As and As complexes as group 1 carcinogens (IARC 2012). The pollution of the environment by As is ascribed to its release via both natural (biogeochemical) and anthropogenic activities (Shukla and Srivastava 2017). Arsenic is consumed as insecticides, pesticides, and herbicides, most of them being As(V)

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compounds with some As(III) compounds, for example, calcium arsenite and copper acetoarsenite (Paris green) as pesticides and methylarsonic acid and dimethylarsinic acid as herbicides (Bencko and Foong 2017). Currently, As is still in practice in the pharmacological as well as glass productions, in the industry of leather stabilizers and toxic baits, and in selected herbicides (dimethylarsinic acid). Numerous organic arsenicals (e.g., roxarsone, C6AsNH6O6; p-arsanilic acid, C6H8AsNO3; and its derivatives) are utilized as feed supplements for fowls and hogs to enhance the percentage of weight gain and to cure and suppress ailments (Bencko and Foong 2017). Though small amount of As compounds in feeds are assimilated by animals and thus through the application of animal excreta as organic fertilizer, As can enter in crops (Roy et al. 2013). Arsenic compounds have been and are still in use for medication of numerous illnesses. Arsenic-containing drugs include Fowler's solution, Donovan's solution, Asiatic pills, arsphenamine, etc. for the treatment of respiratory ailments, head lice, and plague, among others. Arsenic trioxide has been effectively practiced to remediate critical promyelocytic leukemia patients (Alimoghaddam 2014; Minatel et al. 2018). Excluding a few bacterial species that can utilize As compounds for deriving energy, As is toxic to various organisms (Nicomel et al. 2015). However, not all forms of As are toxic. Arsenic poisonousness is associated with its solubility that is in turn altered by pH and redox deviations. For example, the dominant form of As when environmental condition is reducing is the arsenite (AsO_3 −3, As(III)), while in oxygenated conditions, arsenate (AsO4 −3, As(V)) is the prevailing form (Shukla and Srivastava 2017). Inorganic forms (iAs), viz., As(III) and As(V), are deliberated to be highly toxic, the reason may be their bioavailability and their well-known physiological and toxicological effects. Organic forms of As (oAs) are less toxic; other than these forms, numerous methylated arsenicals monomethylarsonic acid [CH3AsO−OOH, MMA(V)], dimethylarsinic acid [(CH3)2AsOO−,DMA(V)], monomethylarsonous acid [CH3As(OH)2, MMA(III)], and dimethylarsinous acid [(CH3)2AsOH, DMA(III)] are the chief metabolites of As metabolism, and several thiolated arsenicals are also upcoming as probable arsenic species in soil and plants (Guo et al. 2017; Awasthi et al. 2017). Groundwater having high level of arsenic is being investigated in various areas of the world, which is known to affect the health of millions of people. South and Southeast Asian countries are the most affected ones (Podgorski et al. 2017). The As-enriched groundwater is extensively used for potable propose as well as in irrigation of agricultural land. These arsenic-contaminated agricultural lands contaminate the growing crops; consequently, arsenic enters in the food chain (Dixit et al. 2015). Human beings most probably get exposed to arsenic via water and food. The food requirements (quantity) and food choices (rice, wheat, vegetables, fruits, fish, chicken, etc.) vary in different regions of the world, at different ages and with different sexes and also during different seasons.

Nowadays more and more research are being concentrated on to assess the influence of As toxicity in the whole world. The current research in the area of arsenic toxocity is revealing the story of arsenic contamination and infiltration and its effect on several crops, food, mushrooms, fruits, vegetables, sea animals, fish, and animal products, resultants in arsenic-loaded commercial foodstuffs formulated from

As-tainted raw material (Zavala and Duxbury 2008; Zhao et al. 2010; Jacob 2016). Thus, the hazard of As exposure becomes relevant not only to people living in As-contaminated regions but also to other parts of the world. This chapter recapitulates the discoveries of As contamination in mushroom, fish, and animals products, along with its probable precautionary and remedial measures available.

2 Arsenic in Food Worldwide

Millions of people around the world are suffering from the toxic effects of arsenicals in many countries because of natural groundwater contamination as well as arsenic in food (McArthur 2019). Arsenic generally occurs in the form of ores; these ores typically comprise sulfide, along with copper, nickel, lead, cobalt, or other metals. Arsenic and its amalgams are movable in the atmosphere. Weathering of rocks alters arsenic sulfides to arsenic trioxide, which arrive in the arsenic cycle as dust or by dissolution in rain, rivers, or groundwater (Bempah 2014). Thus, polluting groundwater by arsenic is a severe hazard to mankind for the entire world. It enters in the food chain producing extensive distribution throughout the plant and animal kingdoms. Though fish, fruits, and vegetables primarily contain organic arsenic, less than 10% of the arsenic in these foods exists in the inorganic form, although the arsenic content of many foods (i.e., milk and dairy products, beef and pork, poultry, and cereals) is mainly inorganic, typically 65–75%. A few recent studies report 85–95% inorganic arsenic in rice and vegetables, which advocate additional research for standardization (Musil et al. 2014; Jackson et al. 2012; Kumarathilaka et al. 2018).

Humans are exposed to this lethal arsenic mainly from air, water, and food. After intake of arsenic-contaminated food, it is treated as a normal constituent of the human body and is transported by the blood to different organs in the body, mainly in the form of MMA after ingestion (Lewchalermvong et al. 2018). It causes a variety of adverse health effects to humans after acute and chronic exposures such as dermal changes (pigmentation, hyperkeratosis, and ulceration) and respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunological, genotoxic, mutagenic, and carcinogenic effects (Vaishaly et al. 2015; Kim and Ryu 2016). Hughes et al. (2003) stated that the body load of arsenic in mice under repeated dose exposure was significantly higher than that under acute exposures; moreover, elimination of arsenic after repeated doses was significantly slower than after an acute dose. He concluded that the actual concentrations of arsenic in edible portions of broiler poultry are higher than the estimates. With the repeated doses, the ratio of liver to muscle arsenic changed dramatically over time, and at day 17, arsenic in the muscle was higher than in the liver. Exposure to 1.38–5.24 μg/kg/day As from chicken consumption, as estimated by Lasky et al. (2004), would be a significant addition to drinking water exposure based on the NRC's recommended maximum contamination level (MCL) of 10 μg/L (~3 L/day, or 30 μg/day; for an adult weighing 70 kg, a daily exposure of 0.43 μg/kg/day).

In connotation to the food, mushroom cultivation has become a multibillion dollar business across the world. Profitable mushroom farming was introduced by the Bangladesh Agricultural Research Council in Mushroom Culture Centre at Savar, Dhaka, in early 1980s, since Bangladesh is one of the most appropriate countries for its farming because of tropical monsoon type climate and low production cost (Rashid et al. 2018). Arsenic contamination is also very high in many regions of Bangladesh which contribute to load of arsenic in mushroom (Hossain et al. 2017). Mushroom fabrication and consumption have increased at a faster rate in the last 20 years than almost any other agricultural food products. Sawdust and rice straw are usually used as media to cultivate mushrooms in Bangladesh. However, wheat straw, oak, gypsum, and beech sawdust have also been used as substrates for mushroom cultivation in many other parts of the world (Rzymski et al. 2016; Rashid et al. 2018). Direct consumer exposures via food may well be a significant and preventable portion of overall exposures to arsenic.

3 Toxic Forms of Arsenic

This metalloid is generally found in numerous chemical forms with different toxicity; thus, inorganic forms of arsenic (arsenite and arsenate) are more toxic, while methylated forms (methylarsonate, MMA and dimethylarsinate, DMA) are deliberated only moderately toxic (Sarkar and Paul 2016). Other arsenic species, like trimethylarsine oxide (TMAO) and tetramethyl arsonium (TETRA), are also considered moderately toxic, whereas arsenobetaine (AsB), arsenocholine (AsC), and other arsenosugars (AsS) show no toxicity (Giri et al. 2016).

4 Arsenic in Mushrooms

Mushrooms are heterotrophic eukaryotic organisms that fit into the kingdom fungi. Around 5.1 million fungal species are found in the world (Tisthammer et al. 2016). More than 75,000 species of fungi subsist, of which more than 15,000 species are macro-fungi (fungi that form fruiting bodies or sporocarps) which are observable to the naked eye. The fruiting body bearing spores is normally called mushroom. Further, more than 2000 mushroom species exist in the environment; out of which merely 22 species are cultivable (Falandysz and Borovička 2013; Rashid et al. 2018). These species like *Agaricus* spp., *Pleurotus* spp., *Lentinus edodes*, *Volvariella volvacea*, and *Auricularia* spp. form a significant part of diet in many countries (Kozarski et al. 2015; Rahi and Malik 2016).

Upon analyzing 300 mushroom species, only half a dozen were found to have abnormally high arsenic levels that ranged from 10 to 2400 mg/kg on d.s. Often, these accumulating species convert poisonous inorganic arsenic to organic derivatives of considerable lower toxicity (Barh et al. 2018). For example, the crown-shaped cup fungus (*S. coronaria*) contains monomethylarsonic acid, whereas in *Laccaria amethystina* arsenic is found as dimethylarsinic acid. In *Sarcodon imbricatus* and in two *Agaricus* species, the detoxification procedure is even more outspoken; these mushrooms were found to comprise arsenobetaine, a harmless metabolite that also occurs in sea fish and crustaceans (Zhang et al. 2015).

Other than arsenic, other metals were also spotted in different mushrooms. Many higher fungi concentrate potential toxic chemical elements such as mercury, cadmium, and even selenium from their substrate. However, accumulation of arsenic is seldom observed. Most mushrooms only contain a few mg/kg of arsenic calculated on dry matter (Melgar et al. 2016; Chen et al. 2018)

4.1 Sources in Mushroom

Mushrooms are recognized for effectively accumulation of numerous trace elements (metals and metalloids such as Se or As), a phenomenon that occurs in their fruiting bodies at levels that may significantly surpass those found in aboveground portions of plants or animal tissues (Falandysz and Drewnowska 2015). On the other hand, the total As content (As total) in the fruiting bodies can greatly differ from concentrations below 0.05 mg kg^{-1} DW up to 1420 mg kg^{-1} DW and is likely determined by species-specific biological features and the level of environmental or substrate contamination (Melgar et al. 2014). It is crucial for food and health safety that the substrates used for mushroom cultivation have the lowest possible content of toxic elements, including arsenic. Among various materials investigated for this purpose including casing soil, horse and chicken manure, shredded wheat straw, as well as rice and corn flour, some of these materials have already been found to contain significant amounts of total arsenic (Mleczek et al. 2016).

4.2 Arsenic and Co-contamination in Mushrooms

Palatable mushrooms may be saprophytes, symbionts, and parasites of various plants and they all need organic matter to grow (heterotrophic organisms); however, the saprophytes are normally used for the controlled production. These mushrooms secrete enzymes to digest nearby foodstuffs and acquire their nourishment from that organic matter (Walker and White 2017). The growth compost, which will be a mix of fodder, straw, corn cobs, water cotton seed meal, or N supplements or perhaps wood logs, will influence the chemical composition and, as a consequence, the nutritionary price of the cultivated mushrooms (Meng et al. 2018).

The adverse health effects of arsenic have long been recognized. The acute toxicity of arsenic ranges from terribly toxic to fully nontoxic, inorganic arsenic being additionally toxic than organic arsenic compounds. The foremost toxic sorts of arsenic are the inorganic arsenic (III) and (V) compounds (Dixit et al. 2015). Methylated forms of arsenic have an occasional acute toxicity; arsenobetaine which is the principal arsenic type in fish and crustaceans is taken into account as nontoxic (Krishnakumar et al. 2016). Although natural soils contain arsenic generally in inorganic forms, in mushroom mostly organic arsenic compounds are found. The arsenic accumulation in certain fungi has been observed (Adriano 2017; Gadd 2016; Huang et al. 2015). Byrne et al. (1995) analyzed a number of mushrooms of various species, and also the main arsenic compound found was arsenobetaine.

Mushroom comprises an imperative nourishment property, and the utilization of consumable mushroom has expanded extensively worldwide because of their dietary value (Seyfferth et al. 2016). Severely growing mushrooms are fit for amassing certain components in huge amount in their natural fruit bodies (Wang et al. 2014). Zhang et al. (2015) reported aggregate total As in 48 types of wild-developed eatable and restorative mushrooms in China. The results showed highest As in *Scleroderma citrinum* (1.70 mg kg^{-1}dw) and the lowest As in *Termitomyces eurrhius* (0.17 mg kg^{-1}dw). In an analysis, Seyfferth et al. (2016) analyzed 40 mushroom samples of 12 types in the USA from two major producing regions for As, Pb, and Cd. Differences were found in total As concentrations (cremini > shiitake) and also in As localization (fruiting body in cremini vs. hymenophore in shiitake). However, As concentration was <1 mg kg^{-1}dw in all mushroom samples. Recently, As speciation analysis was performed in *Elaphomyces* spp. It was found that the As content ranged from 12 to 42 mg kg^{-1}dw in *E. asperulus* and from 120 to 660 mg kg^{-1}dw in *E. granulatus* and *E. muricatus* (Braeuer et al. 2018).

In numerous nations, wild developing mushrooms have been a famous delicacy. A few animal types, for the most part from genera *Agaricus*, *Macrolepiota*, *Lepista*, and *Calocybe*, amass large amounts of cadmium and mercury even in unpolluted and somewhat polluted zones. The convergences of the two metals and furthermore of lead increment impressively in the vigorously contaminated locales, for example, in the region of metal smelters. Present learning of metal speciation in mushrooms is restricted as is information of their bioavailability in man. Accordingly, utilization of the collecting species ought to be confined. Semimetals selenium, arsenic, and antimony don't happen in bothersome dimensions. The developed species, particularly the normal mushroom (*Agaricus bisporus*) and shellfish mushroom (*Pleurotus ostreatus*), contain just low dimensions of these components. Scarce data is accessible on metal disappearance amid conservation and culinary treatment of mushrooms (Seyfferth et al. 2016; Rashid et al. 2018)

4.3 Arsenic Speciation in Mushroom

Smith et al. (1998) has grown *Agaricus bisporus* mushrooms in fertilizer containing either arsenic-sullied mine waste or an arsenate solution. Mushrooms were developed at a little scale mushroom office in Vineland (ON), where the controlled condition considered an expansive number of fruiting bodies (mushrooms) to be created. The aggregate arsenic fixations and speciation were inspected for every treatment more than a few harvests (breaks) utilizing inductively coupled plasma mass spectrometry (ICP−MS) recognition and went from 2.3 to 16 μg·g-1 dry mass in treatment mushrooms. Fruiting bodies from all medicines contained arsenite, dimethylarsinic corrosive (DMA), and arsenobetaine (stomach muscle) and to a lesser degree arsenate and trimethylarsine oxide (TMAO). Arsenic species in arsenic-collecting mushrooms (*Sarcosphaera coronaria*, *Laccaria amethystina*, *Sarcodon imbricatus*, *Entoloma lividum*, *Agaricus haemorrhoidalis*, *Agaricus placomyces*, *Lycoperdon perlatum*) were resolved utilizing HPLC/ICP MS and ion-exchange chromatography. The astounding gatherer *Sarcosphaera coronaria* contained just methylarsonic corrosive and *Entoloma lividum* just arsenite and arsenate. In *Laccaria amethystina*, dimethylarsinic corrosive was the real arsenic compound. *Sarcodon imbricatus* and the two *Agaricus* spp. were found to contain arsenobetaine as the real arsenic species, a form which had recently been discovered just in marine biota (Byrne et al. 1995). The significant level of arsenic in mushrooms was observed to be comparative among phylogenetic gatherings, and arsenobetaine was observed to be the real compound in the *Lycoperdaceae* and *Agaricaceae* families, yet for the most part missing in long-growing mushrooms, proposing the microbial network may impact arsenic speciation in mushrooms. Despite the fact that mushroom is stacked with arsenic and enters in the evolved forms of life, however, different sources are likewise there, for example, fish and creature items (Nearing et al. 2014).

5 Arsenic in Fish

Fish has been recognized as the significant carrier of arsenic (As) for some human populaces; many fish and shellfish endlessly contains very high amount of arsenic than those in the most earthbound organism (Taylor et al. 2017). Arsenic is present principally as organic compounds in marine sustenance. At present rules for As exposure exist only for inorganic As (iAs), which is the significant type of As in drinking water, and can be available at calculable dimensions seafood (Davis et al. 2016) and a predetermined number of other sustenance sources. The reference dosages for iAs depend on investigations from tainted drinking water sources; however, later examinations have discovered impacts of iAs from lower drinking water fixations and from food. Controllers are currently concentrating on distinguishing the effects of As at fixations applicable to those populaces without a particular contaminant specific of As (Davis et al. 2015; Baris et al. 2016).

Arsenobetaine (stomach muscle), the major As species in most fish, is non-dangerous and not utilized in the fish body. Other natural As compounds are arsenosugars and arsenolipids (As sugars and As lipids), which are additionally present at huge amounts in a few sorts of fish and have appeared to be taken up and used by people. These classes of As mixes deliver indistinguishable urinary metabolite as iAs, in particular, dimethylarsinate (DMA); in this way their essence in eating routine could be frustrating to investigations of iAs utilizing biomarkers, for example, pee and blood, or in studies assessing the commitment of other dietary sources to biomarker centralizations of As. Late discoveries have likewise demonstrated that a few types of natural As and their moderate metabolites show cytotoxicity in cell culture (Meyer et al. 2015). Molina-Villalba et al. (2015) propose that further investigations of poisonous quality and metabolic pathway are required.

5.1 Arsenic Sources in Fish

The concentration of As in seawater are low and uniform (1–5 µg/L), with arsenic overwhelmingly present as As(V). In freshwater, As is likewise present principally as iAs, yet focuses can be particularly higher than those in seawater. In spite of the lower As seawater levels, a lot higher groupings of As are found in marine food webs contrasted and freshwater frameworks. This obvious inconsistency might be clarified by the change of iAs to natural As mixes at the base of the marine food web and the higher collection and maintenance of these natural mixes in marine life forms. Arsenic in fish is essentially present as natural As, with some prominent special cases. Shellfish, for the most part, have higher As levels than finfish, and demersal angle frequently contain more As than pelagic fish (Šlejkovec et al. 2014; Taylor et al. 2017). Table 1 summarizes the estimated distributions of As species found in different seafood types.

Assessed As species dispensation, in view of writing and reports, and mean aggregate As fixations for various fish types are delineated in Figs. 1 and 2. It is noticed that evaluation of the extents of natural As compounds in fish is restricted by the modest number of studies and test sizes which report natural As speciation and by contrasts in scientific methodologies between studies (Tyson 2013).

5.2 Arsenic and Co-contamination in Fish

Iron, copper, zinc, and manganese are essential metals since they assume imperative jobs in organic frameworks, while mercury, lead, and cadmium are lethal, even at low concentrations, while the essential metals can likewise create lethal impacts at

Table 1 Estimated distributions of As species found in different seafood types

S.N.	Type of seafood	Arsenic concentration (ug/g wet weight)
1	Pelagic fish	0.005–5.03
2	Cephalopods	0.054–14.6
3	Demersal fish	0.005–5.03
4	Crustaceans	0.118–26.0
5	Mollusks	0.880–7.76
6	Seaweed	0.062–102

Courtesy: Taylor et al. (2017)

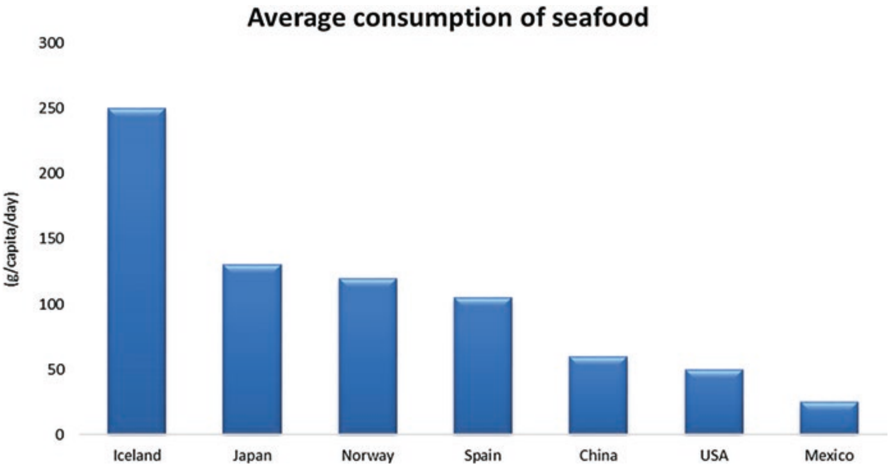

Fig. 1 Seafood consumption by country based on FAOSTAT Food Consumption Database. Countries were chosen to provide a side distribution of dietary patterns, rather than to analyze a particular population

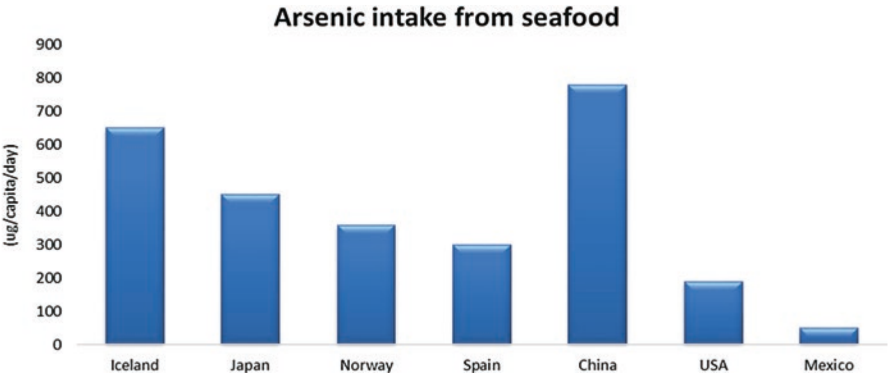

Fig. 2 Hypothetical intake of As species based on estimated distributions of As compounds and seafood consumption data

high concentrations only. Just a couple of metals turned out to be totally barred in the nourishment of human utilization. In this manner, just three metals, lead, cadmium, and mercury, have been incorporated into the controls of the European Association for perilous metals, while the USFDA has incorporated a further three metals, chromium, arsenic, and nickel, in the rundown. The outcome of substantial heavy metal contamination can be unsafe to man, and it frequently ends up requiring to check compound contaminants in food from the marine condition to comprehend their danger levels (Mahmood et al. 2012). Sivaperumal et al. 2007 intends to examine the overwhelming metal concentrations (zinc, copper, cadmium, lead, cobalt, nickel, manganese, chromium, arsenic, selenium, and mercury) in the palatable part of mollusks, shellfish, fish, and fish items gathered from fish advertises in Cochin, Kerala, India, with the end goal to assess their peril level in connection to the greatest lingering limit for human utilization.

5.3 Arsenic Speciation in Fish

Arsenobetaine (AB), the major As species in most fish, is non-dangerous and could not be used in normal metabolism. There are some other more complex natural As compounds such as arsenosugars and arsenolipids (As sugars and As lipids) that are likewise present in huge amounts in a few sorts of fish and have appeared to be taken up and utilized by people. Such complex compounds of As creates indistinguishable urinary metabolite from iAs, to be specific dimethylarsinate (DMA), thusly their quality in eating regimen could be perplexing to investigations of iAs utilizing biomarkers, for example, pee and blood, or in studies assessing the commitment of other dietary sources to biomarker convergences of As (Taylor et al. 2017).

Other discoveries have additionally demonstrated that a few types of natural As and their transitional metabolites show cytotoxicity in cell culture (Meyer et al. 2015). Such studies indicate further requirements of research for the arsenic metabolic pathway (Carlin et al. 2015). Another category of As composites in fish are As lipids, which incorporate unsaturated fats (AsFA), hydrocarbons (AsHC), and glycophospholipids (AsPL).

As-containing alcohols, phosphatidylcholines, and phosphatidylethanolamines have likewise been recognized; however, from now on the portrayal of As lipid mixes is a long way to outright. There is next to no data on the conveyance of As lipids in fish, yet these compounds are connected with slick fish and fish oils. Concentrations of As lipids are higher in pelagic than the demersal fish, and dimensions of 50–62% have been seen in filet of sleek fish (Lischka et al. 2013).

6 Arsenic in Animal Products: Meats, Eggs, and Milk

Arsenic dissemination in an organism's body showed real segment of arsenic dispensed with thorough defecation, pee, and drain. Poultry egg yolk, egg whites, and poultry items hold arsenic in all tissues and organs. Cows and poultry flying creatures raised in endemic zone hold essentially higher concentrations of arsenic. Use of egg, farming products developed in the arsenic toxic soil, thus the produced milk may create arsenicosis and might be considered as an elective way of arsenic pollution (Mazumder et al. 2010).

High concentrations of arsenic have accounted for in grains and vegetables, yet little referred to chicken meat and eggs as a wellspring of arsenic. Human arsenic introduction from poultry items and conceivable ecological pollution from poultry excreta can't be overlooked. This might be of worry for human well-being when people are presented to different sources of arsenic. An abnormal state of arsenic accounted for poultry excreta from chickens expending arsenic in sustenance or water. As the poultry business develops, use of arsenic-rich poultry compost as manure could taint the evolved way of life (Ghosh et al. 2012)

The aftereffects of study led by Ghosh et al. (2012) prove that arsenic in eggs can get exchanged to people through ingestion, bringing about a rise of pee arsenic levels in people. Hoisted arsenic levels can happen in the body if eggs devoured at a higher rate than the arsenic can dispense with from the framework. This may hurt individuals' well-being, particularly in kids, as they are more defenseless to arsenic harming. With arsenic-containing items being mixed up of economically accessible chicken feeds, it is basic that people raising chickens at home know about the potential arsenic pathway presented by these feeds.

6.1 Sources in Animal Products

Bolstering ovens with arsenic-rich nourishment or potentially water add to the gathering of arsenic stacks in its meat and excreta. By and by, cooking of arsenic-inebriated meat may make extra arsenic-rich poisonous side effects for buyers (Sinha and Bhattacharyya 2015). General well-being specialists have communicated worry about the arsenic substance of chicken meat for its job in human dietary exposures (Naujokas et al. 2013).

6.2 Arsenic and Co-contamination in Animal Products

Arsenic may enter natural pecking order through agrarian produces, fishes, and creature items, such as, meat, milk, egg, and so on. It is likewise revealed that arsenic discharges through milk. In this way, use of horticultural produces, angle, meat, milk, milk items, and eggs may cause arsenicosis in person. An investigation by Datta et al. (2012) demonstrated that bovine expended more measure of arsenic through straw than that of water. The information recommended that arsenic transcendently enter cow's body through straw pursued by drinking water.

Arsenic dissemination in the body shows that the hair hold the most extreme concentration pursued by discharged dung, pee, and milk in succession. Hair isn't devoured by people; however, discharge of arsenic through dung and pee of dairy animals debases the encompassing and drain or drain items devoured by people.

Results from Ghosh et al. (2012) give proof that albeit high arsenic level wins in well water for drinking in Bangladesh, the arsenic indicates low natural transmission ability from the body to eggs, and, along these lines, the esteem was underneath the most extreme decent limit for people. Nonetheless, arsenic in drinking water and additionally feed makes a huge commitment to the arsenic collections in eggs and excreta of laying hens.

Examination of egg yolk, egg whites, and distinctive substrates of poultry demonstrated that arsenic focus is held in every one of the organs, including meat. Additionally, the concentration of arsenic in egg yolk and egg whites and poultry items raised in arsenic endemic zone (Mitrapur and Mandal-Hat) is altogether higher than those in the winged animals raised in the nonendemic zone (Akna). In this way, the convergence of arsenic present in egg and poultry items combined with debased nourishments and drain of dairy animals may compel a natural way of life, which on utilization may deliver arsenicosis in people.

6.3 Arsenic Speciation in Animal Products

Arsenic-based medications utilized in poultry generation result in expanded iAs fixations in chicken meat. Past research by the FDA found expanded iAs concentrations in the livers of chickens nourished with added substance, roxarsone (FDA 2011). Moreover, *Clostridium* types of microscopic organisms present in the poultry cecum and in poultry squander have appeared to be fit for changing roxarsone into iAs (Nachman et al. 2013).

The fundamental wellspring of aggregate As to count calories is fish, where add up to As fixations can reach >10 mg/kg. Arsenic in fish is dominatingly present as arsenobetaine (Caumette et al. 2012), a natural As intensify that is non-dangerous and promptly discharged in pee. Later investigations have featured fat solvent arsenolipids which have been accounted for at mg/kg levels in fish oils and in some fish muscle. In vitro cell lethality ponders on the bladder, and liver cells recommend that these arsenolipids have comparable harmfulness to inorganic As introduction (Jackson and Punshon 2015).

7 Arsenic Poisoning and Its Effects on Human Health

Inorganic arsenic is to a great degree dangerous. It causes both intense and unending lethality. At first it goes into the human body through ingestion, inward breath, or skin retention. In the wake of going into the body, it is circulated in several organs including the lungs, liver, kidney, and skin (Hughes et al. 2011).

Intense poisoning: Symptoms of intense inebriation for the most part happen inside 30 min of ingestion yet might be deferred if arsenic is taken with the sustenance. Early clinical side effects at intense arsenic inebriation might be strong agony, shortcoming with flushing skin. Serious sickness and retching, colicky stomach torment, and lavish loose bowels with rice-water stools are the ill effects of arsenic poisoning (Jaishankar et al. 2014).

The ill effects of arsenic cause capillary damage which summed up in vasodilation, transudation of plasma, and vasogenic stun. Arsenic's impact on the mucosal vascular supply, not an immediate destructive activity, prompts transudation of liquid in the gut lumen, mucosal vesical arrangement, and sloughing of tissue parts (Chiocchetti et al. 2018). The patient may whine of muscle issues, deadness in hands and feet, ruddy rashes in the body, and extraordinary thirst. In extreme harming, the skin ends up cool and moist, and some level of circulatory fall for the most part happens alongside kidney harm and diminished pee yield. Sluggishness and perplexity are frequently observed alongside the improvement of a psychosis related with jumpy dreams, fantasies, and incoherence. At last, seizures, unconsciousness, and demise, for the most part because of stun, may follow. Following the gastrointestinal stage, multisystem organ harm may happen (Hong et al. 2014).

The most conspicuous chronic poisoning involves the skin, lungs, liver, and blood frameworks. An underlying steady erythematous flush after some time prompts melanosis, hyperkeratosis, and desquamation. Long haul cutaneous inconveniences incorporate the advancement of multicentric basal cell and squamous cell carcinomas (Lewin and Carucci 2015). Bowen's malady, an uncommon precancerous skin sore, is related with both arsenic and human papillomavirus infections (HPV). Both arsenic and HPV cause malignant growth of the epithelial tissue 79, and one may hypothesize that arsenic cause disease in individuals through the actuation of an oncogenic infection like HPV (Martinez et al. 2011).

8 Summary

Even moderate arsenic exposure may lead to health problems, and thus analyzing and quantifying inorganic arsenic (iAs) exposure from food (mushroom, fish and animal products) for different population groups are essential. By analyzing the data from the several reviews and research articles and collecting reported values of iAs in major food groups, we can have some clue for the health hazards caused by arsenic toxicity. This book chapter may help to estimate for health risk due to the ingestion of food products contaminated with arsenic, both per individual and for total population. Several challenges are there to the advancement of As research and for the conductance of work in this field; likewise there are no accepted models for the study of As-induced carcinogenesis. Among the most thrust areas are arsenic metabolism and its interaction with cellular constituents; possible bioaccumulation of As; interactions with other metals; effects of As on genetic material; development of animal models and cell systems to study effects of As; and a better characterization of human exposures as related to health risks. Other barriers are the apparent lack of interest in the As research; lack of relevant animal models; difficulty with adoption of uniform methodologies; lack of accepted biomarkers; and the need for a central storage repository.

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References

Adriano DC (2017) Uptake and accumulation of metals in bacteria and fungi. In: Biogeochemistry of trace metals. CRC Press, Boca Raton, pp 289–310

Alimoghaddam K (2014) A review of arsenic trioxide and acute promyelocytic leukemia. Int J Hematol-Oncol Stem Cell Res 8(3):44

Awasthi G, Kumar A, Awasthi KK, Singh AP, Srivastva S, Vajpayee P et al (2017) Green synthesis of nanoparticles: an emerging Phytotechnology. In: Green technologies and environmental sustainability. Springer, Cham, pp 339–363

Barh A, Upadhyay RC, Kamal S, Annepu SK, Sharma VP, Shirur M, Banyal S (2018) Mushroom crop in agricultural waste cleanup. In: Microbial biotechnology in environmental monitoring and cleanup. IGI Global, pp 252–266

Baris D, Waddell R, Beane Freeman LE, Schwenn M, Colt JS, Ayotte JD, Ward MH, Nuckols J, Schned A, Jackson B, Clerkin C (2016) Elevated bladder cancer in Northern New England: the role of drinking water and arsenic. JNCI: J Natl Cancer Inst 108(9)

Bempah CK (2014) Arsenic contamination of groundwater in south-western part of Ashanti Region of Ghana. Doctoral dissertation, BTU Cottbus-Senftenberg

Bencko V, Foong FYL (2017) The history of arsenical pesticides and health risks related to the use of agent blue. Ann Agric Environ Med 24(2):312–316

Braeuer S, Borovička J, Goessler W (2018) A unique arsenic speciation profile in Elaphomyces spp. (“deer truffles”)—trimethylarsine oxide and methylarsonous acid as significant arsenic compounds. Anal Bioanal Chem 410(9):2283–2290

Byrne AR, Šlejkovec Z, Stijve T, Fay L, Goessler W, Gailer J, Lrgolic KJ (1995) Arsenobetaine and other arsenic species in mushrooms. Appl Organomet Chem 9(4):305–313

Carlin DJ, Naujokas MF, Bradham KD, Cowden J, Heacock M, Henry HF, Lee JS, Thomas DJ, Thompson C, Tokar EJ, Waalkes MP (2015) Arsenic and environmental health: state of the science and future research opportunities. Environ Health Perspect 124(7):890–899

Caumette G, Koch I, Reimer KJ (2012) Arsenobetaine formation in plankton: a review of studies at the base of the aquatic food chain. J Environ Monit 14(11):2841–2853

Chen S, Yuan B, Xu J, Chen G, Hu Q, Zhao L (2018) Simultaneous separation and determination of six arsenic species in Shiitake (Lentinus edodes) mushrooms: method development and applications. Food Chem 262:134–141

Chiocchetti GM, Vélez D, Devesa V (2018) Effect of subchronic exposure to inorganic arsenic on the structure and function of the intestinal epithelium. Toxicol Lett 286:80–88

Datta BK, Bhar MK, Patra PH, Majumdar D, Dey RR, Sarkar S, Mandal TK, Chakraborty AK (2012) Effect of environmental exposure of arsenic on cattle and poultry in Nadia district, West Bengal, India. Toxicol Int 19(1):59

Davis MA, Higgins J, Li Z, Gilbert-Diamond D, Baker ER, Das A, Karagas MR (2015) Preliminary analysis of in utero low-level arsenic exposure and fetal growth using biometric measurements extracted from fetal ultrasound reports. Environ Health 14(1):12

Davis HT, Aelion CM, Liu J, Burch JB, Cai B, Lawson AB, McDermott S (2016) Potential sources and racial disparities in the residential distribution of soil arsenic and lead among pregnant women. Sci Total Environ 551:622–630

Dixit G, Singh AP, Kumar A, Singh PK, Kumar S, Dwivedi S, Trivedi PK, Pandey V, Norton GJ, Dhankher OP, Tripathi RD (2015) Sulfur mediated reduction of arsenic toxicity involves efficient thiol metabolism and the antioxidant defense system in rice. J Hazard Mater 298:241–251

Falandysz J, Borovička J (2013) Macro and trace mineral constituents and radionuclides in mushrooms: health benefits and risks. Appl Microbiol Biotechnol 97(2):477–501

Falandysz J, Drewnowska M (2015) Macro and trace elements in common Chanterelle (Cantharellus cibarius) mushroom from the European background areas in Poland: composition, accumulation, dietary exposure and data review for species. J Environ Sci Health B 50(5):374–387

FDA (Food and Drug Administration) Final Report on Study 275.30 (2011) Provide data on various arsenic species present in broilers treated with Roxarsone: comparison with untreated birds

Gadd GM (2016) 5 fungi and industrial pollutants. In: Environmental and microbial relationships. Springer, Cham, pp 99–125

Ghosh A, Awal MA, Majumder S, Mostofa M, Khair A, Islam MZ, Rao DR (2012) Arsenic in eggs and excreta of laying hens in Bangladesh: a preliminary study. J Health Popul Nutr 30(4):383

Giri A, Bharti VK, Angmo K, Kalia S, Vivek P, Kumar B (2016) Int J Curr Res Biosci Plant Biol 3(12):105–114

Guo Q, Planer-Friedrich B, Liu M, Li J, Zhou C, Wang Y (2017) Arsenic and thioarsenic species in the hot springs of the Rehai magmatic geothermal system, Tengchong volcanic region, China. Chem Geol 453:12–20

Hong YS, Song KH, Chung JY (2014) Health effects of chronic arsenic exposure. J Prev Med Public Health 47(5):245

Hossain M, Bhattacharya P, Jacks G, von Brömssen M, Ahmed KM, Hasan MA, Frape SK (2017) Sustainable arsenic mitigation–from field trials to implementation for control of arsenic in drinking water supplies in Bangladesh. In: Best practice guide on the control of arsenic in drinking water. IWA Publishing, London, pp 99–116

Huang Q, Jia Y, Wan Y, Li H, Jiang R (2015) Market survey and risk assessment for trace metals in edible fungi and the substrate role in accumulation of heavy metals. J Food Sci 80(7):H1612–H1618

Hughes MF, Kenyon EM, Edwards BC, Mitchell CT, Del Razo LM, Thomas DJ (2003) Accumulation and metabolism of arsenic in mice after repeated oral administration of arsenate. Toxicol Appl Pharmacol 191(3):202–210

Hughes MF, Beck BD, Chen Y, Lewis AS, Thomas DJ (2011) Arsenic exposure and toxicology: a historical perspective. Toxicol Sci 123(2):305–332

International Agency for Research on Cancer (IARC) (2012) 100, Part C

Jackson BP, Taylor VF, Karagas MR, Punshon T, Cottingham KL (2012) Arsenic, organic foods, and brown rice syrup. Environ Health Perspect 120(5):623–626

Jackson BP, Punshon T (2015) Recent advances in the measurement of arsenic, cadmium, and mercury in rice and other foods. Curr Environ Health Rep 2(1):15–24

Jacob T (2016) Poisons in our food. Publications Division Ministry of Information & Broadcasting, New Delhi

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7(2):60–72

Kim S, Ryu DY (2016) A short review of arsenic-induced toxicity. J Prev Vet Med 40(1):46–52

Kozarski M, Klaus A, Jakovljevic D, Todorovic N, Vunduk J, Petrović P, Niksic M, Vrvic M, Van Griensven L (2015) Antioxidants of edible mushrooms. Molecules 20(10):19489–19525

Krishnakumar PK, Qurban MA, Stiboller M, Nachman KE, Joydas TV, Manikandan KP, Mushir SA, Francesconi KA (2016) Arsenic and arsenic species in shellfish and finfish from the western Arabian Gulf and consumer health risk assessment. Sci Total Environ 566:1235–1244

Kumarathilaka P, Seneweera S, Meharg A, Bundschuh J (2018) Arsenic accumulation in rice (*Oryza sativa* L.) is influenced by environment and genetic factors. Sci Total Environ 642:485–496

Lasky T, Sun W, Kadry A, Hoffman MK (2004) Mean total arsenic concentrations in chicken 1989–2000 and estimated exposures for consumers of chicken. Environ Health Perspect 112(1):18

Lewchalermvong K, Rangkadilok N, Nookabkaew S, Suriyo T, Satayavivad J (2018) Arsenic speciation and accumulation in selected organs after oral administration of rice extracts in Wistar Rats. J Agric Food Chem 66(12):3199–3209

Lewin JM, Carucci JA (2015) Advances in the management of basal cell carcinoma. F1000prime reports 7:53

Lischka S, Arroyo-Abad U, Mattusch J, Kühn A, Piechotta C (2013) The high diversity of arsenolipids in herring fillet (*Clupea harengus*). Talanta 110:144–152

Mahmood Q, Rashid A, Ahmad SS, Azim MR, Bilal M (2012) Current status of toxic metals addition to environment and its consequences. In: The plant family Brassicaceae. Springer, Dordrecht, pp 35–69

Martinez VD, Vucic EA, Becker-Santos DD, Gil L, Lam WL (2011) Arsenic exposure and the induction of human cancers. J Toxicol 2011:431287

Mazumder DNG, Ghosh A, Majumdar KK, Ghosh N, Saha C, Mazumder RNG (2010) Arsenic contamination of ground water and its health impact on population of district of Nadia, West Bengal, India. Indian J Community Med: Off Publ Indian Assoc Prev Soc Med 35(2):331

McArthur JM (2019) Arsenic in groundwater. In: Groundwater development and management. Springer, Cham, pp 279–308

Melgar MJ, Alonso J, García MA (2014) Total contents of arsenic and associated health risks in edible mushrooms, mushroom supplements and growth substrates from Galicia (NW Spain). Food Chem Toxicol 73:44–50

Melgar MJ, Alonso J, García MA (2016) Cadmium in edible mushrooms from NW Spain: bioconcentration factors and consumer health implications. Food Chem Toxicol 88:13–20

Meng X, Liu B, Xi C, Luo X, Yuan X, Wang X, Zhu W, Wang H, Cui Z (2018) Effect of pig manure on the chemical composition and microbial diversity during co-composting with spent mushroom substrate and rice husks. Bioresour Technol 251:22–30

Meyer S, Raber G, Ebert F, Taleshi MS, Francesconi KA, Schwerdtle T (2015) Arsenic-containing hydrocarbons and arsenic-containing fatty acids: transfer across and presystemic metabolism in the Caco-2 intestinal barrier model. Mol Nutr Food Res 59(10):2044–2056

Minatel BC, Sage AP, Anderson C, Hubaux R, Marshall EA, Lam WL, Martinez VD (2018) Environmental arsenic exposure: from genetic susceptibility to pathogenesis. Environ Int 112:183–197

Mleczek M, Niedzielski P, Siwulski M, Rzymski P, Gąsecka M, Goliński P, Kozak L, Kozubik T (2016) Importance of low substrate arsenic content in mushroom cultivation and safety of final food product. Eur Food Res Technol 242(3):355–362

Molina-Villalba I, Lacasaña M, Rodríguez-Barranco M, Hernández AF, Gonzalez-Alzaga B, Aguilar-Garduño C, Gil F (2015) Biomonitoring of arsenic, cadmium, lead, manganese and mercury in urine and hair of children living near mining and industrial areas. Chemosphere 124:83–91

Musil S, Pétursdóttir ÁH, Raab A, Gunnlaugsdóttir H, Krupp E, Feldmann J (2014) Speciation without chromatography using selective hydride generation: inorganic arsenic in rice and samples of marine origin. Anal Chem 86(2):993–999

Nachman KE, Baron PA, Raber G, Francesconi KA, Navas-Acien A, Love DC (2013) Roxarsone, inorganic arsenic, and other arsenic species in chicken: a US-based market basket sample. Environ Health Perspect 121(7):818

Naujokas MF, Anderson B, Ahsan H, Aposhian HV, Graziano JH, Thompson C, Suk WA (2013) The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem. Environ Health Perspect 121(3):295–302

Nearing MM, Koch I, Reimer KJ (2014) Arsenic speciation in edible mushrooms. Environ Sci Technol 48(24):14203–14210

Nicomel N, Leus K, Folens K, Van Der Voort P, Du Laing G (2015) Technologies for arsenic removal from water: current status and future perspectives. Int J Environ Res Public Health 13(1):62

Podgorski JE, Eqani SAMAS, Khanam T, Ullah R, Shen H, Berg M (2017) Extensive arsenic contamination in high-pH unconfined aquifers in the Indus Valley. Sci Adv 3(8):e1700935

Rahi DK, Malik D (2016) Diversity of mushrooms and their metabolites of nutraceutical and therapeutic significance. J Mycol 2016:7654123

Rashid MH, Rahman MM, Correll R, Naidu R (2018) Arsenic and other elemental concentrations in mushrooms from Bangladesh: health risks. Int J Environ Res Public Health 15(5):919. https://doi.org/10.3390/ijerph15050919

Roy D, Kumar Das T, Vaswani S (2013) Arsenic: it's extent of pollution and toxicosis: an animal perspective. Vet World 6(1):53

Rzymski P, Mleczek M, Siwulski M, Gąsecka M, Niedzielski P (2016) The risk of high mercury accumulation in edible mushrooms cultivated on contaminated substrates. J Food Compos Anal 51:55–60

Sarkar A, Paul B (2016) The global menace of arsenic and its conventional remediation – a critical review. Chemosphere 158:37–49

Seyfferth AL, McClatchy C, Paukett M (2016) Arsenic, lead, and cadmium in US mushrooms and substrate in relation to dietary exposure. Environ Sci Technol 50(17):9661–9670

Shukla A, Srivastava S (2017) Emerging aspects of bioremediation of arsenic. In: Green technologies and environmental sustainability. Springer, Cham, pp 395–407

Sinha B, Bhattacharyya K (2015) Arsenic toxicity in rice with special reference to speciation in Indian grain and its implication on human health. J Sci Food Agric 95(7):1435–1444

Sivaperumal P, Sankar TV, Nair PV (2007) Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-a-vis international standards. Food Chem 102(3):612–620

Šlejkovec Z, Stajnko A, Falnoga I, Lipej L, Mazej D, Horvat M, Faganeli J (2014) Bioaccumulation of arsenic species in rays from the northern Adriatic Sea. Int J Mol Sci 15(12):22073–22091

Smith M, Shnyreva A, Wood DA, Thurston CF (1998) Tandem organization and highly disparate expression of the two laccase genes lcc1 and lcc2 in the cultivated mushroom Agaricus bisporus. Microbiology 144(4):1063–1069

States JC, Barchowsky A, Cartwright IL, Reichard JF, Futscher BW, Lantz RC (2011) Arsenic toxicology: translating between experimental models and human pathology. Environ Health Perspect 119(10):1356–1363

Taylor V, Goodale B, Raab A, Schwerdtle T, Reimer K, Conklin S, Karagas MR, Francesconi KA (2017) Human exposure to organic arsenic species from seafood. Sci Total Environ 580:266–282

Tisthammer KH, Cobian GM, Amend AS (2016) Global biogeography of marine fungi is shaped by the environment. Fungal Ecol 19:39–46

Tyson J (2013) The determination of arsenic compounds: a critical review. ISRN Anal Chem 2013:835371

Vaishaly AG, Mathew BB, Krishnamurthy NB (2015) Health effects caused by metal contaminated ground water. Int J Adv Sci Res 1(02):60–64

Walker GM, White NA (2017) Introduction to fungal physiology. In: Fungi: biology and applications. Wiley, Hoboken, pp 1–35

Wang XM, Zhang J, Wu LH, Zhao YL, Li T, Li JQ, Wang YZ, Liu HG (2014) A mini-review of chemical composition and nutritional value of edible wild-grown mushroom from China. Food Chem 151:279–285

Zavala YJ, Duxbury JM (2008) Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain. Environ Sci Technol 42(10):3856–3860

Zhang J, Li T, Yang YL, Liu HG, Wang YZ (2015) Arsenic concentrations and associated health risks in Laccaria mushrooms from Yunnan (SW China). Biol Trace Elem Res 164(2):261–266

Zhao FJ, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559

A Brief Status Report on Arsenic in Edible Vegetable Species

Marta Marmiroli

Abstract Over the last few decades, the contamination of groundwater by arsenic (As) has been highlighted as an environmental disaster in many regions of the world. The problem of contamination of groundwater by As is most acute in South and Southeast Asia. However, the problem of As is now well known to be widespread throughout the world. Several authors have conducted long- and short-term studies to monitor the amount of As in vegetables usually in West Bengal, India, and in Bangladesh. However, the reports are also available from other places around the world such as Pakistan and Brazil. This chapter provides a brief status report on the presence of arsenic in vegetables.

Keywords Arsenic · Beans · Green vegetables · Okra · Potato

1 Introduction

Over the last few decades, the contamination of groundwater by geogenic arsenic (As) has been highlighted as an environmental disaster in many regions of the world. The problem of contamination of groundwater by As is most acute in South and Southeast Asia, particularly in the eastern and northeastern regions of India and in Bangladesh. It has been estimated that 60 million people living in those areas are at risk of chronic As poisoning (Chakraborti et al. 2008; Bhattacharya et al. 2011).

Majority of the studies carried out in As-affected regions have focused on As pollution of drinking water trying to decrease As exposure by supplying clean water to local communities. But these measures solve only part of the problem related to As intake. Farmers in Bangladesh and India can nowadays cultivate their land more than three times per year. On one side, this "green revolution" has allowed these countries to become self-sufficient for food but on the other has made the population largely dependent on groundwater irrigation for their food provision

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(Roychowdhury 2008). During the last two decades, thousands of high capacity motorized pumps have been set up to abstract groundwater from aquifers that can be heavily contaminated with As. This agronomic practice will lead to an increase in the topsoil As by a factor of 1.5–2 by the year 2050 (Dittmar et al. 2010). Consequently, increased As concentrations in cultivated lands result in As accumulation in food crops, principally rice but also other vegetables, farmed in these areas (Williams et al. 2006; Signes-Pastor et al. 2008). In addition, rice cultivation practices such as continuous flooding of land contribute heavily to increase the mobility of As in the irrigation land (Spanu et al. 2012; Roberts et al. 2010).

2 Arsenic in Vegetables

Since the beginning of years 2000s, several authors have conducted long- and short-term studies to monitor the amount of As in vegetables usually cultivated in some Indian regions, such as West Bengal, and in Bangladesh but also in other places around the world such as Pakistan and Brazil (Roychowdhury et al. 2002; Arain et al. 2009; Branco Corguinha et al. 2015).

The results from Roychowdhury et al. (2002) revealed that the vegetables containing the highest mean arsenic concentrations in two areas of the Murshidabad district (West Bengal, India) were potato skin and flesh (292.62 and 104 mg/kg), leaf of vegetables (pumpkin, gourd, radish, and other edible herbs) (212.34–294.67 mg/kg), arum leaf (331–341 mg/kg), turmeric powder (334.67 mg/kg), five spices (on average 247 mg/kg), beans (200 mg/kg), and green chili (130 mg/kg). The same author, in a further study on vegetables grown in paddy soils of the same areas, observed that the higher the As in the irrigated groundwater, the higher the arsenic in cultivated land and in different parts of the plants (Roychowdhury 2008). In this work, high concentrations of As were reported in branch (2.8–14.3 mg/kg), leaf (2.1–9.5 mg/kg), trunk (0.3–55 mg/kg), and root (45–130 mg/kg) of plants cultivated in arsenic-contaminated soil (Roychowdhury 2008). The mean As concentration decreases from the root to stem and leaf, which means that As is translocated from the root, more exposed to As-loaded paddy soils, into the aboveground parts in decreasing concentrations from the stem to the leaf.

The problem of irrigation with As-rich water is common to most of the regions of Bangladesh. Williams and colleagues sampled vegetables, pulses, and spices from farmers' fields and homes in several Bengali districts (Williams et al. 2005). There was a wide variation in As levels between and within vegetable types. Based on maximum recorded As levels, the ten vegetables with the highest As values were arum stolon (1.93 μg/g dwt) > brinjal (eggplant) (1.59 μg/g dwt) > cucumber (1.17 μg/g dwt) > lady's finger (1.06 μg/g dwt) > coriander (0.98 μg/g dwt) > potato (0.89 μg/g dwt) > long yard bean (0.87 μg/g dwt) > radish leaf (0.79 μg/g dwt) > giant taro (0.69 μg/g dwt) > papaya (0.69 μg/g dwt). The mean maximum recorded As level for root and tuberous vegetables (0.74 μg/g dwt) was higher than for fruit vegetables (0.56 μg/g dwt) and leafy vegetables (0.39 μg/g dwt). Of notice is the high level of As found in arum (*Colocasia antiquorum*) because this is a widely consumed vegetable, especially by pregnant women in South Asia, since it is a good source of vitamins A and C and Fe. The concentrations of As in pulses and spices were lower compared to those found in vegetable samples (0.03–0.10 μg/g dwt). The average As levels in pulses did not exceed 0.10 μg/g dwt; the average total As concentrations in five types of spices varied widely ranging from 0.04 μg/g dwt in garlic up to 0.49 μg/g dwt in coriander (Williams et al. 2005).

Other studies on vegetables from these same areas, irrigated with As-loaded water, highlighted that in general unpeeled potato (0.654 mg/kg), radish (0.344 mg/kg), arum (0.407 mg/kg), amaranth (0.372 mg/kg), and okra (lady's finger) (0.301 mg/kg) showed the higher As concentrations within a panel of 22 different vegetables, while bitter gourd, bean, tomato, and turmeric showed the lower concentrations of As ranging between 0.021 and 0.003 mg/kg (Bhattacharya et al. 2010).

The As crisis in Southeast Asia has extended also to other Asian states such as Pakistan. In this area the sources of pollution include both edaphic processes and human activities, such as application of inorganic As herbicides, insecticides, and fungicides and the heavy use of phosphate fertilizers. Some areas of Pakistan are facing As-related public health disasters as severe as those in the neighboring Asian country of India (Arain et al. 2009). The work carried out by Arain and colleagues appraised the contribution of water, vegetable, grains, and fish to the population As intake in the villages in the regions surrounding Manchar Lake, one of the largest freshwater lakes in Asia. Besides grains, wheat, sorghum, and maize, containing between 0.317 and 0.256 mg/kg of As, the vegetables with the higher concentrations of As were spinach (0.90 mg/kg), gourd (0.811 mg/kg), and okra (0.894 mg/kg). Among the flavouring spices there were high As concentrations as well, for example, peppermint and coriander contained had 1.2 mg/kg and 0.985 mg/kg As, respectively. Differently from the areas of India and Bangladesh, potatoes (0.256 mg/kg) and other belowground vegetables such as carrot (0.135 mg/kg) and onion (0.048 mg/kg) did not display the highest (eliminate higher) higher As concentrations among the consumed vegetables (Arain et al. 2009).

