

Arsenic Fate and Transport in the Groundwater-Soil-Plant System: An Understanding of Suitable Rice Paddy Cultivation in Arsenic Enriched Areas

P. K. Sahoo and A. Mukherjee

Abstract Irrigation with arsenic (As)-rich groundwater in agricultural soil is one of the major causes for As contamination in rice. This can be observed in Bangladesh where the highest levels of As were reported in rice grains. However, As risk assessment in rice based on the As contaminated groundwater and soil can be misleading, since As accumulation in plant is controlled by a number of factors in the soil–rhizosphere system. In this chapter, we have discussed the impact of As-rich groundwater on rice cultivation, and the major factors which control the fate of As in the soil–rhizosphere–plant system. Soil parameters such as pH, redox potential, and concentrations of phosphorous, sulfur, silica, and iron affect the availability of As in the soil–rhizosphere zone, thus, should be considered in the assessment of As toxicity for rice. Concentration of silica and phosphate compete with arsenite and arsenate respectively during uptake by plants. Environmental factor such as soil flooding condition is also one of the potential factors influencing arsenic accumulation in rice by increasing As mobility in the soil–rhizosphere. In biological factors, rice genotype, which controls the root aeration, is significant in affecting accumulation of As. Therefore, selection of suitable rice genotype besides growing rice in aerobic conditions would be important to minimize As accumulation in rice. The translocation of As from roots to above-ground parts is dependent on As speciation. Although, organic As is more readily translocated, its uptake is much lower compared to inorganic As; thus, inorganic As predominates in grains.

Keywords Arsenic · Rice · Bioavailability · Soil–Rhizosphere system · As uptake mechanism

P. K. Sahoo (✉)

Vale Institute of Technology, Boaventura da Silva, Belém, Pará 66055-090 Brazil
e-mail: prafulla.iitkgp@gmail.com; prafulla.sahoo@vale.com

A. Mukherjee

Department of Geology & Geophysics, Indian Institute of Technology Kharagpur,
Kharagpur, West Bengal 721302, India

D. Sengupta (ed.), *Recent Trends in Modelling of Environmental Contaminants*,
DOI 10.1007/978-81-322-1783-1_2, © Springer India 2014

1 Introduction

Arsenic (As) is a ubiquitous element that ranks 20th among the most abundant elements in the earth's crust (Cullen and Reimer 1989). Its atomic number is 33, and the atomic weight is 74.92. Arsenic is a redox-sensitive element, which exists mainly in four oxidation states, +V (arsenate), +III (arsenite), 0 (arsenic), and -III (arsine). Unlike other toxic elements (Pb, Cu, and Co), As occurs as cation (positively charged ion) and oxyanion (negatively charged ions with oxygen) species. It can occur in the environment both in organic and inorganic forms. Inorganic forms usually associate with many minerals and other elements, especially oxygen, sulfur, and chlorine, while organic forms associate with carbon and hydrogen. The most important inorganic species are arsenate As(V) and arsenite As(III), while the most important organic species are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). The toxicity of As is mainly dependent on the forms of arsenic. Inorganic As species are more toxic to living organisms than organic forms (Meharg and Whitaker 2002). Arsenic toxicity in humans can cause severe health problems ranging from skin lesions to cancers of the brain, liver, kidney, and stomach, and many other cardiovascular and neurological diseases (Smith et al. 1992; Ng et al. 2003; Martinez et al. 2011).