A survey on As in irrigation water and vegetables from the Nawalparasi District of Nepal showed that about more than 36% of the wells exceeded the FAO guideline value for arsenic in irrigation water of 0.1 mg As/ L (FAO 1985; Dahal et al. 2008). In Nepal, farmers have a low awareness regarding the effects of arsenic on agricultural plants, and the contaminations to the food chain are not assessed. In this study, using irrigation water with five different As concentrations (from <0.005 to 1.014 mg/L), it was found that the roots of all vegetable contained higher As contents than shoots > leaves > fruits, with the exception of onion. The highest As contents in potato and brinjal roots were 0.79 and 1.14 mg As/kg, but the highest As concentration (3.45 mg As/kg) was found in cauliflower roots. However, the mean arsenic content in the edible part of cauliflower was 0.61 mg As/kg and in the brinjal fruit was 0.14 mg As/kg (Dahal et al. 2008).

The high As contents within vegetables can be a bioindicator of the levels of As contamination in the irrigation water and most importantly in the whole environment.

However, to assess correctly the risks posed by As in the human diet, As speciation should be established because methylated organic As (o-As; monomethyl arsenic acid, MA, and dimethyl arsenic acid, DMA) is much less toxic than inorganic As (i-As; arsenate and arsenite), which has been classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Diaz et al. 2004). In a work by Signes-Pastor and colleagues, the speciation of As in vegetables collected from villages nearby Calcutta (India) was ascertained (Signes-Pastor et al. 2008). Samples of carrot, kidney bean, radish, tomato, onion, betel nut, cauliflower, brinjal, potato, and spices (coriander seeds, turmeric powder, cumin seeds, mustard, ginger mango, and fenugreek seeds) were collected in farms and local markets. Samples of bulbs and roots, such as carrot (121 mg/kg), radish (167 mg/kg), unpeeled potato (80 mg/kg), and ginger mango (214 mg/kg), showed high As concentrations. The chemical analyses demonstrated that As was mainly present as inorganic arsenite (AsIII), because arsenate (As V) was mostly not detected (Signes-Pastor et al. 2008). Similar results were obtained by Roychowdhury (2008) and Halder and colleagues (2013). In the latter study, it has also been evidenced that leafy vegetables and root vegetables have generally higher concentrations of total As in comparison with non-leafy aboveground vegetables (Halder et al. 2013). Finally, in a recent study on the world risk of As intake through food, it was established that on average for vegetables at least 85% of the total As is in the inorganic, more toxic form; this percentage was about 80% for fruit (Cubadda et al. 2017).

In a study performed in 2013 in Cambodia, Wang and Colleagues highlighted that vegetables contributed to 23.8% of the average As dietary intake, a higher percentage than fish (10.2%) and fruit (13.5%) (Wang et al. 2013). Although with variations among different districts, the fresh weight concentrations of As were higher in carrot (37 ng/g), Chinese radish (22 ng/g), water spinach (morning glory) (57 ng/g), and cucumber (55.2 ng/g) in comparison with other vegetables such as sponge gourd (11.2 ng/g), eggplant (10.3 ng/g), and winter melon (7.1 ng/g) (Wang et al. 2013).

During a recent work carried out in the Bogra province of Bangladesh concerning the source of As in food, it has been evidenced that vegetables can add considerably to the total dietary as intake. Species such as carrot, potato, eggplant, onion, bean, lentil, and chili were analyzed along with fruit (banana, mango, and jackfruit). Bean (0.31 mg/kg), onion (0.29 mg/kg), lentil (0.29 mg/kg), potato (0.27 mg/kg), and banana (0.39 mg/kg) had the highest As contents on a dry weight basis (Islam et al. 2017).

In a study performed in the Samastipur district, Bihar, situated in the eastern part of the Gangetic plain, it has been found that the irrigation using hand pumps and tube wells logged in shallow aquifers resulted in a contamination from As and other metals of several types of vegetables and grains (Kumar et al. 2016). In this work, the vegetables with the highest mean As concentration were luffa (ridge gourd) > eggplant > cucumber > ladyfinger > gourd > mung bean with mean values of 800, 492, 399, 375, 268, and 174 μg/kg, respectively, of As on a dw basis.

Besides India, Bangladesh, and other countries in the Asian continent, there are other parts of the world where As can become an issue into water and food. For example, a work carried out in Spain in 2010 (Matos-Reyes et al. 2010) revealed that some vegetable species can intake high level of As, although these levels were still well below the provisional tolerable daily intake (PTDI) limit of 2.1 μg/day kg body weight (b.w.) (WHO 1993). Green leafy vegetables and roots showed the higher As concentrations in respect to vegetable fruits, bulbs, and pulses. On a dry weight basis, the vegetables with the highest As concentrations were endive (605 ng/g), carrot (241 ng/g), cauliflower (163 ng/g), and chard (131 ng/g), while tomato and zucchini had only 20 ng/g and 38 ng/g of As, respectively. Pulses showed the lowest As concentrations, between 13 ng/g for blank bean and 61 ng/g for chickpea (Matos-Reyes et al. 2010). In this case the source of As is probably from pesticides and fungicides and from the use of phosphates fertilizers, rather than irrigation with As-rich shallow water.

A survey was conducted in southeastern Brazil on fresh vegetable produce purchased from local markets of Unai, Paracatu, and Joao Pinheiro towns located in the northwestern part of Minas Gerais state (Ciminelli et al. 2017). The surveyed towns are located in the Brazilian tropical savanna region, and the main economic activities of the region include agriculture, cattle grazing, and charcoal production. Hence the source of As is likely to come from fertilizers and pesticides. On the other hand, the town of Paracatu is located near a large gold mine, with some residential dwellings situated less than 2 km from the open pit; thus, As comes also from the mining activities. However, the authors did not clarify in their survey the origins of the vegetables analyzed. The highest concentrations of As on a fresh weight basis were found in beans, the lowest in tomato in the following order: bean (0.050 mg/kg), lettuce (0.017 mg/kg), garlic (0.013 mg/kg), potato (0.009 mg/kg), carrot (0.007 mg/kg), cabbage (0.006 mg/kg), and tomato (0.005 mg/kg) (Ciminelli et al. 2017). In a previous study conducted in the Brazilian region of Mato Grosso, it was found that potato can contain 59 mg/kg of As on dry weight basis (Branco Corguinha et al. 2015), while potato tubers cultivated in Chile contained 58 mg/kg dw (Munoz et al. 2002).

In addition, a wide range of aquatic macrophytes used for their role in phytoremediation because of their capacity to accumulate metals in their tissues including As constitute a potential risk to human health due to their consumption as vegetables in certain part of the world such as New Zealand and Hawaii (Robinson et al. 1995). In a study in 2014, Falinski and colleagues assessed As concentrations in edible parts of watercress (*Nasturtium officinale*) and warabi (*Diplazium esculentum*) that were consumed in Hawaii from an As-contaminated area where the soil As reached 356 mg/kg. The total As in the plants of watercress and warabi was 0.572 mg/kg and 0.075 mg/kg, respectively (Falinski et al. 2014).

A very recent review on As in food has been written by Upadhyay et al. (2019). This is an exhaustive compendium of the major sources of As in the diet from grains and vegetables to fish and meat. In this study a complete list of vegetables consumed in countries with issues of As contamination in groundwater but also from other parts of the world is presented. Average As concentrations are also provided, with min-max ranges for most of the entries. Considering all the amount of studies performed to determine As sources in the diet, especially of the southeast Asia regions, there is still a lack of effort in appraising the inorganic As contribution, which is the most severely damaging for human health (Upadhyay et al. 2019).

References

Arain MB, Kazi TG, Baig JA, Jamali MK, Afridi HI, Shah AQ et al (2009) Determination of As levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: estimation of daily dietary intake. Food Chem Toxicol 47:242–248

Bhattacharya P, Samal AC, Majumdar J, Santra SC (2010) Arsenic contamination in rice, wheat, pulses, and vegetables: a study in an As affected area of West Bengal, India. Water Air Soil Pollut 213:3–13

Bhattacharya P, Mukherjee A, Mukherjee AB (2011) Arsenic in groundwater of India. In: Nriagu JO (ed) Encyclopedia of environmental health, vol 1. Elsevier, Burlington, pp 150–164

Branco Corguinha AP, de Souza GA, Cardoso Goncalves V, de Andrade Carvalho C, de Lima WEA, Dias Martins FA, Yamanaka CH, Bohac Francisco EA, Guimaraes Guilherme LR (2015) Assessing arsenic, cadmium, and lead contents in major crops in Brazil for food safety purposes. J Food Compos Anal 37:143–150

Chakraborti D, Rahman MM, Paul K, Chowdhury UK, Sengupta MK, Lodh D, Chanda CR, Saha KC, Mukherjee SC (2008) Arsenic calamity in the Indian subcontinent: what lessons have been learned. Talanta 58:3–22

Ciminelli VST, Gasparon M, Ng JC, Silva GC, Caldeira CL (2017) Dietary As exposure in Brazil: the contribution of rice and beans. Chemosphere 168:996–1003

Cubadda F, Jackson BP, Cottingham KL, Van Horne YO, Kurzius-Spencer M (2017) Human exposure to dietary inorganic arsenic and other arsenic species: state of knowledge, gaps and uncertainties. Sci Total Environ 579:1228–1239

Dahal BM, Fuerhacker M, Mentler A, Karki KB, Shrestha RR, Blum WEH (2008) Arsenic contamination of soils and agricultural plants through irrigation water in Nepal. Environ Pollut 155:157–163

Dıaz OP, Leyton I, Munoz O, Nunez N, Devesa V, Suner MA, Velez D, Montoro R (2004) Contribution of water, bread, and vegetables (raw and cooked) to dietary intake of inorganic arsenic in a rural village of Northern Chile. J Agric Food Chem 52:1773–1779

Dittmar J, Voegelin A, Roberts LC, Hug SJ, Saha GC, Ali MA, Badruzzaman ABM, Kretzschmar R (2010) Arsenic accumulation in a paddy field in Bangladesh: seasonal dynamics and trends over a three-year monitoring period. Environ Sci Technol 44:2925–2931

Falinski KA, Yost RS, Sampaga E, Peard J (2014) Arsenic accumulation by edible macrophytes. Ecotoxicol Environ Saf 99:74–81

FAO (1985) Water quality guidelines for maximum crop production. Food and Agriculture Organization/UN. www.fao.org/docrep/T0551E. 2006/9/13

Halder D, Bhowmick S, Biswas A, Chatterjee D, Nriagu J, Guha MD et al (2013) Risk of As exposure from drinking water and dietary components: implications for risk management in rural Bengal. Environ Sci Technol 47:1120–1127

Islam MS, Ahmed MK, Habibullah-Al-Mamun M, Eaton DW (2017) Arsenic in the food chain and assessment of population health risks in Bangladesh. Environ Syst Decis 37:344–352

Kumar M, Rahman MM, Ramanathan AL, Naidu R (2016) Arsenic and other elements in drinking water and dietary components from the middle Gangetic plain of Bihar, India: health risk index. Sci Total Environ 539:125–134

Matos-Reyes MN, Cervera ML, Campos RC, de la Guardia M (2010) Total content of as, Sb, se, Te and bi in Spanish vegetables, cereals and pulses and estimation of the contribution of these foods to the Mediterranean daily intake of trace elements. Food Chem 122:188–194

Munoz O, Diaz OP, Leyton I, Nunez N, Devesa V, Suner MA, Velez D, Montoro R (2002) Vegetables collected in the cultivated Andean area of northern Chile: total and inorganic arsenic contents in raw vegetables. J Agric Food Chem 50:642–647

Roberts LC, Hug SJ, Dittmar J, Voegelin A, Kretzschmar R, Wehrli B, Cirpka OA, Saha GC, Ali MA, Badruzzaman BM (2010) Arsenic release from paddy soils during monsoon flooding. Nat Geosci 3:53–59

Robinson B, Outred H, Brooks R, Kirkman J (1995) The distribution and fate of arsenic in the Waikato River system, vol 7. Chemi Spec Bioavail, North Island, pp 89–96

Roychowdhury T (2008) Impact of sedimentary arsenic through irrigated groundwater on soil, plant, crops and human continuum from Bengal Delta: special reference to raw and cooked rice. Food Chem Toxicol 46:2856–2864

Roychowdhury T, Uchino T, Tokunaga H, Ando M (2002) Survey of arsenic in food composites from an arsenic-affected area of West Bengal, India. Food Chem Toxicol 40:1611–1621

Signes-Pastor AJ, Mitra K, Sarkhel S, Hobbes M, Burlò F, Carbonell-Barrachina AA (2008) Arsenic speciation in food and estimation of the dietary intake of inorganic arsenic in a Rural Village of West Bengal, India. J Agric Food Chem 56:9469–9474

Spanu A, Daga L, Orlandoni AM, Sanna G (2012) The role of irrigation techniques in arsenic bioaccumulation in rice (*Oryza sativa* L.). Environ Sci Technol 46:8333–8340

Upadhyay MK, Majumdar A, Barla A, Bose S, Srivastava S (2019) An assessment of arsenic hazard in groundwater–soil–rice system in two villages of Nadia district, West Bengal, India. Environ Geochem Health. https://doi.org/10.1007/s10653-019-00289-4

Wang HS, Sthiannopkao S, Chen ZJ, Man YB, Du J, Xing GH (2013) Arsenic concentrations in rice, fish, meat and vegetables in Cambodia: a preliminary risk assessment. Environ Geochem Health 35:745–755

WHO (World Health Organization) (1993) Guidelines for drinking-water quality, 2nd edn. CH, Geneva

Williams PN, Price AH, Raab A, Hossain SA, Feldmann J, Meharg AA (2005) Variation in As speciation and concentration in paddy rice related to dietary exposure. Environ Sci Technol 39:5531–5540

Williams PN, Islam MR, Adomako EE, Raab A, Hossain SA, Zhu YG, Felfmann J, Meharg AA (2006) Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. Environ Sci Technol 40:4903–4908

Potential Exposure to Arsenic and Other Elements from Rice in Bangladesh: Health Risk Index

Mohammad Mahmudur Rahman and Ravi Naidu

Abstract This study evaluates the potential exposure to arsenic (As) and other elements in rice from two severely arsenic (As)-impacted districts (Comilla and Chandpur) of Bangladesh. Rice samples were collected from 99 households and analyzed for this purpose. The mean concentrations of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in rice were 187 μg/kg, 40 μg/kg, 16 μg/kg, 819 μg/kg, 1.8 mg/kg, 7.3 mg/kg, 549 μg/kg, 61 μg/kg, and 8.9 mg/kg, respectively. Food and drinking water contribute 20.2, 0.27, 0.24, 6.9, 20, 100, 5.3, 1.6 and 100 μg of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn per kg bw daily, respectively. Drinking water contributes 92% of the total dietary intake of As to adults whereas food contributes 90-100% for other elements. The estimated health risk index (HRI) for As, Cd, Cr, Cu, Pb, Mn, Ni, and Zn are 67.4, 0.27, 2.3, 0.54, 0.41, 0.73, 0.27, and 0.33, respectively. The results show that As and Cr in food and drinking water pose significant health risks to the study population as the values of HRIs were greater than 1.

Keywords Arsenic · Toxic elements · Rice · Exposure · Health risk index

1 Introduction

Chronic exposure to arsenic (As) through drinking well water poses significant health threats to inhabitants of Bangladesh and many other regions worldwide. More than 100 million people in Bangladesh are at risk from As toxicity, and many are suffering from As-related diseases such as dermal, neurological, cardiovascular, and respiratory and diabetes mellitus along with various types of cancer of the skin

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and different internal organs (Rahman et al. 2009a). Arsenic-contaminated groundwater is also extensively used in agricultural irrigation, especially for growing paddy rice, which accumulates elevated level of As. Drinking water and food (rice and vegetables) are the main exposure pathways of As to the population in Bangladesh. It was reported that consumption of cooked rice was responsible for genetic damage in a section of population from As-impacted area of West Bengal, India, although it was not confirmed whether As contribution from cooked rice is alone responsible or other confounding factors have also influenced the DNA damage observed in that study (Banerjee et al. 2013).

Various reports have already investigated the concentrations of As in foodstuffs, particularly rice and vegetables, as both are the staple foods for inhabitants in severely As-impacted areas of Bangladesh and West Bengal, India (Rahman et al. 2011, 2013; Roychowdhury et al. 2008; Williams et al. 2006). A few articles also estimated the intake of As by adults and children in both areas, and some reports have already demonstrated the level of As in rice from Bangladesh and West Bengal (Chowdhury et al. 2001; Roychowdhury et al. 2003). The current research of Bangladesh and West Bengal was basically focused on As, whereas other potential toxic elements such as Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in food were not considered extensively. Much efforts have been directed to investigate the levels of As in rice; very limited studies emphasized the potential exposure of other elements from rice in Bangladeshi population. Considering this, in this communication, we report exposure of As and other elements in rice from two As-contaminated districts of Bangladesh. The main objective of the present study is to investigate (1) As and other elements present in rice and (2) exposure arising from the daily intake of As and other elements from rice for adult populations. The total exposure was determined using data of As and other elements in drinking water and vegetables from our previous study (Rahman et al. 2013) to determine the health risk index.

2 Materials and Methods

2.1 Sample Collection, Preparation, and Analysis

For this study, a total of 99 rice grain samples were collected from 99 households in two As-contaminated adjacent districts (Comilla and Chandpur) of Bangladesh during 2014. The rate of daily consumption of rice by each adult individual (male and female) was used in our previous study in Bangladesh (Rahman et al. 2011). The collection and washing procedures of rice samples, digestion method for rice, and the analytical procedures for As and other elements were described in our earlier publications (Rahman et al. 2013, 2011).

2.2 Health Risk Index (HRI)

Health risk index was measured as the ratio of estimated exposure of As and other elements from rice and oral reference dose (Cui et al. 2004; Fang et al. 2014). We have also estimated the HRI from drinking water and vegetables based on the data reported in our previous study from Bangladesh (Rahman et al. 2013). Estimated exposure was obtained by dividing daily intake of elements by their oral reference dose. An index of greater than 1 was considered unsafe for human health (USEPA 2002).

Daily intake of element ($\mathrm{DI_E}$) was calculated by using the following equation:

$$\mathrm{DI_E} = \left(\mathrm{CE_R} \times \mathrm{IR_R} + \mathrm{CE_{DW}} \times \mathrm{IR_{DW}} + \mathrm{CE_V} \times \mathrm{IR_V}\right) / \mathrm{BW_A}$$

where CE, IR, and BW_A represent concentration of element, daily intake rate, and average body weight (45 kg) of an adult, respectively (Chowdhury et al. 2003). R, DW, and V represent rice, drinking water, and vegetables, respectively. The daily consumption of As and other elements from rice by adults is calculated by multiplying the median consumption rate of rice with median concentrations of elements observed in rice in this study.

The oral reference doses for As, Cd, Cr, Cu, Pb, Mn, Ni, and Zn are 0.0003, 0.001, 0.003, 0.04, 0.004, 0.14, 0.02, and 0.3 mg/kg/day, respectively (USEPA 1997). No oral dose was listed for Co.

2.3 Analytical Performances

We analyzed standard reference material (SRM) from the National Institute of Standards and Technology (NIST), USA, to verify the accuracy of the digestion method employed in this study. Rice flour (SRM 1568a) was used to verify the results for As and other elements in rice. Rice flour was digested after utilizing the same procedure as that used for rice samples. The analytical results of As and other metals in SRM are presented in Table 1. The percentage of recovery was in good agreement with the certified values.

3 Results and Discussion

3.1 Concentrations of As and Other Elements in Rice

The mean, median, and range of As and other elements present in Bangladeshi rice are also provided in Table 1. The mean As concentration in 99 rice samples was 187 μg/kg (dry wt.) with a range of 57–341 μg/kg. Rahman et al. (2014) reported

Table 1 Concentrations of As and other elements (µg/kg) in NIST SRM and rice samples from Bangladesh

Element	NIST SRM 1568a (rice flour)		Rice grain (*n* = 99)		
	Certified values	Observed values (*n* = 3)	Mean	Median	Range
As	290 ± 30	273 ± 12	187	192	57–341
Cd	22 ± 2	20 ± 1	40	25	1–193
Co	18	16.7 ± 1.2	16	15	8–46
Cr	–	–	819	778	508–1686
Cu[a]	2.4 ± 0.3	2.1 ± 0.6	1.8	1.7	0.7–8.8
Mn[a]	20 ± 1.6	18.9 ± 1.1	7.3	6.9	3.4–16.5
Ni	–	–	549	518	176–1573
Pb	<10	–	61	45	20–432
Zn[a]	19.4 ± 0.5	18.4 ± 0.8	8.9	8.5	5.3–17.5

[a] mg/kg

that the mean concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in Australian-grown rice were 7.5 µg/kg, 21 µg/kg, 144 µg/kg, 2.9 mg/kg, 24.4 mg/kg, 166 µg/kg, 375 µg/kg, and 17.1 mg/kg, respectively. They concluded that concentrations of heavy metals except Cd in Australian-grown rice were higher than Bangladeshi rice on sale in Australia and concentrations of Cd, Cr, Cu, and Ni in Indian rice on sale in Australia were higher than Australian-grown rice (Rahman et al. 2014). They also found that concentrations of Cu and Ni in Vietnamese rice and that of Cd, Cr, Cu, Ni, and Pb in Thai rice on sale in Australia were also higher than Australian-grown rice (Rahman et al. 2014). The concentrations of Mn and Pb in this study were much lower than Australian-grown rice, and concentrations of other elements are comparable. Roychowdhury et al. (2003) reported that the average concentrations of As, Cu, Ni, Mn, and Zn in rice were 232 µg/kg, 3.5, 0.65, 5.9, and 6.6 mg/kg, respectively, from Jalangi block and 233 µg/kg, 2.7, 0.55, 6.7, and 9.6 mg/kg, respectively, for Domkal block in West Bengal. Shraim (2014) analyzed rice samples on sale in Kingdom of Saudi Arabia (KSA) and reported that the mean concentrations of Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb were 0.057, 4.2, 0.012, 0.064, 1.2, 6.1, 0.136, 0.017, and 0.029 mg/kg, respectively. The author also analyzed rice samples sold in Brisbane, Australia, and the mean concentrations of Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb were 0.097, 9.4, 0.018, 1.8, 2.7, 11.4, 0.092, 0.039, and 0.120 mg/kg, respectively (Shraim 2014). The result reveals that concentrations of Mn, Pb in Australian-grown rice were much higher compared to rice sold in KSA as well as Brisbane, Australia, and Zn concentrations were elevated in both studies. The range of As in rice grain was 2–557 µg/kg (dry wt) in our previous work based on 214 rice grain samples collected from 25 villages of Comilla, Manikganj, Munshiganj, and Brahmanbaria districts of Bangladesh (Rahman et al. 2009b).

3.2 *Intake of As and Other Elements from Rice and Other Components*

Based on the elemental concentrations (Table 1) observed in this study in rice and the intake rate of rice [425 g uncooked basis, equivalent to 370 g (fresh weight), considering 13% moisture content in rice grain] observed for 71 adults (males and females, age range 12–80 years) in the previous study (Rahman et al. 2011), we have estimated the daily intake of As and other elements from rice for adults, presented in Table 2. Roychowdhury et al. (2003) reported that the total daily intakes of As, Cu, Ni, Mn, and Zn from rice for adults were 174, 2633, 488, 4493, and 4965 μg, respectively, from Jalangi and 175, 2070, 412, 5062 and 7267 μg, respectively, from Domkal. When we combine As and other elemental contribution from vegetables and drinking water [data derived from Rahman et al. (2013)], the total daily intakes of As, Cu, Ni, Mn, and Zn from food (rice and vegetables) and drinking water were 890, 2400, 123, 4800, and 4100 μg, respectively, for adult males and females. Roychowdhury et al. (2003) reported that the total daily intakes of As, Cu, Ni, Mn, and Zn from food (rice and vegetables) and drinking water were 666, 3436, 710, 7776, and 7869 μg, respectively, for adult males and 583, 3434, 701, 7710, and 7791 μg for adult females, respectively, from Jalangi of West Bengal. In the same study, Roychowdhury et al. (2003) also estimated that the total daily intakes of As, Cu, Ni, Mn, and Zn from food (rice and vegetables) and drinking water were 555, 2867, 527, 8099, and 10,005 μg, respectively, for adult males and 485, 2865, 519, 7703, and 9946 μg for adult females, respectively, from Domkal of West Bengal. Thus, the daily intake of As for adults is higher than Jalangi and Domkal, whereas daily intakes of Cu, Ni, Mn, and Zn are much lower in this study.

Table 2 Daily intake of elements from rice, drinking water, and vegetables for adults in Bangladesh

Element	Intake from rice (μg)	Intake from drinking water (μg)[a]	Intake from vegetables (μg)[a]	Total intake from food and drinking water (μg)	Daily intake (μg or mg per kg BW)	Oral reference dose mg/kg/day	HRI	JECFA's PTDI/PTMI/PTWI values (μg or mg per kg BW)
As	71.0	837	2.3	910.3	20.2	0.0003	67.4	–
Cd	9.3	–	2.9	12.2	0.27	0.001	0.27	7
Co	5.6	1.1	4.4	11.1	0.24	–	–	–
Cr	288	1.9	20.8	310.6	6.9	0.003	2.3	–
Cu	0.6[b]	7.0	0.34[b]	1.0[b]	0.02[b]	0.04	0.54	0.05–0.5[b]
Mn	2.6[b]	336	1.7[b]	4.6[b]	0.10[b]	0.14	0.73	–
Ni	192	3.1	46	240.8	5.3	0.02	0.27	12
Pb	16.7	0.4	56	73.1	1.6	0.004	0.41	25
Zn	3.1[b]	23.1	1.3[b]	4.5[b]	0.1[b]	0.3	0.33	0.3–1.0

[a] Data from Rahman et al. (2013)
[b] Unit as expressed in mg

Previously we estimated that the total daily intake of As from rice and drinking water was 888 µg and 706 µg for adult males and adult females, respectively, from 25 villages of Bangladesh (Rahman et al. 2009b). Smith et al. (2006) reported that the average daily intake of As from cooked rice and drinking water from Munshiganj and Monohardi of Bangladesh was 1180 µg for adults, although they did not consider the intake of As from vegetables. A study from Pabna reported that average daily total As intake for adult female was 174 µg (Kile et al. 2007). Based on another study from Chapai Nawabganj of Bangladesh, Ohno et al. (2007) estimated that the total As intakes from food and drinking water for adult males and females were 180 µg and 96 µg per day, respectively. In a study, it was suggested that differences of As intake could be attributed to regional variations in As contamination of food components and drinking water or from sampling procedures between studies (Rahman et al. 2011). This study employed a household survey method to estimate the As intake from raw food, whereas the other three studies employed duplicate diet methodology to analyze As in cooked food.

The percentage of daily intakes of elements from drinking water and food (rice and vegetables) is presented in Fig. 1. Drinking water contributed the primary route of As intake; food also contributed greatly to the total daily As intake. This study reveals that drinking water is the major contributor for As, whereas food is the major contributors for other elements.

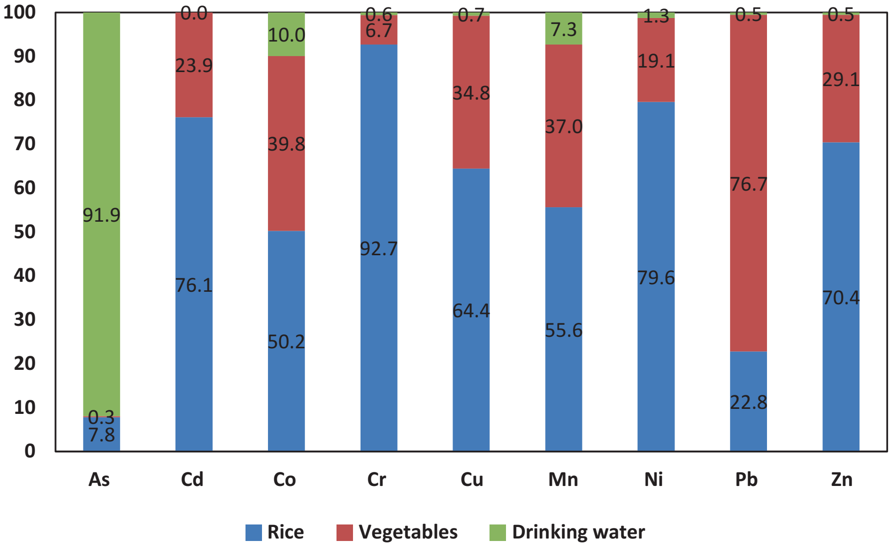

Fig. 1 Percentage contribution of elements from rice, vegetables, and drinking water for adults in Bangladesh

3.3 Health Risk Index (HRI)

Based on the average bw of a Bangladeshi adults (45 kg) (Chowdhury et al. 2003), food and drinking water contribute 20.2, 0.27, 0.24, 6.9, 20, 100, 5.3, 1.6, and 100 μg of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn per kg bw daily, respectively. The estimated HRI for As, Cd, Cr, Cu, Pb, Mn, Ni, and Zn are 67.4, 0.27, 2.3, 0.54, 0.41, 0.73, 0.27, and 0.33, respectively (Table 2). The values of HRIs for As and Cr were greater than 1, suggesting that food and drinking water pose significant health risks to the study population, whereas values of HRIs for other elements were less than 1, suggesting that consumption of the investigated food and drinking water do not pose any health risks for Bangladeshi consumers from other elements such as Cd, Cu, Pb, Mn, Ni, and Zn.

4 Conclusions and Study Limitations

The study reveals that concentrations of As in rice (this study) and drinking water and vegetables (previous study) were elevated. Very high concentrations of Cu, Mn, and Zn were found in rice. The study concluded that drinking water is the major intake route for As, whereas food components are the primary intake source of other elements. Based on the HRIs data, it reveals that As and Cr are the primary concern from dietary intake for Bangladeshi population. The study did not analyze the elemental concentrations in cooked food items which provide the accurate estimation of daily intake of metal/loids, and then the data can be used for potential health risk. We also did not consider all food items people consumed and the water used for food preparation as well as beverages they drink which will be required to include for further studies. Future studies should focus on duplicate diet sampling including cooked food and all other food items and beverages to determine the actual health threats to this section of population.

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References

Banerjee M, Banerjee N, Bhattacharjee P, Mondal D, Lythgoe PR, Martínez M, Pan J, Polya DA, Giri AK (2013) High arsenic in rice is associated with elevated genotoxic effects in humans. Sci Rep 3:2195

Chowdhury UK, Rahman MM, Mandal B, Paul K, Lodh D, Biswas BK, Basu GK, Chanda CR, Saha KC, Mukherjee SC (2001) Groundwater arsenic contamination and human suffering in West Bengal, India and Bangladesh. Environ Sci 8:393–415

Chowdhury UK, Rahman MM, Sengupta MK, Lodh D, Chanda CR, Roy S, Quamruzzaman Q, Tokunaga H, Ando M, Chakraborti D (2003) Pattern of excretion of arsenic compounds [arsenite, arsenate, MMA (V), DMA (V)] in urine of children compared to adults from an arsenic exposed area in Bangladesh. J Environ Sci Health A 38:87–113

Cui Y-J, Zhu Y-G, Zhai R-H, Chen D-Y, Huang Y-Z, Qiu Y, Liang J-Z (2004) Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. Environ Int 30:785–791

Fang Y, Sun X, Yang W, Ma N, Xin Z, Fu J, Liu X, Liu M, Mariga AM, Zhu X (2014) Concentrations and health risks of lead, cadmium, arsenic, and mercury in rice and edible mushrooms in China. Food Chem 147:147–151

Kile ML, Houseman EA, Breton CV, Smith T, Quamruzzaman Q, Rahman M, Mahiuddin G, Christiani DC (2007) Dietary arsenic exposure in Bangladesh. Environ Health Perspect 115:889–893

Ohno K, Yanase T, Matsuo Y, Kimura T, Hamidur Rahman M, Magara Y, Matsui Y (2007) Arsenic intake via water and food by a population living in an arsenic-affected area of Bangladesh. Sci Total Environ 381:68–76

Rahman M, Ng J, Naidu R (2009a) Chronic exposure of arsenic via drinking water and its adverse health impacts on humans. Environ Geochem Health 31:189–200

Rahman MM, Owens G, Naidu R, (2009b) Arsenic levels in rice grain and assessment of daily dietary intake of arsenic from rice in arsenic-contaminated regions of Bangladesh—implications to groundwater irrigation. Environmental Geochemistry and Health 31 (S1):179–187

Rahman M, Asaduzzaman M, Naidu R (2011) Arsenic exposure from rice and water sources in the Noakhali District of Bangladesh. Water Qual Expo Health 3:1–10

Rahman MM, Asaduzzaman M, Naidu R (2013) Consumption of arsenic and other elements from vegetables and drinking water from an arsenic-contaminated area of Bangladesh. J Hazard Mater 262:1056–1063

Rahman MA, Rahman MM, Reichman SM, Lim RP, Naidu R (2014) Arsenic speciation in Australian-grown and imported rice on sale in Australia: implications for human health risk. J Agric Food Chem 62(25):6016–6024

Roychowdhury T, Tokunaga H, Ando M (2003) Survey of arsenic and other heavy metals in food composites and drinking water and estimation of dietary intake by the villagers from an arsenic-affected area of West Bengal, India. Sci Total Environ 308:15–35

Roychowdhury T, Uchino T, Tokunaga H (2008) Effect of arsenic on soil, plant and foodstuffs by using irrigated groundwater and pond water from Nadia district, West Bengal. Int J Environ Pollut 33:218–234

Shraim AM (2014) Rice is a potential dietary source of not only arsenic but also other toxic elements like lead and chromium. Arab J Chem 10:S3434–S3443

Smith NM, Lee R, Heitkemper DT, Cafferky KD, Haque A, Henderson AK (2006) Inorganic arsenic in cooked rice and vegetables from Bangladeshi households. Sci Total Environ 370:294–301

USEPA (1997) Region 9, preliminary remediation goals

USEPA (2002) Risk-based concentration table. Washington, DC

Williams PN, Islam MR, Adomako EE, Raab A, Hossain SA, Zhu YG, Feldmann J, Meharg AA (2006) Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. Environ Sci Technol 40:4903–4908

Preventive and Therapeutic Strategies for Acute and Chronic Human Arsenic Exposure

S. J. S. Flora

Abstract Arsenic, a ubiquitous metalloid, is naturally present in the lithosphere (Earth's crusts, soil, rock, etc.), hydrosphere (surface water, aquifers, deep wells, etc.), atmosphere, and biosphere. In South Asia, Some studies reported that GSH contamination in groundwater in the Ganga- Brahmaputra fluvial plains in India and Padma-Meghna fluvial plains in Bangladesh has been found to have a huge impact on human health, and its consequences have been reported as the world's biggest natural groundwater calamities. After entering into the body, it is distributed in a large number of organs including the lungs, liver, kidney, and skin. The clinical manifestations of arsenic poisoning are myriad, and the correct diagnosis depends largely on awareness of the problem. It is very difficult to diagnose early symptoms of arsenicosis because such non-specific symptoms may also be present in many other diseases. Medicine used for remedy of arsenicosis has been found to be unsatisfactory by repeated application and experience. The number of chelating drugs has been used for the treatment of arsenic poisoning. Some of them have been found to be effective during acute poisoning; however, there is still no safe and effective antidote available for treating chronic arsenicosis. Few natural and herbal extracts too have been attempted with limited success. This chapter reviews some of the fundamentals of arsenic toxicity and also summarizes currently available remedial measures.

Keywords Arsenic · Chelation · Dimercaprol · Melatonin · Taurine · Toxicity

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1 Introduction

Rapid advancements in industrialization as well as inculcation of technological advancements have principally contributed toward adverse events on ecosystem. As a result of these advancements, groundwater contamination appears to be primarily affected (Hughes et al. 1988). Arsenic, a metalloid, has been suggested as one of the major groundwater contaminants. The ubiquitous availability of arsenic in the environment is due to its natural occurrence in the Earth's crust, rocks, soils, and water and through anthropogenic sources.

Arsenic exhibits a dual role (friend and foe) on the nutritional and health condition of humans. Arsenic (in low dosage) safeguards the dietary and health condition of humans. Arsenic has few known medicinal uses as well like oral Fowler's solution in the tonic mixture. It is also used in the treatment of various diseases like leukemia, asthma, malignancies, syphilis, topical eosinophilia, trypanosomiasis, and psoriasis (Zachariae et al. 1974; Smith et al. 1998). Arsenic is also being used as insecticides, weedicides, and rodenticides, agricultural besides few industrial uses. Arsenic is also used in the processing of glass, paper, pigments, textiles, metal adhesives, wood preservatives, and ammunition and also as an alloying agent in the making of transistors, lasers, and semiconductors.

There are many countries (including Argentina, Australia, Bangladesh, Cambodia, Chile, China, Hungary, India, Inner Mongolia, Mexico, Nepal, New Zealand, the Philippines, Taiwan, Thailand, Vietnam, and the United States) in the world where arsenic concentration in drinking water was found to be more than the permissible limit of 10 μg/L according to World Health Organization (2018). Over the last few decades, the occurrence of high concentrations of arsenic in drinking water has been recognized as a major public health concern in several parts of the world. Apparently, there are areas where the concentration still needs to be recognized.

In southern Asian regions, contaminated drinking water is the main cause of arsenic exposure. In previous years, contamination of drinking water by arsenic is elevating day by day in various regions of India. Varied amount of arsenic has been reported in different regions of India (Table 1). West Bengal, Bihar, Uttarakhand, Uttar Pradesh, and some of the northeastern states are highly affected by arsenic contamination of drinking water. In the northeastern states like Tripura, Nagaland, Assam, Manipur, and Arunachal Pradesh, concentration in drinking water was found to be 300 ppb according to the North Eastern Regional Institute of Water and Land Management (Devi et al. 2009). It has been reported that the basin of Ganges and Brahmaputra were contaminated with arsenic. So both the river flows through different states such as Assam, West Bengal, Bihar, Utter Pradesh, etc. and leave arsenic in groundwater. The average amount of arsenic in the basin of these rivers is 200 mg/L (Ghosh et al. 2009; Singh 2015). Some districts of Uttar Pradesh like Ballia and Kheri have also reported to contain a very high amount of arsenic (4800–6300 ppb) (Katiyar and Singh 2014).

Table 1 The status of groundwater arsenic content in different states of India

State	Source of toxicity	Concentration (μg/L)	Reference
Bihar	Groundwater	≥1800	Chakraborti et al. (2009)
Patna		1810	
Purantola		1466	
Kittachawhater		1466	Chakraborti et al. (2009)
Maner		1820	
Bhagalpur		143	
Buxar		1222–1400	
Bhojpur		1630	
Samastipur		626	
Uttar Pradesh	Groundwater	≥1300	Ghosh and Singh (2009)
Ballia		1310	
Mathura		520	
West Bengal	Groundwater	≥500	Chakraborti et al. (2016)
Howrah		50–155	
Hugli		510	
Murshidabaad		2037	
Paragons		1321	
Chhattisgarh	Groundwater	50–1890	
Assam	Groundwater	100–200	Devi et al. (2009)
Manipur	Groundwater	798–986	Devi et al. (2009)
Arunachal Pradesh	Groundwater	618	Devi et al. (2009)

Arsenic toxicity has been recognized a century back. Long-term exposure to arsenic through groundwater or other sources poses several deleterious effects on public health, which include poor morbidity and mortality. Dermatological manifestations, development of carcinomas, and organ-specific toxicity are considered as characteristics of chronic arsenic toxicity.

Early identification of arsenic-affected areas can serve as a milestone for the remediation program and to provide safe drinking water. In groundwaters, the ratio of As^{3+}/As^{5+} varies to a great extent due to variation in redox conditions, sources of water, and environmental conditions.

2 Fate of Arsenic in the Body

In the periodic table, arsenic ranks at the 33rd position as a part of the elements in Group 15 and a member of nitrogen family. The atomic number of arsenic is 33 and atomic weight is 74.921. The presence of arsenic in the environment has been noted in different forms and oxidation states depending on its functioning. Four oxidation states of arsenic have been identified (As^{-3}, As^{0}, As^{+3}, As^{+5}) and classified as organic or inorganic. Arsenic trichloride, arsenic trioxide, and sodium arsenate are some of the inorganic trivalent forms, whereas arsenic pentoxide, lead arsenates, and calcium arsenates are inorganic pentavalent forms. Organic forms of arsenic available in the environment are methylarsonic acid, dimethylarsinic acid (cacodylic acid), and arsenobetaine. Out of these, inorganic form (especially in As^{+3} state) of arsenic appears to be the highly toxic as it has more binding capacity to the sulfhydryl group of proteins and interferes with cell enzymes, cell respiration, and mitosis and disrupts the antioxidant defense status (Flora 2011).

Exposure to arsenic occurs through different routes such as ingestion (either by drinking water or contaminated food) and inhalation (fumes and dust from mining and smelting) and through the skin. Absorption of arsenic compounds is a function of their aqueous solubility, both after inhalation of aerosols or particles and after ingestion. Arsenic in either form (arsenate or arsenite) is readily absorbed through the gastrointestinal tract. However, arsenite has been reported to be absorbed more rapidly than arsenate (Rahman et al. 2012).

Arsenic enters the cells with the help of transporters, such as aquaglyceroporin (aquaporins 7 and 9) which is permeable to As^{3+}. In contrast, As^{5+} utilizes phosphate transporters for cellular uptake (Csanaky and Gregus 2001; Kwong 2004). AQPs are almost present in every organ like the lung, liver, spleen, adipose tissues, and kidney (Tsukaguchi et al. 1999). Uptake of organic methylated MMAIII form is done by the AQP9 channel transporter. These AQP9 are vastly present in the NB4 cell lines, due to which these cell lines are extra sensitive to arsenic. When there is downregulation of AQPs, it results into decreasing arsenic treatment. For example, in case of the K562, a type of chronic myeloid leukemia cell line, it is less sensitive to As^{+3} treatment because there is deficiency in AQP9 expression in that particular cell (Leung et al. 2007). Efflux of arsenic takes place via a variety of proteins, human multidrug resistance proteins (e.g., MRP1/MRP2, ABCC1/ABCC2), which have been recognized as crucial transporters. The MRP family has nine types of transporters which belongs to the class of ATP-binding cassette (ABC) transporters that help in the elimination of drugs outside the body (Haimeur et al. 2004). MRPs form conjugation with metals by sulfate, glucuronide, and glutathione conjugation (Deeley et al. 2006). Arsenic is effluxed majorly through MRP1 and 2 along with glutathione transferase (GST) (Smitherman et al. 2004). Some studies reported that GSH is essential requirement for the conjugation of arsenic-Glutathione conjugates. MRP1/MRP2 transporters help in the transportation of these conjugates in the bile. Both the transporters involved in arsenic efflux are less expressed in tumor and cancer cells which decreases the sensitivity of arsenic treatment (Cole and Deeley 2006).

Absorbed inorganic arsenic binds poorly to plasma proteins and is distributed via the blood to various organs. Concentrations of inorganic arsenic in the tissue vary by valence: As^{+5} exhibits affinity for the bone and teeth, probably due to its chemical similarity to phosphate, whereas As^{+3} is attracted to the high sulfhydryl content of the skin, hair, and nails.

The major portion of arsenic gets absorbed through the gastrointestinal tract; thereafter, it reaches the systemic circulation and is distributed throughout the body including the liver, kidney, lungs, gonads, spleen, etc. In systemic circulation,

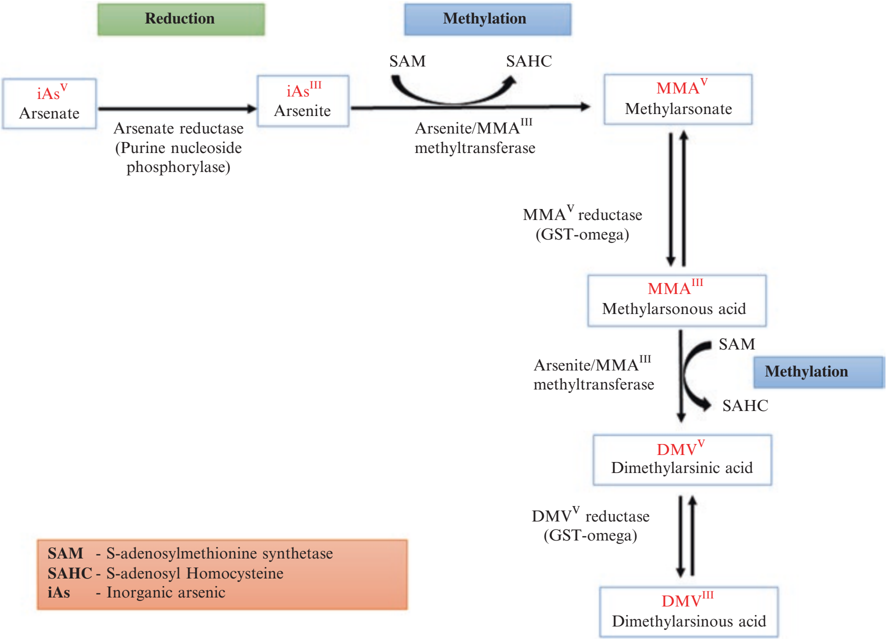


Fig. 1 Schematic representation of arsenic metabolism

arsenic binds with globin protein and is distributed throughout the body. Almost 70% of absorbed arsenic is eliminated through renal clearance. However, the absorbed arsenic gets metabolized in the liver through methylation process by arsenite methyltransferase (cofactor S-adenosylmethionine). Inorganic arsenic is methylated to form monomethylarsonic acid (MMA) leading to further formation of dimethylarsinic acid (DMA) by a methyl donor S-adenosylmethionine which is a principal method of detoxification of toxic inorganic forms of arsenic (Sattar et al. 2016).

Metabolism of arsenic involves two reactions: first is reductive methylation and second is oxidative methylation. Methylation is the predominant metabolic pathway for inorganic arsenic for humans and most laboratory animals (Fig. 1); however exception (inability of arsenic methylation) has been noted in some species especially in guinea pig, marmoset, tamarin, squirrel, monkeys, and chimpanzee. The liver is the major site of biotransformation of arsenic where arsenic methyltransferase enzymes catalyze the methylation process in the presence of S-adenosyl-L-methionine and glutathione (GSH), as methyl donor and essential cofactor, respectively. The reduction and oxidation reactions between As^{+3} and As^{+5} take place in plasma (Flora 2017). While the exact pathway has not been elucidated, most proposed pathways require an initial reduction of As^{+5} to As^{+3}, followed by stepwise addition of methyl groups to form monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Aposhian 1997; Healy et al. 1998). Both MMA and DMA are eliminated through renal excretion. MMA has been noted to be more reactive and toxic and poses toxic effects on the liver, skin, lungs, etc.

3 Probable Mechanism

The fate of arsenic in the body cannot be determined without exploring its metabolism. Various mammalian species can facilitate methylation reaction, and therefore the toxicity of arsenic may vary according to rate and extent of methylation within a species including humans. Oxidative stress is considered to play a major role in arsenic-induced toxicity. This adverse situation normally arises when excess reactive oxygen species (ROS) are generated and react with cellular components.

Oxygen in molecular form reacts with dimethylarsine and forms dimethylarsinic radical and superoxide anion. The second molecule of oxygen then combines and results in a dimethylarsinic peroxyl radical. These arsenic radicals are reported to mediate cellular damage. Further, this free radical-mediated alteration in mitochondrial respiration is considered as one of the important mechanisms of arsenic-induced cell injury, cell death, and cancer. Specifically, inorganic arsenicals induce oxidative stress by inhibiting mitochondrial respiration and enhanced ROS generation that in turn might cause DNA mutations and ultimately contribute to the development of cancer.

DNA-damaging ROS are generated from iron released from ferritin, which is significantly enhanced by DMA (III) and DMA (V) in the presence of ascorbic acid. In this pathway, free iron plays a central role in generating harmful oxygen species by enhancing the conversion of highly reactive $^{\bullet}OH$ radical from O_2^- and H_2O_2 via the Haber–Weiss reaction. Only DMA (III), however, remains active for iron release in the absence of ascorbic acid. Here, it should be noted that arsenate, arsenite, MMA (V), and MMA (III) remain inactive in iron release from ferritin.

Arsenic may induce oxidative stress by cycling between oxidation states of metals, such as As, Fe, etc., or by interacting with antioxidants and increasing inflammation, resulting in the accumulation of free radicals in cells. Major arsenic-induced ROS include superoxide anion ($O2^{\bullet-}$), hydroxyl radical ($^{\bullet}OH$), hydrogen peroxide (H_2O_2), singlet oxygen, and peroxyl radicals. Oxygen-derived radicals form the most important class of radical species generated in living systems because molecular oxygen that has a unique electronic configuration forms $O2^{\bullet-}$ by addition of one electron. Superoxide anions, arising through metabolic processes or after oxygen "activation" by physical irradiation, are considered "primary" ROS. They can further interact directly, through enzyme- or metal-catalyzed processes, with other molecules to generate "secondary" ROS. For instance, •OH generated through superoxide-mediated process involving hydrogen peroxide plays an important role in mediating the genotoxic effects of arsenic. Yamanaka and colleagues (1996) were the first to demonstrate arsenic-induced free radical formation.

Molecular oxygen reacts with dimethylarsine (a trivalent arsenic form and a minor in vivo metabolite of dimethylarsinic acid) to form dimethylarsinic radical and superoxide anion. Further, the addition of another molecule of molecular oxygen results in a dimethylarsinic peroxyl radical, and these arsenic radicals are known to be detrimental to cells.

It is thus clearly evident that arsenic exposure results in ROS generation in various cellular systems; however, the source or mechanism involved remains unclear. Mitochondria are suggested to be one of the important sites of ROS production. In addition to mitochondria, three other sources of ROS have been proposed:

1. Generation of intermediary arsine species may produce significant amounts of free radicals.
2. Methylated arsenic species can release redox-active iron from ferritin. Free iron plays a central role in generating harmful oxygen species by promoting the conversion of $O2^{\bullet-}$ and H_2O_2 into the highly reactive $^{\bullet}OH$ radical through the Haber–Weiss reaction.
3. ROS can be generated during oxidation of arsenite to arsenate.

The mechanisms underlying arsenic-induced organ pathology have been well studied. Once arsenic enters the human body, it can alter signal transduction pathways, which leads to either activation or inhibition of different transcription factors and regulatory proteins that bind to DNA and regulate gene transcription. Free radical-mediated activation of mitogen-activated protein kinases (MAPKs) (p38 MAPK/pJNK pathway), ERK, NRF-2, and NF-κB results in genotoxic stress, cell cycle arrest, apoptosis, and cell death.

4 Toxicity

Arsenic-contaminated ground may lead to several adverse effects on human health, which can be acute and chronic toxicity. Symptoms of acute toxicity generally arise within 30 min of ingestion of arsenic, but in case of food ingestion, it may be delayed up to several hours. After ingestion, at first the patient feels a metallic taste; some patients' breath have a garlic odor, dry mouth, and trouble in taking food. Different clinical signs may also arise due to arsenic acute toxicity which includes severe nausea and vomiting, muscular pain, weakness, pain in abdomen, and copious diarrhea. Some patients complain about cramps in the muscle; unresponsiveness of fingers, hands, and feet; pink-colored marks seen completely on the body; and increase in thirst. In severe cases, the skin of the patients turns out to be cold and clammy, which usually leads to renal damage and reduction in output of urine. Further, cardiac abnormalities in arsenic toxicity include acute cardiomyopathy, subendocardial hemorrhages, and electrocardiographic changes (prolongation in QT intervals and non-specific ST segment) (Saha et al. 1999). Lethargy and misperception are frequently noted in acute arsenic toxicity patients alongside advancement of psychosis with delirium, hallucinations, and delusions and ultimately may lead to seizures, coma, and death. Alternately circulatory insufficiency due to acute toxicity may lead to multisystem organ failure and culminates to death.

Chronic form of arsenic toxicity is more complicated than acute toxicity because diagnosis of chronic toxicity is very difficult. Dermatitis due to arsenic was hardly to choose from variety of other dermatosis. The cause of exposure due to arsenic is revealed only in 50% of cases or less. The utmost chronic toxicity includes the liver, skin, lungs, and blood systems (Flora 2011). Chronic toxicity causes different cutaneous changes which are non-specific. Early it shows the signs of slow erythematous flush, and after some time, it converted into desquamation, hyperkeratosis, and melanosis. Hyperkeratosis is often disrupted and happens on the distal edges. A diffuse desquamation in the palms of hands and soles of the foot is seen in different patients. Upon long-term contact with skin, it increases various skin related problems including cancer of basal cell and squamous cell carcinomas (Saha 1995). Some other symptoms also appear during arsenic exposure which includes anemia and leucopenia thrombocytopenia. The anemia is caused by hemolysis of cells; it is usually normochromic and normocytic. Disruption in metabolism of folate and synthesis of DNA consequence into the development of megaloblastic change (Black 2008; Westhoff et al. 1975). In countries like India and Bangladesh, the occurrence of leucopenia, anemia, and thrombocytopenia from exposure of arsenic needs to be cautiously evaluated by understanding the effect of malnutrition on anemia and leucopenia.

Majority of animals which are used in the laboratory seem to be less susceptible to arsenic than humans. According to some studies, chronic intake of inorganic arsenic (more than 0.05–0.1 mg/kg/day) may lead to some neurological symptoms and hematological toxicity in humans. However, an intake of 0.72–2.8 mg/kg/day dose is toxic for rats, monkeys, and dogs (Drobna et al. 2010; Byron et al. 1967). Arsenic exposure through oral or inhalation routes may produce signs and symptoms of carcinogenicity in humans, but in case of animals, there is no data available on carcinogenicity. Thus, quantitative dose-dependent data from animal studies cannot be correlated to the effects observed in humans. Toxicity induced by different metabolites generally depends on number of species, types of cell, and rate at which arsenic compounds get absorbed. For example, IC_{50} of every form of arsenic changes from cells to cells and in liver cells IC_{50} of $DMA^{III}(GS) \approx As^{+3} << MMA^{III}$, whereas in keratinocytes cells, it is $As^{+3} << DMA^{III}(GS) < MMA^{III}$, in case of bronchial cells IC_{50} value found to be in order of $DMA^{III}(GS) < As^{+3} \approx MMA^{III}$ (Liu et al. 2014).

Arsenic on chronic exposure gets distributed in the body and deposited in different target organs which could lead to organ-specific damage like hepatotoxicity, dermal toxicity, nephrotoxicity, and neurotoxicity. Arsenic is also known for its genotoxic and carcinogenic potential (Fig. 2). In the following paragraph, we discuss different organ-specific toxicities.