Arsenic naturally occurs in many environmental media, such as rocks, soil, sediments, and surface/groundwater, and it can further be released into the aquatic and terrestrial ecosystem via natural and anthropogenic activities (Lombi et al. 2000). According to the World Health Organization (WHO) guideline, the baseline limit of As concentration in safe drinking water is 10 $\mu\text{g/L}$, which is similar to the European Union (EU), US Environmental Protection Agency (USEPA), Netherlands, and Germany limits of As in drinking water (Ahsan and DeIvalls 2011). However, in Bangladesh and many other developing countries, such as India, China, and Nepal, it is set to 50 $\mu\text{g/L}$ (World Bank 2005). Currently, Australia has set a strict national standard of 7 $\mu\text{g/L}$ for acceptable As concentration in drinking water (World Bank 2005). Arsenic poisoning via drinking of As contaminated groundwater is well documented (Smedley and Kinniburgh 2002); however, recent investigation revealed that rice, which is the staple food for nearly half of the world's population, is another potential As exposure pathway to human health (William et al. 2005; Zavala et al. 2008). It can add significant amounts of dietary intake of As than most crops because rice plants have the special ability to soak up As from soil compared to other cereals (Heikens 2006), and use of arsenic-contaminated groundwater for irrigation of rice cultivation (Heikens et al. 2007). However, accumulation of As in rice is influenced by various environmental, geochemical, and biological factors which controls As solubility, bioavailability, and uptake in the soil-rhizosphere-plant system (Walter and Wenzel 2002; Zhao et al. 2010).

This chapter presents the As levels in rice from different parts of the world, assesses the impact of irrigation with As rich-groundwater on soil and paddy rice, and discusses the major factors controlling As behavior in the soil-rhizosphere-plant systems, along with As toxicity to plants. Understanding of these aspects may be helpful to reduce As accumulation in rice grains.

2 Arsenic Concentration in Rice

Several surveys of As concentration in rice grains have been carried out in various countries (Table 1). It was found that As concentration in rice varied widely. The highest level of As, up to 1.85 mg/kg (0.05–1.85 mg/kg), was found in Bangladesh (Meharg and Rahman 2003). Other Asian countries also reported high levels (ranges) of arsenic in rice: China, 0.46–1.18 mg/kg (Sun et al. 2008); Taiwan, 0.1–0.63 mg/kg (Lin et al. 2004); Thailand, 0.06–0.5 mg/kg (Adamako et al. 2011); Japan, 0.07–0.42 mg/kg (Meharg et al. 2009); Korea, 0.24–0.72 mg/kg (Lee et al. 2008); and India, particularly from West Bengal, 0.085–0.66 mg/kg (Roychowdhury et al. 2002). Besides Asian rice, significant arsenic levels were reported from Venezuela (0.19–0.46 mg/kg) by Schoof et al. (1998), France (0.12–0.61 mg/kg) by Williams et al. (2007a), and USA (0.16–0.71 mg/kg) by Zavala et al. (2008).

Rice As values (ranges) from Europe, 0.13–20 mg/kg (Williams et al. 2005); Spain, 0.07–0.21 mg/kg (Williams et al. 2007a); Italy, 0.19–0.22 mg/kg (Williams et al. 2005); and Ghana <0.01–0.15 mg/kg (Adomako et al. 2011) fall into intermediate category. Some parts of the Asian rice also fall into this category, as follows: Philippines, 0–0.25 mg/kg (Williams et al. 2006); Vietnam, 0.09–0.17 mg/kg (Adomako et al. 2011); and Pakistan, 0.01–0.2 mg/kg (Adamako et al. 2011). On contrary, rice from Australia, 0.02–0.04 mg/kg (Williams et al. 2006); Canada, 0.02 mg/kg (Williams et al. 2005); and Egypt (0.02–0.08 mg/kg) (Meharg et al. 2007) is found to contain the lowest levels of As contamination (Table 1). The overall range found among all samples, the lowest grain As (0.01 mg/kg) is nearly two order magnitude difference with that of the highest concentration (1.835 mg/kg). According to the information available to us, in terms of As contamination levels in rice, there is no limit set by EU and US (Francesconi 2007). However, China has regulated the maximum contamination level (MCL) of As in rice as 0.15 mg/kg (Zhu et al. 2008). On comparison with Table 1, it was noticed that the mean values of most of the Asian, USA, and France rice were exceeded the MCL. However, higher enrichment in Asian rice, particularly in Bangladesh, which can be the significant source of dietary As for population of this area and population from other countries import rice from this region.