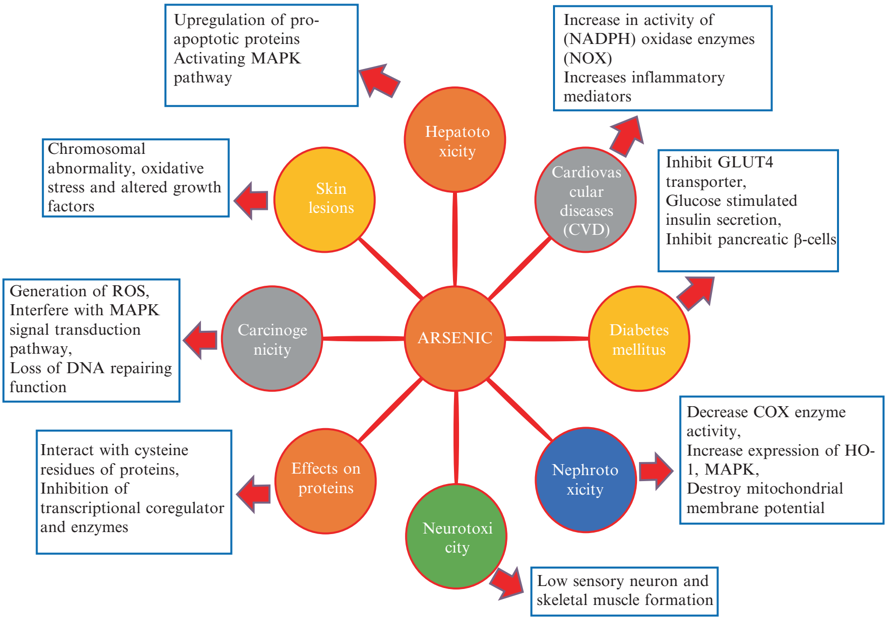


Fig. 2 Arsenic-induced organ-specific toxicity

4.1 Hepatotoxicity

On long-term exposures, arsenic mainly gets accumulated in the liver cells over a period of months or years (Clarkson 2001). Early symptoms due to arsenic accumulation include bleeding in the esophagus known as esophageal varices, accumulation of fluid in the abdomen (ascites), jaundice, or enlargement of the liver. Hepatic lesion sometimes formed later by long-term use of medicines containing arsenic (Fowler's solution) (Chakraborty and Saha 1987; Guha Mazumder et al. 1988). Individuals who are exposed to arsenic more often suffer from cirrhosis, which is a secondary effect due to damage in hepatic blood vessels. All the studies evidently suggest that chronic arsenic toxicity is linked with fibrosis, hepatomegaly, and cirrhosis (Liu and Waalkes 2005). Arsenic also induces different liver diseases including fibrosis, cirrhosis, and hepatomegaly. Toxicity of arsenic is mainly mediated through generation of oxidative stress and activation of c-Jun N-terminal kinases (JNK) and p38 mitogen-activated protein kinases (MAPK) pathway. After activation of these pathways, they result into induction of apoptosis of liver cells. There is upregulation of various pro-apoptotic proteins which induce hepatic cell death (Bashir et al. 2006; Suzuki and Tsukamoto 2006). Portal tract fibrosis was identified using histological examination of the liver (Mazumder 2005). Thus oxidative stress and pro-apoptotic factors are some of the targets which may lead to hepatotoxicity (Li et al. 2007).

4.2 Cardiotoxicity

Long-term inhalation of contaminated air, fumes, and dust containing toxic arsenic trioxide increases the frequency of death in humans from cardiovascular disease (Vineetha and Raghu 2019). Repeated inhalation for a long time may injure heart blood vessels (Bunderson et al. 2002). Intake of contaminated food and drinking water may cause severe effects on the heart including vascular damage (Blackfoot disease) which is endemic in some area of Taiwan where concentration of arsenic in daily used water was around 0.17–0.8 ppm arsenic (Tseng 1977), than normal concentration of about 0.01–0.5 mg As/kg/day. Cardiac arrhythmias, cerebrovascular disease, ischemic heart disease, and hypertension are some other effects (Mumford et al. 2007). There is no data available for organoarsenical-induced cardiovascular toxicity.

Mechanism through which arsenic causes toxicity involves different types of cells, among them is vascular endothelial cells which play crucial role in CVS toxicity. In these cells, there is an increase in activity of nicotinamide adenine dinucleotide phosphate (NADPH) oxidase enzymes (NOX) and deals with the hypertension and disease of vessels (Flora 2011; Liu et al. 2018). Arsenic species bind to these particular enzymes, and free radical generation occurs by ROS and nitric oxide which ultimately upregulate the inflammatory mediators like monocyte chemoattractant protein-1 (MCP-1), heme oxygenase-1 (HO-1), and interleukin-6 (IL-6) (34). These inflammatory mediators are responsible for the CVD. Arsenic also binds with G protein-coupled receptors (GPCR) to amplify signal schemes that regulate NOX-dependent redox signaling (Liu et al. 2018).

4.3 Nephrotoxicity

It is well known that accumulation of arsenic in kidneys on chronic exposure may cause nephrotoxicity in humans. Kidneys have a role in the excretion of arsenic outside the body and convert pentavalent form of arsenic into less soluble trivalent form. Renal route is the principal route for the elimination of arsenic, as well as the main site of converting pentavalent arsenic into the more toxic and less soluble trivalent arsenic. Arsenic causes toxicity in kidney cell, capillaries, glomeruli, and tubules (Schoolmeester and White 1980; Liu et al. 2005). Damage to proximal tubules causes proteinuria and mitochondrial damage in the urine which might sometime lead to renal failure. Arsine-induced hemolysis is one of the probable reasons for tubular necrosis with whole renal failure. To prevent the same hemodialysis is required for the elimination of arsenic bound to hemoglobin.

Higher content of arsenic (inorganic methylated form of arsenic; MMA and DMA) in urine is mainly associated with arsenic-mediated nephrotoxicity (Zheng et al. 2015). Out of several trivalent arsenicals (As^{+3}, MMA^{III}, and DMA^{III}), MMA^{III} shows more cytotoxic effects on human urothelial cells in vitro studies (Zhou and Xi 2018).

4.4 Neurotoxicity

Chronic arsenic exposure may also lead to neural injury. Like the cardiovascular system, arsenic damages both portions of the brain, i.e., central nervous system and peripheral nervous system (Schoolmeester and White 1980; Liu et al. 2005; Zheng et al. 2015). Higher exposure of arsenic (1 mg As/kg/day or more) often causes encephalopathy with other symptoms such as hallucination, seizures, mental confusion, lethargy, headache, and sometimes coma (Prakash et al. 2016). On repeated arsenic exposures, there is a chance of sensory motor polyneuropathy, which resemble Landry–Guillain–Barre syndrome symptoms. Neuropathy takes time to appear, usually 1–5 weeks after an acute exposure to arsenic. As an outcome of neurotoxiicty various primary symptoms include changes in memory function, irritability, loss of sleep, libido, and elevation in urine output (Liu et al. 2019) occur, whereas secondary symptoms are depression, anxiety, panic attacks, and cognitive. Neuropathy detected by using electromyography technique (EMG) suggests diminished amplitude of nerve conduction along with very minute change in conduction velocity. Inhalation of arsenic can also cause neurological defects in humans like peripheral neuropathy of both sensory and motor neurons leading to loss of reflexes and weakness of muscle (Sińczuk-Walczak et al. 2010).

4.5 Dermal Toxicity

From various epidemiological studies, skin disorders have been recognized in human population who drink contaminated water containing arsenic between the levels 0.01 and 0.1 mg As/kg/day and more. After few years of exposure, arsenic causes nonmalignant skin lesions. Primary symptoms may appear as dark pigmentation on the skin (melanosis) and small corn-like elevation diffused and spotted (keratosis). Leucomelanosis (raindrop pigmentation) and hyperkeratosis both are second stage of skin toxicity, and this stage further converted into skin cancer such as Bowen's disease and other cancers (Khan et al. 2003; Huang et al. 2004; Yoshida et al. 2004).

The dermal toxicity is caused by different mechanisms mainly by oxidative stress, chromosomal abnormality, and altered growth factors (Kitchin 2001; Yu et al. 2006). Oxidative stress occurs due to production of ROS which accumulate the unfolded proteins in endoplasmic reticulum and leads to stress in endoplasmic reticulum (Liu et al. 2005). Under these circumstances, the ER membrane-resident sensors PERK, IRE1α, and ATF6α separate the chaperone GRP78 (Gardner et al. 2013) which carry out activation of ER by proteolysis or phosphorylation. IRE1α sensor works as the nuclease and splices XBP-1; it also initiates various pathways which at last activate UPR target genes in the skin. Arsenic also activates p38 MAP kinase and its downstream protein MAPKAPK-2 (Zhang and Kaufman 2004). Thus, UPR and p38 MAP kinase both are responsible for inflammation in the skin.

4.6 Carcinogenicity

Cancer seems to be the end-stage consequence of chronic exposure to inorganic arsenic. Based on epidemiological data, arsenic is classified as class one carcinogen by the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA) (Flora 2011). Due to carcinogenesis, various organs of humans get affected. The relationship between exposure of arsenic through environment and occupational sources to millions of people worldwide increases the risks of cancer of the lungs, skin, liver, kidney, urinary bladder, prostate, and other organs (Chen et al. 1992; Smith et al. 1998; Yu et al. 2000; Zhang and Kaufman 2004). The precise mechanism of carcinogenicity by arsenic intake or exposure is not understood yet, but advancement of carcinogenesis is related to intracellular signal transduction, activation of different transcription factors, and abnormal genes expression.

One of the main mechanisms to cause carcinogenicity is arsenic-induced oxidative stress. Arsenic metabolites like DMA^V increase production of ROS and elevate 8-hydroxydeoxyguanosine which excites cell proliferation and brings carcinogenicity (Kinoshita et al. 2007). It also interferes with MAPK signal transduction pathway, and via AP-1 and NF-kB, they modify several gene expressions and cause cancer (Yang and Frenkel 2002). Regulation of various downstream signaling pathways (EGFR, ERK, cadherins) of carcinogenesis occurs by focal adhesion kinase activation upon arsenic exposure (Liu et al. 2005). Arsenic has several other actions; it can damage DNA, deregulate cell cycle, stimulate angiogenesis, block apoptosis, and cause cancer (Liu et al. 2005; Hays et al. 2006; Klein et al. 2007). Together oxidative stress, genotoxic effects, growth factor expression, and loss of DNA-repairing mechanisms are roughly the possible approaches of carcinogenic action of arsenic.

4.7 Diabetes Mellitus

In some cases it is found that on chronic exposure of arsenic, there is an increased chance of diabetes mellitus. Mainly trivalent form of arsenic leads to the generation of diabetes. It mainly inhibits GLUT4 receptor causing inhibition of insulin secretion. Mammalian target of rapamycin (mTOR) activity and 3-phosphoinositide-dependent kinase-I (PDK-1) activity is inhibited by the arsenic. PDK-1 and mTOR activation are the important steps for the phosphorylation of Akt diabetes (Paul et al. 2007). Akt is mandatory for translocation of GLUT4 and movement of glucose. So, inhibition of PDK-1 and mTOR does not activate the phosphorylation of Akt, and there is loss of insulin-dependent glucose uptake and later outcomes in diabetes (Paul et al. 2007). Another group of researcher studied that the insulin produced from β-cells of the pancreas is the target for arsenic exposure and inhibition of glucose-stimulated insulin secretion by the methylated metabolites may be the important mechanism of arsenic-induced diabetes (Ourshalimian et al. 2018).

Further prolonged exposure to arsenic could decrease PPAR-γ expression and might reduce the sensitivity of insulin and might be responsible for the induction of type II diabetes (Wauson et al. 2002). Replacement of a phosphate group from adenosine triphosphate (ATP) by arsenites slows down glucose metabolism, interrupts energy production, and interferes with ATP-dependent insulin secretion (Tseng 2004). Because of its high affinity for sulfhydryl groups, arsenite forms covalent bonds with this group in insulin, with its receptors, as well as with the other molecules and enzymes involved in glucose metabolism (Tseng 2004). In addition, a significant decrease in glucose-6-phosphatase activity due to chronic exposure to arsenic may cause hypoglycemia in both the liver and kidneys (Pal and Chatterjee 2005). Inorganic arsenic could increase oxidative stress and in turn leads to overexpression of various stress mediators such as NF-κB, JNK/SAPK, and hexosamine, causing insulin resistance and dysfunction of beta cells of the islets of Langerhans.

4.8 Genotoxicity

Generally arsenic is not considered mutagenic due to lack of its ability to cause mutation. The epidemiological data suggest people exposed to higher level of arsenic are more prone to develop genotoxicity (Roy et al. 2018). Free radicals generated by arsenic may cause DNA damage leading to breaks, chromosomal aberration, and micronuclei formation, and reduced repair mechanism may contribute to arsenic-induced genotoxicity. Chronic exposure with arsenic has been reported to increase expression of 8OHdG in humans, and simultaneous enhancement has been recorded in 8-oxoguanine DNA glycosylase level which facilitates its removal (Zhou and Xi 2018).

4.9 Reproductive Toxicity

The epidemiological studies have suggested strong correlation between arsenic exposure and reproductive toxicity in humans**.** The reproductive toxicity studies were based on semen analysis based on its motility, viability, membrane integrity, and DNA integrity. The concentration of arsenic has been found to be directly connected with quality of semen. These perturbations are because of arsenic-mediated endocrine disruption and oxidative stress (Xu et al. 2012). However the clear pathogenic mechanism remains unclear.

Experimental studies have provided valuable insight in understanding of arsenic-mediated reproductive toxicity. Exposure to trivalent and pentavalent arsenic has been reported to produce reproductive toxicity in male rodents. Arsenite form produces more toxic effect by reducing somniferous epithelium and Leydig cells and alters redox balance in testicular milieu (Morakinyo et al. 2010). Exposure to arsenic in rodents causes its accumulation in the epididymis, testicular tissue, prostate gland, and seminal vesicle which further leads to altered enzymatic activity in the testes, reduction in absolute sperm count with abundance of abnormal sperms, and reduced motility. Trivalent and pentavalent forms of arsenic are reported to inhibit spermatogenesis. The trivalent form of arsenic hinders the spermatogenesis possibly via attenuating testosterone synthesis pathway and oxidative stress; downregulating the expression of Ddx3y, C1dn11, and Ocln proteins; and inducing apoptosis (Li et al. 2012). Further trivalent arsenic form represses the capacitation of the sperm and its fusion with the egg and culminates to inhibition of fertilization.

The transcriptional activity of androgen receptor has been found to be repressed in trivalent arsenic exposure, which possibly involves ERK/AKT/NF-kB signaling pathway. Activation of ERK1/ERK2, possibly via free radicals, suppresses the function of Sertoli cells and induces apoptosis in testicular tissues (Rui et al. 2016). Prolonged exposure of arsenic leads to production of heat shock proteins (especially Hspa4l), which may exert cytoprotective effect on germ cells, and further leads to the development of resistance to arsenic-induced germ cell apoptosis (Huang et al. 2016).

5 Management of Arsenic Toxicity

The most important source of arsenic toxicity occurs via drinking water and contaminated food. Thus control of arsenic in groundwater and food samples appears of utmost requirement for prevention of arsenic-mediated toxicity. Further the treatment of acute and chronic arsenic toxicity cases can be done by chelation therapy and herbal therapy (Sharma and Flora 2018; Flora 2009).

5.1 Approaches for Improvement in Water Quality

Limiting arsenic level in groundwater in endemic regions via several measures may reduce the contamination of drinking water and edible vegetables and may reduce risk of arsenic toxicity. The improvement in quality of drinking water leads to slow reversal of some of toxicological aspects of arsenic toxicity as observed through reduced level of arsenicals in urine. Thus restricting groundwater contamination with arsenic appears as one of the putative approaches for limiting arsenic-mediated toxicity in endemic regions of arsenic toxicity. Several strategies, which could procure safe drinking water, are discussed herewith (Murphy et al. 2018).

5.1.1 Rain Water Harvesting

Harvesting of rainwater is best option to collect pure water. It can be collected during rainy season and should store in large tanks for future use. Various strategies are used by people to store rainwater. These types of methods are very useful in that area, where sufficient amount of water supply is not present and quality of water is also very poor.

5.1.2 Treatment of Surface Water

Treatment method is used where surface water is available in sufficient quantity and of good quality. Numerous methods are used for treatment of surface water including pond sand filter, slow sand filter, and filtration using pressure and then treatment by disinfectant small-scale conventional water treatment plants, and surface water treatment plants.

5.1.3 Tube Wells

In various areas of different country, deep tube wells are the only source to deliver water of acceptable quality and quantity. It has been recommended that water should be tested earlier before fitting a tube well to particular area. It should be ensured that deep wells are separated from the shallow contaminated aquifers by comparatively resistant layers. Also monthly testing of tube wells water is also suggested because arsenic concentrations in those wells could vary with time.

5.1.4 Removing Arsenic from the Contaminated Water

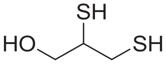
Arsenic contamination is very high in water sources in some areas, but there is no option available other than removing arsenic from drinking water. Various efforts are made to discover an economically possible and virtually operative method to remove arsenic in water. Arsenic removal plant can be the possible approach for big-diameter tube well, other than this arsenic treatment unit used for hand pumps and provide arsenic-free drinking water (Nicomel et al. 2016).

5.2 Chelation Therapy

Chelation is a kind of binding where ions are bound to a particular metal (Hatch et al. 1978). In this particular bonding, two or more discrete coordination bonds form among a multiple bonded ligand and a single central atom (Flora et al. 2008; Flora 2009). These bonded molecules are known as chelating agents.

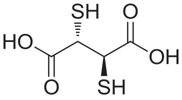
After formation of complex between metals and chelating agent, these complexes get converted into more active forms that are optically active. After the World War II, these agents were particularly used as antidotes for various metal toxicities. British anti-Lewisite (BAL) is the first chelator which was used in World War II as an antidote against Lewisite which is an arsenic-containing agent. After being tested successfully, it was used in the treatment of mercury, arsenicals, and gold toxicity. Other than this, there are several other antidotes/chelators like sodium 2, 3-dimercaptopropane-1-sulfonate (DMPS), meso-2, 3-dimercaptosuccinic acid (DMSA), and D-penicillamine (D-PA) which were discovered for the treatment of metal toxicity. Numbers of in vivo studies suggest that immediate management with BAL, DMPS, and DMSA can stop the adverse effects of inorganic arsenic (Kosnett 2013).

5.2.1 Dimercaprol



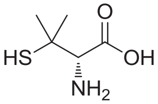
British anti-lewisite (BAL) or dimercaprol (2, 3-dimercapto-1-propanol) is a lipophilic drug that was first discovered during World War II from against Lewisite. According to the World Health Organization, it is listed as essential medicines in essential medicine list. The most operative and harmless medicine is the need of healthcare system. BAL is a dithiol compound having two sulfhydryl groups present in it, which helps in forming a stable product. It's a five-membered heterocyclic rings bound with arsenic and form nontoxic chelate. It is well absorbed in the body and eliminates rapidly due to its short half-life. BAL is an efficient chelator for acute arsenic poisoning (Flora et al. 2008; Flora and Pachauri 2010). Other than its useful effects, it itself has toxic effect to the body. LD50 of BAL for rats is around 0.85 mmol/kg and 1.5 mmol/kg in case of mice (Llobet et al. 1986). It is a well-known antidote for metal toxicity; it shows their action by presence of –SH group in its structure and participates with the thiol groups of enzymes for bonding with arsenic or other metals to form metal–chelate complex and removed out metal through urine. Sometime it exhibits adverse effect like nephrotoxicity and hypertension. BAL treatment must continue until urinary arsenic levels are less than 50 μg/L/24 h. Dose given to patients is 3–5 mg/kg i.m every 4 h for 2–10 days (Flora and Pachauri 2010).

5.2.2 Meso-2, 3-Dimercaptosuccinic Acid (DMSA)



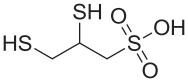
Meso-2, 3-dimercaptosuccinic acid is also known as “Succimer.” DMSA is an active form of dimercaprol and safer than dimercaprol. DMSA have four hydrogens in its structure which is ionizable at a pH 7 which makes DMSA a weak acid and thus unable to enter cells (Ding and Liang 1991). In case of lead and cadmium, meso form of DMSA binds with these metals by bonding through sulfur and oxygen atom, whereas, in case of mercury, it binds to two sulfur atoms of meso-DMSA (Rivera et al. 1989; Aposhian and Aposhian 1990). DMSA is a known antidote for lead poisoning, particularly in case of children because it has less toxicity than DMPS (Flora et al. 2007). It was effective in animal and human cases of arsenic poisoning. According to one study (Flora 1999), oxidative stress induced by arsenic in rats could be reduced by co-administration of N-acetylcysteine and DMSA post arsenic exposure. Meso-DMSA binds metal cations with the thiol groups, which ionize upon complexation. Different forms of DMSA as monoesters were synthesized and found to be more active than the parent compound. These monoesters were able to penetrate cells, target intracellular sites in the body, and effectively reduce arsenic in the cytosol. In patient, dose of DMSA should be approximately 30 mg/kg daily for 5 days which led to substantial increase in arsenic elimination with clinical improvement (Graziano et al. 1992).

5.2.3 D-Penicillamine (D-PA)



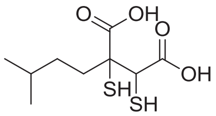
Penicillamine is a D-B, B-dimethylcysteine, obtained by degradation of penicillin, and is being used since 1957 for the treatment of lead poisoning. Currently it is replaced by DMSA for the treatment of lead poisoning. D-PA is also effective against arsenic (Jensen et al. 1991). It is absorbed rapidly from the GI tract, metabolized inside the body, and eliminated through the kidney. D-PA has been described as an actual agent in the management of arsenic poisoning. Oral administration of D-PA as a chelating agent has been reported to reduce arsenic level (Blanusa et al. 2005). Chelation of arsenicals is via sulfhydryl group present in D-PA, and enhancing arsenic removal through urine appears as a plausible protective mechanism. The recommended dose of D-PA is 25 mg/kg (Kavanagh et al. 1998). In comparison to other chelators (like DMSA, DMPS, and BAL), D-PA has been found less effective in arsenic poisoning.

5.2.4 2, 3-Dimercaptopropane-1-sulfonate (DMPS)



2, 3-Dimercaptopropane-1-sulfonic acid or 2,3-dimercaptopropane-1-sulfonate (DMPS) is a derivative of BAL. It is a modified form of 2, 3-dimercaptopropane-1-sulfonic acid as sodium salt. Occurrence of the sulfonic group reduces its solubility in water. With the help of organic anion transport pathway, it enters the intracellular compartment. Without transporter, it cannot pass through membrane and leave extracellularly (Aposhian et al. 1995; Islinger et al. 2001; Flora and Pachauri 2010). DMPS is an effective chelating agent for acute or chronic arsenic poisoning. Toxicity of DMPS is lower than that of dimercaprol and widely used in Russia and the Western world (Andersen 1999). Both DMSA and sodium DMPS have been reported to be useful in the prevention of arsenite- and arsenate-induced developmental toxicity in mice (Bosque et al. 1991; Domingo et al. 1991). Sodium DMPS binds with arsenic and forms insoluble complex. It cannot bind to intracellular component and easily eliminate through the kidney. In adults, DMPS given as oral dose of 200–400 mg daily and intravenous doses of 250 mg every 4–6 ho is recommended.

5.2.5 Monoisoamyl 2, 3-Dimercaptosuccinic Acid (MiADMSA)



Monoisoamyl 2, 3-dimercaptosuccinic acid (MiADMSA) is a new chelating agent and an analogue of DMSA (Flora et al. 2007). It has lipophilic properties and has emerged as a promising drug for the treatment of arsenic toxicity. Various analogues of DMSA were synthesized, and their efficacy was determined against arsenic intoxication. Among these analogues, monoisoamyl DMSA (MiADMSA) was found to be the most effective one and is currently under human clinical trials. Glutathione synthesis which primarily occurs in the liver and brain can be potentiated by MiADMSA administration along with significantly minimizing the level of glutathione disulfide in tissues. It has various properties like ability to cross the membrane and can be used for the treatment of both acute and chronic arsenic toxicity (Pachauri et al. 2013). MiADMSA also acts as a moderate antioxidant in view of its vicinal thiol groups. Owing to its lipophilic property, it easily enters cells, and structure has a C5 branched chain (Flora 2011; Flora et al. 2012; Dwivedi et al. 2011; Gale et al. 1993; Xu et al. 1995). MiADMSA appears more effective through oral route as compared to other routes of administration in animal model. The effective dose is 50 mg/kg (Flora et al. 2012). MiADMSA is still in the clinical developmental stage.

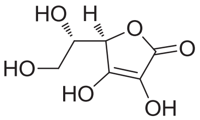
Apart from arsenic, MiADMSA has been reported to reduce copper content, which proposes its plausible use in copper toxicity. In summary MiADMSA is a drug of choice for arsenic with its better ability to blood-brain barrier permeability and lipophilicity (Mehta and Flora 2001; Mehta et al. 2006; Flora et al. 2012). It seems conceivable that MiADMSA could reduce the oxidative stress in tissues each by reducing arsenic from the target organs or by directly scavenging ROS via sulfhydryl group (Flora and Mehta 2009; Mishra et al. 2008).

5.3 Alternative or Supplementary Therapy for the Management of Arsenic Toxicity

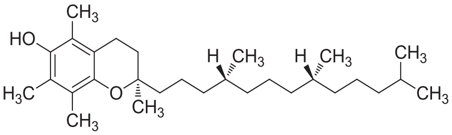
Nutrition plays an important role in preventing the appearance of symptoms of arsenicosis. Population is advised to take high energy value food from animal or plant source for preventing absorption of arsenic. It has been reported that toxicity of arsenic is mediated through free radical generation suggesting antioxidants could be an effective strategy to prevent arsenic absorption and can also be used during chelation treatment (Flora et al. 2013). Among various antioxidants, few commonly used are vitamin E, beta-carotene, and vitamin C. There are a number of animal studies that are available for their efficacy as a preventing agent in arsenicosis as antioxidants (Sharma and Flora 2018). However, no clinical data is available for their potential use in human population. The use of these drugs in market can be governed by the national policy of that country and references of the medical bodies in particular countries.

Antioxidants are known as compounds which interrupt oxidation step of various biologically related molecules by inhibiting the formation of free radicals. These antioxidants are supplied through food as nutrition. Antioxidants show a crucial role in neutralizing injury which is mainly induced through free radical generation and also treat free radical-mediated cellular damage. Arsenic shows their toxic effect by different mechanisms; out of them free radical generation or oxidative stress is one of the major mechanisms. Thus it is important to investigate different molecules that can modulate or enhance the antioxidant system of our body or reduce the generation of reactive oxygen species. In the following paragraphs, we have discussed few important natural or synthetic antioxidants which have been reported to be effective in reducing arsenic-induced oxidative stress in animal models.

5.3.1 Vitamins C and E



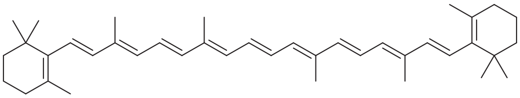
Vitamin C



Vitamin E

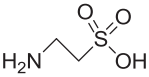
Vitamin C is also known as ascorbic acid. It is well known for its water solubility and is present as ascorbate anion in organisms. It has the scavenging action on free radicals. It also shows its effect in rejuvenation of α-tocopherol (Young and Woodside 2001). Vitamin E, also known as α-tocopherol, possesses fat-soluble vitamin. It is known as powerful endogenous antioxidants mainly found in the cell membrane. Vitamin C and vitamin E exhibit their action by discontinuing the proliferation of free radical and help in maintaining cell membranes integrity. They work together by unsaturated chains of fatty acid. Intake of both vitamins C and E simultaneously help in the recovery of DNA damage by decreasing tumor necrosis factor α (TNF-α) levels and inhibit caspase cascade activation (Ramanathan et al. 2005). Radical formation is one of the chief mechanisms of arsenic-induced toxicity. It has been put forward that ascorbic acid and α-tocopherol both can recover arsenic-induced molecular alterations (Kadirvel et al. 2007).

5.3.2 β-Carotene



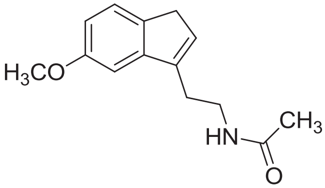
β-Carotene has isoprene units in its structure; it is the member of a carotenoids family. β-Carotene acts as a precursor for retinol which is also known as vitamin A; it has a similar activity as vitamin E due to its lipid solubility (Young and Woodside 2001). The presence of various long chains in the form of conjugation via double bonds in its structure imparts colors to carotene and responsible for its good antioxidative action. β-Carotene acts via removing oxygen-free radicals from body and sometimes diminishes their energy. A dose-response correlation has been described between serum levels of α- and β-carotene and ischemic heart disease patients. Synergistic interaction is involved for ischemic heart disease patients between duration of consuming contaminated water and low serum carotene levels. This interaction was detected with the help of multivariate analysis (Hsueh et al. 1998).

5.3.3 Taurine



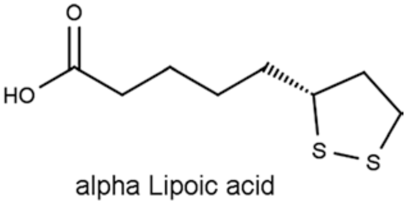
Taurine (2-aminoethanesulfonic acid) is a sulfur-containing amino acid present in the pancreas, muscle, heart, and brain (Ghosh et al. 2009). It is synthesized by the cysteine sulfinic pathway. Its sulfonic group work as zwitterions in physiological pH. It is known for its antioxidant activity act as the precursor of glutathione (Huxtable 1992). It is that compound which is not metabolized and not merged into proteins; it is suggested that it plays a vital role in cell cytosolic functioning. It is studied that taurine efficiently minimizes arsenic-induced cardiac dysfunction like ROS production, cardiomyocyte viability, calcium burden intracellularly, and apoptosis. Outcomes suggest that taurine intake can prevent arsenic-induced myocardial pathophysiology; diminish NF-κB activation via IKK, p38, and JNK MAPK signaling pathways; and signify a capable methodology for the defense of heart tissue against As-induced cardiovascular burden. Flora et al. informed the administration of taurine only expressively minimizes hepatic oxidative stress in arsenic-induced toxicity in rats (100 mg/kg) (Flora et al. 2004).

5.3.4 Melatonin



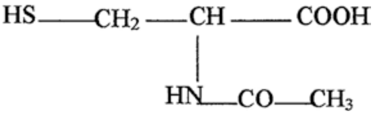
Melatonin, also called as N-acetyl-5-methoxy tryptamine, is a hormone that is produced by the pineal gland in humans and animals and regulates sleep and wake cycle. In human it regulates blood pressure, reproduction, immune system activity, and reduction of oxidative stress by acting as indirect antioxidant and free radical scavenger (Hardeland et al. 1993; Tan et al. 2000). It has been informed that melatonin is superior to other scavengers in nullifying peroxyl radicals. Pieri et al. show that melatonin have five times more activity than glutathione in scavenging free hydroxyl radicals (Pieri et al. 1994). Melatonin crosses the cell membrane because it is very small in size and highly lipophilic in nature. Some studies showed that it is an effective defender of DNA, protein, and lipids in cellular membranes. Upon activation of GPx in the brain, it delivers an indirect defense against free radical attack (Cuzzocrea and Reiter 2002). Melatonin inhibits the induction of free radical which is generated by ingestion of toxins, ionizing radiation, ischemia, and excessive exercise (Pachauri et al. 2012).

5.3.5 α-Lipoic Acid



α-Lipoic acid (LA) is a dithiol antioxidant having low molecular weight, which acts as a cofactor in numerous multienzyme complex systems in mitochondria. It also called as thioctic acid. Alpha-lipoic acid is very useful in treatment of arsenic-induced oxidative stress. It is freely absorbed from the intestine and freely absorption helps into crossing blood-brain barrier. It is provided in the diet, and it has been told that diet taken from outside rises levels of unbound lipoic acid, which acts as a potent antioxidant and reduces oxidative stress both in vitro and in vivo (Bustamante et al. 1998). In addition, LA also has metal chelating activity. According to one study, lipoic acid works as an antidote against arsenic-induced toxicity (89). Its antidote effect occurred through reducing NADH to dihydrolipoic acid (DHLA), which, being a stronger antioxidant than LA, helps in scavenging excess oxidants and recycles another antioxidants such as vitamin E, vitamin C, and glutathione. Also, LA could stimulate antioxidant defense by uplifting the levels of antioxidant molecules (like GSH) via the stimulation of phase II enzymes.

5.3.6 N-Acetylcysteine

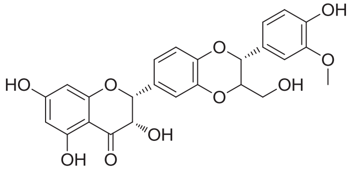


$$\mathrm{HS{-}CH_2{-}\underset{\substack{|\\ HN{-}CO{-}CH_3}}{CH}{-}COOH}$$

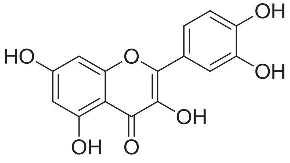
N-Acetylcysteine (NAC) is a thiol-containing compound. It is a precursor of reduced glutathione. It has mucolytic activity. It increases the synthesis of GSH and boosts glutathione S-transferase activity. As an antioxidant, it acts as a scavenger of free radicals. Various studies have been supported the protective effect of NAC in arsenic toxicity (Flora 1999). The reproductive toxicity of arsenic has been found to be reversed by cotreatment of NAC (Reddy et al. 2011), and antioxidant effect in the testes has been conversed as protective mechanism. In another study, treatment with NAC significantly reduces ROS-mediated oxidative stress in the liver of arsenic-exposed animals (Hemalatha et al. 2013). NAC treatment might act as an effective intervention to bring back arsenic-depleted GSH stores (Santra et al. 2007). Combined intake of NAC and succimer after arsenic exposure led to a significant recovery in biochemical variables, indicative of oxidative stress, and arsenic depletion from soft organs (Kannan and Flora 2006).

5.3.7 Silymarin and Quercetin

Silymarin



Quercetin



Silymarin and quercetin are polyphenolic flavonoids with antioxidant properties. They hold anticancer and cytoprotective properties and are extensively available in vegetable sources (Volate et al. 2005). Bioflavonoids, ingested through a well-balanced diet, function with expanded pharmacological actions and avoid a wide variety of human disease (Soria et al. 2007). Bongiovanni et al. (2007) investigated the effect of silymarin and quercetin on arsenite-induced oxidative stress in CHO-K1 cells and report its potential effect. Soria et al. (2007) showed the variance effects of these flavonoids in human breast adenocarcinoma cell lines. Ghosh et al. (2011) demonstrated that a QC and DMSA both combined in form of nanoparticle in a nanocapsulated drug delivery system gave enhanced therapeutic efficacy than bulk form. They showed that there nanoparticle prevents liver fibrosis, inhibits ROS generation, reestablished mitochondrial integrity, and downregulated ROS-induced signaling pathways that led the cells toward p53-dependent apoptosis (Ghosh et al. 2010).

6 Future Direction

There is no specific mechanism being suggested for arsenic toxicity, but from different studies, ROS is found to be the common pathways through which toxicity occurs. Apart from the ROS generation, there are various downstream pathways which get activated by arsenic poisoning. According to some data, it suggests that cellular functions such as proliferation, differentiation, and apoptosis might be controlled by various arsenic-induced signaling pathways.

In the future there is a need to study and discover the exact mechanisms of action along with discovering various target genes which may be involved in the mechanism of arsenic toxicity. In future there is need for an effective and economically viable diagnostic technique with some specific biomarker for early detection of the disease which can help the researcher in finding the best treatment option. Arsenic toxicity is known to be mediated through ROS generation; thus it will also be interesting to investigate new antioxidants which can act both as moderate chelator and antioxidant (Yadav and Flora 2016). Currently no such multifunctional compound is available; however, one such potential drug, MiADMSA, is currently under human trial and may be an answer to most of the concerns facing researchers (Sharma et al. 2018). Another effective strategy could be “Combination Therapy” where either two differently acting chelators could be used or a combined administration of a chelating agent and an antioxidant (natural or synthetic) may lead to better therapeutic effects in the treatment of chronic arsenic poisoning (Mittal et al. 2018).

7 Conclusion

A considerable percentage of the total populations of the world are suffering from chronic arsenicosis due to drinking arsenic-contaminated water. Understanding the chemistry behind arsenic toxicity and its mode of action depends on several factors and is quite complicated. The major determinants for arsenic to cause toxicity are valence state (trivalent/pentavalent), charge at physiological pH, extent of methylation and electrostatic attraction and repulsion to active sites on important macromolecules, and several pharmacokinetic factors like absorption, distribution, metabolism, protein binding, and excretion. With recent advances in technology and the development of animal experimental models for arsenic toxicity, the understanding of the toxicology of arsenic will continue to improve. The management of arsenic toxicity is considerably achieved through chelation therapy; however supportive treatment may provide marginal advantages. The adverse events with existing chelating agents necessitate further research for the development of effective antidote against arsenic toxicity.

References

Andersen O (1999) Principles and recent developments in chelation treatment of metal intoxication. Chem Rev 99(9):2683–2710

Aposhian HV (1997) Enzymatic methylation of arsenic species and other new approaches to arsenic toxicity. Ann Rev Pharmacol Toxicol 37:397–419

Aposhian HV, Aposhian MM (1990) meso-2,3-Dimercaptosuccinic acid: chemical, pharmacological and toxicological properties of an orally effective metal chelating agent. Ann Rev Pharmacol Toxicol 30:279–306

Aposhian HV, Maiorino RM, Gonzalez-Ramirez D, Zuniga-Charles M, Xu Z, Hurlbut KM et al (1995) Mobilization of heavy metals by newer, therapeutically useful chelating agents. Toxicology 97(1–3):23–38

Bashir S, Sharma Y, Irshad M, Nag TC, Tiwari M, Kabra M et al (2006) Arsenic induced apoptosis in rat liver following repeated 60 days exposure. Toxicology 217(1):63–70

Black MM (2008) Effects of vitamin B12 and folate deficiency on brain development in children. Food Nutr Bull 29:S126–S131

Blanusa M, Varnai VM, Piasek M, Kostial K (2005) Chelators as antidotes of metal toxicity: therapeutic and experimental aspects. Curr Med Chem 12(23):2771–2794

Bongiovanni GA, Soria EA, Eynard AR (2007) Effects of the plant flavonoids silymarin and quercetin on arsenite-induced oxidative stress in CHO-K1 cells. Food Chem Toxicol 45(6):971–976

Bosque M, Domingo J, Llobet J, Corbella J (1991) Effects of meso-2,3-dimercaptosuccinic acid (DMSA) on the teratogenicity of sodium arsenate in mice. Bull Environ Contam Toxicol 47(5):682–688

Bunderson M, Coffin JD, Beall HD (2002) Arsenic induces peroxynitrite generation and cyclooxygenase-2 protein expression in aortic endothelial cells: possible role in atherosclerosis. Toxicol Appl Pharmacol 184(1):11–18

Bustamante J, Lodge JK, Marcocci L, Tritschler HJ, Packer L, Rihn BH (1998) Alpha-lipoic acid in liver metabolism and disease. Free Radic Biol Med 24(6):1023–1039

Byron WR, Bierbower GW, Brouwer JB, Hansen WH (1967) Pathologic changes in rats and dogs from two-year feeding of sodium arsenite or sodium arsenate. Toxicol Appl Pharmacol 10(1):132–147

Chakraborti D, Das B, Rahman MM, Chowdhury UK, Biswas B, Goswami AB et al (2009) Status of groundwater arsenic contamination in the state of West Bengal, India: a 20-year study report. Mol Nutr Food Res 53(5):542–551

Chakraborti D, Rahman MM, Ahamed S, Dutta RN, Pati S, Mukherjee SC (2016) Arsenic groundwater contamination and its health effects in Patna district (capital of Bihar) in the middle Ganga plain, India. Chemosphere 152:520–529

Chakraborty AK, Saha KC (1987) Arsenical dermatosis from tubewell water in West Bengal. Ind J Med Res 85:326–334

Chen CJ, Chen CW, Wu MM, Kuo TL (1992) Cancer potential in liver, lung, bladder and kidney due to ingested inorganic arsenic in drinking water. Br J Cancer 66(5):888–892

Clarkson TW (2001) Chapter 61 – Inorganic and organometal pesticides. In: Krieger RI, Krieger WC (eds) Handbook of pesticide toxicology, 2nd edn. Academic, San Diego, pp 1357–1428

Cole SP, Deeley RG (2006) Transport of glutathione and glutathione conjugates by MRP1. Trends Pharmacol Sci 27(8):438–446

Csanaky I, Gregus Z (2001) Effect of phosphate transporter and methylation inhibitor drugs on the disposition of arsenate and arsenite in rats. Toxicol Sci 63(1):29–36

Cuzzocrea S, Reiter RJ (2002) Pharmacological actions of melatonin in acute and chronic inflammation. Curr Top Med Chem 2(2):153–165

Deeley RG, Westlake C, Cole SP (2006) Transmembrane transport of endo- and xenobiotics by mammalian ATP-binding cassette multidrug resistance proteins. Physiol Rev 86(3):849–899

Devi NL, Ch YI, Shihua Q (2009) Recent status of arsenic contamination in groundwater of northeastern India–a review. Rep Opin 1(3):22–32

Ding GS, Liang YY (1991) Antidotal effects of dimercaptosuccinic acid. J Appl Toxicol 11(1):7–14

Domingo JL, Bosque MA, Piera V (1991) meso-2,3-Dimercaptosuccinic acid and prevention of arsenite embryotoxicity and teratogenicity in the mouse. Fundam Appl Toxicol 17(2):314–320

Drobná Z, Walton FS, Harmon AW, Thomas DJ, Stýblo M (2010) Interspecies differences in metabolism of arsenic by cultured primary hepatocytes. Toxicol Appl Pharmacol 245(1):47–56

Dwivedi N, Mehta A, Yadav A, Binukumar BK, Gill KD, Flora SJS (2011) MiADMSA reverses impaired mitochondrial energy metabolism and neuronal apoptotic cell death after arsenic exposure in rats. Toxicol Appl Pharmacol 256(3):241–248

Flora SJS (1999) Arsenic-induced oxidative stress and its reversibility following combined administration of N-acetylcysteine and meso 2,3-dimercaptosuccinic acid in rats. Clin Exp Pharmacol Physiol 26(11):865–869

Flora SJS (2009) Structural, chemical and biological aspects of antioxidants for strategies against metal and metalloid exposure. Oxid Med Cell Longev 2(4):191–206

Flora SJS (2011) Arsenic induced oxidative stress and its reversibility. Free Radic Biol Med 51:257–281

Flora SJS (2017) Arsenic: exposure, toxicology, use and misuse. In: Flora SJS (ed) Encyclopedia of the anthropocene, arsenic: exposure, toxicology, use, and misuse. Reference module in earth systems and environmental sciences

Flora SJS, Mehta A (2009) Monoisoamyl dimercaptosuccinic acid abrogates arsenic-induced developmental toxicity in human embryonic stem cell-derived embryoid bodies: comparison with in vivo studies. Biochem Pharmacol 78(10):1340–1349

Flora SJS, Pachauri V (2010) Chelation in metal intoxication. Int J Environ Res Public Health 7(7):2745–2788

Flora SJ, Pande M, Kannan GM, Mehta A (2004) Lead induced oxidative stress and its recovery following co-administration of melatonin or N-acetylcysteine during chelation with succimer in male rats. Cell Mol Biol (Noisy-le-Grand, France) 50(Online Pub):Ol543–Ol551

Flora SJS, Saxena G, Mehta A (2007) Reversal of lead-induced neuronal apoptosis by chelation treatment in rats: role of reactive oxygen species and intracellular Ca(2+). J Pharmacol Exp Ther 322(1):108–116

Flora SJ, Mittal M, Mehta A (2008) Heavy metal induced oxidative stress & its possible reversal by chelation therapy. Ind J Med Res 128(4):501–523

Flora SJ, Bhadauria S, Pachauri V, Yadav A (2012) Monoisoamyl 2, 3-dimercaptosuccinic acid (MiADMSA) demonstrates higher efficacy by oral route in reversing arsenic toxicity: a pharmacokinetic approach. Basic Clin Pharmacol Toxicol 110(5):449–459

Flora SJS, Shrivastava R, Mittal M (2013) Chemistry and pharmacological properties of some natural and synthetic antioxidants for heavy metal toxicity. Curr Med Chem 20(36):4540–4547

Gale GR, Smith AB, Jones MM, Singh PK (1993) meso-2,3-dimercaptosuccinic acid monoalkyl esters: effects on mercury levels in mice. Toxicology 81(1):49–56

Gardner BM, Pincus D, Gotthardt K, Gallagher CM, Walter P (2013) Endoplasmic reticulum stress sensing in the unfolded protein response. Cold Spring Harb Perspect Biol 5(3):a013169

Ghosh N, Singh R (2009) Groundwater arsenic contamination in India: vulnerability and scope for remedy

Ghosh J, Das J, Manna P, Sil PC (2009) Taurine prevents arsenic-induced cardiac oxidative stress and apoptotic damage: role of NF-kappa B, p38 and JNK MAPK pathway. Toxicol Appl Pharmacol 240(1):73–87

Ghosh D, Ghosh S, Sarkar S, Ghosh A, Das N, Das Saha K et al (2010) Quercetin in vesicular delivery systems: evaluation in combating arsenic-induced acute liver toxicity associated gene expression in rat model. Chem Biol Interact 186(1):61–71

Ghosh S, Dungdung SR, Chowdhury ST, Mandal AK, Sarkar S, Ghosh D et al (2011) Encapsulation of the flavonoid quercetin with an arsenic chelator into nanocapsules enables the simultaneous delivery of hydrophobic and hydrophilic drugs with a synergistic effect against chronic arsenic accumulation and oxidative stress. Free Radic Biol Med 51(10):1893–1902

Graziano JH, Lolacono NJ, Moulton T, Mitchell ME, Slavkovich V, Zarate C (1992) Controlled study of meso-2,3-dimercaptosuccinic acid for the management of childhood lead intoxication. J Pediatr 120(1):133–139

Guha Mazumder DN, Chakraborty AK, Ghose A, Gupta JD, Chakraborty DP, Dey SB et al (1988) Chronic arsenic toxicity from drinking tubewell water in rural West Bengal. Bull World Health Organ 66(4):499–506

Haimeur A, Conseil G, Deeley RG, Cole SP (2004) The MRP-related and BCRP/ABCG2 multidrug resistance proteins: biology, substrate specificity and regulation. Curr Drug Metab 5(1):21–53

Hardeland R, Reiter RJ, Poeggeler B, Tan DX (1993) The significance of the metabolism of the neurohormone melatonin: Antioxidative protection and formation of bioactive substances. Neurosci Biobehav Rev 17(3):347–357

Hatch RC, Clark JD, Jain AV (1978) Use of thiols and thiosulfate for treatment of experimentally induced acute arsenite toxicosis in cattle. Am J Vet Res 39(9):1411–1414

Hays AM, Srinivasan D, Witten ML, Carter DE, Lantz RC (2006) Arsenic and cigarette smoke synergistically increase DNA oxidation in the lung. Toxicol Pathol 34(4):396–404

Healy SM, Casarez EA, Ayala-Fierro F, Aposhian H (1998) Enzymatic methylation of arsenic compounds. V. Arsenite methyltransferase activity in tissues of mice. Toxicol Appl Pharmacol 148(1):65–70

Hemalatha P, Reddy AG, Reddy YR, Shivakumar P (2013) Evaluation of protective effect of N-acetyl cysteine on arsenic-induced hepatotoxicity. J Natl Sci Biol Med 4(2):393–395

Hsueh YM, Wu WL, Huang YL, Chiou HY, Tseng CH, Chen CJ (1998) Low serum carotene level and increased risk of ischemic heart disease related to long-term arsenic exposure. Atherosclerosis 141(2):249–257

Huang C, Ke Q, Costa M, Shi X (2004) Molecular mechanisms of arsenic carcinogenesis. Mol Cell Biochem 255(1–2):57–66

Huang Q, Luo L, Alamdar A, Zhang J, Liu L, Tian M et al (2016) Integrated proteomics and metabolomics analysis of rat testis: mechanism of arsenic-induced male reproductive toxicity. Sci Rep 6:32518

Hughes JP, Polissar L, van Belle G (1988) Evaluation and synthesis of health effects studies of communities surrounding arsenic producing industries. Int J Epidemiol 17(2):407–413

Huxtable RJ (1992) Physiological actions of taurine. Physiol Rev 72(1):101–163

Islinger F, Gekle M, Wright SH (2001) Interaction of 2,3-dimercapto-1-propane sulfonate with the human organic anion transporter hOAT1. J Pharmacol Exp Ther 299(2):741–747

Jensen GE, Christensen JM, Poulsen OM (1991) Occupational and environmental exposure to arsenic – increased urinary arsenic level in children. Sci Total Environ 107:169–177

Kadirvel R, Sundaram K, Mani S, Samuel S, Elango N, Panneerselvam C (2007) Supplementation of ascorbic acid and alpha-tocopherol prevents arsenic-induced protein oxidation and DNA damage induced by arsenic in rats. Hum Exp Toxicol 26(12):939–946

Kannan GM, Flora SJ (2006) Combined administration of N-acetylcysteine and monoisoamyl DMSA on tissue oxidative stress during arsenic chelation therapy. Biol Trace Elem Res 110(1):43–59

Katiyar S, Singh D (2014) Prevalence of arsenic exposure in population of Ballia district from drinking water and its correlation with blood arsenic level. J Environ Biol 35(3):589–594

Kavanagh P, Farago ME, Thornton I, Goessler W, Kuehnelt D, Schlagenhaufen C et al (1998) Urinary arsenic species in Devon and Cornwall residents, UK. A pilot study. Analyst 123(1):27–29

Khan MM, Sakauchi F, Sonoda T, Washio M, Mori M (2003) Magnitude of arsenic toxicity in tube-well drinking water in Bangladesh and its adverse effects on human health including cancer: evidence from a review of the literature. Asian Pac J Cancer Prev 4(1):7–14

Kinoshita A, Wanibuchi H, Wei M, Yunoki T, Fukushima S (2007) Elevation of 8-hydroxydeoxyguanosine and cell proliferation via generation of oxidative stress by organic arsenicals contributes to their carcinogenicity in the rat liver and bladder. Toxicol Appl Pharmacol 221(3):295–305

Kitchin KT (2001) Recent advances in arsenic carcinogenesis: modes of action, animal model systems, and methylated arsenic metabolites. Toxicol Appl Pharmacol 172(3):249–261

Klein CB, Leszczynska J, Hickey C, Rossman TG (2007) Further evidence against a direct genotoxic mode of action for arsenic-induced cancer. Toxicol Appl Pharmacol 222(3):289–297

Kosnett MJ (2013) The role of chelation in the treatment of arsenic and mercury poisoning. J Med Toxicol 9(4):347–354

Kwong YL (2004) Arsenic trioxide in the treatment of haematological malignancies. Expert Opin Drug Saf 3(6):589–597

Leung J, Pang A, Yuen WH, Kwong YL, Tse EW (2007) Relationship of expression of aquaglyceroporin 9 with arsenic uptake and sensitivity in leukemia cells. Blood 109(2):740–746

Li GX, Pei QL, Gao Y, Liu KM, Nie JS, Han G et al (2007) Protective effects of hepatocellular canalicular conjugate export pump (Mrp2) on sodium arsenite-induced hepatic dysfunction in rats. Exp Toxicol Pathol 58(6):447–453

Li Y, Wang M, Piao F, Wang X (2012) Subchronic exposure to arsenic inhibits spermatogenesis and downregulates the expression of ddx3y in testis and epididymis of mice. Toxicol Sci 128(2):482–489

Liu J, Waalkes M (2005) Focal adhesion kinase as a potential target in arsenic toxicity. Toxicol Sci 84(2):212–213

Liu SX, Davidson MM, Tang X, Walker WF, Athar M, Ivanov V et al (2005) Mitochondrial damage mediates genotoxicity of arsenic in mammalian cells. Cancer Res 65(8):3236–3242

Liu S, Sun Q, Wang F, Zhang L, Song Y, Xi S et al (2014) Arsenic induced overexpression of inflammatory cytokines based on the human urothelial cell model in vitro and urinary secretion of individuals chronically exposed to arsenic. Chem Res Toxicol 27(11):1934–1942

Liu J, Zhao H, Wang Y, Shao Y, Zhang L, Xing M (2018) Impacts of simultaneous exposure to arsenic (III) and copper (II) on inflammatory response, immune homeostasis, and heat shock response in chicken thymus. Int Immunopharmacol 64:60–68

Liu S, Wu B, Yu Y, Shen Z (2019) Memory effect of arsenic-induced cellular response and its influences on toxicity of titanium dioxide nanoparticle. Sci Rep. 2019 9(1):107

Llobet JM, Domingo JL, Corbella J (1986) Comparison of the effectiveness of several chelators after single administration on the toxicity, excretion and distribution of cobalt. Arch Toxicol 58(4):278–281

Mazumder DN (2005) Effect of chronic intake of arsenic-contaminated water on liver. Toxicol Appl Pharmacol 206(2):169–175

Mehta A, Flora SJ (2001) Possible role of metal redistribution, hepatotoxicity and oxidative stress in chelating agents induced hepatic and renal metallothionein in rats. Food Chem Toxicol 39(10):1029–1038

Mehta A, Pant SC, Flora SJ (2006) Monoisoamyl dimercaptosuccinic acid induced changes in pregnant female rats during late gestation and lactation. Reprod Toxicol 21(1):94–103

Mishra D, Mehta A, Flora SJ (2008) Reversal of arsenic-induced hepatic apoptosis with combined administration of DMSA and its analogues in guinea pigs: role of glutathione and linked enzymes. Chem Res Toxicol 21(2):400–407

Mittal M, Chatterjee S, Flora SJS (2018) Combination therapy with vitamin C and DMSA for arsenic-fluoride co-exposure in rats. Metallomics 10(9):1291–1306

Morakinyo A, Achema P, Adegoke O (2010) Effect of Zingiber officinale (Ginger) on sodium arsenite–induced reproductive toxicity in male rats. Afr J Biomed Res 13:39–45