3 Arsenic in Groundwater

Arsenic contamination of groundwater has been identified in many countries, including Argentina, Bangladesh, China, Cambodia, India, Japan, Mongolia, Mexico, Nepal, Taiwan, Thailand, Vietnam, and USA (Mandal and Suzuki 2002; Smedley and Kinniburgh 2002). There are a number of people are at risk of chronic arsenic poisoning from drinking As-contaminated water in several parts of the world, however highest number of people at risk from Ganges Delta (Bangladesh and West Bengal, India) (Fig. 1) (Smedley and Kinniburgh 2005; Garelick and Jones 2008).

Table 1 Arsenic concentration (in mg/kg) in rice grains from different countries

Country	Maximum	Minimum	Average	No. of samples	Study (Author/year)
Bangladesh	1.835	0.058	0.49	13	Meharg and Rehman (2003)
China	1.18	0.46	0.82	2	Sun et al. (2008)
India	0.66	0.085	0.3	10	Roychowdhury et al. (2002)
Taiwan	0.63	0.1	0.1	5	Lin et al. (2004)
Thailand	0.5	0.06	0.15	53	Adomako et al. (2011)
Korea	0.72	0.24	0.41	–	Lee et al. (2008)
Japan	0.42	0.07	0.19	26	Meharg et al. (2009)
Vietnam	0.17	0.09	0.12	18	Adomako et al. (2011)
Philippines	0.25	0	0.07	–	Williams et al. (2006)
Pakistan	0.2	0.01	0.09	5	Adomako et al. (2011)
Venezuela	0.46	0.19	0.3	4	Schoof et al. (1998)
Egypt	0.08	0.02	0.05	108	Meharg et al. (2007)
Spain	0.21	0.07	0.13	10	Williams et al. (2007a)
Europe	0.2	0.13	0.15		Williams et al. (2005)
France	0.61	0.12	0.32	22	Williams et al. (2007a)
USA	0.71	0.16	0.29	24	Zavela et al. (2008)
Italy	0.22	0.19	0.14	–	Williams et al. (2005)
Ghana	0.15	<0.01	–	7	Adomako et al. (2011)
Australia	0.04	0.02	0.03	5	Williams et al. (2006)
Canada	–	–	0.02	–	Williams et al. (2005)
Lebanon	0.07	0.01	0.04	11	Adomako et al. (2011)

“–”: not available

Scores of people from China, Vietnam, Taiwan, Chile, Argentina, and Mexico are likely at risk as well (Fig. 1).

3.1 Arsenic Mobility in Groundwater

Based on the As geochemistry, there are three major mechanisms controlling As mobility in the groundwater, which have been reported by various workers. These are:

Oxidation of Pyrite Mobilization of As due to oxidation of arsenic-rich pyrite minerals associated with sediment and rock materials have been identified by many workers (Williams et al. 1996; Kim et al. 2012) (Table 2). Insoluble As-bearing minerals such as arsenopyrite (FeAsS) are rapidly oxidized when in contact with oxygen, releasing soluble As(III) and Fe(II) (Smedley and Kinniburgh 2002). The oxidation of the As-bearing minerals is dependent on availability of oxygen. High oxygen in pyritiferous system suffers by the excess pumping and water-table draw-down. Chakraborti et al. (2001) and Sikdar et al. (2001) observed that water table declined in the Bengal basin because of the agricultural pumping that began in



Fig. 1 Worldwide distribution of arsenic contaminated regions, illustrating numbers of people at risk of chronic As exposure. (Adapted from Garelick and Jones 2008)

Table 2 As concentration in groundwater ($\mu\text{g/L}$) relations with major release mechanism reported from different countries