Mumford JL, Wu K, Xia Y, Kwok R, Yang Z, Foster J et al (2007) Chronic arsenic exposure and cardiac repolarization abnormalities with QT interval prolongation in a population-based study. Environ Health Perspect 115(5):690–694

Murphy T, Phan K, Yumvihoze E, Irvine K, Wilson K, Lean D, Ty B, Poulain A, Laird B, Chan LHM (2018) Groundwater irrigation and arsenic speciation in rice in Cambodia. J Health Pollut 8(19):180911

Nicomel NR, Leus K, Folens K, Voort PVD, Laing GD (2016) Technologies for arsenic removal from water: current status and future perspectives. Int J Environ Res Public Health 13(1):62

Ourshalimian S, Naser AM, Rahman M, Doza S, Stowell J, Narayan KMV, Shamsudduha M, Gribble MO (2018) Arsenic and fasting blood glucose in the context of other drinking water chemicals: a cross-sectional study in Bangladesh. Environ Res 172:249–257

Pachauri V, Dubey M, Yadav A, Kushwaha P, Flora SJS (2012) Monensin potentiates lead chelation efficacy of MiADMSA in rat brain post chronic lead exposure. Food Chem Toxicol 50(12):4449–4460

Pachauri V, Mehta A, Mishra D, Flora SJS (2013) Arsenic induced neuronal apoptosis in guinea pigs is Ca2+ dependent and abrogated by chelation therapy: role of voltage gated calcium channels. Neurotoxicology 35:137–145

Pal S, Chatterjee AK (2005) Prospective protective role of melatonin against arsenic-induced metabolic toxicity in Wistar rats. Toxicology 208(1):25–33

Paul DS, Harmon AW, Devesa V, Thomas DJ, Stýblo M (2007) Molecular mechanisms of the diabetogenic effects of arsenic: inhibition of insulin signaling by arsenite and methylarsonous acid. Environ Health Perspect 115(5):734–742

Pieri C, Marra M, Moroni F, Recchioni R, Marcheselli F (1994) Melatonin: a peroxyl radical scavenger more effective than vitamin E. Life Sci 55(15):Pl271–Pl276

Prakash C, Soni M, Kumar V (2016) Mitochondrial oxidative stress and dysfunction in arsenic neurotoxicity: a review. J Appl Toxicol 36(2):179–188

Rahman MA, Hasegawa H, Lim RP (2012) Bioaccumulation, biotransformation and trophic transfer of arsenic in the aquatic food chain. Environ Res 116:118–135

Ramanathan K, Anusuyadevi M, Shila S, Panneerselvam C (2005) Ascorbic acid and alpha-tocopherol as potent modulators of apoptosis on arsenic induced toxicity in rats. Toxicol Lett 156(2):297–306

Reddy PS, Rani GP, Sainath SB, Meena R, Supriya C (2011) Protective effects of N-acetylcysteine against arsenic-induced oxidative stress and reprotoxicity in male mice. J Trace Elem Med Biol 25(4):247–253

Rivera M, Zheng W, Aposhian HV, Fernando Q (1989) Determination and metabolism of dithiol chelating agents: VIII. Metal complexes of meso-dimercaptosuccinic acid. Toxicol Appl Pharmacol 100(1):96–106

Roy JS, Chatterjee D, Das N, Giri AK (2018) Substantial evidences indicate that inorganic arsenic is a genotoxic carcinogen: a review. Toxicol Res 34(4):311–324

Rui W, Guan L, Zhang F, Zhang W, Ding W (2016) PM2.5-induced oxidative stress increases adhesion molecules expression in human endothelial cells through the ERK/AKT/NF-kappaB-dependent pathway. J Appl Toxicol 36(1):48–59

Saha KC (1995) Chronic arsenical dermatoses from tube- well water in West Bengal during 1983–87. Ind J Dermatol 40(1):1–12

Saha JC, Dikshit AK, Bandyopadhyay M, Saha KC (1999) A review of arsenic poisoning and its effects on human health. Crit Rev Environ Sci Tech 29(3):281–313

Santra A, Chowdhury A, Ghatak S, Biswas A, Dhali GK (2007) Arsenic induces apoptosis in mouse liver is mitochondria dependent and is abrogated by N-acetylcysteine. Toxicol Appl Pharmacol 220(2):146–155

Sattar A, Xie S, Hafeez MA, Wang X, Hussain HI, Iqbal Z, Pan Y, Iqbal M, Shabbir MA, Yuan Z (2016) Metabolism and toxicity of arsenicals in mammals. Environ Toxicol Pharmacol 48:214–224

Schoolmeester WL, White DR (1980) Arsenic poisoning. South Med J 73(2):198–208

Sharma A, Flora SJS (2018) Nutritional management can assist a significant role in alleviation of arsenicosis. J Trace Elem Med Biol 45:11–20

Sharma A, Pachauri V, Flora SJS (2018) Advances in multi-functional ligands and the need for metal-related pharmacology for the management of Alzheimer disease. Front Pharmacol 9:1247

Sińczuk-Walczak H, Szymczak M, Hałatek T (2010) Effects of occupational exposure to arsenic on the nervous system: clinical and neurophysiological studies. Int J Occup Med Environ Health 23(4):347–355

Singh SK (2015) Groundwater arsenic contamination in the Middle-Gangetic Plain, Bihar (India): the danger arrived. Int Res J Environ Sci 4(2):70–76

Smith AH, Goycolea M, Haque R, Biggs ML (1998) Marked increase in bladder and lung cancer mortality in a region of Northern Chile due to arsenic in drinking water. Am J Epidemiol 147(7):660–669

Smitherman PK, Townsend AJ, Kute TE, Morrow CS (2004) Role of multidrug resistance protein 2 (MRP2, ABCC2) in alkylating agent detoxification: MRP2 potentiates glutathione S-transferase A1-1-mediated resistance to chlorambucil cytotoxicity. J Pharmacol Exp Ther 308(1):260–267

Soria EA, Eynard AR, Quiroga PL, Bongiovanni GA (2007) Differential effects of quercetin and silymarin on arsenite-induced cytotoxicity in two human breast adenocarcinoma cell lines. Life Sci 81(17–18):1397–1402

Suzuki T, Tsukamoto I (2006) Arsenite induces apoptosis in hepatocytes through an enhancement of the activation of Jun N-terminal kinase and p38 mitogen-activated protein kinase caused by partial hepatectomy. Toxicol Lett 165(3):257–264

Tan DX, Manchester LC, Reiter RJ, Qi WB, Karbownik M, Calvo JR (2000) Significance of melatonin in antioxidative defense system: reactions and products. Biol Signals Recept 9(3–4):137–159

Tseng WP (1977) Effects and dose – response relationships of skin cancer and blackfoot disease with arsenic. Environ Helth Perspect 19:109–119

Tseng CH (2004) The potential biological mechanisms of arsenic-induced diabetes mellitus. Toxicol Appl Pharmacol 197(2):67–83

Tsukaguchi H, Weremowicz S, Morton CC, Hediger MA (1999) Functional and molecular characterization of the human neutral solute channel aquaporin-9. Am J Phys 277(5):F685–F696

Vineetha VP, Raghu KG (2019) An overview on arsenic trioxide-induced cardiotoxicity. Cardiovasc Toxicol 19(2):105–119. https://doi.org/10.1007/s12012-018-09504-7

Volate SR, Davenport DM, Muga SJ, Wargovich MJ (2005) Modulation of aberrant crypt foci and apoptosis by dietary herbal supplements (quercetin, curcumin, silymarin, ginseng and rutin). Carcinogenesis 26(8):1450–1456

Wauson EM, Langan AS, Vorce RL (2002) Sodium arsenite inhibits and reverses expression of adipogenic and fat cell-specific genes during in vitro adipogenesis. Toxicol Sci 65(2):211–219

Westhoff DD, Samaha RJ, Barnes A Jr (1975) Arsenic intoxication as a cause of megaloblastic anemia. Blood 45(2):241–246

World Health Organization (2018) Arsenic: international programme on chemical safety, pp 1–5

Xu C, Holscher MA, Jones MM, Singh PK (1995) Effect of monoisoamyl meso-2,3-dimercaptosuccinate on the pathology of acute cadmium intoxication. J Toxicol Environ Helth 45(3):261–277

Xu W, Bao H, Liu F, Liu L, Zhu YG, She J et al (2012) Environmental exposure to arsenic may reduce human semen quality: associations derived from a Chinese cross-sectional study. Environ Health Glob Access Sci Source 11:46

Yadav A, Flora SJS (2016) Nano drug delivery systems: a new paradigm for treating metal toxicity. Expert Opin Drug Deliv 13(6):831–841

Yamanaka K, Ohtsubo K, Hasegawa A, Hayashi H, Ohgi H, Kanisawa M, Okada S (1996) Exposure to dimethylarsinic acid, a main metabolite of inorganic arsenics, strongly promotes tumorigenesis initiated by 4-nitroquinoline 1-oxide in the lungs of mice. Carcinogenesis 17:767–770

Yang C, Frenkel K (2002) Arsenic-mediated cellular signal transduction, transcription factor activation, and aberrant gene expression: implications in carcinogenesis. J Environ Pathol Toxicol 21(4):331–342

Yoshida T, Yamauchi H, Fan Sun G (2004) Chronic health effects in people exposed to arsenic via the drinking water: dose-response relationships in review. Toxicol Appl Pharmacol 198(3):243–252

Young IS, Woodside JV (2001) Antioxidants in health and disease. J Clin Pathol 54(3):176–186

Yu RC, Hsu KH, Chen CJ, Froines JR (2000) Arsenic methylation capacity and skin cancer. Cancer Epidemiol Biomark Prev 9(11):1259–1262

Yu HS, Liao WT, Chai CY (2006) Arsenic carcinogenesis in the skin. J Biomed Sci 13(5):657–666

Zachariae H, Sogaard H, Nyfors A (1974) Liver biopsy in psoriatics previously treated with potassium arsenite. A controlled study. Acta Derm Venereol 54(3):235–236

Zhang K, Kaufman RJ (2004) Signaling the unfolded protein response from the endoplasmic reticulum. J Biol Chem 279(25):25935–25938

Zheng LY, Umans JG, Yeh F, Francesconi KA, Goessler W, Silbergeld EK et al (2015) The association of urine arsenic with prevalent and incident chronic kidney disease: evidence from the Strong Heart Study. Epidimiology 26(4):601–612

Zhou Q, Xi S (2018) A review on arsenic carcinogenesis: epidemiology, metabolism, genotoxicity and epigenetic changes. Regul Toxicol Pharmacol 99:78–88

Mechanisms of Arsenic Uptake, Transport, and *in planta* Metabolism in Rice

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Abstract Arsenic (As) in food is a threat for human health, and among all cereal rice is the most important source of the metalloid through diet. The dynamic of the element and the natural ability of rice to uptake, transport, and accumulate the metalloid at grains have motivated important research to be carried out in this regard. Thus, the aim of this chapter is to draw a synthesis on the main factors which ultimately determines As content in rice, from its uptake from the soil solution to its transport, metabolism, and final accumulation in grain. The element is of natural occurrence, varying in concentration, and its chemical species are modified due to a range of factors, such as the soil redox state. Among all As species, arsenite [As(III)] is the most common in anoxic conditions, such as the ones found in flooded paddy rice fields, which form is preferred for rice root uptake. Rice is naturally efficient in As(III) uptake, compared to most crops already studied, which is mainly due to its improved ability to uptake and transport silicon, especially with the aid of aquaporins, as silicic acid and arsenite are chemically analogous. Similarly, the second most important As form, arsenate [As(V)], is mainly uptaken and transported through the phosphate way. After being uptaken, As is transported either via xylem or phloem and is loaded to the grain. Within rice tissues, the element can be metabolized, being reduced, biomethylated, complexed to other elements, or even sequestered into vacuoles. The knowledge regarding the mechanisms of As uptake, transport, and metabolization in rice allows one to draw strategies in order to mitigate the content of this element in the grains, either via management practices or also via breeding and biotechnological approaches.

Keywords As bioavailability · As content · As detoxification · As speciation · Mitigation strategies · *Oryza sativa*

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1 Introduction

Arsenic (As) is listed as a human carcinogen since 1980 by the International Agency for Research on Cancer. Its carcinogenicity is mainly related to the exposure to its inorganic forms (iAs), arsenite [As(III)] and arsenate [As(V)], which are classified as group 1 carcinogenic. The organic species (oAs) monomethylarsonic acid [MMA(V)] and dimethylarsinic acid [DMA(V)] are also potentially carcinogenic for human and are classified in group 2B (revised by Guillod-Magnin et al. 2018). Numerous studies have associated the chronic exposition to high levels of As to health adverse effects, with damages to different organs and systems. Among the diseases associated to As exposure, the most important are keratosis; skin, bladder, and lung cancers; damaged intellectual (brain) function; bronchiectasis; cardiac coronary diseases; and diabetes (revised by Lai et al. 2015).

Rice (*Oryza sativa* L.) presents a high ability in accumulating As, resulting in a concentration ten times higher than any other cereal crops already studied (revised by Guillod-Magnin et al. 2018). Thus, in populations where rice is the major dietary source, the exposure to As can be considered expressive, and the ingestion of this element can represent a significant health risk factor (revised by Islam et al. 2017).

In addition to health problems caused to humans, As presents a negative impact on rice growth and development. The As toxicity results in inhibition in adenosine triphosphate (ATP) synthesis and also culminates in oxidative stress, resulting in a significative reduction in grain yield. Furthermore, under As toxicity conditions, plants may present stunted growth, brown spots, and burned leaves (revised by Bakhat et al. 2017).

Arsenic concentration in soil varies due to its geological genesis and anthropogenic activities, which include metal mining and foundry, As-containing pesticide applications, wood conservants, food additives, and the use of contaminated water in irrigation. Arsenic exists in the environment in different inorganic and organic forms. In paddy flooded soils, the ones where rice is grown in many parts of the world, As(III) is the dominant species, comprising 63% of total As in soil, followed by As(V) with 36%, and finally the methylated (organic) forms DMA(V) and MMA(V) (revised by Mitra et al. 2017). The high concentration of iAs in anaerobic soils associated to the high ability of rice plants in capturing this element constitutes a current and highly relevant threat.

Thus, considering the menace of As contamination in rice grains, it becomes imperative to thoroughly summarize the information already available in the literature and draw a model to synthetize the mechanisms of uptake, transport, and metabolism *in planta*. In this chapter, the proteins involved in the uptake of the different As forms and their association with the uptake of other elements are presented. Chemical modifications in As molecules after being uptaken by the plant will also be described. The plant tolerance mechanisms as well as the hyperaccumulation phenomena are described in details. Furthermore, the translocation from root to shoot, mobilization via phloem, and sulfur's influence on these processes are also addressed.

2 Arsenic Species and Factors Which Affect Its Bioavailability from Soil

The total amount of As present in a given area depends on several factors. The first is related to soil genesis, being soils formed from As-rich bedrocks naturally high in As (Punshon et al. 2017). Other factors comprise any force which increases the element in an area, including natural inputs, e.g., through volcanic emissions, and anthropogenic sources, e.g., the use of As-based pesticides and metal mining, among many others (Zhao et al. 2010). In general, the higher is the total As in soil, the higher plants uptake the element; however, when As level is too high, this correlation became not valid, as high levels of the metalloid in the soil result in the restriction of the absorption of any element by plants (reviewed by Punshon et al. 2017). However, As can be present in different species, i.e., chemical forms, which strongly affect the uptake, translocation, and accumulation of the metalloid in plants and their organs (Marin et al. 1992). The most relevant As species in the context of As rice accumulation are the inorganic and more toxic As(III) and As(V) and the organic forms DMA and MMA (reviewed by Zhao et al. 2010).

A vast range of factors, including physicochemical and biological, govern the species, mobility, and bioavailability of As in soil-water systems (Kumarathilaka et al. 2018a). Rice is grown under flooded conditions in a vast area around the world, and it has a profound impact on the As biogeochemistry and bioavailability to the crop. The anaerobic conditions affect As mobility mainly by influencing As species, soil redox potential, and pH (Yamaguchi et al. 2011). In aerobic soils, As(V) is predominant; however, in anaerobic conditions, As is reduced and As(III) becomes the prevailing species. Due to its lower sorption capacity, it is followed by its desorption from soil minerals. This gives the element more mobility; however, As(V) and organic species can still be found in anaerobic soils, but in lower proportions (Stroud et al. 2011). Bacteria which reduce As(V) and oxide As(III) are also found in the soil. Arsenate reduction by microorganisms occurs through two main ways: As(V) as a final acceptor of electrons during the anaerobic respiration and the detoxification, in which As(V) is reduced to As(III) and pumped to the external side of the microbial cell (Zhao et al. 2010).

Arsenic also interacts with several elements in the soil, more importantly with sulfur (S), iron (Fe), silicon (Si), and phosphorus (P) (Zhao et al. 2010). In the geological environment, As often occurs combined with sulfur-rich minerals (Majzlan et al. 2014), and its release from these minerals depends on natural or anthropogenic processes, such as rock weathering. Regarding Fe, anaerobic conditions provoke its dissolution, and being Fe an important site for As binding, this results in higher As mobility (Yamaguchi et al. 2011). On the other hand, Fe plaque formation in rice roots has possibly also an important role, although not completely established yet, in regulating As absorption and reduction (Seyfferth 2015). Rice genotypes which release more oxygen through their aerenchyma at roots promote Fe plaque formation at the rhizosphere, which decreases As uptake. However, the oxygen released by roots can also oxidize As(III) back to As(V), which is more absorbed by the Fe plaques, i.e., the Fe plaque could keep As in proximity to the roots (reviewed in Awasthi et al. 2017). The presence of As(III)-oxidizer bacteria, such as *Acidovorax* and *Hydrogenophaga* in the Fe plaque which are involved in the As transformation, also influences the concentration of this element in the plant tissues (Hu et al. 2015). The abundance of AsO-Bac (arsenite-oxidizing bacteria) in the root ferric plaques was negatively correlated with As concentration in roots, straw, and grain, indicating that the microorganisms from the iron plaque were actively catalyzing the As transformation and decreasing the absorption of the element by rice (Hu et al. 2015).

Arsenite (as AsO_3^{3-}) is chemically similar to silicate (SiO_4^{4-}) and As(V) (AsO_4^{3-}) analogous to phosphate (PO_4^{3-}) (Zhao et al. 2010). It means that these molecules compete at the same time for retention sites on soil mineral surfaces and for transporters for uptake and translocation in the rice plant (reviewed by Bakhat et al. 2017). Phosphorus is a macronutrient, essential for plant growth, playing important physiological roles (Shen et al. 2011), and Si is a beneficial element, which helps plants to fight biotic and abiotic stresses (Meharg and Meharg 2015). Furthermore, rice is a Si accumulator, being able to contain Si at about 10% of the shoot dry weight, thanks to its highly efficient Si transporters (Yamamoto et al. 2012). The fact that As(III) and SiO_4^{4-}, and As(V) and PO_4^{3-}, compete for binding sites in soil would mean that supplying both SiO_4^{4-} and PO_4^{3-} as fertilizers would help to release more As in the soil solution, which would be more available to plant acquisition. However, research has suggested that the competition for transporters in the plant is more important in the context of As uptake, transport, and accumulation; hence, the application of SiO_4^{4-} and PO_4^{3-}, along sulfur (S) fertilizers, is highly recommended aiming decrease As accumulation by crops (Li et al. 2009; Bakhat et al. 2017).

3 Arsenic Uptake Mechanisms

The iAs uptake from the soil by plants depends on the amount and the chemical form of the element. In aerobic soils, the prevailing form is As(V), strongly sorbed in minerals from the soil, such as Fe oxides. In anaerobic soils, As(V) is reduced to As(III), followed by the desorption from the soil minerals, due to its low sorption capacity, compared to As(V); this is why As(III) is predominant in anaerobic conditions (Suriyagoda et al. 2018). As can also occur in different organic forms in the soil, being the most common the DMA(V) and MMA(V) (revised by Lomax et al. 2012).

Even though the most common arsenic forms in the soil are As(III) and As(V), in rice grains the prevailing types are As(III) and DMA(V). It is not clear yet whether plants are able to convert iAs in oAs. What is well known is the significant role that microorganisms have in this modification and that plants grown in soils without MMA(V) and DMA(V) do not present As methylated forms in their constitution (revised by Ma et al. 2017).

Comparing to other cereals, rice is the one which exhibits the highest capacity to uptake and accumulate As in different organs and grains. This behavior is due to the mobility of reduced As(III) present in anaerobic soils, characteristic of the irrigated (flooded) rice cultivation system in addition to the efficient As(III) capture mechanisms present in rice (Lomax et al. 2012). The uptake of the different As species by rice plants takes place through different processes, involving diverse proteins. In magnitude, rice plants uptake from soil As(III) > As(V) > DMA(V) > MMA(V). The capture of As(V) and As(III) occurs due to the similarity of these molecules with phosphate and silicate, respectively. Arsenate enters the root cells through phosphate transporter proteins (PHT) and As(III) through aquaglyceroporin transporter proteins from various classes and mainly via nodulin 26-like intrinsic protein, an aquaporin. DMA(V) and MMA(V) also use aquaporins to enter in the root cells (revised by Awasthi et al. 2017; Punshon et al. 2017; Suriyagoda et al. 2018). Arsenate is analogous to phosphate, interfering in phosphate metabolism (such as phosphorylation and ATP production). Arsenite binds to the protein's sulfhydryl groups, affecting their structures or catalytic capacity (reviewed in Awasthi et al. 2017).

In rice, the gene family *Pht1* (*OsPT1*-*OsPT13*) encodes for Pi transporters which are located on the plasma membrane (Ye et al. 2017). The As(V) uptake is performed through the transporters OsPHT1;8 (OsPT8) (Wu et al. 2011; Wang et al. 2016), OsPHT1;1 (OsPT1) (Kamiya et al. 2013) and OsPHT1;4 (OsPT4) (Cao et al. 2017; Ye et al. 2017). Rice mutants for *ospt8* showed reduction of 33–57% in As(V) uptake and increased significantly the tolerance to this form of the metalloid, with a 100-fold or higher increase in root length, demonstrating that the uptake of As(V) via OsPHT8 exercises a pronounced toxic effect in root elongation (Wang et al. 2016). The *ospt1* rice mutant presented a reduction in 60% in the As content in the plant (Kamiya et al. 2013). Further, *ospt4* mutants accumulated 16–32% less As and still observed that the xylem of the mutants presented 20–40% less As comparing to the wild types (Cao et al. 2017).

It has been reported that PHT transporters are unidirectional, carrying out the influx of As(V) from soil to root cells (revised by Abbas et al. 2018). In addition to PHT proteins, other proteins can act on As(V) uptake, such as the transcription factor phosphate starvation response 2 (OsPHR2) and phosphate transporter traffic facilitator 1 (OsPHF1) (Wu et al. 2011). The As(V) transport from roots to shoots also occurs through different PHTs (revised by Awasthi et al. 2017).

Aquaporins are membrane channels belonging to the major intrinsic protein (MIP) family. MIPs are classified into three subgroups: aquaporins (AQPs) or specific water channels; glycerol facilitators (GlpFs) permeable to small solutes, such as glycerol; and aquaglyceroporins, a channel permeable to water, glycerol, and small solutes (revised by Thomas et al. 2002). Plant aquaporins are classified in four subfamilies according to their location and homology: plasma membrane intrinsic proteins (PIPs), tonoplast intrinsic proteins (TIPs), nodulin 26-like intrinsic membrane proteins (NIPs), and small and basic intrinsic proteins (SIPs) (Ma et al. 2008).

Aquaporins present an aromatic/arginine (ar/R) region, which acts as a filter for subtract selection. According to the ar/R region, NIPs were divided into NIP I, NIP II, and NIP III. Members belonging to these three subgroups present ability to uptake As(III), however, in different quantities (Ma et al. 2008).

In rice, low silicon 1 (OsLsi1, also named OsNIP2;1) is a silicic acid NIP III aquaporin transporter, which can also inadvertently capture As(III), MMA(V), and DMA(V). In terms of magnitude, OsLsi1 captures As(III) > MMA(V) > DMA(V) (Punshon et al. 2017). Other members of the NIP family also capture As(III), however, at lower rates than OsLsi1 (Ma et al. 2008). OsLsi1 transporter is bidirectional performing in root cells the influx and efflux of As(III), i.e., As(III) can be transported depending on the difference of As concentration between roots cell and soil (revised by Abbas et al. 2018). OsLsi2 is a transporter which is not involved in the As(III) influx to the root cells, but instead in the efflux of this molecule to xylem, being directly associated with the As accumulation in rice grains (Ma et al. 2008). OsLsi1 and OsLsi2 are located on the plasma membrane of root exodermic cells, where the Casparian strips are found. However, with different polar localization, since OsLsi1 locates at the distal side of the cell and OsLsi2 at the proximal side (revised by Zhao et al. 2009; Chen et al. 2017). Rice *oslsi1* mutants present a significant decrease in As(III) uptake, and *oslsi2* mutants show an expressive reduction of As(III) content in xylem, aerial organs, and grains. Thus, it is verified that OsLsi2 has a more pronounced impact on the As(III) accumulation in rice grains than OsLsi1 (Ma et al. 2008).

Some studies have reported the involvement of PIP aquaporins, including OsPIP2;4, OsPIP2;6, and OsPIP2;7 in As(III) uptake and transport. Other transporters, such as OsNRAMP1 (natural resistance-associated macrophage protein 1), have also been suggested as having roles in the uptake and transport of As(III) (revised by Awasthi et al. 2017).

The uptake of methylated (organic) As forms (oAs) is slower than the uptake of the inorganic forms; however, the translocation of the methylated forms is faster than the others. Some organic As species are transported from the soil to xylem via influx Si transporters (Lsi1) and efflux Si transporters (Lsi2) (revised by Abbas et al. 2018). The mechanisms of movement *in planta* are discussed deeper in the Sect. 5 of this chapter.

4 Arsenic Metabolism in Plant

4.1 Arsenate Reduction

Speciation analysis of As in plant tissues demonstrates that the most prevailing form found is As(III), even in plants exposed to As(V) (Zhao et al. 2009), demonstrating a high As(V) reduction capacity. In a study with plants grown in hydroponic conditions with nutritional solution supplemented with As(III) or As(V), it was verified that As(III) remained stable; however, As(V) was rapidly reduced to As(III). Thus, As(III) represented from 92% to 99% of the total amount of As found in rice roots (Xu et al. 2007). Both roots and shoots are able to reduce As(V); however, roots are more important, considering that As(III) is the most abundant form found in xylem of many different plant species (reviewed in Zhao et al. 2010).

Rice presents two genes encoding for As(V)-reductase, viz., *OsACR2.1* and *OsACR2.2*, which are involved in the reduction of As(V) (Duan et al. 2007). The products of these genes were purified from *E. coli* and demonstrate the capacity to reduce As(V) to As(III) in vitro, being OsACR2.1 the one which presented higher reductase activity comparing to OsACR2.2; however, both presented phosphatase activity. The expression of *OsACR2.1* in the plant increased significatively after the As(V) exposure, while *OsACR2.2* was expressed only in roots exposed to As(V) and in less quantity comparing to *OsACR2.1*. The genes, *OsHAC1;1* and *OsHAC1;2* (*high arsenic content 1*), were also identified as As(V)-reductases in rice (Shi et al. 2016). *OsHAC1;1* and *OsHAC1;2* were able to reduce As(V) to As(III) and, when expressed in *E. coli* deficient in As(V)-reductases, reestablished the As tolerance. When *OsHAC1;1* and *OsHAC1;2* were overexpressed, a significant increase in the As(III) efflux to the medium and lesser accumulation of As in rice were reported. Furthermore, a decreased amount of As was identified in the grains of the studied lines.

Glutaredoxin also plays an important role in As(V) reduction, regulating the As(III) levels in the cell; however, the complete mechanism is not well known yet (reviewed in Zhao et al. 2009). Two rice glutaredoxins, OsGrx_C7 and OsGrx_C2.1, were expressed in *E. coli* mutant strains, in yeast, and in *A. thaliana* and were important in response to As stress (Verma et al. 2016). OsGrxs expressed in *E. coli* promoted tolerance to As(V) and As(III) and in yeast demonstrated less As(III) intracellular accumulation and higher extracellular glutathione (GSH) accumulation. An in vitro experimentation showed that purified OsGrxs glutaredoxin presents similar activities of GSH-disulfide oxidoreductase, glutathione reductase, and As(V)-reductase.

Recently, it was reported the role of the vacuolar phosphate transporter (VPT) in As(V) tolerance in *A. thaliana* (Luan et al. 2018). The *vpt1* mutant presented tolerance to As toxicity and lesser As accumulation, while VPT1-overexpressing lines were more sensible to the stress and presented more As accumulation, comparing to the corresponding wild type. For plants which were grown under optimal Pi conditions, the loss of function of the VPT1 increased the levels of Pi in the cytosol, which suppress the expression of the PHT1-type (*phosphate transporter1*), decreasing the As accumulation, which is chemically similar to Pi and enters into the cell through Pi transporters.

4.2 Arsenic Complexation and Sequestration

4.2.1 Methylation

Biomethylation of the As species has been considered a potential detoxification mechanism in microorganisms. This process results in the conversion of inorganic and toxic As to the less toxic MMA(V), DMA(V), trimethylarsenic oxide [TMAO(V)], and trimethylarsine [TMAs(III)] (Rahman and Hassler 2014). The intermediate trivalents are structurally different from the pentavalent ones, and they are more reactive and less carcinogenic (reviewed in Bastías and Beldarrain 2016). It was demonstrated that As(III) is tenfold more toxic than As(V) and that monomethylarsonite [MMA(III)] and dimethylarsonite [DMA(III)] are more toxic than As(V) and As(III) (Rahman and Hassler 2014). However, As(V) and As(III) are more toxic than MMA(V) and DMA(V). Finally, TMAO is the less toxic As form, among the most common forms.

The As methylation mechanism was described via Challenger, in studies with fungus (Zhao et al. 2010). In this system, As(III) is the initial substrate for methylation catalyzed by S-adenosylmethyltransferase (ArsM) using as methyl group donor, S-adenosyl-L-methionine. ArsMs are able to methylate As(III) sequentially in mono-, di-, and trimethyl generating as the final compost the TMA gas, which is volatilized. Enzymes involved in As methylation were detected in prokaryotic and eukaryotic cells (reviewed in Chen et al. 2017). The encoding gene for As(III) S-adenosyl methionine methyltransferase (ArsM) was identified in the bacteria *Rhodopseudomonas palustris* and catalyzes the formation of methylated As intermediates, viz., DMA(V) and TMAO, resulting in TMAs(III), a gas, as the final product. In the seaweed *Cyanidioschyzon merolae*, two ArsM enzymes were identified, and in mammals, AS3MT, homologous to the ArsM bacterial, was also identified. Transgenic rice expressing RpArsM (Rp – *Rhodopseudomonas palustris*) was able to produce methylated As and presented tenfold more volatile As compared to wild type (Meng et al. 2011). Arsenic accumulation in rice grains was lower in T1 generation, including As(III) and As(V) concentration.

Rice grain may contain organic and inorganic As forms. Arsenite and DMA are the more typical ones. In addition to these forms, rice can present As(V), MMA, and occasionally tetramethylarsonate. There are still reports of the presence of arsenobetaine (AsB) and arsenocholine (AsC) (reviewed in Bastías and Beldarrain 2016). However, some investigations showed that plants supplied with only iAs in hydroponic conditions presented small amounts of methylated species in their tissues and xylem, giving evidences on the As biomethylation in plants, even though at low levels (reviewed in Zhao et al. 2010). However, it has been reported that rice is not able to methylate inorganic As in vivo; thus the methylated species should have been originated from the rhizosphere, via microbial methylation (Lomax et al. 2012; Jia et al. 2013).

Rice genome presents genes which encode for proteins with the UbiE/Coq5 motif, belonging to the same protein family as the bacterial genes ArsM (Norton et al. 2008). However, no As methyltransferase enzyme has been identified so far. Rice absorbs methylated As through the OsLsi1 transporter, which transports SiO_4^{4-} and As(III) (Li et al. 2009).

A recent study demonstrated that the reduction and complexation at roots are important steps for As(V) and MMA(V) metabolism in rice, but not for DMA(V) (Mishra et al. 2017). As(V) and MMA(V) induced the thiols synthesis in rice, and a diversity of complexes As(V)-thiol and MMA(V)-thiol was formed in rice roots, including various homologous of GSH and phytochelatins (PC). Furthermore, the predominance of MMA(III) in roots and shoots was reported and demonstrated that during the growth period, the rice plant can accumulate high levels of MMA(III) in tillers, which can also be transported to grains.

4.2.2 Tolerance and Detoxification Mechanisms

After entry into cells, metals and metalloids form complexes, by binding to metals, which include GSH, PCs, metallothioneins, nicotianamine, organic acids, and amino acids. GSH and PCs present high affinity for binding to metals due to their thiol groups (reviewed in Zhang et al. 2018). As(III) possesses high affinity with the sulfhydryl (-SH) groups of the thiol peptides of GSH and PCs, and when complexed to them, As(III) is detoxified in the plant (Pal and Rai 2010; Batista et al. 2014). GSH is synthetized in two steps: in the first, the dipeptide γ-glutamylcysteine (γ-EC) is produced from L-glutamate and L-cysteine, in an ATP-dependent reaction, catalyzed by γ-EC synthetase (γ-ECS). GSH is synthetized in two steps: 1) the dipeptide γ-glutamylcysteine (γ-EC) is produced from L-glutamate and L-cysteine, in an ATP-dependent reaction, catalyzed by γ-EC synthetase (γ-ECS); 2) one glycine is added to the C-terminal dipeptide portion, thus producing glutathione, in an ATP-dependent reaction, catalyzed by glutathione synthetase (Hell and Bergmann 1990). PCs are synthetized through the transpeptidation of the GSH γ-glutamylcysteinyl peptides by the catalytic activity of the PC synthase (PCS) (Pal and Rai 2010). Rice genotypes exposed to stress by As(V) and As(III) presented differences in the expression of some transporters, such as GST (Glutathione S-transferase – catalyzes the conjugation of the reduced form of glutathione with toxic substrates for detoxification) and γ-ECS including the PCS which were upregulated in the genotype which accumulated more As(V) and As(III) (Rai et al. 2011).

It was demonstrated that the CRT transporter (chloroquine resistance transporter) like from rice, OsCLT1, presents an important role in the GSH homeostasis, probably mediating the exportation of γ–EC and GSH from plastids to the cytoplasm. The *Osclt1* mutant exhibited lower PC contents, when treated with As, resulting in lower As accumulation in roots and high or similar accumulation in shoots (Yang et al. 2016). Overexpression of genes encoding for enzymes involved in PC synthesis increases the tolerance and accumulation of metals in plants. The overexpression of *OsPCS1* under the control of the 35S promoter from CaMV (Cauliflower mosaic vírus) in rice decreased As accumulation in grains (Hayashi et al. 2017). The reduction of As accumulation in rice grains was attributed to the expression of *OsPCS1* in other tissues, blocking the As translocation to grain by the action of OsABCC1, which acts sequestering As into vacuole. T-DNA knockout lines of *OsPCS1* presented sensitivity to higher As(III) accumulation, highlighting even more the importance of PCs in As translocation (Uraguchi et al. 2017). Two genes encoding for PCS were identified in rice, viz., *OsPCS1* and *OsPCS2*, being the first more sensitive to As activation than the latter (Hayashi et al. 2017).

Inside the vacuole, As is mainly sequestered when in PC-As or GSH-As complexes, in this way, the transporters responsible for sequestering these complexes present a crucial role in As detoxification (Batista et al. 2014; Zhang et al. 2018).

As(III) sequestering by the vacuole is mediated by a transporter, member of the ABC transporter family (ATP binding cassette) (reviewed in Briat 2010). After being chelated by PC, As can be sequestered to vacuole, mediated by the C-type ABC transporter (ABCC). In rice, a similar ABC transporter, OsABCC1, is needed for the As(III)-PC vacuolar sequestering and As detoxification, reducing As accumulation in grains (Batista et al. 2014; Song et al. 2014). Knockout of *OsABCC1* increased As sensitivity. In roots, *OsABCC1* is expressed in the exodermis and pericycle. However, *Osabcc1* did not present decreases in As accumulation comparing to the wild type, probably due the absence of OsABCC1, resulting in rise of As toxicity and inducing the biosynthesis of thiol compounds which bind As in the cytoplasm. On the other hand, in shoots, *Osabcc1* presented decreases in As accumulation in the node I but increased the As allocation to flag leaf and grain. These findings suggest that OsABCC1 constraints As translocation to grain by sequestering the element into the vacuoles of the phloem companion cells in rice nodes.

A recent work demonstrated that sequestering As into vacuole of root and phloem cells inhibits the As translocation for the grain (Deng et al. 2018). For this purpose, a transgenic rice line expressing *ScYCF1* (*Saccharomyces cerevisiae yeast cadmium factor*) and *OsABCC1* genes, the ones involved in As sequestering into the vacuole, under the control of the *RCc3* promoter (*root-specific cDNA clone3*) in the radicular cortex and internodal phloem cells and the bacterial gene for γ-glutamylcysteine synthetase controlled by the maize ubiquitin, was tested. These transgenic plants presented decreased As translocation from root to shoot and from internodal phloem to the grain. It was reported also a decrease in 70% in As accumulation in rice without affecting agronomic traits.

Sulfur helps in As detoxification through binding As(III) to thiol-rich peptides. This mechanism also contributes in keeping As in roots, restricting its translocation to tillers (Rai et al. 2011). The involvement of S in preventing As toxicity was also demonstrated in other study, in which S treatment (5.0 mM) in plants increased As accumulation in roots due the complexing of As with thiolic ligands as nonprotein thiols and PCs, which restricted As translocation to shoot (Dixit et al. 2015). Moreover, enzymes involved in the S assimilation pathway and downstream thiolic metabolites were upregulated with the increase of S supplementation. The decrease of the transcription of *Lsi2*, which product is an As(III) transporter, is probably the reason for the lower As content in the shoot.

Through As(III) complexing with thiol groups for transportation to the vacuole, a strategy is to express ABC transporters and PCS simultaneously, which can maximize As sequestering to vacuole as well as the utilization of root-specific promoters which can control the expression of genes in the development of rice genotypes presenting low As grain content (Chen et al. 2017).

4.2.3 Hyperaccumulation

The engineering for As hyperaccumulation depends basically on the development of plants which are more tolerant to As in a way to accumulate biomass and plants which have the ability to store significantly more As in the surface or any organ or tissue which do not direct As for the grain (Dhankher et al. 2002). In these plants, the formation of complexes As(III) with GSH and PC and the transportation into the cellular vacuoles of roots and shoots constitute an important mechanism to deal with As stress (Souri et al. 2017). Despite diverse plants are able to hyperaccumulate and detoxify high levels of potentially toxic elements, few species are known as As hyperaccumulators, such as *Pteris vittata*, *P. criteca*, *P. longifolia*, *P. umbrosa*, and *Pityrogramma calomelanos* (reviewed in Kumar et al. 2015).

In order to develop plants able to accumulate As in their surface, the co-expression of two bacterial genes was performed in *A. thaliana*, viz., *arsC* and *γ-EC*, under the control of the leaf-specific promoter of the rubisco's small subunity (Dhankher et al. 2002). The gene *arsC* produced the reduction of As(V) to As(III) in leaves and conferes to the plant the potential of complexing As with the thiol groups in the surface. The product of the *γ-EC* gene acts in the synthesis of the γ-EC dipeptide, the first enzyme involved in the PC synthesis. The hybrid line *ArsC9* + *γ-EC* presented a substantially lower concentration of As when comparing to the corresponding wild type.

Oxidative stress induced by the reactive oxygen species production is one of the main toxic effects of As; however, strong oxidative forces in hyperaccumulating plants can constitute an important detoxification strategy (Souri et al. 2017). Souri and co-workers (2017) describe diverse studies which show a positive correlation between an improved antioxidant capacity, especially in the cover regions of the plant, and the tolerance to As and other metals in hyperaccumulating plants.

4.2.4 Molecular Strategies for Developing Rice with Less As Grain Content

Chen and co-workers (2017) described some genes in rice that can be used for genome editing using the CRISPR/Cas9 (cluster regularly interspaced short palindromic repeats-associated nuclease Cas9) technology, aiming the development of a rice genotype with lower As accumulation. *OsPht1:8*, *Lsi1*, and *Lsi2* are involved in the uptake and As transportation, and *OsPT4* was also reported as a potential candidate for obtaining rice genotypes with less As content (Ye et al. 2017). *OsPT4* overexpressing lines presented sensitivity to As when grown in hydroponic system supplemented with As(V). However, *OsPT4* CRISPR lines presented an opposing phenotype. Regarding As accumulation, *OsPT4-ox* increased twofold in this element in shoots and roots, As absorption in 23–45% and 22–30% in straw and grain. In OsPT4-cr lines, As accumulation decreased 17–30% comparing to the wild type.

However, other strategies can be applied, based on the understanding of the expression profile of genes differentially expressed in rice when subjected to As stress, taking into account the differences in absorption and As metabolism in rice genotypes. In this regard, the identification of rice genotypes contrasting for As accumulation, association, and QTL mapping is also important (Tuli et al. 2010). Diverse studies have focused on the transcriptional, metabolic, and proteic alterations in plants under stress by As; the mechanisms involving the transportation, translocation, and detoxification of hyperaccumulator plants comprise an important source of information to deal with this stress (Souri et al. 2017).

5 As Translocation *in planta*

After being captured by rice roots, As may be translocated to many different parts of the plant, just as occur to many other elements, including essential, beneficial, and even other toxic elements. It is an important part of the "journey of this element from soil to the rice grain" (Awasthi et al. 2017). The literature on this theme is growing constantly; however, some mechanisms are still unknown, and others were only studied in arabidopsis or other species; thus for rice these aspects have to be further investigated (Kumarathilaka et al. 2018b).

It is important to mention that the uptake from soil and translocation within the plant may be performed by similar mechanisms, i.e., same transporters (Kumarathilaka et al. 2018b). However, as the uptake was discussed in the third section of this chapter, in this part, we aim to present and discuss the mobilization of this element after being captured by plants. This mobility deserves special attention, because understanding the features of the process can be a key knowledge to drive efficient management and breeding strategies (including biotechnological approaches) in the aim of mitigating the content of As in rice grains, which is, ultimately, the last objective of investigating the problem. In other words, the literature has suggested an expressive number of strategies which could be applied in order to decrease As in rice grains, being the translocation of the element already captured by plant to other tissues in detriment to the grain one of the most promising (Punshon et al. 2017).

An important motivation for this is that although rice is remarkably efficient in As uptake from soil when comparing to most other crops, as already discussed in Sect. 3 of this chapter, fortunately from the human consumption point of view, most of these As do not reach the grain, being "dispersed during the journey" from soil to grain (Lindsay and Maathuis 2017). In fact, after being captured by plant, firstly most of the As remains in the roots, and secondly it is accumulated in stems – with special importance of the upper nodes and leaves, then grain husks, and finally the grain (Zhao et al. 2009; Batista et al. 2014; Chen et al. 2015, 2017). Among the reasons for that is the As metabolism in the plant, which was discussed in Sect. 4 of this chapter, in which As is complexed to other forms, affecting its mobility, or sequestered. Part of the remaining points will be addressed here.

As earlier exposed in this chapter, As can be present in different chemical forms (presenting different levels of toxicity), which strongly determines differences during the mobilization between tissues and organs (Marin et al. 1992; Awasthi et al. 2017). The fact that As(III) is analogous to silicate and As(V) to phosphate means that for translocation *in planta*, As shares the pathways of the respective analogous elements, just as occur for uptake (reviewed by Suriyagoda et al. 2018).

An interesting contrast between As uptake and translocation is that the As species most efficiently captured from the soil (the inorganic forms) are not the most efficiently translocated inside the plant and especially to the grain, being in this case the organic forms, mainly DMA (reviewed by Zhao et al. 2013 and Awasthi et al. 2017). To magnify this contrast, it has been shown that regarding uptake, DMA(V) is captured from soil in a rate of one twentieth of that of As(III); however the translocation to the rice grain is around 100-fold more efficient (Abedin et al. 2002; Lomax et al. 2012).

The mobility of As species in rice plants follows the order: DMA(V), followed by MMA(V), and only then the inorganic forms (reviewed by Kumarathilaka et al. 2018b). To illustrate it, Zhao et al. (2012), by labeling As(III) with ^{73}As radioactive tracer, showed that only 10% of the As(III) captured by roots were distributed to shoot, mainly in leaves and stems, and about 3.3% reached the grain. Literature has suggested reasons for that. One is that while As(III) is translocated to rice grain primarily via the phloem pathway, DMA is transported to grain via both the phloem and xylem pathways (Carey et al. 2010). Also, from feeded cut flag leaves, DMA and MMA were efficiently translocated to rice grain, whereas As(V) was reduced to As(III) and retained in this tissue (Carey et al. 2011a, b). Other reasons are related to As metabolism, in which As(III) is suggested to be readily complexed by thiol compounds such as PCs and sequestered in the vacuoles, resulting in decreased mobility within the plant tissue (Liu et al. 2010; Song et al. 2010), whereas for DMA(V), there is a lack of complexing (Kumarathilaka et al. 2018b) (see Sect. 4 for a more detailed discussion on As metabolism).

5.1 As Mobilization from Root to Shoot

In general, the translocation of As from root to shoot can be considered inefficient in rice, being the ratio shoot/root of As concentrations ranging from 0.11 to 0.31 (Marin et al. 1992; Zhao et al. 2009). Considering that As is also toxic to the plant (Sharma 2012), it has been suggested that keeping the metalloid away from photosynthetic tissues is possibly an important strategy that lets some plant species tolerate As (Lindsay and Maathuis 2017).

After arsenic is uptaken by roots, many transporters are involved in its translocation. The element uses both active and passive ways to move along the plant, i.e., transporters that, respectively, use and do not use energy of the metabolism; however the extent of the contribution of each of these types in moving As is a question to be still answered (Kumarathilaka et al. 2018b). All major forms of As can be translocated from roots to shoot via xylem, being As(III) the prevailing form in this sap (reviewed by Zhao et al. 2009 and Suriyagoda et al. 2018).

Transporters are required, though, to load the element inside xylem. As(V) is presumably loaded through Pi transporters and As(III) by aquaporins (Verbruggen et al. 2009). Wu et al. (2011) performed an extensive study investigating the contribution of the Pi transport pathway in As mobilization in rice, and they found that the overexpression of the phosphate transporter OsPht1;8 increased the xylem loading of As(V). Other regulators of phosphate transport, viz., OsPHF1 (phosphate transporter traffic facilitator 1) and PHR2 (phosphate starvation response 2), also have an effect on As(V) transport (Wu et al. 2011). On the other hand, for As(III) the OsLsi2 (OsNIP2;1) transporter was found as involved in xylem loading (Ma et al. 2008; Fleck et al. 2013) as well as OsNRAMP1 – natural resistance-associated macrophage protein transporter (Tiwari et al. 2014). For organic As, much less is known about the translocation within the plant, comparing to iAs (Zhao et al. 2013). A recent study has shown that OsPTR7 (OsNPF8.1), a putative peptide transporter in rice, is involved in DMA(V) long-distance transport and thus accumulation in rice grain (Tang et al. 2017) also suggested for MMA(V) (Kumarathilaka et al. 2018b). An important point to highlight is that although As(V) and As(III) share, respectively, the phosphate and silicate ways, both As forms are less mobile than phosphate and silicate.

5.2 Phloem Transport

The last step regarding the accumulation of As in rice is the translocation to the grain. Arsenic, as well as most of other elements, including nutrients, is transported to rice grains mainly via the phloem (Carey et al. 2010, 2011a, b), by transporters situated in upper steam nodes (Song et al. 2014; Chen et al. 2015). Xylem plays a minor role in delivering nutrients, which includes other elements such as As, to developing seeds, possibly due to limited transpiration rate of these tissues (Bauer and Hell 2006).

For phloem loading, OsPHT1;8 and OsPHT1;1 have been suggested for As(V) and OsPTR7 for DMA(V) and MMA(V); however for As(III), transporters have still to be investigated, being suggested that inositol transporters (INT), already found in arabidopsis (Duan et al. 2016), could play similar role in rice (reviewed by Kumarathilaka et al. 2018b). Finally, for grain loading, As(V) is transported through OsPHT1;8 and DMA(V), and MMA(V), through OsPTR7. Once more, for As(III) inositol transporters (INT) and OsNIP2;2 can only be suggested as transporters, as further studies are required in rice to better elucidate this mechanism (reviewed by Kumarathilaka et al. 2018b).

Stem nodes have been proved to be of high importance for As storage and transport in rice. They have been suggested to act as a filter restricting As(III) distribution to grains being Lsi2 (OsNIP2;1) the transporter which plays a decisive role in this process (Chen et al. 2015). Also, OsABCC1, located at the tonoplast in the phloem cells from the node, was shown as responsible for the sequestration of As(III)–PC (As complexed) in the vacuoles (Song et al. 2014).

It is well known that there is a symplastic discontinuity between the maternal (plant) and the filial (seed) tissues, which could affect the As deposition in grains. DMA(V) has been proved to be several times more mobile to grain than any inorganic As form (Carey et al. 2010). Furthermore, DMA(V) not only reaches the grain more expressively but also permeates readily in the endosperm, whereas As(III) shows a strong tendency to accumulate in the ovular vascular traces, located on the surface of the grain (reviewed by Zhao et al. 2013).

In summary, rice grains, especially polished rice, tend to present a higher content of DMA(V) in comparison with As(III), As(V), and MMA(V). The positive aspect of this information is that DMA(V) is expressively less toxic for human consumption than the inorganic forms, and in addition to the small amount of total As which usually reaches the rice grain, it is suggested that DMA(V) in rice would not be a very high cause of concern regarding health risk (Zhao et al. 2013).

5.3 Sulfur's Influence on As Accumulation in Rice

As earlier discussed, As and S present a strong relationship in soil (Majzlan et al. 2014). In the same way, in the journey from soil uptake to the final deposit, S has been found to affect As acquisition, translocation, and accumulation in rice (Zhang et al. 2011; Dixit et al. 2015; Hashimoto and Kanke 2018). The element plays a crucial role in As regulation through complexation of As by S-containing ligands GSH and PCs (Mishra et al. 2013). These As-thiol complexes are subsequently transported to vacuoles as an As detoxification process (Song et al. 2010).

Considering the importance of S in As regulation and taking also into account that it is an essential nutrient for plant growth, S mineral fertilization has been broadly suggested as an important mitigation alternative for reducing As in rice grain (Bakhat et al. 2017).

6 Final Considerations and Future Perspectives

Arsenic in rice has been considered a menace for consumers worldwide, deserving especial attention regarding the development of different strategies in the aim of mitigate this situation. Numerous strategies have been suggested with this aim, such as related to water and soil management, e.g., supplying silicate and phosphate fertilizers and the cultivation under rainfed conditions, and postharvest management, e.g., polishing the grain and even cooking it with an extra volume of water. On the other hand, another group of strategies comprise the development of improved rice cultivars, able to deal with the As in the soil, either by minimizing the absorption from soil or by the reduction of the translocation to the grain, through sequestering the element into other tissues.

Understanding the mechanisms involved in the uptake and transport of As in rice, as presented and discussed in the present chapter, is of fundamental importance for rice breeders to define specific targets in breeding programs. These genotypes can be obtained through biotechnology techniques, such as plant transformation and gene editing. Mutation breeding is also a powerful tool. In addition, it could be achieved through conventional approaches, via hybridizations, generation advancing, and selection of superior lines, requiring, though, genetic variability in rice germplasm. It has to be pointed out that more than probably, integrating different breeding approaches, in addition to improvements in management, will lead to advances in mitigating the problem of the presence of As in rice, one of the most important staple food for humankind.

References

Abbas G, Murtaza B, Bibi I, Shahid M, Niazi NK, Khan MI, Amjad M, Hussain M, Natasha (2018) Arsenic uptake, toxicity, detoxification, and speciation in plants: physiological, biochemical, and molecular aspects. Int J Environ Res Public Health 15:59

Abedin MJ, Feldmann J, Meharg AA (2002) Uptake kinetics of arsenic species in rice plants. Plant Physiol 128:1120–1128

Awasthi S, Chauhan R, Srivastava S, Tripathi RD (2017) The journey of arsenic from soil to grain in rice. Front Plant Sci 8:1007

Bakhat HF, Zia Z, Fahad S, Abbas S, Hammad HM, Shahzad AN, Abbas F, Alharby H, Shahid M (2017) Arsenic uptake, accumulation and toxicity in rice plants: possible remedies for its detoxification: a review. Environ Sci Pollut Res Int 24:9142–9158

Bastías JM, Beldarrain T (2016) Arsenic translocation in rice cultivation and its implication for human health. Chil J Agric Res 76:114–122

Batista BL, Nigar M, Mestrot A, Rocha BA, Barbosa Júnior F, Price AH, Raab A, Feldmann J (2014) Identification and quantification of phytochelatins in roots of rice to long-term exposure: evidence of individual role on arsenic accumulation and translocation. J Exp Bot 65:1467–1479

Bauer P, Hell R (2006) Translocation of Iron in plant tissues. In: Barton LL, Abadia J (eds) Iron nutrition in plants and Rhizospheric microorganisms, 1st edn. Springer, Switzerland, pp 279–288

Briat J (2010) Arsenic tolerance in plants: “Pas de deux” between phytochelatin synthesis and ABCC vacuolar transporters. Proc Natl Acad Sci U S A 107:20853–20854

Cao Y, Sun D, Ai H, Mei H, Liu X, Sun S, Xu G, Liu Y, Chen Y, Ma LQ (2017) Knocking out OsPht1;4 gene decreases arsenic uptake by rice plants and inorganic arsenic accumulation in rice grains. Environ Sci Technol 51:12131–12138

Carey AM, Scheckel KG, Lombi E, Newville M, Choi Y, Norton GJ, Charnock JM, Feldmann J, Price AH, Meharg AA (2010) Grain unloading of arsenic species in rice. Plant Physiol 152:309–319

Carey AM, Norton GJ, Deacon C, Scheckel KG, Lombi E, Punshon T, Guerinot ML, Lanzirotti A, Newville M, Choi Y, Price AH, Meharg AA (2011a) Phloem transport of arsenic species from flag leaf to grain during grain filling. New Phytol 192:87–98

Carey AM, Lombi E, Donner E, de Jonge MD, Punshon T, Jackson BP, Guerinot ML, Price AH, Meharg AA (2011b) A review of recent developments in the speciation and location of arsenic and selenium in rice grain. Anal Bioanal Chem 402:3275–3286

Chen Y, Moore KL, Miller AJ, McGrath SP, Ma JF, Zhao FJ (2015) The role of nodes in arsenic storage and distribution in rice. J Exp Bot 66:3717–3724

Chen Y, Han Y-H, Cao Y, Zhu Y-G, Rathinasabapathi B, Ma LQ (2017) Arsenic transport in rice and biological solutions to reduce arsenic risk from rice. Front Plant Sci 8:268

Deng F, Yamaji N, Ma JF, Lee S, Jeon J, Martinoia E, Lee Y, Song W (2018) Engineering rice with lower grain arsenic. Plant Biotechnol J 16:1691–1699

Dhankher OP, Li Y, Rosen BP, Shi J, Salt D, Senecoff JF, Sashti NA, Meagher RB (2002) Engineering tolerance and hyperaccumulation of arsenic in plants by combining arsenate reductase and γ-glutamylcysteine synthetase expression. Nat Biotechnol 20:1140–1145

Dixit G, Singh AP, Kumar A, Singh PK, Kumar S, Dwivedi S, Trivedi PK, Pandely V, Norton GJ, Dhankher OP, Tripathi RD (2015) Sulfur mediated reduction of arsenic toxicity involves efficient thiol metabolism and the antioxidant defense system in rice. J Hazard Mater 298:241–251

Duan G, Zhou Y, Tong Y, Mukhopadhyay R, Rosen BP, Zhu Y (2007) A CDC25 homologue from rice functions as an arsenate reductase. New Phytol 174:311–321

Duan G-L, Hu Y, Schneider S, McDermott J, Chen J, Sauer N, Rosen BP, Daus B, Liu Z, Zhu YG (2016) Inositol transporters AtINT2 and AtINT4 regulate arsenic accumulation in Arabidopsis seeds. Nat Plants 2:15202

Fleck AT, Mattusch J, Schenk MK (2013) Silicon decreases the arsenic level in rice grain by limiting arsenite transport. J Plant Nutr Soil Sci 176:785–794

Guillod-Magnin R, Brüschweiler BJ, Aubert R, Haldimann M (2018) Arsenic species in rice and rice-based products consumed by toddlers in Switzerland. Food Addit Contam Part A Chem Anal Control Expo Risk Assess 35:1164–1178

Hashimoto Y, Kanke Y (2018) Redox changes in speciation and solubility of arsenic in paddy soils as affected by sulfur concentrations. Environ Pollut 238:617–623

Hayashi S, Kuramata M, Abe T, Takagi H, Ozawa K, Ishikawa S (2017) Phytochelatin synthase OsPCS1 plays a crucial role in reducing arsenic levels in rice grains. Plant J 91:840–848

Hell R, Bergmann L (1990) γ-Glutamylcysteine synthetase in higher plants: catalytic properties and subcellular localization. Planta 180:603–612

Hu M, Li F, Liu C, Wu W (2015) The diversity and abundance of As(III) oxidizers on root iron plaque is critical for arsenic bioavailability to rice. Sci Rep 5:13611

Islam S, Rahman MM, Rahman MA, Naidu R (2017) Inorganic arsenic in rice and rice-based diets: health risk assessment. Food Control 82:196e202

Jia Y, Huang H, Zhong M, Wang F, Zhang L, Zhu Y (2013) Microbial arsenic methylation in soil and rice rhizosphere. Environ Sci Technol 47:3141–3148

Kamiya T, Islam MR, Duan G, Uraguchi S, Fujiwara T (2013) Phosphate deficiency signaling pathway is a target of arsenate and phosphate transporter OsPT1 is involved in As accumulation in shoots of rice. Soil Sci Plant Nutr 59:580–590

Kumar S, Dubey RS, Tripathi RD, Chakrabarty D, Trivedi PK (2015) Omics and biotechnology of arsenic stress and detoxification in plants: current updates and prospective. Environ Int 74:221–230

Kumarathilaka P, Seneweera S, Meharg A, Bundschuh J (2018a) Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors-a review. Water Res 140:403–414

Kumarathilaka P, Seneweera S, Meharg A, Bundschuh J (2018b) Arsenic accumulation in rice (*Oryza sativa* L.) is influenced by environment and genetic factors. Sci Total Environ 642:485–496

Lai PY, Cottingham KL, Steinmaus C, Karagas MR, Miller MD (2015) Arsenic and rice: translating research to address health care providers' needs. J Pediatr 167:797–803

Li RY, Ago Y, Liu WJ, Mitani N, Feldmann J, McGrath SP, Ma JF, Zhao FJ (2009) The rice aquaporin Lsi1 mediates uptake of methylated arsenic species. Plant Physiol 150:2071–2080

Lindsay ER, Maathuis FJ (2017) New molecular mechanisms to reduce arsenic in crops. Trends Plant Sci 22:1016–1026

Liu WJ, Wood BA, Raab A, McGrath SP, Zhao FJ, Feldmann J (2010) Complexation of arsenite with phytochelatins reduces arsenite efflux and translocation from roots to shoots in Arabidopsis. Plant Physiol 152:2211–2221

Lomax C, Liu WJ, Wu L, Xue K, Xiong J, Zhou J, McGrath SP, Meharg AA, Miller AJ, Zhao FJ (2012) Methylated arsenic species in plants originate from soil microorganisms. New Phytol 193(3):665–672

Luan M, Liu J, Liu Y, Han X, Sun G, Lan W, Luan S (2018) Vacuolar phosphate transporter 1 (VPT1) affects arsenate tolerance by regulating phosphate homeostasis in Arabidopsis. Plant Cell Physiol 59:1345–1352

Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proc Natl Acad Sci U S A 105:9931–9935

Ma L, Wang L, Jia Y, Yang Z (2017) Accumulation, translocation and conversion of six arsenic species in rice plants grown near a mine impacted city. Chemosphere 183:44e52

Majzlan J, Drahota P, Filippi M (2014) Parageneses and crystal chemistry of arsenic minerals. Rev Mineral Geochem 79:17–184

Marin AR, Masscheleyn PH, Patrick WH (1992) The influence of chemical form and concentration of arsenic on rice growth and tissue arsenic concentration. Plant Soil 139:175–183

Meharg C, Meharg AA (2015) Silicon, the silver bullet for mitigating biotic and abiotic stress, and improving grain quality, in rice? Environ Exp Bot 120:8–17

Meng XY, Qin J, Wang LH, Duan GL, Sun GX, Wu HL, Chu CC, Ling HQ, Rosen BP, Zhu YG (2011) Arsenic biotransformation and volatilization in transgenic rice. New Phytol 191:49–56

Mishra S, Wellenreuther G, Mattusch J, Stärk HJ, Küpper H (2013) Speciation and distribution of arsenic in the non-hyperaccumulator macrophyte *Ceratophyllum demersum*. Plant Physiol 163:1396–1408

Mishra S, Mattush J, Wennrich R (2017) Accumulation and transformation of inorganic and organic arsenic in rice and role of thiol-complexation to restrict their translocation to shoot. Sci Rep 7:40522

Mitra A, Chatterjee S, Moogouei R, Gupta DK (2017) Arsenic accumulation in rice and probable mitigation approaches: a review. Agronomy 7:67

Norton GJ, Lou-Hing DE, Meharg AA, Price AH (2008) Rice-arsenate interactions in hydroponics: whole genome transcriptional analysis. J Exp Bot 59:2267–2276

Pal R, Rai JPN (2010) Phytochelatins: peptides involved in heavy metal detoxification. Appl Biochem Biotechnol 160:945–963

Punshon T, Jackson BP, Meharg AA, Warczack T, Scheckel K, Guerinot ML (2017) Understanding arsenic dynamics in agronomic systems to predict and prevent uptake by crop plants. Sci Total Environ 581–582:209–220

Rahman MA, Hassler C (2014) Is arsenic biotransformation a detoxification mechanism for microorganisms? Aquat Toxicol 146:212–219

Rai A, Tripathi P, Dwivedi S, Dubey S, Shri M, Kumar S, Tripathi PK, Dave R, Kumar A, Singh R, Adhikari B, Bag M, Tripathi RD, Trivedi PK, Chakrabarty D, Tuli R (2011) Arsenic tolerances in rice (*Oryza sativa*) have a predominant role in transcriptional regulation of a set of genes including sulphur assimilation pathway and antioxidant system. Chemosphere 82:986–995

Seyfferth AL (2015) Abiotic effects of dissolved oxyanions on iron plaque quantity and mineral composition in a simulated rhizosphere. Plant Soil 397:43–61

Sharma I (2012) Arsenic induced oxidative stress in plants. Biologia 67:447–453

Shen J, Yuan L, Zhang J, Li H, Bai Z, Chen X, Zhang W, Zhang F (2011) Phosphorus dynamics: from soil to plant. Plant Physiol 156:997–1005

Shi S, Wang T, Chen Z, Tang Z, Wu Z, Salt DE, Chao D, Zhao F (2016) OsHAC1;1 and OsHAC1;2 function as arsenate reductases and regulate arsenic accumulation. Plant Physiol 172:1708–1719

Song WY, Park J, Mendoza-Cozatl DG, Suter-Grotemeyer M, Shim D, Hortensteiner S, Geisler M, Weder B, Rea PA, Rentsch D, Schroeder JI, Lee Y, Martinoia E (2010) Arsenic tolerance in Arabidopsis is mediated by two ABCC-type phytochelatin transporters. Proc Natl Acad Sci U S A 107:21187–21192

Song WY, Yamaki T, Yamaji N, Ko D, Jung KH, Fujii-Kashino M, An G, Martinoia E, Lee Y, Ma JF (2014) A rice ABC transporter, OsABCC1, reduces arsenic accumulation in the grain. Proc Natl Acad Sci U S A 111:15699–15704

Souri Z, Karimi N, Sandalio LM (2017) Arsenic Hyperaccumulation strategies: An overview. Front Cell Dev Biol 5:67

Stroud JL, Khan MA, Norton GJ, Islam MR, Dasgupta T, Zhu YG, Price AH, Meharg AA, McGrat SP, Zhao FJ (2011) Assessing the labile arsenic pool in contaminated paddy soils by isotopic dilution techniques and simple extractions. Environ Sci Technol 45:4262–4269

Suriyagoda LDB, Dittert K, Lambers H (2018) Mechanism of arsenic uptake, translocation and plant resistance to accumulate arsenic in rice grains. Agric Ecosyst Environ 253:23–37

Tang Z, Chen Y, Chen F, Ji Y, Zhao FJ (2017) OsPTR7 (OsNPF8. 1), a putative peptide transporter in rice, is involved in dimethylarsenate accumulation in rice grain. Plant Cell Physiol 58:904–913

Thomas D, Bron P, Ranchy G, Duchesne L, Cavalier A, Rolland J-P, Raguénès-Nicol C, Hubert J-F, Haase W (2002) Aquaglyceroporins, one channel for two molecules. Biochim Biophys Acta 1555:181–186

Tiwari M, Sharma D, Dwivedi S, Singh M, Tripathi RD, Trivedi PK (2014) Expression in *Arabidopsis* and cellular localization reveal involvement of rice NRAMP, OsNRAMP1, in arsenic transport and tolerance. Plant Cell Environ 37:140–152

Tuli R, Chakrabarty D, Trivedi PK, Tripathi RD (2010) Recent advances in arsenic accumulation and metabolism in rice. Mol Breed 26:307–323

Uraguchi S, Tanaka N, Hofmann C, Abiko K, Ohkama-Ohtsu N, Weber M, Kamiya T, Sone Y, Nakamura R, Takanezawa Y, Kiyono M, Fujiwara T, Clemens S (2017) Phytochelatin synthase has contrasting effects on cadmium and arsenic accumulation in rice grains. Plant Cell Physiol 58:1730–1742

Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or cadmium excess in plants. Curr Opin Plant Biol 12:364–372

Verma PK, Verma S, Meher AK, Pande V, Mallick S, Bansiwal AK, Tripathi RD, Dhankher OP, Chakrabarty D (2016) Overexpression of rice glutaredoxins (OsGrxs) significantly reduces arsenite accumulation by maintaining glutathione pool and modulating aquaporins in yeast. Plant Physiol Biochem 106:208–217

Wang P, Zhang W, Mao C, Xu G, Zhao F-J (2016) The role of OsPT8 in arsenate uptake and varietal difference in arsenate tolerance in rice. J Exp Bot 67:6051–6059

Wu Z, Ren H, McGrath SP, Wu P, Zhao F-J (2011) Investigating the contribution of the phosphate transport pathway to arsenic accumulation in Rice. Plant Physiol 157:498–508

Xu XY, McGrath SP, Zhao FJ (2007) Rapid reduction of arsenate in the medium mediated by plant roots. New Phytol 176:590–599

Yamaguchi N, Nakamura T, Dong D, Takahashi Y, Amachi S, Makino T (2011) Arsenic release from flooded paddy soils is influenced by speciation, Eh, pH, and iron dissolution. Chemosphere 83:925–932

Yamamoto T, Nakamura A, Iwai H, Ishii T, Ma JF (2012) Effect of silicon deficiency on secondary cell wall synthesis in rice leaf. J Plant Res 125:771–779

Yang J, Gao MX, Hu H, Ding XM, Lin HW, Wang L, Xu JM, Mao CZ, Zhao FJ, Wu ZC (2016) OsCLT1, a CRT-like transporter 1, is required for glutathione homeostasis and arsenic tolerance in rice. New Phytol 211:658–670

Ye Y, Li P, Xu T, Zeng L, Cheng D, Yang M, Luo J, Lian X (2017) OsPT4 contributes to arsenate uptake and transport in rice. Front Plant Sci 8:2197

Zhang J, Zhao QZ, Duan GL, Huang YC (2011) Influence of sulphur on arsenic accumulation and metabolism in rice seedlings. Environ Exp Bot 72:34–40

Zhang J, Martinoia E, Lee Y (2018) Vacuolar transporters for cadmium and arsenic in plants and their applications in phytoremediation and crop development. Plant Cell Physiol 59:1317–1325

Zhao FJ, Ma JF, Meharg AA, McGrath SP (2009) Arsenic uptake and metabolism in plants. New Phytol 181:777–794

Zhao FJ, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559

Zhao F-J, Stroud JL, Khan MA, McGrath SP (2012) Arsenic translocation in rice investigated using radioactive ^{73}As tracer. Plant Soil 350:413–420

Zhao F-J, Zhu YG, Meharg AA (2013) Methylated arsenic species in rice: geographical variation, origin, and uptake mechanisms. Environ Sci Technol 47:3957–3966

Molecular Physiology of Arsenic Uptake, Transport, and Metabolism in Rice

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Abstract Arsenic (As) becomes a global problem by affecting both plant and human health. It is a nonessential toxic metalloid that can be readily taken up by plant root and accumulated inside the plant tissue causing detrimental effects. Rice, the major crop, is greatly affected by As due to high contamination of As in paddy soil and its ability to accumulate heaps of As inside the tissues. Besides As being a group I carcinogen, it affects human health through the food chain. In the situation, the major aim is to develop rice cultivars with less As accumulation to decrease toxic effects, thereby elevating production and quality of rice. For this, a deep understanding on all of everything of As from soil to grains is quite essential. This review encompasses uptake and transportation of As, transporters, accumulation and toxicity, and detoxification mechanisms against As in rice. Impact of As on health and economy is also summarized and in addition, development of As tolerant plant is also discussed.

Keywords Arsenic · Rice · Transporter · Toxicity · Tolerant

1 Introduction

Arsenic is a naturally occurring highly toxic metalloid where its inorganic form is classified as a type 1 carcinogenic agent by the International Agency for Research on Cancer (IARC 2012). Accumulation of this metalloid in soil depends on various factors like burning of fossil fuels and the use of fertilizers, pesticides, etc. Kumar et al. (2015) reported rice as an efficient accumulator of arsenic due to its capability to uptake and transport arsenic. For half of the world population, rice is the main staple food and it is widely cultivated. Sohn (2014) reported that rice can accumulate more arsenic than other cereals, and it is up to 92 mg Kg^{-1} in straw and up to 2 mg Kg^{-1} in grains (Williams et al. 2005). The efficient accumulation of As in rice is due to higher mobilization of arsenite [As(III)] because of anaerobic condition and

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transport of arsenite through Si transport pathway (Takahashi et al. 2004; Zhao et al. 2010). The inorganic forms of arsenic harm the metabolic pathways in cells by interacting with the sulfhydryl groups of proteins and replacing the phosphate in ATP (Tripathi et al. 2007). Thus, the growth of plant and yield is lowered due to arsenic toxicity (Carbonell Barrachina et al. 1995). The toxic effects of arsenic in plants include reduction of extension in root, necrosis, shrinkage of plant parts, and chlorosis of leaves (Carbonell-Barrachina et al. 1998). Arsenic can heavily hamper the growth of plants by reducing accumulation of biomass, lowering reproductive capacity, etc. (Garg and Singla 2011). Duxbury and Panaullah (2007) reported about the reduced yield of rice due to the presence of arsenic. They added that in the conventional field of Bangladesh rice yields decreased from 7.5 to 2.5 t ha^{-1} due to increased concentration of arsenic from 12 to 60 mg kg^{-1}. Stunted growth, scorching on leaves, and brown spots are the phytotoxicity symptoms of arsenic contamination in rice plants growing in 60 mg kg^{-1} arsenic-containing soil (Bakhat et al. 2017). Exposure to arsenic lowers the intensity of plant transpiration (Stoeva and Bineva 2003). Beyond the control level of ROS (reactive oxygen species) are generated by the inorganic species of arsenic, and thus it causes oxidative stress (Tripathi et al. 2012). Metabolic processes of plants are also affected by higher concentration of arsenic, and it may lead to the death of plants. The major part of the plant to get exposed to arsenic is the roots, and due to the translocation of arsenic, its accumulation varies from the root to other parts of the plants. It is reported that accumulation of arsenic in the Ratna variety of *Oryza sativa* (Aman rice) is in the following order: root > basal stem > median stem > apical stem > leaves > grains (Bhattacharya et al. 2014; Liu et al. 2004). Farooq et al. (2016) reported that As availability and solubility in rice plants can be changed by water management practices and changing the concentration of other minerals present in soil.

Duan et al. (2013) and Brackhage et al. (2014) reported that the uptake of some essential minerals like zinc (Zn) and iron (Fe) by plants is also limited by arsenic. In the metabolism of arsenic into plants, transporters play a very critical role (Schroeder et al. 2013). They added that transporters transport not only the essential minerals or molecules for plants but also some harmful components like arsenic. Different arsenic species are taken up and translocated by plants through some distinct pathways and transporters. Zhao et al. (2010) revealed that different studies on transporters reflect their role in the transport and metabolism of arsenic in plants. Thus, to develop engineering techniques to limit As uptake, accumulation in plants, and migration into the food chain, a brief understanding of transport mechanism of As is important. In this review, molecular physiology of arsenic uptake, transport, and metabolism in rice has been discussed.

2 Arsenic Uptake and Transport in Rice Plant

Uptake and transport of arsenic in rice plant takes place through different mechanisms. One of them involves phosphate transporters (Catarecha et al. 2007). Wu et al. (2011) reported that the transport of As from the root to the shoot and uptake of As(V) from the soil take place through these transporters. Another mechanism involves participation of aquaporin channels in which methylated As species and As(III) are taken up (Ma et al. 2008; Li et al. 2009). As arsenite is the analogue of silicic acid, it utilizes the Si transporter to enter the plant body. Lsi1 and Lsi2 transporter controls the accumulation of Si as well as As in rice, and the expression of these transporters controls the accumulation of Si and As in rice (Ma et al. 2007). The transport of As across the cells and tissues is facilitated by the presence of OsLsi1 and OsLsi2 in both sides of cells (Ma et al. 2007). Li et al. (2009) revealed that through the above mentioned transporter (OsLsi1), uncharged methylated As species can be taken up by the roots of rice. Lsi1 also acts as a bidirectional channel by releasing the uptaken As(III) in the rhizosphere (Zhao et al. 2010). They added that in various organs and shoots, the remaining As is distributed by transporting across the shoots or in the vacuoles of roots, and As may be sequestered.

In aerobic soils, the dominant As species is As(V) which enters into the plant roots through phosphate (Pi) transporters because of the similarities between Pi and oxyanion chemical structure of As(V). Francesconi and Kuehnelt (2002) reported that methylated arsenic species [monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)] are present in trace amount in soil. The source of origin of methylated arsenic species is the soil microorganisms and the past use of pesticides. The uptake of MMA and DMA may take place through nodulin 26-like intrinsic protein. Marin et al. (1992) reported the higher phytotoxicity of MMA and DMA and added that it may be due to higher translocation of these arsenic species from the root to the shoot. It is reported that the uptake of methylated arsenic species is lower than the inorganic arsenic species, but the translocation is higher (Raab et al. 2007). Meharg et al. (2009) reported the higher toxicity of inorganic As species than methylated As species. Syu et al. (2015) conducted an experiment on three As levels and six genotypes of rice and indicated that there is no correlation between As concentration in soil and in rice plants. They added that the environment and genotypes play an important role in the concentration of As in rice grain. The dominant species found in rice grain are As(III) and DMA. Accumulation of arsenic species was many times higher in the root than the shoot and raw rice grain (Rahman et al. 2007a). In the roots of rice, concentration-dependent uptake of MMA can be described by Michaelis–Menten kinetics, but the uptake of DMA cannot be described by the linear function or Michaelis–Menten equation.

It is reported that high-affinity phosphate transporters are responsible for the uptake of As(V) in *Oryza sativa*. Wu et al. (2011) reported that uptake and translocation of As(V) is increased by the overexpression of OsPht1;8. They added that OsPht1;8 expression is regulated by the transcription factor OsPHR2. Kamiya et al. (2013) mentioned that As(V) is also taken up by OsPht1;1 which is present in the plasma membrane. Xu et al. (2008) reported that in flooded soil, uptake of As through Pi transport pathway is a minor way because in the anaerobic environments the main form of As is As(III). Several studies are reported to characterize the different proteins to uptake As(III) in plants. Li et al. (2014) and Mukhopadhyay et al. (2014) mentioned that the various routes for the uptake of As(III) include membrane channels, plant aquaporins, etc. Uptake of As(III) in rice mainly takes place through silicon (Si) influx transporter and NIP2;1 (also named OsLsi1). Ma et al. (2008) reported that in rice As(III) influx is mediated by OsNIP2;1 which is present in both endodermal and exodermal cells. Mosa et al. (2012) mentioned that some plasma membrane intrinsic proteins contribute to the uptake of As(III) in plants.

3 Arsenic Transporters in Rice Plant

Through different types of transporters, plants take their beneficial mineral elements from the earth's crust. But in different times, nonessential and harmful elements are also taken up by the transporters due to lack of selectivity. The different transporters which help in the transport of As in rice are as follows:

1. **Phosphate transporters (PHTs: OsPHT1;1, OsPHT1;8):** Rice roots absorb arsenate from the soil through phosphate transporters (PHTs). Different scientists reported a number of phosphate transporters for the uptake of As(V). Examples of some phosphate transporter include OsPT1 and OsPT8. Zhao et al. (2010) revealed that various phosphate transporter proteins are involved in the root-to-shoot transport of As(V). In addition to this for the uptake and transport of As(V), various phosphate transporter regulators are also involved (Wu Z et al. 2011).
2. **Aquaglyceroporins:** Arsenite [As(III)] finds its pathway into paddy plants through nodulin 26-like intrinsic proteins. Xu et al. (2015) reported that in *Arabidopsis thaliana*, As(III) transports through the nodulin 26-like intrinsic proteins. Zhao et al. (2010) revealed that As(III) is also taken up by the silicon transporter OsNIP2;1 (Lsi1). In anaerobic condition of paddy soil, As(III) is predominantly found, and in aerobic conditions, As(V) is found. Thus, when paddy rice fields are not present in submerged condition for a long time, the soil condition turns into aerobic, and then rice roots predominantly absorb As(V) from the soil. When oxygen is released by the rice roots, As(III) can also be changed to As(V) through oxidation (Seyfferth et al. 2010). Mosa et al. (2012) reported that through the different classes of aquaglyceroporins, methylated As species and As(III) are transported. In rice plants, the phosphate transporters which help in the uptake of As(V) and As(III) are OsNIP1;1, OsNIP2;1 (Lsi1), OsNIP3;1, OsNIP2;2 (Lsi6), OsPIP2;4, OsPIP2;6, and OsPIP2;7. In the transportation of As from the root to the shoot, OsLsi2 contributes and Nramp1 (natural resistance-associated macrophage protein) helps in the loading of As in xylem. In the epidermis of the root, another aquaglyceroporin Lsi1 acts as an effluxer of As.
3. **ABCC:** ATP-binding cassette transporter helps in vacuolar sequestration of As(III) complexed with thiolic compounds. Arsenic is transported into the seeds through the phloem. Song et al. (2014) reported that after entering the plants, As exists in its reduced form.

4. **Inositol transporters (INTs)** are known to be involved in phloem loading of As(III) in *Arabidopsis* and thus in the transportation of As(III) to the seeds. It is reported that in the grains of rice, As(III) transportation is helped by inositol transporters (INTs). OsPTR7 (putative peptide transporter) helps in the long-distance transport of DMA. The transporter of As(V) and As(III) in grains are yet to be revealed though Lsi2 has been considered as a probable candidate (Table 1).

Table 1 Some arsenic transporters and their location in rice

SN	Name of transporter	As species	Location	Processes	References
1	OsPHT1;8	As(V)	Plasma membrane	Uptake	Wu et al. (2011) and Jia et al. (2011)
2	OsPHT1;1	As(V)	Plasma membrane	Uptake; root to shoot translocation	Kamiya et al. (2013)
3	OsNIP1;1	As(III)	Plasma membrane	Uptake	Ma et al. (2008)
4	OsNIP3;1	As(III)	Plasma membrane	Uptake	Ma et al. (2008)
5	OsNIP3;2	As(III)	Plasma membrane	Transport	Bienert et al. (2008)
6	OsNIP3;3	As(III)	Plasma membrane	Transport	Katsuhara et al. (2014)
7	OsLsi1	As(III), MMA, DMA	Plasma membrane	Influx	Ma et al. (2008) and Bienert et al. (2008)
8	OsLsi2	As(III)	Plasma membrane	Efflux, xylem loading	Ma et al. (2008)
9	OsLsi6	As(III)	Plasma membrane	Uptake	Ma et al. (2008)
10	OsPIP2;4	As(III)	Plasma membrane	Putative bi-directional permease	Mosa et al. (2012)
11	OsPIP2;6	As(III)	Plasma membrane	Putative bi-directional permease	Mosa et al. (2012)
12	OsPIP2;7	As(III)	Plasma membrane	Putative bi-directional permease	Mosa et al. (2012)
13	OsABCC1	As(III)–PCs	Tonoplast	Transport into vacuoles	Song et al. (2014)
14	OsNRAMP1	As(III)	Plasma membrane	Xylem loading (enter pericycle cell)	Tiwari et al. (2014)

4 Factors Affecting Arsenic Uptake and Transport

4.1 Soil pH

Soil pH directly affects the availability and solubility of arsenic because speciation and leaching of arsenic depends on the pH of the soil (Quazi et al. 2011; Chatterjee et al. 2013). Both higher and lower pH influence the uptake and accumulation of arsenic by paddy rice. It is because Fe oxyhydroxide compounds become more soluble at very low pH (Signes-Pastor et al. 2007) and enhance the uptake of arsenic by plants. Bhattacharya et al. (2010) reported the negative relation between soil pH and arsenic concentration in rice. Otherwise, many authors also supported the positive relation between soil pH and arsenic accumulation (Campbell et al. 1985; Ahmed et al. 2011).

4.2 Soil Texture

The bioavailability of arsenic to rice plant is also controlled by soil texture (Adriano 2001). Soils which have more surface area and finer texture (e.g., clayey and silt soil) have a higher potential for scavenging arsenic due to the presence of iron oxides (Quazi et al. 2011). Thus, paddy plants growing in sandy and loamy soil show more toxic effects of arsenic (Quazi et al. 2011).

4.3 Arsenic Speciation

Arsenic is present in the soil in inorganic and organic forms (species). Arsenate (As(V)) and arsenite (As(III)) are the commonly found inorganic form, and organic forms include monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). The order of toxicity of arsenic species is as follows: As(III) > As(V) > MMA > DMA (Baig et al. 2010). Arsenite is generally found in the submerged paddy soil, i.e., in the anaerobic soil. In the paddy soil, due to microbial action, arsenite is transformed into other forms of arsenic (Islam et al. 2004). Marin et al. (1992) reported that the bioavailability of arsenic to rice plants is in the following order: As(III) > MMA > As(V) > DMA. Rice roots take up all the forms of arsenic, but the rate of uptake is different for different forms (Abedin et al. 2002).

4.4 Redox Conditions

Redox chemistry controls the accumulation of metal in paddy which takes place due to arsenic speciation and its mobility in soil (Williams et al. 2007). Otherwise in oxidized condition, arsenic is present as arsenate and is adsorbed on Fe oxyhydroxide phases (Lauren and Duxbury 2005). But in submerged paddy field condition, arsenite (As(III)) is present and readily available for the uptake of plants due to the conversion of As(V) to As(III) and due to the dissolution of Fe oxides (Takahashi et al. 2004). Rhizospheric microbes may increase the availability of arsenic to rice plants by secreting siderophores to the root–plaque interface which results in the solubilization of ferric ion (Kraemer 2004; Bhattacharya et al. 2012).

4.5 Organic Matter

Another important factor which plays an important role in the uptake and accumulation of arsenic in rice is the presence of organic matter. The chemical nature and complexes of organic matter (OM) regulate the mobility of arsenic in the soil (Williams et al. 2011). The presence of higher amount of OM in the soil results in the reduction of arsenic solubility (Pikaray et al. 2005). OM directly affects the availability of As to plant due to the formation of organoarsenic compounds. Other authors also reported about the lowered content of arsenic in rice grains growing in higher OM content soil (Rahaman et al. 2011; Fu et al. 2011) .On the contrary, some researchers also reported the positive relation between accumulation of arsenic in rice grains and soil OM. The mobility of arsenic from the solid phase can be increased by the presence of higher amount of OM in the soil by modulating the activity of microbes and soil redox potential (Turpeinen et al. 1999).

4.6 Genotype Variation in Rice

Various researchers reported that accumulation of arsenic in rice grains differs with rice varieties (Norton et al. 2010). It is reported that arsenic accumulation was highest in the BR11 variety (1.77 mg kg^{-1}) than the others (Meharg et al. 2003). IR 50, White Minikit, and Red Minikit rice variety were good arsenic accumulators (0.24–0.31 mg kg^{-1}) than Nayanmani, Jaya, Ratna, Ganga-kaveri, and Lal Sanna (0.14–0.20 mg kg^{-1}); maximum accumulation was found. In White Minikit, maximum arsenic accumulation was found (0.31 mg kg^{-1}), and the opposite was in Jaya (0.14 mg kg^{-1}) (Bhattacharya et al. 2010). The cultivar "TN1" and "ZYQ8" accumulate higher arsenic in the vegetative parts and roots, while lowest arsenic was found in "JX-17" cultivar (Zhang and Duan 2008). The variation of arsenic concentration in the different rice variety may be influenced by environmental conditions, genetic differences, and the presence of a different level of arsenic in the irrigation water and soils (Zhang and Duan 2008; Norton et al. 2009a). Norton et al. (2009a) conducted a field-based experiment in Bangladesh with 76 rice cultivars and in multiple environments at two field sites each in Bangladesh, India, and China (Norton et al. 2009b); four- to fivefold variations were observed in the grain arsenic concentration among cultivars. The difference in arsenic accumulation in grains may be due to differences in root anatomy, which controls root aeration, porosity (Wu et al. 2011), Fe plaque formation on the root surfaces (Liu et al. 2004), phytochelatins (PCs) (Duan et al. 2011), rhizosphere interactions, and differences in the arsenic tolerance gene (Dasgupta et al. 2004).

5 Accumulation of Arsenic and Toxicity in Rice Plant

As accumulation is tenfold higher in rice than other cereal crops (Williams et al. 2007) which is a serious concern as rice is the staple food of half of the world's population (Fahad et al. 2016). The accumulation varies with the differences of the plant parts which have different abilities to accumulate; thus accumulation is not uniform. The root serves as the main part for the accumulation of As, and the accumulation declines from the root to the aerial part of the plant which follows the trend as root ˃ straw ˃ grain. Several studies have reported the highest As accumulation in the root and then gradual decrease in the stem, leaves, and grain (Rahman et al. 2007a; Liu et al. 2014). However, As accumulation of the harmful level does not occur in plant tissues growing in uncontaminated environment. Under contaminated environment, the accumulation is significantly increased which becomes toxic to humans through consumption which is evident from the study of Ullah (1998). He reported that in Bangladesh, the normal irrigated soil contains 4–8 mg kg^{-1} of arsenic, while in areas where irrigation with arsenic-contaminated water is carried out, the soil arsenic concentration can be up to 83 mg kg^{-1}.

Different transporters are involved in the accumulation of arsenic in plant cells such as phosphate transporters for arsenate (As(V)) and nodulin 26-like intrinsic protein (NIP) for arsenite (As(III)) (Catarecha et al. 2007; Li et al. 2009). It has been observed that uptake of As in rice root is achieved through the transporter Lsi1 and Lsi2 whereas translocation to vegetative parts and grains through the xylem and phloem, respectively (Yamaji and Ma 2011; Carey et al. 2010). As accumulation in grain differs in different rice genotypes and varies up to 7-fold and 40-fold in rice varieties of different countries and same country, respectively, indicating rice genotypes and environmental factors play an important role in the accumulation of As in rice grain (Syu et al. 2015). Norton et al. (2013) also reported that factors like cultivar type, cultivated place, and processing determine the accumulation of As in rice. Thus, the As concentration in rice from different parts of the globe varies greatly. Meharg et al. (2009) reported that rice of Ghana had the lowest median arsenic concentration (20 ng g^{-1}), followed by India (50 ng g^{-1}), while the USA, Italy, and Thailand had the highest arsenic concentration, with China and Bangladesh being intermediate which is in accordance with the study of Zavala and Duxbury (2008). The As levels in rice grain of China and Taiwan reached up to 0.7 mg kg^{-1} and 0.10 mg kg^{-1}, respectively (Xie and Huang 1998; Lin et al. 2004). Similarly, in Canada, Egypt, and Australia, the rice grain As concentration was found to be 0.02 mg kg^{-1}, 0.02–0.08 mg kg^{-1}, and 0.09–0.33 mg kg^{-1}, respectively (Meharg et al. 2007; Fransisca et al. 2015). According to Meharg and Rahman (2003), the highest level of As was reported in Bangladesh which is up to 1.85 mg kg^{-1} (0.05–1.85 mg kg^{-1}). Factors like soil pH (Bhattacharya et al. 2010; Ahmed et al. 2011) and soil organic matters (Rahaman et al. 2011) also influence the accumulation. Toxicity of As depends not only on the concentration in plant tissues but also on the species. Arsenic induces an adverse effect on plants by interfering with several metabolisms. It causes reduction of root biomass (Banejad and Olyaie 2011), reduction in the number of rice leaf and width of leaf blade (Shaibur et al. 2006), reduction in the transpiration intensity (Stoeva and Bineva 2003), chlorosis, and necrosis in aerial plant parts (Carbonell-Barrachina et al. 1998). It reduces biomass accumulation, reproductive capacity, and fruit production, thereby affecting the whole plant growth and yield (Garg and Singla 2011). Khan et al. (2010) reported that growth and yield of rice decreased markedly in paddy soils of Bangladesh, containing >13 mg As kg^{-1}. Duxbury and Panaullah (2007) also reported that increase in arsenic concentration in soil of Bangladesh resulted in the decrease of rice yields. Moreover, being a redox-active metalloid, As increases production of reactive oxygen species (ROS) causing oxidative stress (Shri et al. 2009; Tripathi et al. 2012). ROS are damaging to DNA, protein, and lipids, which lead to disturbances in various metabolisms. Mehrag and Hartley-Whitaker (2002) reported that As inhibits various cellular functions by interacting with sulfhydryl (-SH) groups of enzymes and proteins of the cell. It has also been reported that As hampers ATP production and oxidative phosphorylation (Tripathi et al. 2007). As arsenic enters in the plants through phosphate transporters as a phosphate analogue, it also altered phosphate metabolism (Meharg and Macnair 1994).

6 Plant's Protective Mechanisms Against Arsenic

Plant operates various protective mechanisms to combat the deleterious impact of As which include restriction of uptake and transport (Mei et al. 2012; Wu et al. 2017), phytochelatin (PC)-dependent detoxification that binds the metalloid (Rausch and Wachter 2005), and stimulation of the activity of antioxidant system which includes catalase (CAT), superoxide dismutase (SOD), ascorbate peroxidase (APX), guaiacol peroxidase (GPX), glutathione reductase (GR), glutathione, and ascorbate (Dave et al. 2013). PCs are heavy metal-binding peptides which have the general structure $(\gamma\text{-glu-cys})_n\text{gly}$ where n varies from 2 to 11. PCs are synthesized enzymatically using GSH by phytochelatin synthase (PCS) which is activated on heavy metal exposure (Thangavel et al. 2007). Induction of As tolerance in rice through the higher level of PCs and PC synthase activity has been observed (Tripathi et al. 2012). Liu et al.

(2010) reported reduction in the concentration of free arsenic in the cytoplasm by complexation and vacuolar sequestration of As–PC complex at acidic pH (5.5).

It has been observed that in response to the detrimental effects of As, many antioxidant molecules are also stimulated in plants (Singh et al. 2015). Dave et al. (2013) found that As induced differential responses of antioxidant enzymes in rice plant owing to variable accumulation of As. Nath et al. (2014) reported elevation of SOD activity during As stress in rice. Singh et al. (2016) also observed As stress enhanced the SOD activity by 1.9- and 2.2-fold in the shoot and twofold and threefold in the root in dose-dependent manner than the control. Moreover, upregulation of Cu/Zn SOD during arsenic stress in rice seedlings was also demonstrated by Shri et al. (2009). CAT activity enhanced twofold and threefold in the shoot and 2.3- and 3.9-fold in the root of rice plant under As stress, as reported by Singh et al. (2016). The study of Nath et al. (2014) also revealed that CAT activity increased in rice under As stress. It has been reported that the activity of CAT increased at 7 days by 39% and 52% and 43% and 44% at 15 days in shoots and roots, respectively, under As stress, which was being more in roots (Khan and Gupta 2018). Upregulation of APX activity has been reported in rice seedlings exposed to As (Shri et al. 2009). As accumulation induced synthesis of peroxide in the early stage of plant development (Stoeva et al. 2005). Singh et al. (2016) reported APX activity increased upon As(V) exposure both in the root and shoot than the control. The study of Singh et al. (2016) showed that GPX activity was enhanced to 22 and 36% in the shoot and 35 and 77% in the root, at As(V) 25 μM and As(V) 50 μM, respectively, than the control. Khan and Gupta (2018) also reported GPX activity in As-stressed rice plants increased by 34% and 41% in rice shoots and roots, respectively, at 7 days, whereas at 15 days, it was 32% in shoots and 53% in roots. Moreover, increment in the GR activity in both the root and shoot was also observed. It has been reported GR activity rapidly increased by 28 and 48% in the 0.5 and 1 mM As-treated rice seedlings, respectively, compared with the control (Rahman et al. 2015). Nath et al. (2014) reported there was significant increase in AsA and GSH content in the root and shoot as compared to controls after 24 and 48 h of As treatment. But in the study of Rahman et al. (2015), the rice seedlings treated with 0.5 and 1 mM As showed 33 and 51% decrease in AsA content, respectively, compared with the control, whereas GSH content in the 0.5 and 1 mM As-treated rice seedlings increased by 48 and 82%, respectively, with respect to the control. Dave et al. (2013) also reported abundance increased in the glutathione content on exposure to As.

7 Impact on Health and Economy by Arsenic

The critical toxicant As is present at very high concentration in the groundwater of more than 70 countries worldwide (Zhao et al. 2010) affecting both plant product and human health. Rice consumption is one of the main sources of human As exposure which is observed from the study of Li et al. (2011) in Chinese population, where it was found that rice contributes up to 60% of the total dietary As. Moreover, rice contributes almost 50% of the total dietary As among the West Bengal and Bangladesh population (Signes-Pastor et al. 2008). Consumption of contaminated rice causes a serious threat to millions of human health, as well as cattle health through the consumption of the contaminated straw. According to the Joint Food and Agriculture Organization and the World Health Organization (FAO/WHO) Expert Committee on Food Additives, the maximum level of inorganic As in polished rice is 0.2 mg kg^{-1} (US FDA 2015; Signes-Pastor et al. 2016). According to Zhao et al. (2010), As is considered as a class I carcinogen and food chain contaminant. Consumption of rice is one of the major pathways for As exposure to humans (Chung et al. 2014). Several studies reveal a substantial relationship of rice intake with both urinary arsenic and prevalent skin lesions (Gilbert et al. 2011; Melkonian et al. 2013). According to Kazi et al. (2009), the common mode of arsenic toxicity in humans is the inactivation of the enzyme system by binding through various biological ligands. Alava et al. (2015) reported that As undergoes a series of biotransformation in the gastrointestinal tract, including oxidation, reduction, methylation, and thiolation. As toxicity causes deleterious health impacts, including hyperpigmentation, keratosis, skin and internal cancers, and vascular diseases (Gibb et al. 2011; Argos et al. 2010). Among the various effects of As poisoning, melanosis and keratosis are the most common in the affected people (Karim 1999).

Arsenic toxicity mainly depends on the speciation where the inorganic arsenic is more toxic than the organic form to human health. The inorganic As on chronic exposure causes several disorders in the various biological systems of humans like the digestive system, respiratory system, cardiovascular system, hematopoietic system, endocrine system, renal system, neurological system, reproductive system, etc. that leads to cancer as reviewed by Santra et al. (2013). It has also been reviewed that comparable peripheral vascular disorders with varying degrees of severity include Raynaud's syndrome and acrocyanosis due to arsenic exposure. A study of Sen and Chaudhuri (2008) revealed that arsenic has a significant effect on stillbirth percentage among pregnant women and has been recognized as a reproductive toxicant in humans. Furthermore, it has also been reported that As exposure is associated with atherosclerosis, Alzheimer's disease, and diabetes (Anawar et al. 2002; Chakraborti et al. 2001). McCarty et al. (2011) reviewed that arsenic can compromise fetal health, including birth weight, fetal mortality, infant mortality, intelligence, and development.

In plants, As exposure induces ROS production, lipid peroxidation, and damaged DNA, RNA, and proteins (Hartley-Whitaker et al. 2001; Srivastava et al. 2011). Arsenic causes oxidative stress to plants which leads to inhibition of plant production. It inhibits plant growth and development by interfering with the metabolic processes (Marin et al. 1993). Its toxicity inhibited seed germination, plant growth, and fruit and grain yield of rice (Abedin and Meharg 2002; Jahan et al. 2003; Abedin et al. 2002). According to Rahman et al. (2007b), As toxicity reduces chlorophyll content in rice, thereby reducing rice growth and production. Alam and Islam (2011) reported various arsenic-related problems in rice production such as less tillering, shorter plants (height), plants do not flower timely, grains do not mature timely, more grains remain unfilled, etc. which eventually resulted in rice yield reduction. Plant production declines so as the economic situation declines. Moreover, As contamination causes deterioration of land quality and soil health.

8 Development of Arsenic-Tolerant Plant

Plant tolerant to As, mainly for crop plant, is greatly needed as As highly affects plant growth and yield and human health through food chain. There are various mechanisms that plants evolve to cope with metal toxicity. The operating mechanisms may vary with different species, and even within the one plant species, more than one mechanism could be in operation. The strategies that plants have evolved to cope metal toxicity involve restriction of metal uptake or transport and internal tolerance mechanisms. Plant As resistivity differs in different plant varieties (Choudhury et al. 2011). Arsenic tolerance mechanisms mainly involve inhibition of uptake by roots, efflux from the roots, and chelation by cysteine-rich thiol-reactive peptides and sequestration (Chen et al. 2016; Duan et al. 2012). It has been reported that As accumulation and tolerance depend on *PvPACR3*, an As(III) efflux protein, as well as on nonprotein thiols in *P. vittata* (Singh et al. 2006; Watanabe et al. 2014). According to the study of Song et al. (2014), one of the important steps of As detoxification metabolism is the sequestration of the As(III)–PC complex in vacuoles. It has been reported that phytochelatin (PC) production increased with the increase of the accumulation of As in rice which reduced the As transportation to the grain (Batista et al. 2014). In *Arabidopsis*, resistivity to As increased by two transporters AtABCC1 and AtABCC2 localized in the vacuole and the expression of γ-ECS gene (γ-glutamylcysteine synthetase) or AtPCS1 (PC synthase) (Li et al. 2004, 2006; Song et al. 2010). Song et al. (2014) identified OsABCC1, a novel vacuole transporter, which can transport As(III)–PCs across the tonoplast. As efflux to the external medium may be a key approach in improving As tolerance which was demonstrated by the study of Chen et al. (2016) in *Pteris vittata*. However, according to Zhao et al. (2009), it remains unclear whether As(III) efflux helps in the detoxification of As in plants.

Through genetic engineering and plant breeding technique, tolerant plant to As can be developed. Several studies have been reported by the introduction of novel genes or alterations in gene expression characteristics, and the ability of plants to resist against As increased. Gasic and Korban (2007), Mandal (2015), and Zanella et al. (2016) demonstrated an increase of resistivity of tobacco plant and *Brassica juncea* to As by genetic engineering plants with overexpression of the *ACR2* gene of *Arabidopsis thaliana*-reduced As. According to Duan et al. (2012), transgenic rice plants exhibited 30% lower arsenic concentration in comparison to wild-type plants having similar arsenic translocation factor. Plant breeding also plays an important role in developing As-tolerant plant by crossing low As accessions with high As accessions. Sohn (2014) revealed that in some rice strains, up to 20-fold lower As accumulation has been detected compared with others. One of the chief problems of As is its accumulation in edible parts of crop plants which impart health hazard

Table 2 Genes responsible for the modulation of As accumulation and tolerance in rice

Sl no.	Name of gene	Consequences	References
1.	*OsPht1;8 (OsPT8)*	Decreased As(V) uptake	Wang et al. (2016)
		Increased As(V) tolerance	
2.	*Lsi1 (OsNIP2;1)*	Decreased As accumulation in straw	Ma et al. (2008)
3.	*OsHAC1;1 and OsHAC1;2*	Increased As(III) efflux into the external medium	Shi et al. (2016)
		Decrease As accumulation in rice grain	
4.	*OsGrx_C7* and *OsGrx_C2.1*	Decreased As accumulation	Verma et al. (2016)
		Enhanced As tolerance	
5.	*OsNRAMP1*	Increased As tolerance and accumulation	Tiwari et al. (2014)
6.	*OsABCC1*	Increased As tolerance	Song et al. (2014)
7.	*Lsi2*	Decreased As accumulation	Ma et al. (2008)
8.	*OsCLT1*	Lower As accumulation in roots but higher or similar As accumulation in shoots	Yang et al. (2016)
9.	*arsM*	Decreased As content in rice grain	Meng et al. (2011)
10.	*Pht1;8* and *PHR2*	Increased uptake and translocation of phosphate and As(V)	Wu et al. (2011)
11.	*ACR3*	Increased As(III) efflux	Duan et al. (2012)
		Decreased As accumulation in rice grain	
12.	*OsPIP2;4*, *OsPIP2;6* and *OsPIP2*	Increased As(III) tolerance	Mosa et al. (2012)
13.	*GSTL2*	Increased As tolerance	Kumar et al. (2013)

through consumption, so development of plant where As deposition in edible parts in very least is needed to prevent the hazardous effects imposed by As. The identification of specific inositol transporters (INTs) and nodulin 26-like intrinsic proteins (NIPs) which can lower the seed As level gives a promising step for the developing plant with least accumulation of As in grain (Duan et al. 2015; Lindsay and Maathuis 2016), but still more deep investigation is needed to produce As-free rice (Table 2).

9 Conclusion

Arsenic, a nonessential highly toxic metalloid, enters in plants mainly in the form of arsenate (As(V)) and arsenite (As(III)) through phosphate transporter and aquaporin channels, respectively, and get accumulated into the plant tissues. Accumulation of As leads to several harmful effects in both plants and animals as low quality and quantity of plant yield and hampering health on consumption of the As-contaminated crops. Plants are operating various defense systems to combat the toxic effects of As where transporters are crucial as they are involved in uptake translocation and detoxification process. Limiting the amount of As uptake by plants will reduce the accumulation in plant tissues that can help in protecting the plants from toxicity imposed by As. To develop As to save rice and crops, more research is necessary to gain a better knowledge on uptake, translocation, accumulation, and detoxification of As.

References

Abedin MJ, Meharg AA (2002) Relative toxicity of Arsenite and arsenate on germination and early seedling growth of rice (*Oryza sativa* L.). Plant Soil 243:57–66

Abedin MJ, Feldmann J, Meharg AA (2002) Uptake kinetics of arsenic species in rice plants. Plant Physiol 128:1120–1128

Adriano DC (2001) Trace elements in the terrestrial environments: biogeochemistry bioavailability, and risks of metals. Springer, New York, pp 47–71

Ahmed ZU, Panaullah GM, Gauch H, McCouch SR, Tyagi W, Kabir MS, Duxbury JM et al (2011) Genotype and environment effects on rice (*Oryza sativa* L.) grain arsenic concentration in Bangladesh. Plant Soil 338:367–382

Alam MS, Islam MA (2011) Assessing the effect of arsenic contamination on modern rice production: evidences from a farm level study. Bangladesh J Agric Econ XXXIV:15–28

Alava P, Laing GD, Tack F, De Ryck T, deWiele TV et al (2015) Westernized diets lower arsenic gastrointestinal bioaccessibility but increase microbial arsenic speciation changes in the colon. Chemosphere 119:757–762

Anawar HM, Akai J, Mostofa KM, Safiullah S, Tareq SM et al (2002) Arsenic poisoning in groundwater: health risk and geochemical sources in Bangladesh. Environ Int 27:597–604

Argos M, Kalra T, Rathouz PJ, Chen Y, Pierce B, Parvez F et al (2010) Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study. Lancet 376:252–258

Baig JA, Kazi TG, Shah AQ et al (2010) Biosorption studies on powder of stem of *Acacia nilotica*: removal of arsenic from surface water. J Hazard Mater 178:941–948

Bakhat HF, Zia Z, Fahad S et al (2017) Arsenic uptake, accumulation and toxicity in rice plants: possible remedies for its detoxification: a review. Environ Sci Pollut Res Int 24:9142–9158

Banejad H, Olyaie E (2011) Application of an artificial neural network model to rivers water quality indexes prediction – a case study. J Am Sci 7:60–65

Batista BL, Nigar M, Mestrot A, Rocha BA, Junior FB, Price AH et al (2014) Identification and quantification of phytochelatins in roots of rice to long-term exposure: evidence of individual role on arsenic accumulation and translocation. J Exp Bot 65:1467–1479

Bhattacharya P, Samal AC, Majumdar J, Santra SC (2010) Accumulation of arsenic and its distribution in rice plant (*Oryza sativa* L.) in gangetic West Bengal, India. Paddy Water Environ 8:63–70

Bhattacharya S, Gupta K, Debnath S et al (2012) Arsenic bioaccumulation in rice and edible plants and subsequent transmission through food chain in Bengal basin: a review of the perspectives for environmental health. Toxicol Environ Chem 94:429–441

Bhattacharya P, Jovanovic D, Polya D et al (2014) Best practice guide on the control of arsenic in drinking water. IWA Publishing, London

Bienert GP, Schuessler MD, Jahn TP et al (2008) Metalloids: essential, beneficial or toxic? Major intrinsic proteins sort it out. Trends Biochem Sci 33:20–26

Brackhage C, Huang JH, Schaller J et al (2014) Readily available phosphorous and nitrogen counteract for arsenic uptake and distribution in wheat (*Triticum aestivum* L.). Sci Rep 4:4944

Campbell JA, Stark JH, Carlton-Smith CH (1985) International Symposium on Heavy Metals in the Environment, vol 1. CEP Consultants, Athens, Greece

Carbonell Barrachina A, Burlo Carbonell F, Mataix Beneyto J et al (1995) Arsenic uptake, distribution, and accumulation in tomato plants: effect of arsenite on plant growth and yield. J Plant Nutr 18:1237–1250

Carbonell-Barrachina A, Aarabi MA, Delaune RD, Gambrell RP, Patrick WHJ et al (1998) Bioavailability and uptake of arsenic by wetland vegetation: effects on plant growth and nutrition. J Environ Sci Health 33:45–66

Carey AM, Scheckel KG, Lombi E, Newville M, Choi Y, Norton GJ, Charnock JM, Feldmann J, Price AH, Meharg AA et al (2010) Grain unloading of arsenic species in rice. Plant Physiol 152:309–319

Catarecha P, Segura MD, Franco-Zorrilla JM, García-Ponce B, Lanza M, Solano R, Paz-Ares J, Leyva A et al (2007) A mutant of the Arabidopsis phosphate transporter PHT1;1 displays enhanced arsenic accumulation. Plant Cell 19:1123–1133

Chakraborti D, Rahman MM, Paul K, Chowhury UK, Chanda CR, et al (2001) Groundwater arsenic contamination in south East Asia, with special reference to Bangladesh and West Bengal, India. Arsenic in the Asia Pacific Adelaide, South Australia, pp 1–4

Chatterjee S, Datta S, Mallick PH et al (2013) Use of wetland plants in bioaccumulation of heavy metals. In: Plant-based remediation processes. Springer, Berlin, pp 117–139

Chen Y, Fu JW, Han YH, Rathinasabapathi B, Ma LQ et al (2016) High As exposure induced substantial arsenite efflux in As-hyperaccumulator *Pteris vittata*. Chemosphere 144:2189–2194

Choudhury B, Chowdhury S, Biswas AK (2011) Regulation of growth and metabolism in rice (*Oryza sativa* L.) by arsenic and its possible reversal by phosphate. J Plant Interact 6:15–24

Chung JY, Yu SD, Seoub HY et al (2014) Environmental source of arsenic exposure. J Prev Med Publ Health 47:253–257

Dasgupta T, Hossain SA, Meharg AA et al (2004) An arsenate tolerance gene on chromosome 6 of rice. New Phytol 163:45–49

Dave R, Tripathi RD, Dwivedi S et al (2013) Arsenate and arsenite exposure modulate antioxidants and amino acids in contrasting arsenic accumulating rice (*Oryza sativa* L.) genotypes. J Hazard Mater 262:1123–1131

Duan GL, Hu Y, Liu WJ et al (2011) Evidence for a role of phytochelatins in regulating arsenic accumulation in rice grain. Environ Exp Bot 71:416–421

Duan G, Kamiya T, Ishikawa S, Arao T, Fujiwara T et al (2012) Expressing ScACR3 in rice enhanced arsenite efflux and reduced arsenic accumulation in rice grains. Plant Cell Physiol 53:154–163

Duan G, Liu W, Chen X et al (2013) Association of arsenic with nutrient elements in rice plants. Metallomics 5:784–792

Duan GL, Hu Y, Schneider S, McDermott J, Chen J, Sauer N, Rosen BP, Daus B, Liu Z, Zhu YG et al (2015) Inositol transporters AtINT2 and AtINT4 regulate arsenic accumulation in Arabidopsis seeds. Nat Plants 2:15202

Duxbury JM, Panaullah GM (2007) Remediation of arsenic for agriculture sustainability, food security and health in Bangladesh. FAO, Rome, pp 1–28

Fahad S, Hussain S, Saud S, Hassan S, Chauhan BS, Khan F, Ihsan MZ, Ullah A, Wu C, Bajwa AA et al (2016) Responses of rapid Viscoanalyzer profile and other rice grain qualities to exogenously applied plant growth regulators under high day and high night temperatures. PLoS ONE 11:e0159590

Farooq MA, Islam F, Ali B, Najeeb U, Mao B, Gill RA, Yan G, Siddique KHM, Zhou W et al (2016) Arsenic toxicity in plants: cellular and molecular mechanisms of its transport and metabolism. Environ Exp Bot 132:42–52

Francesconi KA, Kuehnelt D (2002) Arsenic compounds in the environment. In: Frankenberger JWT (ed) Environmental chemistry of arsenic. Marcel Dekker, New York, pp 51–94

Fransisca Y, Small DM, Morrison PD, Spencer MJS, Ball AS, Jones OAH et al (2015) Assessment of arsenic in Australian grown and imported rice varieties on sale in Australia and potential links with irrigation practices and soil geochemistry. Chemosphere 138:1008–1013

Fu Y, Chen M, Bi X et al (2011) Occurrence of arsenic in brown rice and its relationship to soil properties from Hainan Island, China. Environ Pollut 159:1757–1762

Garg N, Singla P (2011) Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms. Environ Chem Lett 9:303–321

Gasic K, Korban SS (2007) Transgenic Indian mustard (*Brassica juncea*) plants expressing an Arabidopsis phytochelatin synthase (AtPCS1) exhibit enhanced As and Cd tolerance. Plant Mol Biol 64:361–369

Gibb H, Haver C, Gaylor D, Ramasamy S, Lee JS, Lobdell D, Wade T, Chen C, White P, Sams R et al (2011) Utility of recent studies to assess the National Research Council 2001 estimates of cancer risk from ingested arsenic. Environ Health Perspect 119:284–290

Gilbert DD, Cottingham KL, Gruber JF, Punshon T, Sayarath V, Gandolfi AJ, Baker ER, Jackson BP, Folt CL, Karagas MR et al (2011) Rice consumption contributes to arsenic exposure in US women. Proc Natl Acad Sci 108:20656–20660

Hartley-Whitaker J, Ainsworth G, Meharg AA et al (2001) Copper- and arsenate-induced oxidative stress in Holcus lanatus L. clones with different sensitivity. Plant Cell Environ 24:713–722

IARC (2012) Biological agents. IARC Monogr Eval Carcinog Risks Hum:100B. PMID:18335640

Islam FS, Gault AG, Boothman C et al (2004) Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. Nature 430:68

Jahan I, Hoque S, Ullah SM, Kibria MG et al (2003) Effects of arsenic on some growth parameters of rice plant. Dhaka Univ J Biol Sci 12:71–77

Jia HF, Ren HY, Gu M, Zhao JN, Sun SB, Zhang X et al (2011) The phosphate transporter gene OsPht1;8 is involved in phosphate homeostasis in rice. Plant Physiol 156:1164–1175

Kamiya T, Islam R, Duan G et al (2013) Phosphate deficiency signaling pathway is a target of arsenate and phosphate transporter OsPT1 is involved in As accumulation in shoots of rice. J Soil Sci Plant Nutr 59:80–590

Karim MM (1999) Arsenic in ground water and health problem in Bangladesh. Wat Res 34:304–310

Katsuhara M, Sasano S, Horie T, Matsumoto T, Rhee J, Shibasaka M et al (2014) Functional and molecular characteristics of rice and barley NIP aquaporins transporting water, hydrogen peroxide and arsenite. Plant Biotechnol 31:213–219

Kazi TG, Arain MB, Baig JA, Jamali MK, Afridi HI, Jalbani N et al (2009) The correlation of arsenic levels in drinking water with the biological samples of skin disorders. Sci Total Environ 407:1019–1026

Khan E, Gupta M (2018) Arsenic–silicon priming of rice (*Oryza sativa* L.) seeds influence mineral nutrient uptake and biochemical responses through modulation of Lsi-1, Lsi-2, Lsi-6 and nutrient transporter genes. Sci Rep 8:10301

Khan SI, Ahmed AKM, Yunus M, Rahman M, Hore SK, Vahter M, Wahed MA (2010) Arsenic and cadmium in food-chain in Bangladesh – an exploratory study. J Health Popul Nutr 28:578–584

McCarty KM, Hanh HT, Kyoung-Woong K et al (2011) Arsenic geochemistry and human health in South East Asia. Rev Environ Health 26:71–78

Kraemer SM (2004) Iron oxide dissolution and solubility in the presence of siderophores. J Aquat Sci 66:3–18

Kumar N, Mallick S, Yadava RN, Singh AP, Sinha S et al (2013) Co-application of selenite and phosphate reduces arsenite uptake in hydroponically grown rice seedlings: toxicity and defence mechanism. Ecotoxicol Environ Saf 91:171–179

Kumar S, Dubey RS, Tripathi RD et al (2015) Omics and biotechnology of arsenic stress and detoxification in plants: current updates and prospective. Environ Int 74:221–230

Lauren JG, Duxbury JM (2005) Management strategies to reduce arsenic uptake by rice. In: Symposium on the behaviour of arsenic in aquifers, soils and plants: implications for management, Dhaka, pp 16–18

Li YJ, Dhankher OP, Carreira L, Lee D, Chen A, Schroeder JI, Balish RS, Meagher RB et al (2004) Overexpression of phytochelatin synthase in *Arabidopsis* leads to enhanced arsenic tolerance and cadmium hypersensitivity. Plant Cell Physiol 45:1787–1797

Li YJ, Dankher OP, Carreira L, Smith AP, Meagher RB et al (2006) The shoot-specific expression of gamma-glutamylcysteine synthetase directs the long-distance transport of thiol-peptides to roots conferring tolerance to mercury and arsenic. Plant Physiol 141:288–298

Li RY, Ago Y, Liu WJ et al (2009) The rice aquaporin Lsi1 mediates uptake of methylated arsenic species. Plant Physiol 150:2071–2080

Li G, Sun GX, Williams PN, Nunes L, Zhu YG et al (2011) Inorganic arsenic in Chinese food and its cancer risk. Environ Int 37:1219–1225

Li G, Santoni V, Maurel C (2014) Plant aquaporins: roles in plant physiology. Biochim Biophys Acta-Gen Subj 1840:1574–1582

Lin HT, Wong SS, Li GC et al (2004) Heavy metal content of rice and shellfish in Taiwan. J Food Drug Anal 12:176

Lindsay ER, Maathuis FJM (2016) *Arabidopsis thaliana* NIP7;1 is involved in tissue arsenic distribution and tolerance in response to arsenate. FEBS Lett 590:779–786

Liu WJ, Zhu YG, Smith FA et al (2004) Do iron plaque and genotypes affect arsenate uptake and translocation by rice seedlings (*Oryza sativa* L.) grown in solution culture. J Exp Bot 55:1707–1713

Liu WJ, Wood BA, Raab A, McGrath SP, Zhao FJ, Feldmann J et al (2010) Complexation of arsenite with phytochelatins reduces arsenite efflux and translocation from roots to shoots in Arabidopsis. Plant Physiol 152:2211–2221

Liu CW, Chen YY, Kao YH, Maji SK et al (2014) Bioaccumulation and translocation of arsenic in the ecosystem of the Guandu wetland, Taiwan. Wetlands 34:129–140

Ma JF, Yamaji N, Mitani N et al (2007) An efflux transporter of silicon in rice. Nature 448:209–213

Ma JF, Yamaji N, Mitani N et al (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proc Natl Acad Sci 105:9931–9935

Mandal A (2015) Transgenic tobacco plants expressing *ACR2* gene of *Arabidopsis thaliana* exhibit reduced accumulation of arsenics and increased tolerance to arsenate. Omics international conference

Marin AR, Masscheleyn PH, Patrick WH (1992) The influence of chemical form and concentration of arsenic on rice growth and tissue arsenic concentration. Plant Soil 139:175–183

Marin AR, Pezeshki SR, Masscheley PH, Choi HS et al (1993) Effect of dimethyl arsenic acid (DMAA) on growth, tissue arsenic, and photo- synthesis of rice plants. J Plant Nutr 16:865–880

Meharg AA, Adomaco E, Lawgali Y, Deacon C, Williams P et al (2007) Food Standards Agency contract C101045: levels of arsenic in rice–literature review, pp 1–65

Meharg AA, Macnair MR (1994) Relationship between plant phosphorus status and the kinetics of arsenate influx in clones of Deschampsia cespitosa (L.) Beauv. that differ in their tolerance to arsenate. Plant Soil 162:99–106

Meharg AA, Rahman M (2003) Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption. Environ Sci Technol 44:229–234

Meharg AA, Williams PN, Adomako E, Lawgali YY, Deacon C, Villada A, Cambell RCJ, Sun G, Zhu YG, Feldmann J et al (2009) Geographical variation in total and inorganic arsenic content of polished (white) rice. Environ Sci Technol 43:1612–1617

Mehrag AA, Hartley-Whitaker J (2002) Arsenic uptake and metabolism in arsenic resistant and non resistant plant species. New Phytol 154:29–43

Mei XQ, Wong MH, Yang Y, Dong HY, Qiu RL, Ye ZH et al (2012) The effects of radial oxygen loss on arsenic tolerance and uptake in rice and on its rhizosphere. Environ Pollut 165:109–117

Melkonian S, Argos M, Hall MN, Chen Y, Parvez F, Pierce B, Cao H, AschebrookKilfo B, Ahmed A, Islam T et al (2013) Urinary and dietary analysis of 18,470 Bangladeshis reveal a correlation of rice consumption with arsenic exposure and toxicity. PLoS One 8:e80691

Mosa KA, Kumar K, Chhikara S et al (2012) Members of rice plasma membrane intrinsic proteins subfamily are involved in arsenite permeability and tolerance in plants. Transgenic Res 21:1265–1277

Mukhopadhyay R, Bhattacharjee H, Rosen BP (2014) Aquaglyceroporins: generalized metalloid channels. Biochim Biophys Acta-Gen Subj 1840:1583–1591

Nath S, Panda P, Mishra S, Dey M, Choudhury S, Sahoo L, Panda SK et al (2014) Arsenic stress in rice: redox consequences and regulation by iron. Plant Physiol Biochem 80:203–210

Norton GJ, Duan G, Dasgupta T et al (2009a) Environmental and genetic control of arsenic accumulation and speciation in rice grain: comparing a range of common cultivars grown in contaminated sites across Bangladesh, China, and India. Environ Sci Technol 43:8381–8386

Norton GJ, Islam MR, Deacon CM et al (2009b) Identification of low inorganic and total grain arsenic rice cultivars from Bangladesh. Environ Sci Technol 43:6070–6075

Norton GJ, Deacon CM, Xiong L et al (2010) Genetic mapping of the rice ionome in leaves and grain: identification of QTLs for 17 elements including arsenic, cadmium, iron and selenium. Plant Soil 329:139–153

Norton GJ, Adomako EE, Deacon CM, Carey AM, Price AH, Meharg AA et al (2013) Effect of organic matter amendment, arsenic amendment and water management regime on rice grain arsenic species. Environ Pollut 177:38–47

Pikaray S, Banerjee S, Mukherji S et al (2005) Sorption of arsenic onto Vindhyan shales: role of pyrite and organic carbon. Curr Sci 88:1580–1585

Quazi S, Datta R, Sarkar D (2011) Effects of soil types and forms of arsenical pesticide on rice growth and development. Int J Environ Sci Technol 8:445–460

Raab A, Williams PN, Meharg A et al (2007) Uptake and translocation of inorganic and methylated arsenic species by plants. Environ Chem 4:197–203

Rahaman S, Sinha AC, Mukhopadhyay D et al (2011) Effect of water regimes and organic matters on transport of arsenic in summer rice (*Oryza sativa* L.). J Environ Sci 23:633–639

Rahman MA, Hasegawa H, Rahman MM, Rahman MA, Miah MAM et al (2007a) Accumulation of arsenic in tissues of rice plant (*Oryza sativa* L.) and its distribution in fractions of rice grain. Chemosphere 69:942–948

Rahman A, Hasegawa H, Mahfuzur Rahman M, Nazrul Islam M, Majid Miah MA, Tasmen A et al (2007b) Effect of arsenic on photosynthesis, growth and yield of five widely cultivated rice (*Oryza sativa* L.) varieties in Bangladesh. Chemosphere 67:1072–1079

Rahman A, Mostofa MG, Alam M, Nahar K, Hasanuzzaman M, Fujita M et al (2015) Calcium mitigates arsenic toxicity in rice seedlings by reducing arsenic uptake and modulating the antioxidant defense and glyoxalase systems and stress markers. Biomed Res Int 2015:1–12

Rausch T, Wachter A (2005) Sulfur metabolism: a versatile platform for launching resistant and non-resistant plant species. New Phytol 154:29–43

Santra SC, Samal AC, Bhattacharya P, Banerjee S, Biswas A, Majumdar J et al (2013) Arsenic in Food chain and community health risk: a study in Gangetic West Bengal. Procedia Environ Sci 18:2–13

Schroeder JI, Delhaize E, Frommer WB et al (2013) Using membrane transporters to improve crops for sustainable food production. Nature 497:60

Sen J, Chaudhuri ABD (2008) Arsenic exposure through drinking water and its effect on pregnancy outcome in Bengali women. Arh Hig Rada Toksikol 59:271–275

Seyfferth AL, Webb SM, Andrews JC et al (2010) Arsenic localization, speciation, and co-occurrence with iron on rice (*Oryza sativa* L.) roots having variable Fe coatings. Environ Sci Technol 44(21):8108–8113

Shaibur MR, Kitajima N, Sugawara R, Kondo T, Huq SMI, Kawai S (2006) Physiological and mineralogical properties of arsenic-induced chlorosis in rice seedlings grown hydroponically. Soil Sci Plant Nutr 52:691–700

Shi S, Wang T, Chen Z, Tang Z, Wu Z, Salt DE et al (2016) OsHAC1; 1 and OsHAC1; 2 function as arsenate reductases and regulate arsenic accumulation. Plant Physiol 172:1708–1719

Shri M, Kumar S, Chakrabarty D, Trivedi PK, Malick S, Mishra P, Shukla D, Mishra S, Srivastava S, Tripathi RD, Tuli R et al (2009) Effect of arsenic on growth, oxidative stress, and antioxidant system in rice seedling. Ecotoxicol Environ Saf 72:1102–1110

Signes-Pastor A, Burlo F, Mitra K et al (2007) Arsenic biogeochemistry as affected by phosphorus fertilizer addition, redox potential and pH in a west Bengal (India) soil. Geoderma 137:504–510

Signes-Pastor AJ, Mitra K, Sarkhel S, Hobbes M, Burlo F, De Groot WT, Carbonell-Barrachina AA et al (2008) Arsenic speciation in food and estimation of the dietary intake of inorganic arsenic in a rural village of West Bengal, India. J Agric Food Chem 56:9469–9474

Signes-Pastor AJ, Carey M, Meharg AA et al (2016) Inorganic arsenic in rice based products for infants and young children. Food Chem 191:128–134

Singh N, Ma LQ, Srivastava M, Rathinasabapathi B (2006) Metabolic adaptations to arsenic induced oxidative stress in *Pteris vittata L.* and *Pteris ensiformis L.* Plant Sci 170:274–282

Singh AP, Dixit G, Kumar A, Mishra S, Singh PK, Dwivedi S, Trivedi PK, Chakrabarty D, Mallick S, Pandey V, Dhankher OP, Tripathi RD et al (2016) Nitric oxide alleviated arsenic toxicity by modulation of antioxidants and thiol metabolism in rice (*Oryza sativa* L.). Front Plant Sci 6:1272

Singh VP, Singh S, Kumar J, Prasad SM et al (2015) Hydrogen sulfide alleviates toxic effects of arsenate in pea seedlings through up-regulation of the ascorbateglutathione cycle: possible involvement of nitric oxide. J Plant Physiol 181:20–29

Sohn E (2014) Contamination: the toxic side of rice. Nature 514:S62–S63

Song WY, Park J, Mendoza-Cózatl DG, Suter-Grotemeyer M, Shim D, Hortensteiner S, Geisler M, Weder B, Rea PA, Rentsch D, Schroeder JI, Lee Y, Martinoia E et al (2010) Arsenic tolerance in *Arabidopsis* is mediated by two ABCC-type phytochelatin transporters. Proc Natl Acad Sci 107:21187–21192

Song WY, Mendoza-Cozatl DG, Lee Y, Schroeder JI, Ahn SN, Lee HS et al (2014) Phytochelatin–metal(loid) transport into vacuoles shows different substrate preferences in barley and Arabidopsis. Plant Cell Environ 37:1192–1201

Srivastava S, Suprasanna P, D'Souza SF et al (2011) Redox state and energetic equilibrium determine the magnitude of stress in *Hydrilla verticillata* upon exposure to arsenate. Protoplasma 48:805–815

Stoeva N, Bineva T (2003) Oxidative changes and photosynthesis in Oat plants grown in As- contaminated soil. Bulg J Plant Physiol 29:87–95

Stoeva N, Berova M, Zlatev Z et al (2005) Effect of arsenic on some physiological parameters in bean plants. Biol Plant 49:293–296

Syu CH, Huang CC, Jiang PY, Lee CH, Lee DY et al (2015) Arsenic accumulation and speciation in rice grains influenced by arsenic phytotoxicity and rice genotypes grown in arsenic-elevated paddy soils. J Hazard Mater 286:179–186

Takahashi Y, Minamikawa R, Hattori KH et al (2004) Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods. Environ Sci Technol 38:1038–1044

Thangavel P, Long S, Minocha R et al (2007) Changes in phytochelatins and their biosynthetic intermediates in red spruce (*Picea rubens* Sarg.) cell suspension culture under cadmium and zinc stress. Plant Cell Tissue Organ Cult 88:201–216

Tiwari M, Sharma D, Dwivedi S, Singh M, Tripathi RD, Trivedi PK et al (2014) Expression in Arabidopsis and cellular localization reveal involvement of rice NRAMP, OsNRAMP1, in arsenic transport and tolerance. Plant Cell Environ 37:140–152

Tripathi RD, Srivastava S, Mishra S, Singh N, Tuli R, Gupta DK, Maathuis FJM (2007) Arsenic hazards: strategies for tolerance and remediation by plants. Trends Biotechnol 25:158–165

Tripathi P, Mishra A, Dwivedi S, Chakrabarty D, Trivedi PK, Singh RP, Tripathi RD et al (2012) Differential response of oxidative stress and thiol metabolism in contrasting rice genotypes for arsenic tolerance. Ecotoxicol Environ Saf 79:189–198

Turpeinen R, Pantsar-Kallio M, Häggblom M et al (1999) Influence of microbes on the mobilization, toxicity and biomethylation of arsenic in soil. Sci Total Environ 236:173–180

Ullah SM (1998) Arsenic contamination of groundwater and irrigated soils of Bangladesh. In: International conference on arsenic pollution of groundwater in Bangladesh: causes, effects and remedies. Community Hospital, Dhaka, p 133

US Food and Drug Administration (2015) Questions & answers: arsenic in rice and rice products. US. FDA, Silver Spring

Verma PK, Verma S, Meher AK, Pande V, Mallick S, Bansiwal AK et al (2016) Overexpression of rice glutaredoxins (OsGrxs) significantly reduce sarsenite accumulation by maintaining glutathione pool and modulating aquaporins in yeast. Plant Physiol Biochem 106:208–217

Wang P, Zhang W, Mao C, Xu G, Zhao FJ et al (2016) The role of OsPT8 in arsenate uptake and varietal difference in arsenate tolerance in rice. J Exp Bot 67:6051–6059

Watanabe T, Kouho R, Katayose T, Kitajima N, Sakamoto N, Yamaguchi N, Shinano T, Urimoto H, Osaki M et al (2014) Arsenic alters uptake and distribution of sulphur in Pteris vittata. Plant Cell Environ 37:45–53

Williams PN, Price AH, Raab A et al (2005) Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. Environ Sci Technol 39:5531–5540

Williams PN, Villada A, Deacon C et al (2007) Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. Environ Sci Technol 41:6854–6859

Williams PN, Zhang H, Davison W et al (2011) Organic matter solid phase interactions are critical for predicting arsenic release and plant uptake in Bangladesh paddy soils. Environ Sci Technol 45:6080–6087

Wu Z, Ren H, McGrath SP et al (2011) Investigating the contribution of the phosphate transport pathway to arsenic accumulation in rice. Plant Physiol 111

Wu C, Huang L, Xue SG, Pan WS, Zou Q, Hartley W, Mo JY et al (2017) Effect of arsenic on spatial pattern of radial oxygen loss and iron plaque formation in rice. Trans Nonferrous Met Soc China 27:413–419

Xie ZM, Huang CY (1998) Control of arsenic toxicity in rice plants grown on an arsenic-polluted paddy soil. Commun Soil Sci Plant 29:2471–2477

Xu XY, McGrath SP, Meharg AA et al (2008) Growing rice aerobically markedly decreases arsenic accumulation. Environ Sci Technol 42:5574–5579

Xu W, Dai W, Yan H et al (2015) Arabidopsis NIP3; 1 plays an important role in arsenic uptake and root-to-shoot translocation under arsenite stress conditions. Mol Plant 8:722–733

Yamaji N, Ma JF (2011) Further characterization of a rice silicon efflux transporter, Lsi2. Soil Sci Plant Nutr 57:259–264

Yang J, Gao MX, Hu H, Ding XM, Lin HW, Wang L et al (2016) OsCLT1, a CRT-like transporter 1, is required for glutathione homeostasis and arsenic tolerance in rice. New Phytol 211:658–670

Zanella L, Fattorini L, Brunetti P, Roccotiello E, Cornara L, D'Angeli S, Della Rovere F, Cardarelli M, Barbieri M, Sanità di Toppi L, Degola F, Lindberg S, Altamura MM, Falasca G et al (2016) Overexpression of AtPCS1 in tobacco increases arsenic and arsenic plus cadmium accumulation and detoxification. Planta 243:605–622

Zavala YJ, Duxbury JM (2008) Arsenic in rice. 1. Estimating normal levels of total arsenic in rice grain. Environ Sci Technol 42:3856–3860

Zhang J, Duan GL (2008) Genotypic difference in arsenic and cadmium accumulation by rice seedlings grown in hydroponics. J Plant Nutr 31:2168–2182

Zhao FJ, Ma JF, Meharg AA, McGrath SP et al (2009) Arsenic uptake and metabolism in plants. New Phytol 181:777–794

Zhao FJ, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559

Safeguarding Rice from Arsenic Contamination Through the Adoption of Chemo-agronomic Measures

Sudhakar Srivastava, Penna Suprasanna, and Rudra Deo Tripathi

Abstract Arsenic accumulation in rice grains is a serious issue. This is due to the fact that rice is consumed all over the world in different forms by children to adults and also in particular high amount in certain regions of the world. Further, rice, from both arsenic contaminated and rather uncontaminated areas, has been found to have higher than permissible levels of As in grains (0.2 mg kg^{-1} dw). The presence of arsenic has also been detected in rice-based food products including baby foods. Hence, there is a greater need to devise feasible low-cost practices to reduce arsenic in rice grains. A number of chemical-based agronomic, feasible approaches have been studied till date which do hold a promise for achieving desirable arsenic reduction in rice grains. The present chapter discusses up-to-date knowledge on strategies for arsenic reduction in rice grains.

Keywords Arsenic · Nitrogen · Rice · Silica · Soil inversion · Sulfur · Thiourea

1 Introduction

The metalloid, arsenic (As), is a ubiquitously present environmental toxin whose contamination in groundwater and soil in various parts of the world is a huge problem. The most affected areas include the Southeast Asian countries like Bangladesh, India, Vietnam, China, Pakistan, etc. The scale of the problem is huge as the affected area is highly densely populated and, therefore, millions of people are threatened by

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As contamination (Ravenscroft et al. 2009). The limit of As in groundwater is 10 ppb, while the limit set for As in rice is 0.2 mg kg-1 dw as per the WHO standard (Majumder et al. 2013; Sohn 2014). There are several reports which indicate the level of As in groundwater and rice grains exceeds several folds in Bengal delta region in India and Bangladesh. The rice grains from other parts of the world have been analyzed for As, and concentrations higher than the recommended limits have been observed (Williams et al. 2007; Rahman et al. 2014; Upadhyay et al. 2019). The intake of As from rice therefore acts as a major exposure route for humans for the As-contaminated areas as well as for those living in other parts of the world (Upadhyay et al. 2019). Arsenic is recognized as a carcinogenic element, and studies indicate an increased risk of cancer in people living in As-affected countries (Bangladesh) as compared to other countries (Meharg et al. 2009).

Rice cultivation is practiced mostly under submerged conditions, which create anaerobic environment in the field. Arsenic chemistry in soil and the concentrations of various As species depends on physicochemical conditions including pH and redox potentials. In anaerobic conditions, As predominantly exists as arsenite [As(III)], whereas in aerobic conditions, arsenate [As(V)] is the major species. Arsenite exits as free arsenious acid (H_3AsO_3) in a wide range of pH. Rice is one of the best accumulators of silica in the form of silicic acid. Silica acts as a beneficial element for rice plants and can accumulate up to 10% of its biomass. Rice roots express silicic acid transporters to a significantly higher level as compared to other crop plants. Arsenious acid and silicic acid are chemically analogous and are taken up and transported by rice through silicic acid transporters (Ali et al. 2009). Therefore, a unique combination of such factors (anaerobic conditions, As(III) predominance, highly expressed silicic acid transporters), rice plants accumulate As in higher amounts as compared to other crop plants like wheat and maize (Awasthi et al. 2017). There are other unique features of rice that also contribute to its ability to accumulate higher As. Rice roots release oxygen through roots to maintain aerobic conditions in rhizospheric zone around roots. The release of oxygen causes ferrous ion to oxidize to ferric ion that precipitates around root surface. This is known as iron plaque. Apart for complexing iron, iron plaque also binds other metals including As. Further, in rhizospheric zone, As(III) may also reoxidize to As(V) to a certain extent. Therefore, iron plaque acts as a reservoir of As around roots allowing higher As intake and may also act as a deterrent by As(III) to As(V) conversion by altering rate of As uptake (Tripathi et al. 2014). The mechanisms of As uptake and transport within the plant are yet to be fully resolved. However, the need of the hour is to study and design suitable low-cost and feasible strategies to reduce As in rice grains. On the basis of knowledge of As chemistry and speciation, and rice plants habit, several approaches have been proposed and studied. These approaches hold positives and negatives that need to be optimized appropriately in the coming years. In this chapter, various agronomic measures including inorganic and organic amendments are discussed.

2 Arsenic-Elemental Interactions

As discussed above, As(III) and silicic acid compete with each other during uptake and transport by rice plants as they share same transporters. Similarly, As(V) is analogous to phosphate, and therefore the uptake of As(V) occurs through phosphate transporters like OsPHT1;1 and OsPHT1;8 in rice (Wu et al. 2011a, b; Kamiya et al. 2013). Further, upon accumulation in rice plants to high levels, As affects the concentrations of other essential metals like calcium (Ca), zinc (Zn), selenium (Se), etc. (Chauhan et al. 2017). The interaction of various essential metals with As affects the overall health of plants, their potential to tolerate As stress, and the eventual As accumulation in various plant parts including rice grains. Therefore, several laboratory-, pot-, or field-based studies focused on studying As-elemental interactions and to optimize elemental concentration so as to achieve desirable As reduction in rice grains.

In a study on the evaluation of the effects of Si addition in two rice cultivars, Zhendao 10 and Nanjing 44, Li et al. (2019) found that low Si decreased As in Nanjing 44, while high Si increased As concentrations. In the other variety, Si addition did not show any significant impact on As concentrations. Si addition led to an increase in P concentration in both genotypes but did not affect iron plaque formation on rice roots. Thus, the study suggests that Si-As interactions depend on the soil, environment, and genotype of rice. Agostinho et al. (2017) tested the impact of different types of silica sources (wollastonite, slag) supplied via soil and one as foliar spray along with different P amendments on rice plant growth, on Si and P levels, and also on the level of other elements including As. The application of P and wollastonite reduced soil As as well as grain As to a significant extent. The interactive effects of silica (Si) with As are probably the most studied ones. In pot experiments to evaluate interactions of silica, iron plaque, and radial oxygen loss (ROL), Wu et al. (2016) observed that the indica genotypes having greater ROL than hybrid genotypes produced more iron plaque and also had higher As adsorption in iron plaque. Silica amendment (10–40 mg/kg as SiO_2 gel) further increased the level of iron but decreased that of As in iron plaque probably due to occupation of adsorption sites by itself (Liu et al. 2014). Nonetheless, silica addition induced significant decline in As concentrations roots, straw, and husk. Indica rice genotypes also had a lower level of inorganic As in grains than hybrid genotypes. Although the level of inorganic As in grains was not affected by silica, the level of DMA was significantly reduced. The positive effects of silica addition were reflected in increased biomass of plants including grains. Silica is a beneficial element for rice plants, and silica application in different chemical forms and by different methods has been found to improve rice growth and yield (Liu et al. 2014; Tripathi et al. 2013; Detmann et al. 2012). Silica addition can enhance rice tolerance to As toxicity (Fleck et al. 2013) with increase in growth of plants (Guo et al. 2007; Tripathi et al. 2013). Seyfferth et al. (2016) utilized rice husk as a source of Si (1% w/w application in soil), as rice husk contains less As than rice straw, and found that inorganic As concentration in grains decreased by 25−50% without any negative impact on Cd concentrations of grains and grain yield. Earlier, Seyfferth and Fendorf (2012) used two silicate minerals (diatomaceous earth and silica gel) to evaluate the effect of Si on As concentrations in rice. They found that diatomaceous earth Si addition either did not change or increased As in grains. However, the addition of Si in the form of Si gel led to a decreased As in grains. Use kaolin to reduce As in rice grains. Kaolin is a Si- and Al-rich low-cost adsorbent and is readily available. The use of kaolin along with As in soil was found to reduce As concentration of rice grains to below detection limit (Arnamwong et al. 2016).

Sanglard et al. (2014) demonstrated that As (25 micromolar)-induced impairment of carbon fixation and photosynthetic rages in wild-type and *lsi1* mutant rice was correlated to the effect on stomatal and mesophyll conductance. This Si addition (2 mM) caused an increase in Si and up to 48% decrease in As concentration in leaves in WT plants and *lsi1* mutant. However, the alleviation of photosynthetic toxicity was seen to be stronger in WT plants as compared to *lsi1* mutant. Li et al. (2009) also observed a reduction in grain As concentration in rice in pot study when Si was supplied as silica gel (SiO_2). However, they reported an increase in DMA concentration in grains. In contrast to the positive reports, Lee et al. (2014) investigated the effects of Si addition in field conditions and observed that Si application resulted in an increase in the concentration of both As and Si. This in turn caused more toxicity to rice and greater As accumulation. Hence, the form of Si, the amount of Si, the genotype in concern, the environmental conditions, etc. need to be optimized to achieve desirable As reduction in grains and avoid any negative impact.

The uptake of As(V) faces competition with phosphate. Hence, As(V)-phosphate interactions have also been studied by a few researchers. However, the results obtained were variable and did not yield desirable success. In fact, it was observed that phosphate increased soil As(V) concentrations through replacement of adsorbed As(V). Further, As(V) adsorbed in iron plaque around rice roots was also replaced by phosphate. This led to an increase in As(V) concentration in soil and in root rhizosphere that in turn led to an increase in As concentration in rice plants (Hossain et al. 2009; Talukder et al. 2011; Wu et al. 2011a, b). Zou et al. (2018) conducted a pot study on a field soil contaminated with both As and Pb to understand interactive effects of ferrous sulfate and water management on rice plants. The application of ferrous sulfate in non-flooded conditions increased iron plaque formation allowing greater sequestration of As and Pb. Plant growth and biomass was significantly increased in ferrous sulfate treatment in non-flooded conditions. The ferrous sulfate addition resulted in significant decrease in As concentration but an increase in Pb concentrations in rice grains in both flooded and non-flooded conditions. Hence, a combination of appropriate ferrous sulfate amendment and water management can be beneficial but needs to be evaluated for the changes in other elements. Islam et al. (2019) evaluated a set of strategies including alternate wetting and drying/continuous flooding and Si and P fertilization on soil and arsenic. AWD treatments as well as Si addition were found to significantly decrease As concentration in pore water and also in rice (12–21% by AWD, 21% by Si at 20 mg/kg); however, P fertilization did not affect As in rice. Grain yield was significantly decreased by As (58.6% at 20 mg/kg As); however, it was increased by AWD by 13%.

Sulfur (S) is an important element in the context of As detoxification by plants. As in the form of As(III) is complexed by thiol (-SH)-containing ligands: glutathione (GSH) and phytochelatins (PCs). Further, GSH either itself acts as an antioxidant or helps in the operation of ascorbate-glutathione cycle for scavenging of reactive oxygen species (ROS). GSH is also required for the reduction of As(V) to As(III) in the process of As detoxification (Srivastava et al. 2007; Liu et al. 2010; Zhang et al. 2011). In an aquatic plant, *Hydrilla verticillata*, additional S supply was found to increase the As tolerance potential of plants (Srivastava and D'Souza 2009). Hence, keeping in mind the importance of S, studies have been conducted to evaluate the impact of variable S supply on rice plants. Dixit et al. (2015a) evaluated the impact of high S supply on As tolerance and As accumulation in rice plants. They found that in the presence of high S, As was restricted to roots by increased complexation, and the translocation of As from root to shoot was reduced. In contrast, in condition of low S supply, As translocation to shoot was increased. The authors further demonstrated that high S supply also modulated protein and amino acid profile of rice plants and increased thiol metabolism. These effects led to enhanced tolerance of rice plants to As stress (Dixit et al. 2015b). Zhang et al. (2016) also reported that S application decreased As concentration in rice grains (44%). The decrease was observed mainly in As(V) and As(III) concentrations; however, DMA concentration was not affected. The S-mediated effects were attributable to changes in the expression of various genes and transporters of As. Srivastava et al. (2016) grew rice seedlings in three different S supplies, 0.798 mM S (normal S), 0.2 mM S (low S), and 0.003 mM S (zero S), for 7 days given the As(III) stress of 20 μM for 7–15 days. They observed that As concentrations in roots and shoots were declined with the S supply changing from normal to zero. The reduction in As concentration at 15 days in roots was from 1536 $\mu g g^{-1}$DW to 1062 and in shoots from 58 $\mu g g^{-1}$DW to 16 $\mu g g^{-1}$DW at 15 days at normal and zero S supply, respectively. They found that while sulfate transporters were upregulated to maintain sulfate pool, the expression of As transporters (Lsi1 and Lsi2) was downregulated to minimize As load in reduced S supply. However, an increase in thiol metabolites (cysteine, GSH, and PCs) was observed upon As exposure. Thus, S plays a crucial role in As tolerance of rice plants and can regulate As accumulation effectively.

Essential elemental supplementation influences As tolerance in crop plants, and hence appropriate nutrition regime could be useful in augmenting tolerance responses. Srivastava et al. (2019) monitored responses of rice seedlings subjected to As stress in conditions of variable nitrogen (N) supply (low nitrogen, LN, and high nitrogen, HN). It was found that LN supply to As-stressed rice seedlings was able to increase As tolerance with improved growth and root phenotype. Importantly, As concentration in LN+As in roots was significantly lower (848 $\mu g\ g^{-1}$ dw) than that in As-alone treatment (1434 $\mu g\ g^{-1}$ dw). Similarly, nitrate supplementation-mediated reduction in As toxicity in *Solanum lycopersicum* has been reported by Gupta and Seth (2019). Kumar et al. (2014) studied the interaction of As with Se, an important antioxidant. They found that growth of rice seedlings as well as As tolerance was significantly increased in As+Se treatment. It has been suggested that

Se might compete with As for uptake leading to reduction in As accumulation and stress (Malik et al. 2011). Further, Se adds to antioxidant potential of plants allowing them to combat ROS with greater efficiency (Malik et al. 2012). Chauhan et al. (2017) also observed that selenite [Se(IV)] supplementation to As(III)-treated rice seedlings resulted in a decrease in As concentration in roots and shoot of rice seedlings. Further, oxidative stress was significantly reduced with decrease in ROS, lipid peroxidation, prooxidant enzyme activity (NADPH oxidative), etc. in As+Se than in As-alone treated seedlings. Se supplementation also increased the phenolic content (gallic acid, ferulic acid, rutin, protocatechuic acid) and thiol metabolism enzymes. Further, improvement in the nutrient element levels (Fe, Cu, Zn, Mn, Mo, Co) was observed. Therefore, Se supplementation brings about holistic changes in plant metabolism and As uptake and transport to enhance the tolerance of plants to As stress.

In a study on the interaction of calcium (10 mM) with As(V) (0.5 and 1 mM) in rice seedlings during a 5-day treatment period, Rahman et al. (2015) observed that As(V) stress = negatively affected plant growth, to induce oxidative stress and to decrease antioxidants and glyoxalase enzymes along with an increase in As accumulation. The calcium supply was able to mitigate toxic effects of As(V) causing a decline in As accumulation. In an earlier work by Rai et al. (2012), also Ca supply was found to impart tolerance to calli of *B. juncea* under As stress. However, the accumulation of As was found to increase upon Ca supply in calli. Further, changes in As speciation were also observed with increase in As(III) levels in Ca plus As(V) treatment than in As(V)-alone one.

3 Chemical Amendments

3.1 Thiourea and Redox Molecules

As discussed above, GSH and PCs play crucial roles in combating As stress by plants by As complexation and by regulating ROS levels (Srivastava et al. 2016). Apart from this, the ratio of reduced glutathione (GSH)/oxidized glutathione (GSSG) as well as other redox couples like ascorbate/dehydroascorbate, NADPH/NADP, and NADH/NAD is also maintained when ROS are regulated effectively and plant metabolism operates with no negative impact. The maintenance of redox state is crucial as any disturbance to redox balance is linked to the extent of stress caused by As (Srivastava et al. 2011). Kuramata et al. (2011) reported that variable redox conditions of soil in pot-grown and field-grown rice seedlings resulted in differences in As species [As(V), As(III), DMA] in rice seedlings. Srivastava et al. (2014) conducted laboratory experiments by using a redox-active molecule, thiourea (TU), for the evaluation of As stress amelioration in rice seedlings. It was observed that TU supplementation ameliorated As stress in rice seedlings and also caused reduction in As concentrations in shoot. There were changes in thiol metabolism of seedlings. In addition, the expression of As transporters (Lsi1 and Lsi2) was altered in redox-dependent manner. Hence, redox state maintenance by TU supplementation was found to be the prime player behind As stress tolerance of rice seedlings. Earlier, Shri et al. (2009) have also found positive influence of GSH and cysteine supplementation in As(III)-/As(V)-stressed rice seedlings in terms of improved growth and reduced oxidative stress.

3.2 Biochar and Organic Matter Amendment

The burning of rice straw is a common practice among farmers. However, burning temperature leads to the formation of either black carbon (~350 °C) or biochar (400–700 °C) or ash (full oxidation). These processes influence elemental levels and properties of ash (Schaller et al. 2018). Rice straw application after harvest is a routine practice to keep the field covered and to provide nutrients already accumulated in rice plants back to the soil. Schaller et al. (2018) evaluated the impact of addition of fresh rice straw in the form of black carbon or ash after burning. They found that fresh rice straw increased the level of As in soil, while in the form of black carbon, minor change in soil As was observed. The authors derived net ratios of elemental mobilization from soil/no soil experiments and found them to be <1 for Si and P indicating immobilization in soil while >1 for Fe and As suggesting increased mobilization in soil. The authors concluded that burning rice straw on the field to black carbon not only saves additional fertilization costs in the next crop but also reduces As mobilization. Modified biochar and modified biochar plus zerovalent iron applications have been found to significantly reduce bioavailable water-soluble As and decrease As uptake in the shoot and root of *Brassica campestris* (Li et al. 2018). Wu et al. (2017) used rice straw biochar modified by red mud combining features of both red mud and biochar like surface area, metal oxides, porous structure, etc., for the removal of As in laboratory conditions. The adsorption potential of red mud-modified biochar was ten times higher for As(V) and As(III) than untreated biochar. Lin et al. (2019) have demonstrated that the application of Fe-Mn-modified biochar composite (FMBC) in soil altered soil properties increasing soil redox and decreased soil-available As. The activities of soil enzymes were also increased except alkaline phosphatase. In addition, changes in the microbial composition of soil were also noticed with increase in abundance of *Proteobacteria* and *Firmicutes*. Thus, biochar amendments affect soil properties holistically. Earlier work by Liu et al. (2017), who used an amino biochar modified via nano zerovalent iron (ABC/NZVI), also demonstrated changes in rhizospheric microbiota in As-contaminated paddy soil. While proportion of *Geobacter* increased, that of *Nitrososphaera* decreased different growth stages of rice crop. It was found that ABC/NZVI immobilized As in soil and therefore led to decline in As concentration in rice straw.

The role of organic matter (OM) in the mobilization/immobilization of metals is well known (Gao et al. 2018; Stanislawska-Glubiak et al. 2015). Peat is a rich source of OM and is frequently used as organic fertilizer to improve physical and chemical properties of soil. Peat application also affects the mobility of metals and metalloids, and these effects are also modulated by the presence of oxides and hydroxides of metals like Fe (Liu et al. 2015; Yu et al. 2017). In a recent pot study, the combined application of woody peat and iron nitrate [$Fe(NO_3)_3$] was found to cause significant decline in pore water As and Cd. It also led to a decrease in mobile fractions of As and Cd. The application of increasing concentration of $Fe(NO_3)_3$ along with peat caused increase in As immobilization by crystalline Fe oxides and also resulted in higher iron plaque formation on rice roots and consequently reduced grain As and Cd accumulation (Wang et al. 2019).

3.3 Hormones and Other Metabolites

Plant growth and development involve the integration of many environmental and endogenous signals that determine plant structure and physiology together with the intrinsic genetic program. Fundamental to this process are plant hormones or phytohormones which include auxins, gibberellins (GAs), cytokinins, abscisic acid (ABA), ethylene, jasmonic acid (JA), and brassinosteroids (BRs). Pandey and Gupta (2015) studied the effect of the co-application of selenium (Se) and auxin on morphological and biochemical characteristics in rice seedlings exposed to As stress. When used together, Se and auxin were more effective in reducing As-induced stress compared to individual treatments. Also, there are evidences indicating that auxins can promote modification of membrane properties, thereby alleviating toxic effects. Several studies have reported the involvement of ethylene in response to abiotic stress, and few experiments have shown an increased production of ethylene and reduced plant growth and development when exposed to toxic levels of heavy metals (Maksymiec et al. 2007; DalCorso et al. 2010; Khan et al. 2015). It has been suggested that brassinosteroids play a crucial role in response to heavy metal toxicity. Their ability to improve the effectiveness of antioxidant systems by elevating the activity and levels of enzymatic and nonenzymatic antioxidants has made their use a potential strategy for increasing crop resistance to heavy metal stress and significant increase in plant growth and development (Sharma et al. 2013).

Singh et al. (2015) demonstrated the positive results of salicylic acid, a plant hormone, supplementation on rice seedlings under As stress. They found that As stress hampered seedling growth and induced oxidative stress, while SA application reverted the toxic effects. As concentrations were also significantly reduced in the shoot and root of As+SA-treated rice seedlings than As-alone ones. The co-application of SA was found to impart greater effects than pretreatment of SA for 3 days before application of As stress. Further, the role of nitric oxide (NO) in

SA-mediated As toxicity reduction in rice was also demonstrated by Singh et al. (2017). It was found that SA supply increased endogenous NO level through increase in the activity of nitrate reductase enzyme. The exogenous supply of NO was also found to reduce As stress in rice seedlings. Therefore, a concerted action of NO and SA has been proposed by Singh et al. (2015, 2017) in As toxicity reduction in rice. GABA (γ-aminobutyric acid) has been postulated to act as a central regulator for harmonized changes in carbon, nitrogen, and sulfur metabolism during As stress in *Brassica juncea* (Pathare et al. 2013). Kumar et al. (2017) studied the impact of short- and long-term GABA supply on the performance of rice seedlings under As stress. They observed that in the condition of GABA accumulation, the expression of important As transporters (*OsLsi1* and *OsLsi2*) was downregulated resulting into decreased As accumulation in rice. The long-term supply of GABA was also found to induce antioxidant enzyme activities and prevent stress effects on physiological parameters like water use efficiency, photosynthetic efficiency, etc. Further, it was revealed that upon GABA supply, the level of unsaturated fatty acids and amino acids like proline, cysteine, and polyamines was also maintained at a higher level in rice seedlings than that of As-alone stressed seedlings (Kumar et al. 2019).

3.4 Other Agronomic Approaches

Very recently, a novel approach was adopted by Huhmann et al. (2019) to reduce As contamination in rice. The researchers inverted the soil layers by removing a total of 40 cm of soil (with top layer of 20 cm and two layers of 10 cm) and then inverted the layers: top soil layer was kept in the lowest position, and the lowest soil layer was kept at top. The technique led to a decline in soil As but also organic carbon, nitrogen, and phosphorus by 40%, and the low levels could be maintained for four cropping seasons. The result of reduced As burden on rice crops was evident in 15–30% increased paddy yields. However, the authors did mention that such an approach might too become nonfunctional within a few decades due to re-buildup of As via irrigation water.

Dolphen and Thiravetyan (2019) tested the combination of microbe and a potential amendment for reducing arsenic in rice grains. They found that leonardite, an iron- and aluminum-rich material, had the maximum As adsorption efficiency (91.86%) than bagasse fly ash, rice husk ash, and sawdust fly ash, at 2 mg L-1 initial As concentration and 1% of adsorbent. They also identified *Bacillus pumilus* as potential microbe for reducing As in rice grains due to its high siderophore-producing ability. A combination of leonardite and microbe (*B. pumilus*, *Pseudomonas* sp., or *B. thuringiensis*) was found to significantly reduce As in rice grains below 0.2 mg Kg-1 permissible limit through downregulation of Lsi1, Lsi2, and OsPT4 transporters during heading stage.

4 Conclusion

It is clear from the above discussion that As is a ubiquitously present environmental contaminant which affects plant growth and productivity. A number of feasible agronomic options are available to mitigate As stress and to reduce As concentration in the produce especially rice grains. However, the obvious fact is that the effectiveness of each strategy is influenced by the treatment method, chemical composition, genotype of rice in concern, and environmental factors. Therefore, concerted research efforts are needed to develop optimized low-cost, feasible solutions to suit best for the environmental conditions, soil properties, and rice genotypes for the particular area. This would result in obtaining good rice yields with low As accumulation in grains.

References

Agostinho FB, Tubana BS, Martins MS, Datnoff LE (2017) Effect of different silicon sources on yield and silicon uptake of rice grown under varying phosphorus rates. Plan Theory 6:35

Ali W, Isayenkov SV, Zhao FJ, Maathuis FJM (2009) Arsenite transport in plants. Cell Mol Life Sci 66:2329–2339

Arnamwong S, Suksabye P, Thiravetyan P (2016) Using kaolin in reduction of arsenic in rice grains: effect of different types of kaolin, pH and arsenic complex. Bull Environ Contam Toxicol 96:556–561

Awasthi S, Chauhan R, Srivastava S, Tripathi RD (2017) The journey of arsenic from soil to grain in rice. Front Plant Sci 8:1007

Chauhan R, Awasthi S, Tripathi P, Mishra S, Dwivedi S, Niranjan A, Mallick S, Tripathi P, Pande V, Tripathi RD (2017) Selenite modulates the level of phenolics and nutrient element to alleviate the toxicity of arsenite in rice (*Oryza sativa* L.). Ecotoxicol Environ Saf 138:47–55

DalCorso G, Farinati S, Furini A (2010) Regulatory networks of cadmium stress in plants. Plant Signal Behav 5:663–667

Detmann KC, Araújo WL, Martins SCV, Sanglard LMVP, Reis JV, Detmann E, Rodrigues FA, Nunes-Nesi A, Fernie AR, DaMatta FM (2012) Silicon nutrition increases grain yield, which, in turn, exerts a feed-forward stimulation of photosynthetic rates via enhanced mesophyll conductance and alters primary metabolism in rice. New Phytol 196:752–762

Dixit G, Singh AP, Kumar A, Dwivedi S, Deeba F, Kumar S et al (2015a) Sulfur alleviates arsenic toxicity by reducing its accumulation and modulating proteome, amino acids and thiol metabolism in rice leaves. Sci Rep 5:16205

Dixit G, Singh AP, Kumar A, Singh PK, Kumar S, Dwivedi S et al (2015b) Sulfur mediated reduction of arsenic toxicity involves efficient thiol metabolism and the antioxidant defense system in rice. J Hazard Mater 298:241–251

Dolphen R, Thiravetyan P (2019) Reducing arsenic in rice grains by leonardite and arsenic-resistant endophytic bacteria. Chemosphere 223:448–454

Fleck AT, Mattusch J, Schenk MK (2013) Silicon decreases the arsenic level in rice grain by limiting arsenite transport. J Plant Nutr Soil Sci 176:785–794

Gao J, Lv J, Wu H, Dai Y, Nasir M (2018) Impacts of wheat straw addition on dissolved organic matter characteristics in cadmium-contaminated soils: insights from fluorescence spectroscopy and environmental implications. Chemosphere 193:1027–1035

Guo W, Zhu YG, Liu WJ, Liang YC, Geng CN, Wang SG (2007) Is the effect of silicon on rice uptake of arsenate (AsV) related to internal silicon concentrations, iron plaque and phosphate nutrition? Environ Pollut 148:251–257

Gupta P, Seth CS (2019) Nitrate supplementation attenuates As(V) toxicity in *Solanum lycopersicum* L.cv Pusa Rohini: insights into As(V) sub-cellular distribution, photosynthesis, nitrogen assimilation, and DNA damage. Plant Physiol Biochem 139:44–55

Hossain MB, Jahiruddin M, Loeppert RH, Panaullah GM, Islam MR, Duxbury JM (2009) The effects of iron plaque and phosphorus on yield and arsenic accumulation in rice. Plant Soil 317:167–176

Huhmann BL, Harvey CF, Uddin A, Choudhury I, Ahmed KM, Duxbury JM, Ellis T, van Geen A (2019) Inversion of high-arsenic soil for improved rice yield in Bangladesh. Environ Sci Technol 53(7):3410–3418

Islam S, Rahmn MM, Naidu R (2019) Impact of water and fertilizer management on arsenic bioaccumulation and speciation in rice plants grown under greenhouse conditions. Chemosphere 214:606–613

Kamiya T, Islam MR, Duan G, Uraguchi S, Fujiwara T (2013) Phosphate deficiency signaling pathway is a target of arsenate and phosphate transporter *OsPT1* is involved in As accumulation in shoots of rice. Soil Sci Plant Nutr 59:580–590

Khan AL, Waqas M, Hussain J, Al-Harrasi A, Hamayun M, Lee IJ (2015) Phytohormones enabled endophytic fungal symbiosis improve aluminum phytoextraction in tolerant *Solanum lycopersicum*: an examples of *Penicillium janthinellum* LK5 and comparison with exogenous GA3. J Hazard Mater 295:70–78

Kumar A, Singh RP, Singh PK, Awasthi S, Chakrabarty D, Trivedi PK, Tripathi RD (2014) Selenium ameliorates arsenic induced oxidative stress through modulation of antioxidant enzymes and thiols in rice (*Oryza sativa* L.). Ecotoxicology 23:1153–1163

Kumar N, Dubey AK, Upadhyay AK, Gautam A, Ranjan R, Srikrishna S, Sahu N, Behera SK, Mallick S (2017) GABA accretion reduces Lsi-1 and Lsi-2 gene expressions and modulates physiological responses in *Oryza sativa* to provide tolerance towards arsenic. Sci Rep 7:8786

Kumar N, Gautam A, Dubey AK, Ranjan R, Pandey A, Kumari B, Singh G, Mandotra S, Chauhan PS, Srikrishna S, Dutta V, Mallick S (2019) GABA mediated reduction of arsenite toxicity in rice seedling through modulation of fatty acids, stress responsive amino acids and polyamines biosynthesis. Ecotoxicol Environ Saf 173:15–27

Kuramata M, Abe T, Matsumoto S, Ishikawa S (2011) Arsenic accumulation and speciation in Japanese paddy rice cultivars. Soil Sci Plant Nutr 57:248–258

Lee CH, Huang HH, Syu CH, Lin TH, Lee DY (2014) Increase of as release and phytotoxicity to rice seedlings in as-contaminated soils by Si fertilizer application. J Hazard Mater 276:253–261

Li RY, Stroud JL, Ma JF, McGrath SP, Zhao FJ (2009) Mitigation of arsenic accumulation in rice with water management and silicon fertilization. Environ Sci Technol 43:3778–3783

Li L, Zhu C, Liu X, Li F, Li H, Ye J (2018) Biochar amendment immobilizes arsenic in farmland and reduces its bioavailability. Environ Sci Pollut Res 25:34091–34102

Li R, Zhou Z, Xu X, Xie X, Zhang Q, Liu Y (2019) Effects of silicon application on uptake of arsenic and phosphorus and formation of iron plaque in rice seedlings grown in an arsenic-contaminated soil. Bull Environ Contam Toxicol (in press)

Lin L, Li Z, Liu X, Qiu W, Song Z (2019) Effects of Fe-Mn modified biochar composite treatment on the properties of As-polluted paddy soil. Environ Pollut 244:600–607

Liu WJ, Wood BA, Raab A, McGrath SP, Zhao FJ, Feldmann J (2010) Complexation of arsenite with phytochelatins reduces arsenite efflux and translocation from roots to shoots in Arabidopsis. Plant Physiol 152:2211–2221

Liu CP, Wei L, Zhang SR, Xu XH, Li FB (2014) Effects of nanoscale silica sol foliar application on arsenic uptake, distribution and oxidative damage defense in rice (*Oryza sativa* L.) under arsenic stress. RSC Adv 4:57227

Liu C, Yu H-Y, Liu C, Lie F, Xu X, Wang Q (2015) Arsenic availability in rice from a mining area: is amorphous iron oxide-bound arsenic a source or sink? Environ Pollut 199:95–101

Liu S, Lu Y, Yang C, Liu C, Ma L, Dang Z (2017) Effects of modified biochar on rhizosphere microecology of rice (*Oryza sativa* L.) grown in As-contaminated soil. Environ Sci Pollut Res 24:23815–23824

Majumder A, Saha N, Ghosh S, Sarkar S, Kole SC (2013) In vitro assessment of arsenicals bioaccumulating potential of soil bacteria. J Environ Biol 34:841–846

Maksymiec W, Wojcik M, Krupa Z (2007) Variation in oxidative stress and photochemical activity in *Arabidopsis thaliana* leaves subjected to cadmium and excess copper in the presence or absence of jasmonate and ascorbate. Chemosphere 66:421–427

Malik JA, Kumar S, Thakur P, Sharma S, Kaur N, Kaur R et al (2011) Promotion of growth in mungbean (*Phaseolus aureus* Roxb.) by selenium is associated with stimulation of carbohydrate metabolism. Biol Trace Elem Res 143:530–539

Malik JA, Goel S, Kaur N, Sharma S, Singh I, Nayyar H (2012) Selenium antagonises the toxic effects of arsenic on mungbean (*Phaseolus aureus* Roxb.) plants by restricting its uptake and enhancing the antioxidative and detoxification mechanisms. Environ Exp Bot 77:242–248

Meharg AA, Williams PN, Adamako E, Lawgali YY, Deacon C, Villada A, Cambell RCJ, Sun GX, Zhu YG, Feldmann J, Raab A, Zhao FJ, Islam R, Hossain S, Yanai J (2009) Geographical variation in total and inorganic arsenic content of polished (white) rice. Environ Sci Technol 43:1612–1617

Pandey C, Gupta M (2015) Selenium and auxin mitigates arsenic stress in rice (*Oryza sativa* L.) by combining the role of stress indicators, modulators and genotoxic assay. J Hazard Mater 287:384–391

Pathare V, Srivastava S, Suprasanna P (2013) Evaluation of effects of arsenic on carbon, nitrogen, and sulfur metabolism in two contrasting varieties of *Brassica juncea*. Acta Physiol Plant 35:3377–3389

Rahman MA, Rahman MM, Reichman SM, Lim RP, Naidu R (2014) Arsenic speciation in Australian-grown and imported rice on sale in Australia: implications for human health risk. J Agric Food Chem 62:6016–6024

Rahman A, Mostofa MG, Alam MM, Nahar K, Hasanuzzaman M, Fujita M (2015) Calcium mitigates arsenic toxicity in rice seedlings by reducing arsenic uptake and modulating antioxidant defense and glyoxalase systems and stress markers. BioMed Res Int 2015:340812

Rai AN, Srivastava S, Paladi RK, Suprasanna P (2012) Calcium supplementation modulates arsenic-induced alterations and augments arsenic accumulation in callus cultures of Indian mustard (*Brassica juncea* (L.) Czern.). Protoplasma 249:725–736

Ravenscroft P, Brammer H, Richards K (2009) Arsenic pollution, a global synthesis, RGS-IBG book series. Wiley-Blackwell, Oxford

Sanglard LMVP, Martins SCV, Detmann KC, Silva PEM, Lavinsky AO, Silva MM, Detmann E, Araujo WL, DaMatta FM (2014) Silicon nutrition alleviates the negative impacts of arsenic on the photosynthetic apparatus of rice leaves: an analysis of the key limitations of photosynthesis. Physiol Plant 152:355–366

Schaller J, Wang J, Islam MR, Planer-Friedrich B (2018) Black carbon yields highest nutrient and lowest arsenic release when using rice residuals in paddy soils. Sci Rep 8:17004

Seyfferth AL, Fendorf S (2012) Silicate mineral impacts on the uptake and storage of arsenic and plant nutrients in rice (*Oryza sativa* L.). Environ Sci Technol 46:13176–13183

Seyfferth AL, Morris AH, Gill R, Kearns KA, Mann JN, Paukett M, Leskanic C (2016) Soil incorporation of silica-rich rice husk decreases inorganic arsenic in rice grain. J Agric Food Chem 64:3760–3766

Sharma P, Kumar A, Bhardwaj R (2013) Plant steroidal hormone epibrassinolide regulate – heavy metal stress tolerance in *Oryza sativa* L. by modulating antioxidant defense expression. Environ Exp Bot 122:1–9

Shri M, Kumar S, Chakrabarty D, Trivedi PK, Mallick S, Misra P, Shukla D, Mishra S, Srivastava S, Tripathi RD, Tuli R (2009) Effect of arsenic on growth, oxidative stress, and antioxidant system in rice seedlings. Ecotoxicol Environ Saf 72:1102–1110

Singh AP, Dixit G, Mishra S, Dwivedi S, Tiwari M, Mallick S, Pandey V, Trivedi PK, Chakrabarty D, Tripathi RD (2015) Salicylic acid modulates arsenic toxicity by reducing its root to shoot translocation in rice (*Oryza sativa* L.). Front Plant Sci 6:340

Singh AP, Dixit G, Kumar A, Mishra S, Kumar N, Dixit S, Singh PK, Dwivedi S, Trivedi PK, Pandey V, Dhankher OP, Norton GJ, Chakrabarty D, Tripathi RD (2017) A protective role of nitric oxide and salicylic acid for arsenite phytotoxicity in rice (*Oryza sativa* L.). Plant Physiol Biochem 115:163–173

Sohn E (2014) The toxic side of rice. Nature 514:S62–S63

Srivastava S, D'Souza SF (2009) Increasing sulfur supply enhances tolerance to arsenic and its accumulation in *Hydrilla verticillata* (L.f.) Royle. Environ Sci Technol 43:6308–6313

Srivastava S, Mishra S, Tripathi RD, Dwivedi S, Trivedi PK, Tandon PK (2007) Phytochelatins and antioxidant systems respond differentially during arsenite and arsenate stress in *Hydrilla verticillata* (L.f.) Royle. Environ Sci Technol 41:2930–2936

Srivastava S, Suprasanna P, D'Souza SF (2011) Redox state and energetic equilibrium determine the magnitude of stress in *Hydrilla verticillata* upon exposure to arsenate. Protoplasma 248:805–815

Srivastava AK, Srivastava S, Mishra S, D'Souza SF, Suprasanna P (2014) Identification of redox-regulated components of arsenate (AsV) tolerance through thiourea supplementation in rice. Metallomics 6:1718–1730

Srivastava S, Akkarakaran JJ, Sounderajan S, Shrivastava M, Suprasanna P (2016) Arsenic toxicity in rice (*Oryza sativa* L.) is influenced by sulfur supply: impact on the expression of transporters and thiol metabolism. Geoderma 270:33–42

Srivastava S, Pathare VS, Sounderajan S, Suprasanna P (2019) Nitrogen supply influences arsenic accumulation and stress responses of rice (*Oryza sativa* L.) seedlings. J Hazard Mater 367:599–606

Stanislawska-Glubiak E, Korzeniowska J, Kocon A (2015) Effect of peat on the accumulation and translocation of heavy metals by maize grown in contaminated soils. Environ Sci Pollut Res 22:4706–4714

Talukder ASMHM, Meisner CA, Sarkar MAR, Islam MS (2011) Effect of water management, tillage options and phosphorus status on arsenic uptake in rice. Ecotoxicol Environ Saf 74:834–839

Tripathi P, Tripathi RD, Singh RP, Dwivedi S, Goutam D, Shri M, Trivedi PK, Chakrabarty D (2013) Silicon mediates arsenic tolerance in rice (*Oryza sativa* L.) through lowering of arsenic uptake and improved antioxidant defense system. Ecol Eng 52:96–103

Tripathi RD, Tripathi P, Dwivedi S, Kumar A, Mishra A, Chauhan PS, Norton GJ, Nautiyal CS (2014) Roles for root iron plaque in sequestration and uptake of heavy metals and metalloids in aquatic and wetland plants. Metallomics 6:1789

Upadhyay MK, Shukla A, Yadav P, Srivastava S (2019) A review of arsenic in crops, vegetables, animals and food products. Food Chem 276:608–618

Wang X, Yu H-Y, Li F, Liu T, Wu W, Liu C, Liu C, Zhang X (2019) Enhanced immobilization of arsenic and cadmium in a paddy soil by combined applications of woody peat and $Fe(NO_3)_3$: possible mechanisms and environmental implications. Sci Total Environ 649:535–543

Williams PN, Raab A, Feldmann J, Meharg AA (2007) Market basket survey shows elevated levels of as in South Central US processed rice compared to California: consequences for human dietary exposure. Environ Sci Technol 41:2178–2183

Wu C, Ye ZH, Shu WS, Zhu YG, Wong MH (2011a) Arsenic accumulation and speciation in rice are affected by root aeration and variation of genotypes. J Exp Bot 62:2889–2898

Wu ZC, Ren HY, McGrath SP, Wu P, Zhao FJ (2011b) Investigating the contribution of the phosphate transport pathway to arsenic accumulation in rice. Plant Physiol 157:498–508

Wu C, Zou Q, Xue S-G, Pan W-S, Huang L, Hartley W, Mo J-Y, Wong M-H (2016) The effect of silicon on iron plaque formation and arsenic accumulation in rice genotypes with different radial oxygen loss (ROL). Environ Pollut 212:27–33

Wu C, Huang L, Xue S-G, Huang Y-Y, Hartley W, Cui M-Q, Wong M-H (2017) Arsenic sorption by red mud-modified biochar produced from rice straw. Environ Sci Pollut Res 24:18168–18178

Yu H-Y, Wang X, Li F, Li B, Liu C, Wang Q, Lei J (2017) Arsenic mobility and bioavailability in paddy soil under iron compound amendments at different growth stages of rice. Environ Pollut 224:136–147

Zhang J, Zhao QZ, Duan GL, Huang YC (2011) Influence of sulphur on arsenic accumulation and metabolism in rice seedlings. Environ Exp Bot 72:34–40

Zhang J, Zhao CY, Liu J, Song R, Du YX, Li JZ, Sun HZ, Duan GL, Zhao QZ (2016) Influence of sulfur on transcription of genes involved in arsenic accumulation in rice grains. Plant Mol Biol Report 34:556–565

Zou L, Zhang S, Duan D, Liang X, Shi J, Xu J, Tang X (2018) Effects of ferrous sulfate amendment and water management on rice growth and metal(loid) accumulation in arsenic and lead co-contaminated soil. Environ Sci Pollut Res 25:8888–8902

Agricultural Water Management Practices and Environmental Influences on Arsenic Dynamics in Rice Field

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Abstract Rice plant cultivation around the world requires huge volume of fresh water, and depending on the soil constituents and enrichment profiling of elements present, uptake of metal(loid)s varies. Arsenic (As) predominates in its inorganic form in the soil system and gets altered in concentration of bioavailable fraction depending on various soil physico-chemical parameters and water application strategies used for rice cultivation. There is a proven correlation between different irrigation management processes and arsenic dissolution and mobility dynamics in soil system. Ferrous-manganese oxyhydroxides, phosphate, sulphur, silicate, and different soil organic matter (OM) compositions affect soil-As release from bound fractions in soil. Active microbial biomass, radial oxygen loss, and redox changes along with pH can potentially alter the plant available fraction of As in soil. With seasonal variation, irrigation practice applies several strategies of water management like continuously flooded, periodical irrigation, intermittent flooding, and sprinkler dripping and involves different field designs like permanent raised bed or occasional raised bed. As a way to nutrient-enriched rice cultivation, pisciculture in paddy field is also in practice. This chapter aims to discuss all the possible irrigation practices for rice cultivation alongside the soil environmental conditions that either triggers faster dissolution of As or hinders the mobility of being bioavailable.

Keywords Arsenic dynamics · Rice cultivation · Water management practices · Field designing · Soil physico-chemical influences

1 Introduction

Arsenic ($_{74.924}As^{33}$) is a natural contaminant of the soil and food chain. The high accumulation of As, especially inorganic arsenic in rice (*Oryza sativa* L.), leads to health hazards among populations where rice consumption is maximal (Upadhyay

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et al., 2019). The dynamic chemistry of As in paddy fields plays a major role in high As content of groundwater aquifers. Around the globe, particularly in Asian countries including India, Pakistan, Bangladesh and China, where rice is considered to be the staple food, As content exceeds the permissible limit prescribed by WHO. In irrigation waters, during the non-flooded period, As is incorporated in Fe hydroxides present in the soil, and during the flooded period, As is released from soil to water due to reductive dissolution of Fe-oxyhydroxide complexes and also due to the reduction of As from arsenate [As(V)] to highly soluble arsenite [As(III)] (Takahashi et al. 2004; Majumdar and Bose 2017). Due to the conventional application of anaerobic flooded conditions for rice cultivation, rice plants get enriched with the highly mobilized As(III) released from the soil. Paddy rice has shown to be a potent accumulator of arsenic compared to any other cereal crops (Williams et al. 2009), and efficient practical measures are essential to decrease As transfer from soil to grain. Arsenic concentrations in flooded waterlogged environments are always found to be higher than in dry aerobic environments (Norton et al. 2017), without the addition of any arsenic as a control. Arsenate is the predominant species in aerobic soils, while arsenite predominates in anaerobic soils. Arsenic accumulation in rice shoots and grains was seen to considerably increase under the flooded conditions. The effect of flooding-induced arsenite mobilization was reported to be consistent in the soil solution (Li et al. 2009). The concentration of inorganic As, to be particular As(III), gets highly enhanced in the soil solution from the dissolution of Fe-Mn complexes and As(V) conversion in the aqueous phase resulting in greater grain loading compared to aerobic soil where arsenic bioavailability is considerably less (Xu et al. 2008). Due to the presence of less soluble arsenite and higher insoluble arsenate, soil elements remain bound to the solid phase in aerobic conditions resulting in lower fractions of arsenic bioavailability. Thereby, growing of rice in aerobic conditions will result in low As accumulation in rice straw and grain during both vegetative and reproductive stages of rice growth, contrary to rice grown under flooded conditions.

Rice plants efficiently take up arsenic in the form of arsenite through the silicon transport pathway. Soils consist of competitive elements like iron, phosphorus, sulphur and silicon which strongly interact with the As during its transport from soil to plants. In plants, As(V) is reduced to As(III), which is removed via phytochelatin complexation, a thiol-rich peptide that helps in arsenic detoxification (Zhao et al. 2010; Srivastava et al., 2016). In general, there are two different types of transporters that mediate the transport of arsenite from the external medium to the xylem. NIP subfamily of aquaporin transporters in rice transport arsenite rather than arsenate. Mutation in OsNIP2;1 (also called as Lsi1, a silicon influx transporter) can result in decreasing the arsenite uptake (Majumdar and Bose 2018). Likewise, in artificial rice mutants that are defective in Lsi2, another transporter of silicon from soil to rice root, arsenate translocation, to the xylem via the same channel protein and accumulation in grains via shoot get minimized. Mutation in Lsi2 has a greater impact on arsenic accumulation in shoots and grain in field-grown rice than Lsi1 (Ma et al. 2008).

Arsenic contamination of groundwater is an outcome of natural and/or anthropogenic sources, which is presently a serious challenge in the large-scale consumption of groundwater for drinking and other purposes. Millions of people depend on groundwater containing elevated levels of As for drinking, which may cause serious risks to human health. Prolonged exposure to As contaminants by drinking groundwater causes arsenicosis, a chronic superficial disease characterized by skin lesions with patches of dark pigmentation on palms of the hands and feet (Shanker and Shanker 2014). Various mechanisms like flocculation, adsorption, oxidation, coagulation, etc. are being used to mitigate As toxicity in groundwater. The supply of safe drinking water is of global concern which has been furthered due to the arsenic toxicity of groundwater aquifers in Bangladesh, India and other Asian countries. One of the main barriers to supplying safe drinking water is the lack of appropriate water options for millions of people who are exposed only to arsenic-contaminated water sources. In a survey, it was observed that the proportion of families (around 54%) that drank arsenic-contaminated water was significantly lower than the baseline survey (87%) of Bangladesh (Hoque et al. 2004). It is better to recommend cluster-based piped water systems rather than the household-based options for arsenic-contaminated areas. Natural release of arsenic in groundwater causing contamination occurs mostly in and around the alluvial river basin deltas of South and Southeast Asia where shallow groundwater is used in the Bengal basin for several purposes such as irrigating rice fields that leads to the possible gradual accumulation of As in rice grain from As-rich soil deposits (Shrivastava et al. 2014, 2017). Rice-straw As content increases when soil-As concentrations increase, whereas the toxicity of As to rice results in reduced grain-As concentrations (Panaullah et al. 2009). In arsenic affected regions, agricultural sustainability, food quality and consumer health assessment have a direct association with the As-induced rice yield reductions and subsequent accumulation in straw and grain (Upadhyay et al. 2018).

Therefore, significant practical measures are required to mitigate the issue of enhanced As uptake in the paddy rice. There are two restriction methods that can be applied – irrigation water regime management and Si fertilization. Both are effective measures used to reduce As accumulation in rice. Though the addition of silicon increased As concentration in the soil solution, silicon fertilization greatly reduced straw to grain-As transport. Silicon has influenced the As speciation in rice grain and husk by inducing the process of intracellular methylation. Silicon decreases the inorganic As concentration in grain while increasing the concentration of dimethyl arsenic acid (DMA) corresponding to the total arsenic content in the soil. In soils with a higher arsenic concentration, DMA accounted for 10–80% of grain-As, while only 3–52% of the total arsenic concentration was accounted for DMA in grains of rice grown in soils with lower arsenic concentration (Arao et al. 2009). The accumulation of DMA in rice grain is probably because DMA translocates from shoots/roots to grains more readily than inorganic arsenic.

2 Factors Influencing Arsenic Mobility

2.1 *Oxidation Reduction Potential*

The effects of redox potential and pH on arsenic speciation and solubility are major factors that influence arsenic mobility (Barla et al. 2017). The solubility, bioavailability, mobility and toxicity of As depend on its oxidation state (Majumdar et al., 2018). When soil redox levels are high (500–200 Mv), arsenic solubility is low, and the majority, i.e. ~66% to 98%, of As present in the solution is As(V). Under moderately reduced soil conditions (0–100 mV), As solubility is controlled by the dissolution of Fe-oxyhydroxides. When reduced to 200 mV, the soluble arsenic content increases 13-fold compared to the soluble As content at 500 mV (Masscheleyn et al. 1991). In general, both As(V) and As(III) are subjected to chemical and microbial redox changes and biomethylation reactions in soils and natural waters.

2.2 *Microbial Biomass*

The rate of inhibition for culturable soil microbial populations under As pollution would follow the order bacteria > fungi > actinomycetes. Micronutrients can influence the bacterial diversity in the sludge environment as well as during waste degradation. There exists an antagonistic inhibitory effect on the enzymes urease, acid phosphatase and protease, out of which, urease appears to be the most sensitive indicator (Wang et al. 2011).

2.3 *pH*

The diagenesis of iron oxide minerals along with the reduction of arsenate in terms of mobility and dissociation can be checked together when As(V) is compared with the As(III) sorption onto an amorphous iron oxide (HFO), goethite and magnetite at different solution compositions. Adsorption of As(V) onto HFO or goethite is more at an acidic pH range of 5–6 compared to As(III) which preferably binds to these with higher affinity at a pH range of 7–8 in the solid phase. Depending on the solid-to-solution ratio and variation in mineral complexation with surface area, the pH can change during which arsenate-arsenite sorption will be equal and shift towards low pH values. Phosphate might compete for sorption sites in the same environment (Dixit and Hering 2003). In the presence of HFO or goethite, the reduction of As(V) and its mobility might get decreased to some extent as the pH tends to become neutral. However, the minimizing specific surface area and sorption site density could increase arsenic mobility that accompanies transformation of amorphous iron oxides to more crystalline forms. Under aerobic conditions and pH 7, because of the sorption and precipitation on Fe-oxyhydroxides, As solubility is low. Generally, maximum solubilization of As occurs when the pH is around 11 (Al-Abed et al. 2007).

2.4 Organic Carbon

Speciation and mobilization of arsenic get influenced in presence of organic matter (OM) content in chromated copper arsenate (CCA) – contaminated soils were identified under unsaturated and aerobic conditions when a range of organic matter varying between 0.5% and 15% was taken. In soil extracts, water-soluble arsenic speciation, arsenate [As(V)], arsenite [As(III)], monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMAA) can be assessed by HPLC-ICP-MS, and solvent extraction method can be applied for the solid phase [As(III), As(V)] determination. The As(V) is regarded as the predominant form in soil-bound phase and less mobile arsenic species (Sarkar et al., 2017). But the organic matter content does not influence the arsenic speciation in the soluble fraction, i.e. neither As(V) reduction nor arsenic biomethylation occurred. An increase in the dissolved organic carbon content promoted both As(V) and As(III) solubilization in soils. The organic matter contents of 7.5% and 15% have entailed the persistence of soluble As(V) due to the high content of dissolved organic compounds which prevented its sorption onto the soil (Dobran and Zagury 2006). The ecological risk of aerobic CCA-polluted soils rich in humic substances might result in the enhanced availability of soluble As(V) when compared to the generation of more toxic and more mobile As(III).

2.5 Effect of Radial Oxygen Loss

The rate of radial oxygen loss plays an important role in the transfer of As from the soil to the plant system (Awasthi et al. 2017). Mei et al. in 2012 observed that the concentration of As in plant parts decreased substantially with an increase in the rate of ROL. Moreover, ROL also influenced rhizosphere O_2, pH, EH, and Fe plaque formation (Mei et al. 2012). Increased rhizosphere oxygen induces more Fe^{2+} and Mn^{2+} to be oxidized leading to a corresponding increase in plaque formation. This, in turn, increases arsenic sequestration and deposition at the rhizosphere, thereby inhibiting its translocation into the plant system (Li et al. 2011). Hence, breeding rice varieties with promising rates of ROL can be beneficial in abating arsenic concentration in plants as in Fig. 1.

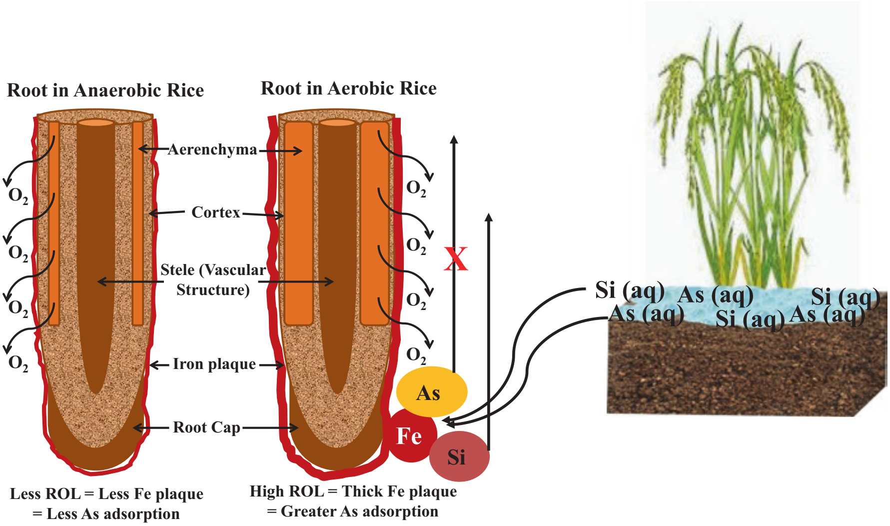


Fig. 1 Iron plaque formation and arsenic restriction in rice root soil

3 Water Treatment Methods

3.1 Co-precipitation of Arsenic Using Fe-Oxyhydroxides

In irrigation waters, As is incorporated in Fe-hydroxide in the soil during the non-flooded period, whereas As is released from soil to water due to reductive dissolution of Fe-hydroxide phase and reduction of As from As(V) to As(III) during the flooded period (Takahashi et al. 2004). The household treatment filtration process includes co-precipitation of dissolved arsenic by addition of ferric and hypochlorite salts to the ground well water and passing through another set of filtration using a bucket sand filter which was reported to be effective in removing a considerable amount of arsenic from the ground well water (Meng et al. 2001). Experiments in consecutive batches were conducted for investigating the combined effects of minerals like silicate, phosphate and bicarbonate for the removal of dissolved arsenic from Bangladesh groundwater and spiked imitated water by iron hydroxides. The adsorption constants of anion sorption to iron hydroxides show its affinity with decreasing pattern as follows: arsenate > phosphate > arsenite > silicate > bicarbonate. The removal of As(III) at lower concentrations was reported to be possible using phosphate, silicate and bicarbonate. The remaining As(V) content after iron hydroxide treatment increased bicarbonate and phosphate solutions which contain both the anions (Meng et al. 2002).

3.2 Silicon Fertilizers

The silicon fertilizers were used in order to reduce the As accumulation in rice to cope with the possible mitigation of rice arsenic toxicity threatening human health. H_3AsO_3 is considered to be the predominant arsenic species in the rice field stagnant water. H_4SiO_4 along with H_3AsO_3 follows a similar transporter uptake pathway, while external silica implication has been proposed to reduce As uptake and grains loading. The addition of silicon has increased the As concentration in the soil solution, whereas the silicon fertilization method has decreased the As concentration in straw and grain.

Application of two different silicate minerals differs in solubility ($+Si_L$, diatomaceous earth; $+Si_H$, Si-gel) and was evaluated to the soils which are altering in mineral composition on arsenic content in rice. The $+Si_L$ addition has a contrasting result of either no change or decreased porewater arsenic content but did not change or enhance the grain-As loading compared to the (+As-Si) control. The $+Si_H$ addition, on the contrary, has increased the As concentration in porewater, but it significantly reduced the grain-As loading compared to the (+As-Si) control. Only the $+Si_H$ addition has resulted in the increase of straw to husk Si content. A negative correlation was reported within total grain-straw-As with the porewater Si, and the relationship was altered between both the soils that exhibited different mineral contents. Due to the active competition between H_4SiO_4 and H_3AsO_3 for the adsorption sites on soil solids and subsequent plant uptake, these results get changed (Seyfferth and Fendorf 2012). The presence of bicarbonate and silicate triggers the effect of phosphate on As(V) adsorption negatively. After iron hydroxide treatment, the remaining arsenate concentration was increased in the bicarbonate and phosphate solutions (Meng et al. 2002).

3.3 Addition of Organic Matter

Organic matter (OM) present naturally is found in all surface soil with diverse percentage and gets percolated to groundwaters to some extent. Because of several practical sources of OM and hygienic reasons, the presence of OM is undesirable in groundwater, particularly for drinking purposes. In several areas, due to the increase in the amount of OM, there are several significant effects on drinking water treatments. The presence of OM creates several hindrances during drinking water treatment processes like:

(a) Unwanted colour, taste and odour problems.
(b) Coagulant and disinfectant dose needs to be applied in high amount for OM removal making the water quality undesirable.
(c) Promoted bacterial diversity and other microbial activities.
(d) Heavy metals and organic pollutants get intensified due to the higher affinity of OM towards these pollutants to adhere.

Nowadays, surface water sources are continuously being enriched with natural OM with changed colour, which has an adverse effect on water purification system for drinking purposes. Coagulation and flocculation are the two most common and economically feasible approaches for removing OM from drinking water involving a two-step sedimentation and sand filtration (Matilainen et al. 2010). Quantitative assessment and characterization of OM is an important parameter in order to improve and optimize these processes. It is also important to understand and predict the characteristic chemical interaction of OM in different steps of the treatment. Methods used in the characterization of natural OM include resin adsorption, size exclusion chromatography (SEC), fluorescence spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Quantification of water dispersed OM can be predicted with parameters including UV-Vis spectroscopic measurement of total organic carbon (TOC) and specific UV-absorbance (SUVA) assessment. Recently, methods have been developed by which the OM structures can be assessed in a better predictive way like multidimensional NMR, pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) and Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) (Matilainen et al. 2011).

4 Types of Rice Cultivation

Rice crops can be differentially cultivated by varying the amount of water fed to agricultural fields. Depending on the amount of water saturation, soil properties such as redox potential (Kohnke and Bradfield 1935), pH, macro- and micronutrient availability (Misra and Tyler 1999), etc. significantly vary, in turn influencing arsenic speciation and uptake pattern in plants (Hu et al. 2013a, b). The following classification summarizes the variation in As uptake by plants and the corresponding effects on grain yield with different modes of irrigation employed throughout the cultivation process starting from seeding to harvesting.

4.1 Conventional or Anaerobic Cultivation

Rice crops are conventionally cultivated by the continuous flooding of water and maintaining the fields at constant waterlogged conditions. This process of cultivation is known as anaerobic cultivation in which the soil remains in a reduced state. Iron oxides and hydroxides form a major part of soil mineral content. Arsenic in the form of arsenate ion $(AsO_4)^{3-}$ and its conjugate acids have a tendency to strongly bind to iron(III) oxides (α-Fe_2O_3), oxide hydroxides (α-,γ- FeOOH) and poorly crystalline ferrihydrite (Sherman and Randall 2003). The decreased redox potential of the soil leads to the reductive desorption of arsenic from these iron

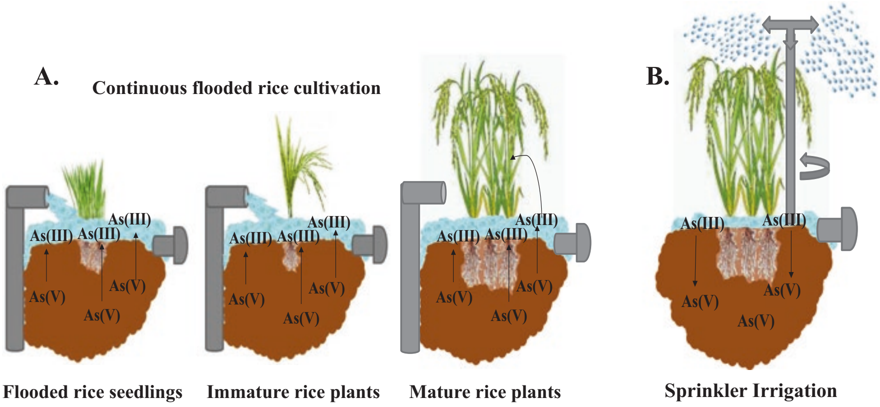


Fig. 2 Rice cultivation under (**a**) continuous flooded and (**b**) sprinkler irrigation

oxyhydroxides and also the reductive dissolution of iron oxyhydroxides into the solution phase, thereby solubilizing adsorbed or co-precipitated arsenic (Takahashi et al. 2004) and resulting in higher accumulation in rice grain (Fig. 2a). Reductive dissolution of iron oxyhydroxides contributes more towards As mobility and bioavailability than just microbial reduction of arsenate to arsenite because at a pH range of 6–9, As(III) is bound to iron oxides to a greater extent than As(V), and hence the reduced arsenite also tends to bind with free Fe oxides (Dixit and Hering 2003). Shankar and Shanker (2014) professed that the activity of indigenous metal-reducing bacteria along with the reductive dissolution of Fe and Al metal oxides is the substantial release mechanism of As, directly affecting the mobility of As. Plants grown under flooded conditions have shown to accumulate maximum arsenic compared to other modes of cultivation. Therefore, anaerobic conditions markedly increase arsenic mobility and bioavailability, mainly in the form of arsenite into the soil solution (Li et al. 2009). In their study in 2009, Li et al. noticed that, although the soil solution contained no DMA (Dimethyl Arsenate), plants grown in the same soil contained strikingly high amounts of the same. This indicated that methylation occurred *in planta* (inside the plant system). The extent of methylation also seemed to increase proportionally with an increase in As bioaccumulation signifying that methylation is a response to As stress in plants. Thereby, this phenomenon indirectly abates As toxicity by transforming inorganic As to its organic form. Nevertheless, the concentration of inorganic As in grain still remains the maximum for conventionally cultivated rice (Li et al. 2009). Highly flooded conditions throughout growth and reproductive phases of rice plants enable maximum productivity and grain yield which is the primary advantage of anaerobic cultivation. However, it is still not an optimum method considering the lethal accumulation of consumable arsenic in rice grains.

4.2 Deficit Irrigation Practices

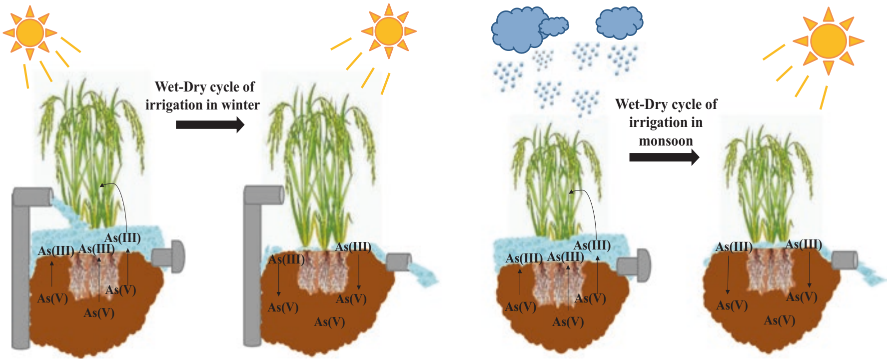
Deficit irrigation, unlike conventional irrigation, uses lesser water for cultivation. Based on this principle, rice cultivation can further be classified into the following types.

- *Aerobic cultivation*

Contrary to anaerobic cultivation, aerobic or dry cultivation is performed in the absence of continuous flooding and waterlogged conditions. In this mode of cultivation, the soil remains in an oxidized state. Oxidized iron (Fe III) effectively binds to arsenic present in the soil. Hence, arsenic mobility is significantly decreased during aerobic conditions. Also, if aerobic conditions continuously prevail, arsenic in the soil transforms predominantly to arsenate (AsV) which is less toxic compared to arsenite (AsIII) (Brannon and Patrick 1987). All these factors suggest that the bioavailability of arsenic and its uptake by plants are significantly low during dry cultivation. Although this method seems to overcome the major drawback of anaerobic cultivation, it is still not preferable for the cultivation of rice. There are two major liabilities in this method. One is that there is a substantial yield decline when rice is aerobically cultivated continuously over a long period. This is possibly caused by the build-up of nematodes and other soil pathogens due to prolonged dry soil conditions (Ventura et al. 1981). The other is the tendency of plants to hyper-accumulate cadmium on account of increased Cd bioavailability during aerobic conditions (Hu et al. 2013a, b). The mobility and bioavailability of Cd in the soil are contrary to that of As. Hence, even though As accumulation is far less during aerobic cultivation, Cd accumulation poses a major threat.

- *Cultivation using intermittent irrigation*

Intermittent irrigation is one of the most optimum methods known for rice cultivation (Fig. 3). As the name suggests, rice crops are neither grown in continuously



Groundwater application when water outlet is closed

Intermediate dry phase while water outlet is open

Rainwater fed cultivation/ closed water outlet

Intermediate dry phase/ Open water outlet

Fig. 3 Rice cultivation with intermittent irrigation approaches with seasonal variation flooded and waterlogged conditions nor in continuously dry or aerobic conditions. In this type of cultivation, the crops are intermittently irrigated or grown in periodic flooded and dry conditions. The growth cycle of any plant can be divided into two phases – vegetative and reproductive phase. Growing rice crops aerobically in any one of these phases shows a significant reduction in As accumulation. Li et al. observed that draining water after flowering for rice grown in continuously flooded conditions decreased grain-As concentration compared to flooding after flowering for rice crops grown in a continuous aerobic condition which seemed to increase grain-As concentration. This suggests that post flowering uptake of water plays a major role in grain-As accumulation. This is because As passes to the grain directly through the xylem if maintained in flooded conditions post flowering, whereas As has to be translocated from plant tissues to the grain through the phloem if maintained in aerobic conditions post flowering. The lesser probability of the latter condition suggests that it is an effective strategy to mitigate grain-As in rice (Li et al. 2009). In the southern USA, allowing fields to dry out completely for 10–14 days before panicle initiation resulted in a profound reduction in As uptake by plants but with a potential decrease in yield compared to flooded cultivation (Brammer 2009). Also, As-induced straight-head disease or spikelet sterility was observed to be effectively reduced when mid-season draining of fields was performed (Zhao et al. 2010). Thereby, intermittent irrigation is efficacious in mitigating As in rice. Although the grain yield obtained through this method is not as abundant as conventional irrigation methods, it does not substantially decline as seen in continuous aerobic cultivation.

- *Cultivation using sprinkler irrigation*

Another method of deficit irrigation is the adoption of sprinklers. Long-term adoption of this method is said to substantially decrease As concentration in rice (Fig. 2b). The transfer coefficient of As was also found to be lower for sprinkler-irrigated crops compared to flooded crops. In their field study, Jimenez et al. observed that in sprinkler-irrigated rice, the proportion of organic As was maximum among the total As concentration of rice grain. Moreover, sprinkler-irrigated rice had very low concentrations of inorganic rice when compared to flood-irrigated rice samples. Hence, they inferred that sprinkler-irrigated rice is the safest for human consumption (Jimenez et al. 2014). While employing this mode of cultivation, the total average concentration of As in rice samples was found to be very close to the concentration found in irrigation water, indicating that this method substantially reduces As bioavailability and bioaccumulation in plants. Therefore, beyond agronomic advantages such as water conservation in regions with high scarcity, sprinkler irrigation proves to be very effective in alleviating chronic As intoxication in highly exposed populations (Spanu et al. 2012).

4.3 Alternate Methods

Some of the alternative methods of water management that would mitigate As uptake in rice crops are discussed below.

- Rain-fed agriculture: In places where groundwater is highly contaminated with arsenic, farmers can resort to using rainwater to irrigate crops. However, during monsoons, if the field is in the form of a slope, the continuous flow of rainwater tends to flush out all the top surface elements in the soil along with arsenic to nearby lands. Although As gets effectively removed, plants also lose vital nutrients essential for growth. On the other hand, if the field is concave, with slight depression towards the centre, rainwater gets collected and stagnates in the field. Initially, the rainwater may aid deeper percolation of As. But eventually, if the soil gets saturated, it can affect plant growth by increasing As mobility and bioavailability. Therefore, rain-fed irrigation greatly reduces crop yield due to the reducing number of growing seasons per annum and especially due to the risks mentioned above, suggesting that it is not an economically feasible option to farmers (Sharma et al. 2014).
- Alternative sources of non-contaminated water such as surface water from rivers or storage ponds can be used to irrigate crops. Deep arsenic-free groundwater is also an option. They should however not be exploited for large volume pumping to irrigate agricultural fields because they need to be preserved as a safe source of drinking water (Dittmar et al. 2010). Other drawbacks in using deep water extractions include costly installation, availability of As-free deep aquifers, an uncertainty of groundwater recharge mechanisms, a risk of saltwater intrusion in coastal areas and presence of very high concentrations of dissolved Fe and Mn (Shankar and Shanker 2014). New deep wells can be drilled without disturbing the aquifers to extract arsenic-free groundwater. Although this method will greatly increase crop yield without As contamination, there is a high risk of these wells getting contaminated with As over prolonged usage (Sharma et al. 2014).
- Contaminated water can be cleared of arsenic by allowing them to flow through barren soil rich in iron oxyhydroxides. This way, arsenic gets bound to iron oxyhydroxides, and the clarified flow-through can be used for irrigation (Dittmar et al. 2010). However, the feasibility of this approach must be further studied.
- A considerable amount of As can be removed from extracted groundwater that naturally contains a high concentration of Fe. The simplest method is to allow the extracted water to stand for a day. The As and Fe will oxidize, react and finally sediment. The clear water can be decanted for further use. The efficiency of this process can be enhanced by the use of sand filters (Sharma et al. 2014). This has been observed to be feasible in open irrigation channels maintained at aerobic conditions (Ravenscroft et al. 2009). However, if maintained at extended anaerobic conditions, there is a high risk of As to desorb and solubilize into the water (Sharma et al. 2014).

5 Management via Field Design

The agricultural field can be designed in such a way as to enable reduced As accumulation and uptake by plants. Some potential designs are mentioned below.

- *Permanent raised beds*

Growing rice on permanent raised beds with water in surrounding furrows is an efficient water management regime to mitigate As concentrations in both straw and grain of rice crops. This method reduces total As concentration in the soil, caused due to irrigation, by up to 30% (Talukder et al. 2011). Rice grown on raised beds that remain at a higher redox potential accumulated less As compared to conventionally grown rice (Li et al. 2009). The raised soil helps to drain excess water naturally and maintains it in a near aerobic condition. Duxbury Panaullah (2007) showed that this method counteracted yield losses unlike most of the other methods that showed promising results in mitigating As in rice plants. It also seemed to save nearly 30–40% of the required irrigation water, with better utilization of fertilizers and considerably less run-off. Thereby, many farmers prefer this method of cultivation due to better yields, water savings, lower tillage and labour costs and especially the production of safer crops (Duxbury Panaullah 2007).

- *Periodically raised beds*

Furrow-irrigated periodically raised beds, similar to permanent raised beds, significantly reduce As bioaccumulation compared to conventional anaerobic rice cultivation (Talukder et al. 2011). In order to reduce leaching of arsenic from furrows, they can be lined with plastic sheets, and the beds can be periodically moistened by splashing water from these flooded furrows (Brammer 2009). Furrow irrigation reduces water consumption rates because seasonal floods are not established and farmers only use water that is sufficient enough to saturate the soil. Owing to the comparatively oxidized state of furrow-irrigated fields, Fe-oxyhydroxides are quite stable, and a greater portion of the soil's intrinsic As pool remain unavailable to the plants (Aide et al. 2016).

6 Factors Influencing Arsenic Mitigation During Irrigation Practices

6.1 Effect of Silicon and Its Compounds

Silicon enhances plant resistance to biotic and abiotic stresses and hence is a very beneficial element to rice crops. It increases shoot length and biomass of rice seedlings (Guo et al. 2007). The reduced form of inorganic As, arsenite, is taken up by plants through the Si uptake pathway, unlike arsenate which is imbibed through phosphate channels. Hence, Si fertilizers effectively compete with As for uptake by the plant system, thereby significantly reducing As bioaccumulation in rice straw, husk and also grain to a certain extent (Majumdar et al., 2019). This inhibitory effect was observed even though the addition of Si significantly increased As concentration in the soil solution, presumably because of the replacement of arsenite present in Fe-As complexes with silicic acid. Apart from reducing bioaccumulation of As, Si also influenced As speciation in grain by decreasing the concentration of As and increasing the concentration of DMA (Li et al. 2009). Soil rich in Si, such as those developed from volcanic ash, showed very good yield benefits along with considerably less As accumulation in rice plants (Zhao et al. 2010).

6.2 Effect of Phosphate

In aerated soils where arsenate (AsV) is the predominant form of bioavailable As, the addition of phosphate greatly reduced As bioaccumulation in rice plants (Brammer 2009). The principle behind this phenomenon is that phosphate and arsenate are imbibed through the same phosphate uptake channels (Srivastava et al. 2018). These channels have a greater affinity towards phosphate, and so it effectively competes and replaces arsenate. Heavy application of phosphate during aerobic cultivation seemed to reduce As bioaccumulation by up to 80% (Talukder et al. 2012). On the other hand, uptake of arsenite, the predominant species during anaerobic cultivation (Xu et al. 2008), is not influenced by phosphate application (Abedin et al. 2002) and hence leads to adverse effects (Jahiruddin et al. 2005). Therefore, aerobic rice cultivation with P amendment has significant potential in As mitigation.

6.3 Effect of Sulphur

Hu et al. in 2007 found that the addition of sulphur considerably enhanced iron plaque formation in the root system and rhizosphere of rice plants. Iron plaque plays a major role in sequestering As and decreasing its bioavailability to the plant system. They also observed that the addition of sulphate (SO_4^{2-}) gave better results compared to elemental sulphur at the same rate of application. This phenomenon has a very good potential to ameliorate As uptake and accumulation in rice. Application of sulfur compounds in the form of thiol is also reported as a potential reducer of arsenic toxicity in various water macrophytes and rice plant (Mishra et al. 2008; Srivastava and D'souza 2010).

7 Association and Application of Rizi-pisciculture

As a traditional way of rice cultivation, water log condition in rice fields is maintained as an integrated part of rice cultivation in China from ancient time (Renkui et al. 1995) and expanded to Thailand (Little et al. 1996), Vietnam (Berg 2002), India (Victor et al. 1994; Das 2002) and Bangladesh (Haroon and Pittman 1997). Rice cultivation in association with fish farming is termed as 'rizi-pisciculture' (an FAO report after Coche 1967). Although water stagnant condition can enhance the arsenic uptake in rice plant due to higher translocation of arsenite [As(III)], application of fish cultivation in water log condition might be profitable to some extent in certain aspects. Fish farming can certainly increase the paddy growth and total grain yield by 6–15% as reported by Schuster (1955). Alternatively, due to the activity of fishes, organic fertilizer amendment increases coming from fish excreta. Reports also suggest that mineralization of organic matter in rice fields gets increased in the association of fish farming with greater aeration of the soil-aqueous system (Coche 1967) which leads to the maintenance of oxidized condition in rice field rather any prevailing reduced condition in absence of pisciculture. This condition can resulted in lesser dissolution of arsenate [As(V)] from Fe-Mn complexes, being converted to arsenite, and hence the chance of arsenic toxicity might get reduced to some extent. Also, fishes can absorb arsenic present in an aqueous phase (as preferably in As(III) form) via their gills and bio-convert that inorganic form of arsenic to a non-toxic organic form of arsenic known as arsenobetaine and arsenocholine (Eislar 1988). Thus, a certain amount of soluble inorganic arsenic can get stored to the fish tissue itself, rather being transferred to the rice plant tissue, which in turn is no longer a toxic form to its consumer. So the application of fish farming can be an option to cope with partial arsenic contamination in rice plant but with some limitations. Association of pisciculture needs specialized field preparation, labour management, rice seedling damage risk and likely so. Also, a bulk amount of water is required where rice varieties that can tolerate prolonging water stagnancy can only be opted. Thus the application of rizi-pisciculture is a practice of conditions based.

8 Summary

Water management practices are an important parameter for controlling the mobility of water-soluble fraction of any elemental content in the soil system. The conventional idea of waterlogged irrigation for the better growth of rice production is a matter of conflict between scientific research findings and habit of conventional practices. Over the period of time, application of irrigation patterns are getting changed to more suitable practices for rice growth and yield, managing the chance of arsenic contamination in rice grain. Research reports suggest that aerobic or dry phase cultivation of rice can minimize arsenic uptake by rice plant but compromises the production efficiency, whereas implication of periodical dry-wet phase or intermittent water irrigation resulted in maintenance of aerobic-anaerobic complement which enhances the grain yield with minimized risk of arsenic accumulation in rice grain. Elemental dissolution in soil-aqueous phase and competitive translocation via different transporters play crucially in arsenic uptake and accumulation in rice tissues. Silicon, phosphate, sulphur, root iron plaque, organic content, microbial activity and soil pH-ORP are all influencing parameters to regulate the arsenic dynamics in soil system which in turn modulates the arsenic in plant parts. Aquaculture in conjugation with rice cultivation can be an option to minimize arsenic translocation in rice plant that also has some limitations within suggesting the best way to mitigate arsenic contamination to be the water management with occasional application of competitive nutrient elements.

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References

Abedin MJ, Feldmann J, Meharg AA (2002) Uptake kinetics of arsenic species in rice plants. Plant Physiol 128(3):1120–1128

Aide M, Beighley D, Dunn D (2016) Arsenic uptake by rice (*Oryza sativa* L.) having different irrigation regimes involving two southeastern Missouri soils. Int J Appl Agric Res 11:71–81

Al-Abed SR, Jegadeesan G, Purandare J, Allen D (2007) Arsenic release from iron rich mineral processing waste: influence of pH and redox potential. Chemosphere 66(4):775–782

Arao T, Kawasaki A, Baba K, Mori S, Matsumoto S (2009) Effects of water management on cadmium and arsenic accumulation and dimethylarsenic acid concentrations in Japanese rice. Environ Sci Technol 43(24):9361–9367

Awasthi S, Chauhan R, Srivastava S, Tripathi RD (2017) The journey of arsenic from soil to grain in rice. Front Plant Sci 8:1007

Barla A, Shrivastava A, Majumdar A, Upadhyay MK, Bose S (2017) Heavy metal dispersion in water saturated and water unsaturated soil of Bengal delta region, India. Chemosphere 168:807–816

Berg H (2002) Rice monoculture and integrated rice-fish farming in the Mekong Delta, Vietnam-economic and ecological considerations. Ecol Econ 41(1):95–107

Brammer H (2009) Mitigation of arsenic contamination in irrigated paddy soils in South and South-east Asia. Environ Int 35(6):856–863

Brannon JM, Patrick WH (1987) Fixation, transformation, and mobilization of arsenic in sediments. Environ Sci Technol 21(5):450–459

Coche AG (1967) Fish culture in rice fields a world-wide synthesis. Hydrobiologia 30(1):1–44

Das DN (2002) Fish farming in rice environments of North Eastern India. Aquac Asia 7(2):43–47

Dittmar J, Voegelin A, Roberts LC, Hug SJ, Saha GC, Ali MA, Badruzzaman ABM, Kretzschmar R (2010) Arsenic accumulation in a paddy field in Bangladesh: seasonal dynamics and trends over a three-year monitoring period. Environ Sci Technol 44(8):2925–2931

Dixit S, Hering JG (2003) Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ Sci Technol 37(18):4182–4189

Dobran S, Zagury GJ (2006) Arsenic speciation and mobilization in CCA-contaminated soils: influence of organic matter content. Sci Total Environ 364(1–3):239–250

Duxbury JM, Panaullah G (2007) Remediation of arsenic for agriculture sustainability, food security and health in Bangladesh. FAO Water Working Paper. FAO, Rome, p 28

Eisler R (1988) Arsenic hazards to fish, wildlife, and invertebrates: a synoptic review (No. 12). Fish and Wildlife Service, US Department of the Interior

Guo W, Zhu YG, Liu WJ, Liang YC, Geng CN, Wang SG (2007) Is the effect of silicon on rice uptake of arsenate (AsV) related to internal silicon concentrations, iron plaque and phosphate nutrition? Environ Pollut 148(1):251–257

Haroon AKY, Pittman KA (1997) Rice-fish culture: feeding, growth and yield of two size classes of Puntius gonionotus Bleeker and Oreochromis spp. in Bangladesh. Aquaculture 154(3–4):261–281

Hoque BA, Hoque MM, Ahmed T, Islam S, Azad AK, Ali N, Hossain M, Hossain MS (2004) Demand-based water options for arsenic mitigation: an experience from rural Bangladesh. Public Health 118(1):70–77

Hu ZY, Zhu YG, Li M, Zhang LG, Cao ZH, Smith FA (2007) Sulfur (S)-induced enhancement of iron plaque formation in the rhizosphere reduces arsenic accumulation in rice (*Oryza sativa* L.) seedlings. Environ Pollut 147(2):387–393

Hu P, Huang J, Ouyang Y, Wu L, Song J, Wang S, Li Z, Han C, Zhou L, Huang Y, Luo Y (2013a) Water management affects arsenic and cadmium accumulation in different rice cultivars. Environ Geochem Health 35(6):767–778

Hu P, Li Z, Yuan C, Ouyang Y, Zhou L, Huang J, Huang Y, Luo Y, Christie P, Wu L (2013b) Effect of water management on cadmium and arsenic accumulation by rice (*Oryza sativa* L.) with different metal accumulation capacities. J Soils Sediments 13(5):916–924

Jahiruddin M, Islam M R, Shah M A L, Rashid M A, Rashid M H, Ghani M A (2005) Arsenic in the water-soil-crop systems: PETRRA-BRRI-BAU-AAS study. Paper presented at Symposium on the Behavior of Arsenic in Aquifers, Soils and Plants: Implications for Management, Organized by CYMMIT, IDB Bhaban, Dhaka, 16–18 January 2005

Kohnke H, Bradfield R (1935) Factors affecting the redox potential of soils. Soil Sci Soc Am J 16. (2001:85–85

Li RY, Stroud JL, Ma JF, McGrath SP, Zhao FJ (2009) Mitigation of arsenic accumulation in rice with water management and silicon fertilization. Environ Sci Technol 43(10):3778–3783

Li H, Ye ZH, Wei ZJ, Wong MH (2011) Root porosity and radial oxygen loss related to arsenic tolerance and uptake in wetland plants. Environ Pollut 159(1):30–37

Little DC, Surintaraseree P, Innes-Taylor N (1996) Fish culture in rainfed rice fields of northeast Thailand. Aquaculture 140(4):295–321

Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proc Natl Acad Sci 105(29):9931–9935

Majumdar A, Bose S (2017) Toxicogenesis and metabolism of arsenic in rice and wheat plants with probable mitigation strategies: in arsenic: risks of exposure. In: Behaviour in the environment and toxicology, vol 1. Nova Science Publishers, U.S., pp 149–166

Majumdar A, Bose S (2018) A glimpse on uptake kinetics and molecular responses of arsenic tolerance in Rice plants. In: Mechanisms of arsenic toxicity and tolerance in plants, vol 1. Springer, Singapore, pp 299–315

Majumdar A, Barla A, Upadhyay MK, Ghosh D, Chaudhuri P, Srivastava S, Bose S (2018) Vermiremediation of metal (loid)s via Eichornia crassipes phytomass extraction: a sustainable technique for plant amelioration. J Environ Manag 220:118–125

Majumdar A, Upadhyay MK, Kumar JS, Barla A, Srivastava S, Jaiswal MK, Bose S (2019) Ultrastructure alteration via enhanced silicon uptake in arsenic stressed rice cultivars under intermittent irrigation practices in Bengal delta basin. Ecotoxicol Environ Saf 180:770–779

Masscheleyn PH, Delaune RD, Patrick WH Jr (1991) Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ Sci Technol 25(8):1414–1419

Matilainen A, Vepsäläinen M, Sillanpää M (2010) Natural organic matter removal by coagulation during drinking water treatment: a review. Adv Colloid Interf Sci 159(2):189–197

Matilainen A, Gjessing ET, Lahtinen T, Hed L, Bhatnagar A, Sillanpää M (2011) An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere 83(11):1431–1442

Mei XQ, Wong MH, Yang Y, Dong HY, Qiu RL, Ye ZH (2012) The effects of radial oxygen loss on arsenic tolerance and uptake in rice and on its rhizosphere. Environ Pollut 165:109–117

Meng X, Korfiatis GP, Christodoulatos C, Bang S (2001) Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system. Water Res 35(12):2805–2810

Meng X, Korfiatis GP, Bang S, Bang KW (2002) Combined effects of anions on arsenic removal by iron hydroxides. Toxicol Lett 133(1):103–111

Mishra S, Srivastava S, Tripathi RD, Trivedi PK (2008) Thiol metabolism and antioxidant systems complement each other during arsenate detoxification in *Ceratophyllum demersum* L. Aquat Toxicol 86:205–215

Misra A, Tyler G (1999) Influence of soil moisture on soil solution chemistry and concentrations of minerals in the calcicoles Phleum phleoides and *Veronica spicata* grown on a limestone soil. Ann Bot 84(3):401–410

Moreno-Jiménez E, Meharg AA, Smolders E, Manzano R, Becerra D, Sánchez-Llerena J, Albarrán Á, López-Piñero A (2014) Sprinkler irrigation of rice fields reduces grain arsenic but enhances cadmium. Sci Total Environ 485:468–473

Norton GJ, Shafaei M, Travis AJ, Deacon CM, Danku J, Pond D, Cochrane N, Lockhart K, Salt D, Zhang H, Dodd IC (2017) Impact of alternate wetting and drying on rice physiology, grain production, and grain quality. Field Crop Res 205:1–13

Panaullah GM, Alam T, Hossain MB, Loeppert RH, Lauren JG, Meisner CA, Ahmed ZU, Duxbury JM (2009) Arsenic toxicity to rice (*Oryza sativa* L.) in Bangladesh. Plant Soil 317(1–2):31

Ravenscroft P, Brammer H, Richards K (2009) Arsenic pollution: a global synthesis, vol 28. Wiley, New York

Renkui C, Dashu N, Jianguo W (1995) Rice fish culture in China: the past, present, and future. In Rice fish culture in China. IDRC, Ottawa, pp 3–14

Sarkar SR, Majumdar A, Barla A, Pradhan N, Singh S, Ojha N, Bose S (2017) A conjugative study of *Typha latifolia* for expunge of phyto-available heavy metals in fly ash ameliorated soil. Geoderma 305:354–362

Schuster WH (1955) Fish culture in conjunction with rice cultivation. World Crops 7(11–14):67–70

Seyfferth AL, Fendorf S (2012) Silicate mineral impacts on the uptake and storage of arsenic and plant nutrients in rice (*Oryza sativa* L.). Environ Sci Technol 46(24):13176–13183

Shankar S, Shanker U (2014) Arsenic contamination of groundwater: a review of sources, prevalence, health risks, and strategies for mitigation. Sci World J 2014:304524

Sharma AK, Tjell JC, Sloth JJ, Holm PE (2014) Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. Appl Geochem 41:11–33

Sherman DM, Randall SR (2003) Surface complexation of arsenic (V) to iron (III) (hydr) oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. GeochimicaetCosmochimicaActa 67(22):4223–4230

Shrivastava A, Barla A, Yadav H, Bose S (2014) Arsenic contamination in shallow groundwater and agricultural soil of Chakdaha block, West Bengal, India. Front Environ Sci 2:50

Shrivastava A, Barla A, Singh S, Mandraha S, Bose S (2017) Arsenic contamination in agricultural soils of Bengal deltaic region of West Bengal and its higher assimilation in monsoon rice. J Hazard Mater 324:526–534

Spanu A, Daga L, Orlandoni AM, Sanna G (2012) The role of irrigation techniques in arsenic bioaccumulation in rice (*Oryza sativa* L.). Environ Sci Technol 46(15):8333–8340

Srivastava S, D'souza SF (2010) Effect of variable sulfur supply on arsenic tolerance and antioxidant responses in *Hydrilla verticillata* (Lf) Royle. Ecotoxicol Environ Saf 73:1314–1322

Srivastava S, Upadhyay MK, Tripathi RD, Dhankher OP (2016) Arsenic transport, metabolism and toxicity in plants. Int J Plant Environ 2:1–2

Srivastava S, Upadhyay M, Srivastava A, Abdelrahman M, Suprasanna P, Tran LS (2018) Cellular and subcellular phosphate transport machinery in plants. Int J Mol Sci 19:1914

Takahashi Y, Minamikawa R, Hattori KH, Kurishima K, Kihou N, Yuita K (2004) Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods. Environ Sci Technol 38(4):1038–1044

Talukder ASMHM, Meisner CA, Sarkar MAR, Islam MS (2011) Effect of water management, tillage options and phosphorus status on arsenic uptake in rice. Ecotoxicol Environ Saf 74(4):834–839

Talukder ASMHM, Meisner CA, Sarkar MAR, Islam MS, Sayre KD, Duxbury JM, Lauren JG (2012) Effect of water management, arsenic and phosphorus levels on rice in a high-arsenic soil–water system: II arsenic uptake. Ecotoxicol Environ Saf 80:145–151

Upadhyay MK, Shukla A, Yadav P, Srivastava S (2018) A review of arsenic in crops, vegetables, animals and food products. Food Chem 276:608–618

Upadhyay MK, Majumdar A, Barla A, Bose S, Srivastava S (2019) An assessment of arsenic hazard in groundwater–soil–rice system in two villages of Nadia district, West Bengal, India. In: Environmental geochemistry and health, pp 1–15

Ventura W, Watanabe I, Castillo MB, De la Cruz A (1981) Involvement of nematodes in the soil sickness of a dry land rice-based cropping system. Soil Sci Plant Nutr 27(3):305–315

Victor TJ, Chandrasekaran B, Reuben R (1994) Composite fish culture for mosquito control in rice fields in southern India. Southeast Asian J Trop Med Public Health 25(3):522–527

Wang Q, He M, Wang Y (2011) Influence of combined pollution of antimony and arsenic on culturable soil microbial populations and enzyme activities. Ecotoxicology 20(1):9–19

Williams PN, Lei M, Sun G, Huang Q, Lu Y, Deacon C, Meharg AA, Zhu YG (2009) Occurrence and partitioning of cadmium, arsenic and lead in mine impacted paddy rice: Hunan, China. Environ Sci Technol 43(3):637–642

Xu XY, McGrath SP, Meharg AA, Zhao FJ (2008) Growing rice aerobically markedly decreases arsenic accumulation. Environ Sci Technol 42(15):5574–5579

Zhao FJ, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559

Biotechnological Strategies to Reduce Arsenic Content in Rice

Natasha Das, Surajit Bhattacharya, and Mrinal K. Maiti

Abstract Rice (*Oryza sativa*) grain containing above a certain threshold level of arsenic (As) is a significant contributor of dietary As intake that acts as a major risk factor for several human diseases. When As-contaminated water is used for irrigation in paddy field, the entry vis-à-vis mobilization of these heavy metal(loid)s from roots to grains inside the plant is facilitated. Amongst several strategies in practice, biotechnological strategies are the most effective ones to reduce the accumulation of heavy metal(loid)s in rice grains. To employ this strategy, identification of the genetic factors associated with As uptake, translocation, accumulation and detoxification in rice plant is very much essential. Some major genes as potential targets for biotechnological applications are discussed here in the context of As-stress mitigation in rice plants. Along with the endogenous rice genes for genetic engineering application, a few genes used for heterologous expression studies to reduce As accumulation in rice from other plants and microorganisms have also been reviewed. The new molecular techniques as biotechnological tools will lead mankind in the quest for food and nutritional security by producing safer rice grains.

Keywords Arsenic uptake and transport · Arsenic accumulation · Endogenous gene silencing · Genetic engineering · Heterologous expression · Transgenic rice

1 Introduction

Rice is the primary crop for food, culture and economy in Asia apart from being indispensable in standard diet for half of the world's population. Not only in Asia, the consumption of rice is increasing in significant proportion throughout Europe

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(http://airea.net/images/siteimages/EU27-Rice.pdf) and countries like the USA as a healthy gluten-free carbohydrate source (Batres-Marquez et al. 2009). Accumulation of heavy metal such as cadmium (Cd) and metalloids like arsenic (As) in rice grains is a serious health hazard particularly in the eastern part of India and Bangladesh. Recent report (Jang et al. 2016) warned that in more than 42 countries, the level of As in drinking water frequently exceeds the WHO standard guideline (10 μg/l) (Mandal and Suzuki 2002; Srivastava et al. 2011; Jang et al. 2016). Amongst the long list of 42 nations, countries like Australia and China are also included. Moreover, several researches point out that intake of rice as cereal or rice product such as rice snacks, baby food, etc. is responsible for As exposure in infants and children (Karagas et al. 2016). The presence of these heavy metal and metalloids [metal(loid)s] in drinking water is a precursor of major health hazards to the human and animals of not only in the affected belt; but also these poisonous elements entering into the food chain are well capable of causing severe human and animal health problems to even those residing outside the affected belt. Further, the fact that metalloid As cannot be destroyed or degraded makes this a matter of serious concern worldwide. Therefore, this food chain contaminations by heavy metal(loid)s convert the problem from a point source to diffuse source, instantly increasing the severity of the situation. Usually heavy metal(loid)s (such as arsenic, lead, cadmium, etc.) present in the soils or irrigated water enter into the plant cells through root system and are subsequently transported from root to shoot before finally accumulating in the reproductive or storages parts (fruits or seed) of the plant. The presence of these metal(loid)s above the threshold level in the common edible plant parts (roots, leaves stem, tuber, fruit or seed) causes toxicity to the herbivores including human beings. Amongst all the heavy metal(loid)s, As is of primary importance in this regard for their carcinogenic activity (Smith et al. 2002; Nawrot et al. 2006). The International Agency for Research on Cancer (IARC) recognizes As and As compounds as group 1 carcinogens. Similarly, in the plant system as well, As hampers the overall growth and causes severe physiological disorders which can ultimately result in death of the plant (Stoeva et al. 2005). Thus, attempts to reduce these heavy metal(loid)s, especially As accumulation in rice grain, demand special scientific intervention and are indispensable from the point of view of both agriculture and human health. Therefore, ample knowledge about the processes of uptake, transport and accumulation of As in crop plants, especially in rice, leading to their biomagnification in storage parts is of urgent need so as to develop comprehensive strategies to mitigate As accumulation in rice grains.

2 Heavy Metal(loid) Toxicity Is Directly Related to Plant's Requirement of Mineral Nutrients

Plants require different metal elements for a wide range of physiological processes, which help in overall plant growth, development and reproduction. The essential metals (Ca, Mg, Fe, Zn, Cu, Co, Cr, Mn and Ni) are quintessential for plants to maintain various biochemical and physiological functions in their biologically relevant oxidation state at certain threshold concentrations. The term heavy metals especially in biological sense is generally used for those metals and semimetals or metalloids that can cause potential toxicity for plants, animals (including human) or environment (Tchounwou et al. 2012). Heavy metal(loid)s are frequently present naturally in soils, but many anthropogenic activities (e.g. mining, agriculture, sewage processing, the metal industry and automobiles) increase their ubiquity in the environment resulting in concentrations that are toxic to both animals and plants. These nonessential metals(oids) like arsenic (As), lead (Pb), mercury (Hg) and cadmium (Cd) cause phytotoxicity and severely affect plant physiology by inducing stress symptoms. According to the US Agency for Toxic Substances and Disease Registry (ATSDR) Priority List of Hazardous Substances in 2017 (https://www.atsdr.cdc.gov/SPL), these four elements have been ranked first, second, third and seventh, respectively.

Contamination of cultivable land with heavy metal(loid) pollutants possesses a serious risk for agriculture and serves as a major source of heavy metal(loid) exposure to human populations upon entering the food chain via consumption of heavy metal-contaminated plant parts. Plants being immobile organisms have very limited mechanism against stress prevention and face specific challenges by environmental metal(loid) ion concentrations while absorbing sufficient mineral micronutrients for their continued growth and development but at the same time dealing with toxic levels of both the essential and nonessential metal(loid)s. Plants obtain essential elements from the soil, but due to their faulty selectivity towards metal(loid) ion absorbance, they tend to take up nonessential elements when these toxic elements are bioavailable (Clemens and Ma 2016). Amongst all these toxic metals(oids), As has been found to cause maximum damage to human population through dietary uptake of plant-derived foods cultivated in contaminated soil. Since metal(loid) homeostasis in plants is associated with the mobilization, uptake, binding/chelation, trafficking, storage as well as both long- and short-distance transport of metal(loid) elements, the regulation of these processes plays a crucial role in accumulation of As in different plant parts (Clemens 2001). Therefore, deciphering the molecular mechanisms of As uptake, absorption, transport and translocation by plants is not only of general scientific interest but could significantly contribute towards increasing the scientific basis for reducing As contamination in food supplies leading to improvement of the nutritional value of diet.

3 Effect of Arsenic in Plant System

Arsenic is one of the nonessential metal(loid)s and is highly toxic to the plants. Generally, plants have the ability to counter the detrimental effects of heavy metal(loid)s by a range of different detoxification mechanisms. The detoxification processes include binding with root exudates or cell wall constituents, uptake through transport and efflux of metal(loid) from plasma membrane, increasing sequestration and compartmentalization into the vacuole via chelation by metallothioneins (MTs) and phytochelatins (PCs). However, when the As species are not detoxified, it affects the overall growth of the plant and causes severe physiological disorders including death of the plant species (Stoeva et al. 2005). The first exposed location from where the As is uptaken in plant is the root, which shows reduced proliferation and extension of tissue following As exposure. Apart from phenotypically observable symptoms, a lot of physiological processes are also influenced by As toxicity at the same time. Plant cellular membranes tend to get damaged that leads to electrolyte leakage due to oxidative stress generated following As toxicity (Singh et al. 2006). Often, the oxidative stress caused by As is also responsible for lipid peroxidation as evident by increased production of malondialdehyde, a product of lipid peroxidation. Moreover, As exposure has also been demonstrated to induce antioxidant defence mechanisms, and as a result, the synthesis of ascorbate, the γ-Glu-Cys-Gly tripeptide glutathione (GSH) and the GSH oligomer ([γ-Glu-Cys]*n*-Gly) phytochelatin (PC) increases throughout the plant body, especially in the roots (Schmöger et al. 2000; Li et al. 2004; Geng et al. 2006; Singh et al. 2006; Khan et al. 2009), while increased level of anthocyanin accumulates in leaves (Catarecha et al. 2007). Further, As toxicity has also been associated with reduction in the intensity of plant transpiration (Stoeva and Bineva 2003).

Normally, plants take up As from soil mainly as arsenate As(V), which interferes with different metabolic processes within the plant species that require phosphate. Following its entry inside the plant cells, As(V) has the ability to shatter the energy flow by competing with PO_4^{3-} and forming unstable adenosine diphosphate-As(V) during ATP (adenosine triphosphate) synthesis (Meharg and Hartley-Whitaker 2002; Cozzolino et al. 2010). On the other hand, the mode of action of arsenite As(III) varies significantly from that of As(V) inside plant cells following its direct uptake or conversion of As(V) into As(III) by arsenate reductase. Being a thiol-reactive agent, As(III) can bind to vicinal sulfhydryl groups (up to three) of proteins that often leads to obvious negative effect on the structural as well as on the catalytic function of the protein (Kitchin and Wallace 2006; Tripathi et al. 2007; Zhao et al. 2010). Improper folding of proteins due to As(III) binding may result into inactivation of necessary enzymes. Apart from protein-/enzyme-binding property, As(III) also plays the role of cross-linking agent and binds to cofactors, thiol-containing molecules such as the antioxidant GSH and PC (Ha et al. 1999; Raab et al. 2004; Song et al. 2010), thus affecting several physiological function normally carried out by GSH and PC.

4 Strategies of Reducing the Accumulation of Heavy Metal(loid)s in Rice Grain

Metal(loid) pollutants have been an integral part of human civilization since its very inception. However, rapid industrial development has played a key role in intensifying the heavy metal(loid)s toxicity in the biosphere, leading to severe environmental and health hazards. The contamination of these toxic metal(loid)s in the agricultural soils occurs because of excessive fertilizer (phosphate) application in cultivated fields and the use of sewage sludge as a soil amendment or sometimes due to naturally high background levels due to microbiological-geochemical activities (Dorlhac de Borne et al. 1998). These heavy metal(loid)s have been accounted to be accumulated in notable amount in the consumable parts of crop plants, and their subsequent internalizing in the food chain raises the question of potential health hazards (Verbruggen et al. 2009). These toxic elements present in the food chain following ingestion are absorbed in the digestive tract in the consumer's body and are accumulated in the kidney or liver. Accumulation in high levels causes stomach irritation leading to vomiting and diarrhoea and sometimes even death. Moreover, rice, the most cultivated and consumed crop in eastern India, is highly efficient in arsenic (As) assimilation than other cereal crops (Williams et al. 2007) and contains more amount of inorganic arsenic in the grains (Schoof et al. 1999). Therefore, attempts to reduce the toxicity caused by arsenic in rice grain demand special scientific intervention and become indispensable from the point of view of both agriculture and human health.

In order to reduce the accumulation of the toxic heavy metalloid As in rice grains, three possible strategies can be employed (Fig. 1):

(I) Agronomic practices: These include various traditional methods of minimizing or decontaminating heavy metal(loid)s in the soil such as soil amendments, fertilizer management, water management, etc.

(II) Bioremediation and phytoremediation approaches: Use of various microbes and accumulator plants to clean up the toxic metal(loid)s from the soil. Both these strategies could be used for remediation of these toxic elements in the soil, which can significantly reduce the uptake, transfer and their subsequent accumulation in rice grains.

(III) Application of molecular biology techniques: These involve the direct application of the DNA analysis and recombinant DNA tools for screening of the desired genetic variants from breeding progeny and transgenic lines to overcome the uptake, transfer and accumulation of heavy metal(loid)s in rice grains.

Although all these strategies can be useful for controlling accumulation of As in rice, the cost-intensive and low efficiency at low metal concentrations in soil (Hammaini et al. 2003) have severely hindered the use of conventional agronomic practices for efficient As removal. Therefore, in recent years much research has focussed on using modern biotechnological tools to develop safer transgenic plants exploiting mainly two strategies, i.e. (a) identifying and utilizing the endogenous critical genes involved in As uptake, transport and sequestration within the plant tissue and (b) identifying and utilizing genes other than endogenous origin for reducing the uptake and accumulation of As in rice plants. Fundamentally, the genetic engineering or biotechnological techniques involve either overexpression of endogenous or heterologous target genes or silencing/downregulation of target genes.

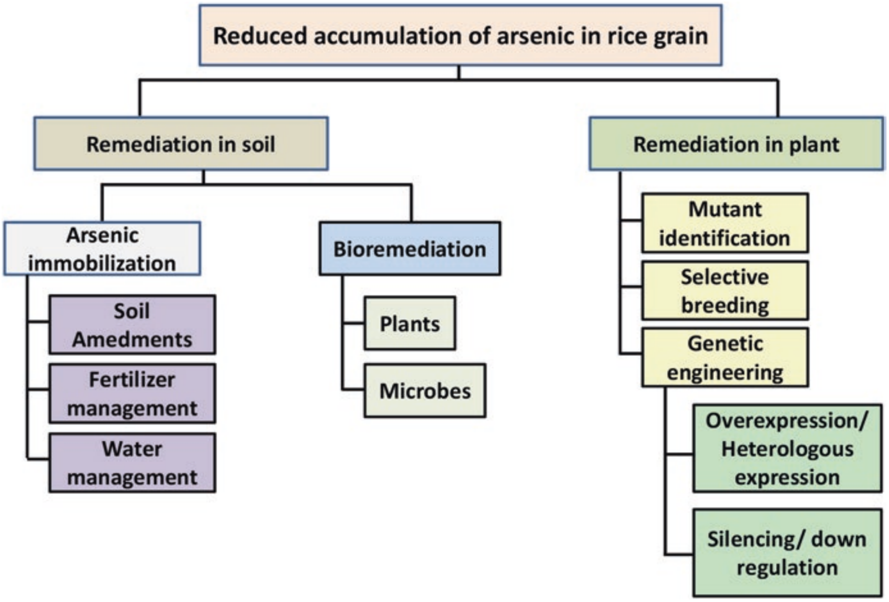

Fig. 1 Schematic representation of the various strategies for reducing the accumulation of arsenic in rice grain

4.1 Identifying Endogenous Target Genes: Genes Associated with As Uptake, Translocation, Accumulation and Detoxification in Rice Plant

4.1.1 Targeting Genes Involved in Arsenic Uptake in Rice Plants

In soil, As exists both as inorganic and organic species but is found predominantly in inorganic forms of arsenate As(V) and arsenite As(III). The dominant form of arsenic in aerobic environment is As(V), whereas in anaerobic environmental condition like flooded rice paddy field, As(III) is found to be the prevailing form. Derivatives of As(III), i.e. mono-, di- and trimethylated As(III) (MMA^{III}, DMA^{III}, TMA^{III}), are volatile in nature. On the other hand, the different organic species of As(V), which are monomethylarsonic acid (MMA^{V}), dimethylarsinic acid (DMA^{V}) and trimethylarsine oxide ($TMAO^{V}$), are found in very low amount in soil (Finnegan and Chen 2012). In case of plants, it is the inorganic forms of As that are predominantly taken up from the soil due to the imperfect selectivity of the endogenous transporters while acquiring necessary elemental ions from the soil. Amongst the different forms of As, the foremost species taken up by plants is As(V), which being an analogue of inorganic phosphate (Pi) can be easily transported across one cell to another, through the internal plasma membrane located Pi transporter (PHT) proteins (Ullrich-Eberius et al. 1989; Wu et al. 2011; Finnegan and Chen 2012) (Fig. 2). Till date, a few Pi transporters, i.e. OsPT1–OsPT8, have been identified in rice plant that facilitates the cellular uptake of As (Wu et al. 2011). Interestingly, a two- to threefold higher expression of OsPT8 compared to OsPT2 in Aus rice variety Kasalath showed an increased tolerance to As(V) compared to *japonica* variety Nipponbare (Wang et al. 2016). This observation combined with the finding that OsPT8 mutant of both Kasalath and Nipponbare rice varieties demonstrated significant reduction in As(V) uptake leading to elevated As(V) tolerance (Wang et al. 2016) clearly established the importance of OsPT8 in rice As(V) uptake. Further, in a recent study, four members of rice Pi transporter family, i.e. OsPT1, OsPT2, OsPT4 and OsPT8, have been elucidated to play an important role in uptake of As(V) by rice roots (Ye et al. 2017). Furthermore, of the various PHTs involved in As(v) uptake in rice, the T-DNA-mediated insertion in OsPHT1;4 gene developed mutant rice lines that not only demonstrated reduced As concentration in xylem sap of the immature plants but also accumulated significantly less amounts of total and inorganic As in the grains of the mature plants (Cao et al. 2017). Similar mutation in another rice PHT gene, i.e. OsPHT1;8, resulted in both increased tolerance and up to 57% reduced uptake of As(V) (Wang et al. 2016). Although both these studies showed the effect of mutating PHTs controlling the As content in rice plants, since no analysis of phosphate content was provided, the true extent of their suitability for mitigating As accumulation in rice remains unanswered.

On the other hand, nodulin 26-like intrinsic protein (NIP) class of aquaporin channels are responsible for uptake and transport of As(III) and nondissociated methylated As in plants (Zhao et al. 2010; Mosa et al. 2012; Clemens and Ma 2016) (Fig. 2). Although several members of NIP transporters, viz. OsNIP1;1, OsNIP2;2, OsNIP3;1, OsNIP3;2, OsNIP3;3, have been reported to facilitate As(III) uptake in rice (Clemens and Ma 2016), the silicic acid (Si) transporter OsLsi1 (OsNIP2;1), belonging to NIP group of transporters localized on the distal side in the root cells of rice, has been found to play a crucial role in As(III) uptake in rice (Ma et al. 2008). The uptaken As(III) is then effluxed into the stele and xylem tissues by the activity of proximally localized silicon efflux transporter OsLsi2 for xylem loading of As(III) (Ma et al. 2008) (Fig. 2). Most interestingly, mutations in the OsLsi1 significantly affected the As(III) uptake in rice (Ma et al. 2008). Moreover, OsLsi2 mutants of rice demonstrated reduced transportation leading to decreased accumulation of As(III) in shoots and grains of rice (Ma et al. 2008), indicating the potential of these transporters to develop low As-accumulating rice plants. Another class of aquaporin proteins, i.e. plasma membrane intrinsic proteins (OsPIPs) such as OsPIP2;4, OsPIP2;6 and OsPIP2;7, have been reported to be involved in As(III) uptake and transport in rice (Mosa et al. 2012). Overexpression analysis of these transporters in *Arabidopsis* not only resulted in enhanced As(III) tolerance and higher biomass accumulation but also displayed no significant accumulation of As in shoots and roots of transgenic plants even after long-term exposure (Mosa et al. 2012). This interesting observation has been attributed to the bidirectional permeability for As(III) of OsPIPs making them particularly suitable for transgenic approaches for generating plants with reduced As content even when grown in As-contaminated soil.

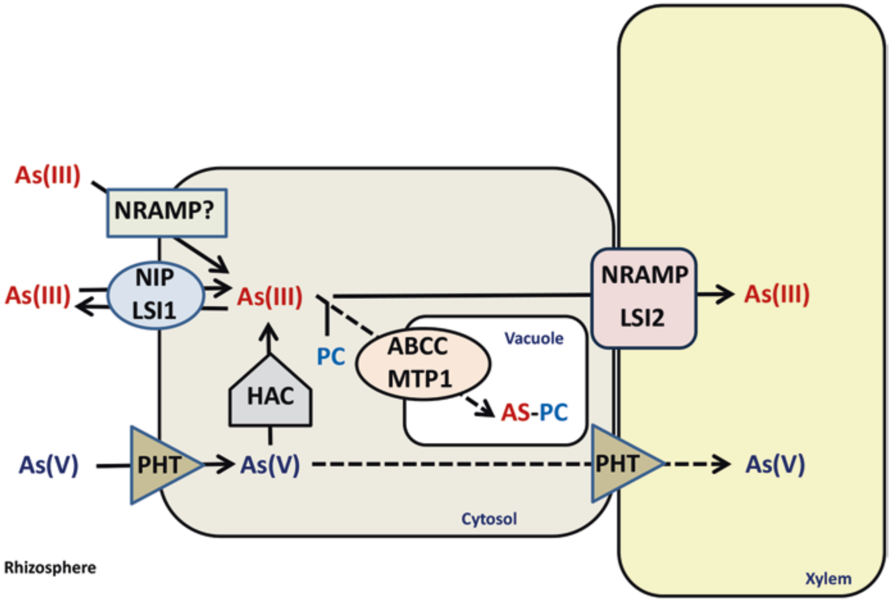

Fig. 2 A schematic representation of the various factors and transporters involved in As uptake in rice roots and the subsequent As transport through xylem up to the grains. PHT: Phosphate transporters are involved in the uptake of As(V), whereas aquaporins (NIP, Lsi1) and NRAMP1 (natural resistance-associated macrophage protein) are involved in the uptake of As(III). As(III) is sequestered into vacuoles either directly by metal transporter protein (MTP1) or by complexing with thiolic compounds via the action of C-type ATP-binding cassette transporter (ABCC). OsLsi2 and NRAMP1 help in xylem loading and root-to-shoot transport of As

Further, the iron transporter OsNRAMP1 (Natural Resistance-Associated Macrophage Protein 1), which has previously been reported to be involved in Cd accumulation in rice (Takahashi et al. 2011), has also been suspected to be involved in As(III) uptake and transport in rice (Tiwari et al. 2014) (Fig. 2). The heterologous expression of OsNRAMP1 in *Arabidopsis* has resulted in an increased tolerance and accumulation of As(III) compared to untransformed control *Arabidopsis* plants. However, so far no work has been carried out to control As accumulation in rice plants using this transporter. Recently, a metabolite and/or xenobiotic compound transporter belonging to multidrug and toxic compound extrusion (MATE) protein family, OsMATE2, has been identified to be involved in As accumulation in rice plants (Das et al. 2018). Most importantly, endosperm-specific silencing of this OsMATE2 transporter demonstrated reduction in As accumulation in rice grains of transgenic rice lines in comparison to untransformed control plants (Das et al. 2018). Although a few transporter proteins involved in uptake and accumulation of As in rice plants have been identified, the transporters involved in loading of As from xylem to phloem and subsequently into seeds of rice are yet unknown. Recently in *Arabidopsis*, inositol transporters (AtINT2 and AtINT4) responsible for loading inositol in phloem have been identified to be responsible for the uptake of As(III) in the phloem tissues (Duan et al. 2016). Identifying the rice counterparts of these transporters thus becomes a matter of utmost importance. However, even though the manipulation of these transporters and their expression can be used to minimize As transport accumulation in rice grains, the fact that these transporters are also involved in transportation of essential or beneficial elements for plant growth and development, genetic modification of transporters can lead to severe structural or yield-related compromises for the transgenic plants. Therefore, the outcome of manipulating transporter expressions on the balance of other essential metabolites need to be critically assessed before employing transgenic strategies for reducing grain As content in rice.

4.1.2 Targeting Genes Involved in Arsenic Speciation in Rice Plants

Once inside the plant system, the speciation of As is regulated by enzyme arsenate reductase (AR), which reduces As(V) to As(III), thereby making the As(III) the dominant species inside the plant body (Fig. 2). In rice, two AR genes, i.e. OsHAC1;1 and OsHAC1;2, have been identified with differing expression pattern (Shi et al. 2016). Although both OsHAC1;1 and OsHAC1;2 are primarily expressed in the roots, OsHAC1;1 expression is mostly in epidermis, root hairs and pericycle layer along with significant abundance in stems and nodes (Xu et al. 2017). On the other hand, OsHAC1;2 expression is predominant in epidermis, outer cortex layers and endodermis. Interestingly, OsHAC1;1 or OsHAC1;2 knock out in rice not only reduced the As(III) efflux to external media but also increased the As accumulation in the shoots of rice plants (Shi et al. 2016). Further, overexpression of OsHAC1;1 or OsHAC1;2 significantly decreased As accumulation in grains by increasing the efflux of As(III) to the external media (Shi et al. 2016). Recently, another member of rice AR family, i.e. OsHAC4, has been identified having no expression in leaves but with high expression in the epidermal elongation and maturation zone and exodermis of the roots (Xu et al. 2017). Similar to the results observed with OsHAC1;1 or OsHAC1;2, overexpression of OsHAC4 reduced As accumulation in rice shoots, whereas downregulation of OsHAC4 significantly reduced As(III) efflux resulting in increased accumulation of As in the shoots. The results observed clearly highlight the importance of As(V) to As(III) interconversion and their eventual accumulation in rice plants and signify the potential of these AR family members in mitigating As accumulation in rice.

4.1.3 Targeting Genes Involved in Arsenic Chelation and Vacuolar Transport

Inside the plant cell, the reduced As(III) is normally transported to vacuoles either through tonoplast-bound metal transporter proteins such as OsMTP1 (Das et al. 2016) or in the form of As(III)-phytochelatin complex following its complexion with phytochelatins (PC) through the transporters belonging to C-type ATP-binding cassette (ABC) family, viz. OsABCC1 and OsABCC2 (Song et al. 2014) (Fig. 2). Recent report documented that the heterologous expression of the OsMTP1 in tobacco significantly increased the As tolerance and accumulation ability, indicating the potential application of this membrane-bound transporter to mitigate As accumulation in rice (Das et al. 2016). On the other hand, PCs being the group of thiol-rich small peptides are one of the most critical components of plant defence against heavy metal(loid) stress (Grill et al. 1987). The PCs produced by the activity of phytochelatin synthase (PCS) form PC-As complexes with the As(III) and subsequently sequester the bound As(III) inside the vacuole to reduce the toxic effect. Recently, rice genome has been found to contain at least two functionally distinct copies of PCS genes, i.e. OsPCS1 and OsPCS2 (Das et al. 2017). In an interesting approach, endosperm-specific simultaneous downregulation of both OsPCS1 and OsPCS2 resulted in significant reduction of the grain As content in rice that was hypothesized to reduce PC content in grains (Das et al. 2017), which clearly establishes PCS as an ideal target to develop rice plants with reduced grain As content.

One of the most important part of rice plant that acts as the controlling point of As transport and its eventual distribution and accumulation in the grain is the node (Yamaji and Ma 2014; Zhao et al. 2014). It is implied that the nodes act as barrier to As(III) by limiting its movement into the grains (Chen et al. 2015). Furthermore, it is assumed that the ABCC transporters sequester PC-As complex in vacuoles in nodal cells limiting the transport of As from the nodes to the grains of rice (Song et al. 2014; Clemens and Ma 2016). It must be noted that As(III) forms complex with PCs before sequestration into vacuole, and PC is synthesized from the precursor glutathione (GSH) by the transpeptidation reactions carried out by the PCS enzyme mentioned earlier. Moreover, the observation that at the nodal region of rice, OsABCC1 is localized in the phloem companion cells of the vascular bundle further strengthens the importance of OsABCC1 in As accumulation in rice grains. Knockout of OsABCC1 in rice although resulted in increased As susceptibility and elevated As content in grains compared to wild-type plants, establishing the fact that OsABCC1 plays an important role in limiting As transport to the rice grain from the nodes (Song et al. 2014). Further in a very recent study, with the aim to increase As vacuolar sequestration in rice, OsABCC1 has been concomitantly expressed along with the yeast cadmium factor (ScYCF1) under the control of a root-specific promoter. Most importantly, the transgenic rice lines not only demonstrated a steep decline in root-to-shoot and internode-to-grain translocation of As but also resulted in significant reduction of grain As content without affecting the agronomic trait (Deng et al. 2018).

4.1.4 Targeting Genes of Regulatory Factors

Apart from the genes directly involved in uptake, transport and sequestration of As in rice plants, there are various regulatory factors which are postulated to play important role in mitigating As stress in rice plants and thus can act as potential targets for biotechnological applications. Further, several sequencing and transcriptomic analyses have indicated the involvement of a number of phytohormones, transcription factors, microRNAs, etc. in As stress responses of plants (Norton et al. 2008; Yu et al. 2012; Srivastava et al. 2013, 2015). The first level of regulation is carried out by the phytohormones such as ethylene, abscisic acid and salicylic acid, which act as important mediators in regulating the responses of plants when exposed to various heavy metal(loid)s including As (Song et al. 2012; Srivastava et al. 2013; Alves et al. 2017). Transcription factors have long been identified as master regulators for most metabolic processes, and a few transcription factors such as WRKY6 and WRKY45 have been found to play crucial roles in As uptake and transport in *Arabidopsis* (Castrillo et al. 2013; Wang et al. 2014). However, not much information about the functioning of these transcription factor homologs have been obtained from rice plants till date. Very recently a R2R3 Myb family transcription factor OsARM1 (Arsenite-Responsive Myb1) has been identified as a critical regulator of intercellular As transporters in rice plant (Wang et al. 2017). Although overexpression of OsARM1 increased sensitivity to As(III), the root-to-shoot translocation of As was significantly reduced due to downregulation of crucial As transporters OsLsi1, OsLsi2 and OsLsi6 in transgenic rice plants (Wang et al. 2017). On the other hand, small non-coding RNAs especially microRNAs (miRNAs) have been identified as another important regulating factor controlling the gene expression by regulating the transcription and/or translation of target genes. Recently, it has been documented that the overexpression of an As-responsive miRNA, miR528 results in increased sensitivity and altered oxidative stress responses in transgenic rice (Liu et al. 2015), clearly establishing the role of miRNAs in directly controlling As-stress response in rice plants. Although many other As-responsive miRNAs have been identified in several plants, more in-depth studies are of critical importance not only to decipher the exact roles of these miRNAs but also to use them in biotechnological applications for mitigating As uptake and accumulation in plants, including rice.

4.2 Utilizing Genes Other Than Endogenous Origin for Genetic Engineering Application

Apart from targeting the endogenous genes for controlling As uptake, transport and eventual accumulation in rice grains, a few genes from other plants and microorganisms have also been used for heterologous expression studies to reduce As accumulation in rice. Considering the role of PCS in chelation and eventual transport of As inside the vacuole, heterologous expression of a *Ceratophyllum demersum* PCS gene (CdPCS1) in rice was carried out to limit root-to-shoot As transport and limiting As accumulation in the grains (Shri et al. 2014). The transgenic rice plants expressing CdPCS1 showed significantly increased As accumulation in root and shoot but reduced As content in rice grain and husk, indicating a successful implementation of the adopted strategy (Shri et al. 2014). Another interesting approach to limit As accumulation in grain could be to develop transgenic plants capable of volatilizing inorganic As uptaken from the soil/environment. In case of bacteria, S-adenosyl-methionine-dependent methyltransferase (arsM) is known to convert As(III) to the gaseous trimethylarsine (TMA); however, in plants, this conversion process is not observed due to the absence of *arsM* gene (Messens and Silver 2006). Overexpression of *arsM* gene from gram-negative purple non-sulphur bacterium *Rhodopseudomonas palustris* in rice significantly increased the volatile As species in transgenic plants, suggesting potential application of this *arsM* gene for controlling As accumulation (Meng et al. 2011). In a similar approach, the expression of the *arsM* gene of soil fungus *Westerdykella aurantiaca* induced elevated arsenic methylation and volatilization leading to reduced grain As content in transgenic rice plants in comparison to the untransformed control plants, clearly highlighting the importance of the adapted strategy to mitigate As accumulation in rice grains (Verma et al. 2017).

5 Prospecting the New Molecular Techniques Towards Attaining Reduced Arsenic in Rice

Transgenic technology mediated through plant tissue transformation by *Agrobacterium tumefaciens* and particle bombardment and DNA uptake into protoplast in economically important plant species has revolutionized agriculture. However, the transgene integration at random sites in the plant genome and the variable level of transgene expression associated with complexity and position of the integrated recombinant DNA in the plant genome in turn may lead to undesirable phenotypes or gene silencing or potential side effect due to redundant mutation. The advent of a few novel genome manipulation methods has demonstrated a significant impact on agricultural biotechnology sector in recent times. Targeted genome engineering (TGE)/targeted editing of the genomes of particular plant species allows both fundamental research and application in crop improvement without 'position' effect caused by random integration and significantly helps in the production of genetically modified plant variety with desired traits.

Homologous recombination (HR) based gene targeting (GT) offers many advantages over traditional transformation techniques. HR ensures transgene integration in a precise manner, transgene expression at the desirable/ high level, and also insertion of single copy transgene obviates the unknown 'position' effect thereby produce safer transgenic crop. Other novel genome-editing systems in practice for various organisms include zinc finger nucleases (ZFNs), transcription activator-like effector nucleases (TALENs) and clustered regularly interspaced short palindromic repeats/ Cas9 (CRISPR/Cas9). The bacterial RNA-guided CRISPR/Cas9 system is nowadays preferred over other tools for precise gene editing with genome. Rice, on the other hand, as a model plant has been used for building technological platforms and testing novel strategies for genetic improvements, which can be extrapolated to other cereal crops. It is true that transgenic technologies have identified a few genetic markers, which can be used as a tool for marker assisted breeding for selecting low As rice. Nowadays due to availability of precise gene-editing technology, alteration of endogenous genes (with respect to expression or activity) is possible that will give rise to new information regarding metabolism of As in rice and other plant species, so that information about new genes can be utilized for producing low-As rice.

Although there is advent of modern tools, still genetic engineering in rice (and other plant species) faces several challenges in applying genome-editing technologies. Performing genome engineering in most of the *indica* rice cultivars that are recalcitrant to tissue culture is till now very challenging; for that reason most of the genome editing-related studies have been carried out in *japonica* rice varieties. However, a recent study by Tang et al. (2017) succeeded to develop *indica* rice lines and their hybrids with extremely low Cd content in grains using the CRISPR/Cas9-mediated *OsNramp5* gene editing system. In future, similar approach can be used to reduce grain As levels in other rice cultivars, which expedite the development of toxic metal/metalloid-safe rice through precision breeding.

6 Conclusion

Commercialization of transgenic or genome-edited rice is also an issue with respect to biosafety towards humans (animals) and environment that comes under different country's government regulations. However, several countries (developed and developing) in the world have already accepted the genetically modified crops including food crops for commercial production on case-to-case basis considering the scientific merits and benefit/risk balance ratio. Nevertheless, there is a great potential of biotechnological tools (both transgenic and genome editing) helping mankind to achieve food and nutritional security by producing safer rice grains with no or minimum toxic elements.

References

Alves LD, Monteiro CC, Carvalho RF, Ribeiro PC, Tezotto T, Azevedo RA, Gratao PL (2017) Cadmium stress related to root-to-shoot communication depends on ethylene and auxin in tomato plants. Environ Exp Bot 134:102–115

Batres-Marquez SP, Jensen HH, Upton J (2009) Rice consumption in the United States: recent evidence from food consumption surveys. J Am Diet Assoc 109(10):1719–1727

Cao Y, Sun D, Ai H, Mei H, Liu X, Sun S et al (2017) Knocking out OsPT4 gene decreases arsenate uptake by rice plants and inorganic arsenic accumulation in rice grains. Environ Sci Technol 51:12131–12138

Castrillo G, Sánchez-Bermejo E, de Lorenzo L, Crevillén P, Fraile-Escanciano A, Mohan TC (2013) WRKY6 transcription factor restricts arsenate uptake and transposon activation in Arabidopsis. Plant Cell 25:2944–2957

Catarecha P, Segura MD, Franco-Zorrilla JM, García-Ponce B, Lanza M, Solano R et al (2007) A mutant of the Arabidopsis phosphate transporter PHT1; 1 displays enhanced arsenic accumulation. Plant Cell 19:1123–1133

Chen Y, Moore KL, Miller AJ, McGrath SP, Ma JF, Zhao FJ (2015) The role of nodes in arsenic storage and distribution in rice. J Exp Bot 66:3717–3724

Clemens S (2001) Molecular mechanisms of plant metal tolerance and homeostasis. Planta 212:475

Clemens S, Ma JF (2016) Toxic heavy metal and metalloid accumulation in crop plants and foods. Annu Rev Plant Biol 67:489–512

Cozzolino V, Pigna M, Di Meo V, Caporale AG, Violante A (2010) Effects of arbuscular mycorrhizal inoculation and phosphorus supply on the growth of *Lactuca sativa* L. and arsenic and phosphorus availability in an arsenic polluted soil under non-sterile conditions. Appl Soil Ecol 45:262–268

Das N, Bhattacharya S, Maiti MK (2016) Enhanced cadmium accumulation and tolerance in transgenic tobacco overexpressing rice metal tolerance protein gene *OsMTP1* is promising for phytoremediation. Plant Physiol Biochem 105:297–309

Das N, Bhattacharya S, Bhattacharyya S, Maiti MK (2017) Identification of alternatively spliced transcripts of rice phytochelatin synthase 2 gene *OsPCS2* involved in mitigation of cadmium and arsenic stresses. Plant Mol Biol 94(1–2):167–183

Das N, Bhattacharya S, Bhattacharyya S, Maiti MK (2018) Functional characterization of a rice MATE family transporter OsMATE1 implicates its role in arsenic accumulation. Plant Mol Biol 98(1–2):101–120

Deng F, Yamaji N, Ma JF, Lee SK, Jeon JS, Martinoia E et al (2018) Engineering rice with lower grain arsenic. Plant Biotechnol J 16:1691–1699

Dorlhac de Borne F, Elmayan T, De Roton C, De Hys L, Tepfer M (1998) Cadmium partitioning in transgenic tobacco plants expressing a mammalian metallothionein gene. Mol Breed 4:83–90

Duan GL, Hu Y, Schneider S, McDermott J, Chen J, Sauer N et al (2016) Inositol transporters atint2 and atint4 regulate arsenic accumulation in Arabidopsis seeds. Nat Plants 2:15202

Finnegan P, Chen W (2012) Arsenic toxicity: the effects on plant metabolism. Front Physiol 3:182

Geng CN, Zhu YG, Hu Y, Williams P, Meharg AA (2006) Arsenate causes differential acute toxicity to two P-deprived genotypes of rice seedlings (*Oryza sativa* L.). Plant Soil 279:297–306

Grill E, Winnacker EL, Zenk MH (1987) Phytochelatins, a class of heavy-metal-binding peptides from plants, are functionally analogous to metallothioneins. Proc Natl Acad Sci U S A 84(2):439–443

Ha SB, Smith AP, Howden R, Dietrich WM, Bugg S, O'Connell MJ, Goldsbrough PB, Cobbett CS (1999) Phytochelatin synthase genes from *Arabidopsis* and the yeast, *Schizosaccharomyces pombe*. Plant Cell 11:1153–1164

Hammaini A, Gonzalez F, Ballester A, Blazquez ML, Munoz JA (2003) Simultaneous uptake of metals by activated sludge. Miner Eng 16:723–729

Jang YC, Somanna Y, Kim H (2016) Source, distribution, toxicity and remediation of arsenic in the environment – a review. Int J Appl Environ Sci 11:559–581

Karagas MR, Punshon T, Sayarath V, Jackson BP, Folt CL, Cottingham KL (2016) Association of rice and rice-product consumption with arsenic exposure early in life. JAMA Pediatr 170:609–616

Khan I, Ahmad A, Iqbal M (2009) Modulation of antioxidant defence system for arsenic detoxification in Indian mustard. Ecotoxicol Environ Saf 72:626–634

Kitchin KT, Wallace K (2006) Arsenite binding to synthetic peptides: the effect of increasing length between two cysteines. J Biochem Mol Toxicol 20:35–38

Li Y, Dhankher OM, Carreira L, Lee D, Chen A, Schroeder JI, Balish RS, Meagher RB (2004) Overexpression of phytochelatin synthase in *Arabidopsis* leads to enhanced arsenic tolerance and cadmium hypersensitivity. Plant Cell Physiol 45:1787–1797

Liu F, Liu XN, Ding C, Wu L (2015) The dynamic simulation of rice growth parameters under cadmium stress with the assimilation of multi-period spectral indices and crop model. Field Crop Res 183:225–234

Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proc Natl Acad Sci U S A 105(29):9931–9935

Mandal B, Suzuki K (2002) Arsenic round the world: a review. Talanta 58:201–235

Meharg AA, Hartley-Whitaker J (2002) Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. New Phytol 154:29–4310

Meng XY, Qin J, Wang LH, Duan GL, Sun GX, Wu HL et al (2011) Arsenic biotransformation and volatilization in transgenic rice. New Phytol 191:49–456

Messens J, Silver S (2006) Arsenate reduction: thiol cascade chemistry with convergent evolution. J Mol Biol 362:1–17

Mosa KA, Kumar K, Chhikara S, Mcdermott J, Liu Z, Musante C et al (2012) Members of rice plasma membrane intrinsic proteins subfamily are involved in arsenite permeability and tolerance in plants. Transgenic Res 21:1265–1277

Nawrot T, Plusquin M, Hogervorst J, Roels HA, Celis H, Thijs L, Vangronsveld J, Van Hecke E, Staessen JA (2006) Environmental exposure to cadmium and risk of cancer: a prospective population-based study. Lancet Oncol 7:119–126

Norton GJ, Lou-Hing DE, Meharg AA, Price AH (2008) Rice–arsenate interactions in hydroponics: whole genome transcriptional analysis. J Exp Bot 59(8):2267–2276

Raab A, Feldmann J, Meharg AA (2004) The nature of arsenic phytochelatin complexes in *Holcus lanatus* and *Pteris cretica*. Plant Physiol 134:1113–1122

Schmöger MEV, Oven M, Grill E (2000) Detoxification of arsenic by phytochelatins in plants. Plant Physiol 122:793–802

Schoof RA, Yost LJ, Eickhoff J, Crecelius EA, Cragin DW, Meacher DM, Menzel DB (1999) A market basket survey of inorganic arsenic in food. Food Chem Toxicol 37(8):839–846

Shi SL, Wang T, Chen Z, Tang Z, Wu ZC, Salt DE et al (2016) OsHAC1;1 and OsHAC1;2 function as arsenate reductases and regulate arsenic accumulation. Plant Physiol 172:1708–1719

Shri M, Dave R, Dwivedi S, Shukla D, Kesari R, Tripathi RD, Trivedi PK, Chakrabarty D (2014) Heterologous expression of *Ceratophyllum demersum* phytochelatin synthase, CdPCS1, in rice leads to lower arsenic accumulation in grain. Sci Rep 4:5784

Singh HP, Batish DR, Kaur S, Arora K, Kohli RK (2006) α-Pinene inhibits growth and induces oxidative stress in roots. Ann Bot 98(6):1261–1269

Smith AH, Lopipero PA, Bates MN, Steinmaus CM (2002) Public health – arsenic epidemiology and drinking water standards. Science 296:2145–2146

Song WY, Park J, Mendoza-Cózatl DG, Suter-Grotemeyer M, Shim D, Hörtensteiner S et al (2010) Arsenic tolerance in Arabidopsis is mediated by two ABCC-type phytochelatin transporters. Proc Natl Acad Sci U S A 107:21187–21192

Song W, Zheng AZ, Shao HB, Chu L, Brestic M, Zhang Z (2012) The alleviative effect of salicylic acid on the physiological indices of the seedling leaves in six different wheat genotypes under lead stress. Plant Omics: J Plant Omics Mol Biol 5:486–493

Song WY, Yamaki T, Yamaji N, Ko D, Jung KH, Fujii-Kashino M, An G, Martinoia E, Lee Y, Ma JF (2014) A rice ABC transporter, OsABCC1, reduces arsenic accumulation in the grain. Proc Natl Acad Sci U S A 111:15699–15704

Srivastava S, Suprasanna P, D'Souza SF (2011) Redox state and energetic equilibrium determine the magnitude of stress in *Hydrilla verticillata* upon exposure to arsenate. Protoplasma 48:805–815

Srivastava S, Srivastava AK, Suprasanna P, D'Souza SF (2013) Identification and profiling of arsenic stress-induced microRNAs in *Brassica juncea*. J Exp Bot 64:303–315

Srivastava S, Srivastava AK, Sablok G, Deshpande T, Suprasanna P (2015) Transcriptomics profiling of Indian mustard (*Brassica juncea*) under arsenate stress identifies key candidate genes and regulatory pathways. Front Plant Sci 6:646

Stoeva N, Bineva T (2003) Oxidative changes and photosynthesis in oat plants grown in as-contaminated soil. Bulg J Plant Physiol 29(1–2):87–95

Stoeva N, Berova M, Zlatev Z (2005) Effect of arsenic on some physiological parameters in bean plants. Biol Plant 49:293–296

Takahashi R, Ishimaru Y, Senoura T, Shimo H, Ishikawa S, Arao T, Nakanishi H, Nishizawa NK (2011) The OsNRAMP1 iron transporter is involved in Cd accumulation in rice. J Exp Bot 62:4843–4850

Tang L, Mao B, Li Y, Lv Q, Zhang L, Chen C et al (2017) Knockout of OsNramp5 using the CRISPR/Cas9 system produces low Cd-accumulating indica rice without compromising yield. Sci Rep 7:14438

Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2012) Heavy metal toxicity and the environment. Molecular. Clin Environ Toxicol Experientia Suppl 101:133–164

Tiwari M, Sharma D, Dwivedi S, Singh M, Tripathi RD, Trivedi PK (2014). Expression in Arabidopsis and cellular localization reveal involvement of rice NRAMP, OsNRAMP1, in arsenic transport and tolerance. Plant Cell Environ 37:140–152

Tripathi RD, Srivastava S, Mishra S, Singh N, Tuli R, Gupta DK et al (2007) Arsenic hazards: strategies for tolerance and remediation by plants. Trends Biotechnol 25:158–165

Ullrich-Eberius CI, Sanz A, Novacky AJ (1989) Evaluation of arsenate- and vanadate-associated changes of electrical membrane potential and phosphate transport in Lemna gibba-G1. J Exp Bot 40:119–128

Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or cadmium excess in plants. Curr Opin Plant Biol 12(3):364–372

Verma S, Verma PK, Meher AK, Bansiwal AK, Tripathi RD, Chakrabarty D (2017) A novel fungal arsenic methyltransferase, WaarsM reduces grain arsenic accumulation in the transgenic rice plant. J Hazard Mater 344:626–634

Wang H, Xu Q, Kong YH, Chen Y, Duan JY, Wu WH et al (2014) Arabidopsis WRKY45 transcription factor activates PHOSPHATE TRANSPORTER1;1 expression in response to phosphate starvation. Plant Physiol 164:2020–2029

Wang L, Bei X, Gao J, Li Y, Yan Y, Hu Y (2016) The similar and different evolutionary trends of MATE family occurred between rice and *Arabidopsis thaliana*. BMC Plant Biol 16:207

Wang FZ, Chen MX, Lu LJ, Xie LJ, Yuan LB, Qi H et al (2017) OsARM1, an R2R3 MYB transcription factor, is involved in regulation of the response to arsenic stress in rice. Front Plant Sci 8:1868

Williams PN, Villada A, Deacon C, Raab A, Figuerola J, Green AJ, Feldmann J, Meharg AA (2007) Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. Environ Sci Technol 41(19):6854–6859

Wu Z, Ren H, McGrath SP, Wu P, Zhao FJ (2011) Investigating the contribution of the phosphate transport pathway to arsenic accumulation in rice. Plant Physiol 157:498–508

Xu J, Shi S, Wang L, Tang Z, Lv T, Zhu X et al (2017) OsHAC4 is critical for arsenate tolerance and regulates arsenic accumulation in rice. New Phytol 215(3):1090–1101

Yamaji N, Ma JF (2014) The node, a hub for mineral nutrient distribution in graminaceous plants. Trends Plant Sci 19:556–563

Ye Y, Li P, Xu T, Zeng L, Cheng D, Yang M et al (2017) OsPT4 contributes to arsenate uptake and transport in rice. Front Plant Sci 8:2197

Yu LJLYF, Liao B, Xie LJ, Chen L, Xiao S et al (2012) Comparative transcriptome analysis of transporters, phytohormone and lipid metabolism pathways in response to arsenic stress in rice (*Oryza sativa*). New Phytol 195:97–112

Zhao FJ, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559

Zhao FJ, Moore KL, Lombi E, Zhu YG (2014) Imaging element distribution and speciation in plant cells. Trends Plant Sci 19:183–192