Country	As in groundwater	Major release mechanism	References
USA	Up to 12,000	Oxidation of As-rich sulfides	Schreiber et al. (2000)
Thailand	1.25–5114	Oxidation of As-rich sulfides	Williams et al. (1996)
Korea	23–178	Oxidation of As-rich sulfides	Kim et al. (2012)
Bangladesh	Up to 640	Reductive dissolution of Fe or Mn (hydro)oxides	Harvey et al. (2002)
Bangladesh	6–934	Reductive dissolution of Fe or Mn (hydro)oxides	Bibi et al. (2008)
India	0.77–1059	Reductive dissolution of Fe or Mn (hydro)oxides	Bhattacharyya et al. (2008)
Nepal	< 10–740	Reductive dissolution of Fe or Mn (hydro)oxides	Gurung et al. (2005)
China	0.6–572	Reductive dissolution of Fe or Mn (hydro)oxides	Guo et al. (2008)
Taiwan	Up to 12,000	Reductive dissolution of Fe or Mn (hydro)oxides	Chen and Liu (2007)
Vietnam	1–741	Reductive dissolution of Fe or Mn (hydro)oxides, oxidation of As-rich sulfides ^a	Naguyen and Itoi (2009)
USA	11–2620	Reductive dissolution of Fe or Mn (hydro)oxides, Desorption from Fe (hydro)oxides	Welch and Lico (1998)
India	0.82–538	Reductive dissolution of Fe or Mn (hydro)oxides, Desorption from Fe (hydro)oxides ^a	Kar et al. (2010)
Argentina	7–14,969	Desorption from Fe (hydro)oxides	Bhattacharya et al. (2006)

^a Minor mechanism

the 1970s. Subsequently, in 1978, first As contamination in the Bengal Basin was detected. The rate of oxidation of pyrite is dependent on the redox potential (Eh) and pH. The release of Fe from pyrite oxidation can form Fe oxides that can immobilize As.

Reductive Dissolution of Fe Oxyhydroxides Arsenic in Fe-oxyhydroxides is mobilized when the environment becomes anaerobic (Smedley and Kinniburgh 2002). Bhattacharya et al. (1997) first proposed the reductive dissolution of Fe oxyhydroxides process for arsenic release. After that, many other studies have been reported this mechanism (Welch and Lico 1998; Harvey et al. 2002; Bibi et al. 2008; Gurung et al. 2005; Chen and Liu 2007; Bhattacharyya et al. 2008; Guo et al. 2008; Kar et al. 2010) (Table 2). McArthur et al. (2001) stated that the good correlation between As and HCO_3^- in groundwater is an indication of reduction. Other studies from Bengal basin reported that low Eh, O_2 , NO_3^- , and SO_4^{2-} , and high Fe and Mn in groundwater are the indication of reducing conditions (Bhattacharya et al. 1997; Dowling et al. 2002). Similarly, Kim et al. (2009) and Sahoo et al. (2013) stated that the higher arsenic concentration in groundwater associated with lower Eh, NO_3^- , and

SO_4^{2-} , and higher alkalinity, Fe, and PO_4 is the indication of reductive dissolution of Fe (hydr)oxides.

Desorption of Fe-Oxyhydroxides Besides anaerobic conditions for releasing As from Fe oxyhydroxides, there is also effect of pH, particularly at $\text{pH} > 8.5$, which can cause mobilization of As from Fe-oxides. This is indentified by some workers (Bhattacharya et al. 2006; Kar et al. 2010) (Table 2).

4 Impact of As-Rich Groundwater on Paddy Cultivation

Arsenic concentration in paddy fields can occur naturally via weathering processes, and/or by anthropogenic activities such as mining (Zhu et al. 2008), pesticide use, fertilizer application (Williams et al. 2007b), and irrigation with As contaminated groundwater (Mehrag and Rahman 2003; Williams et al. 2006). However, irrigation with As contaminated groundwater plays a dominant role, especially in Asian countries where groundwater-irrigated rice cultivation has increased dramatically over the past few decades to maintain the country's food security. In the long term, use of this As-contaminated irrigation water can cause elevated As concentration in paddy soils and crops (Heikens et al. 2007; Hossain et al. 2008; Baig et al. 2011). Several field studies from Bangladesh and West Bengal showed that irrigation with As-rich groundwater increases the As levels in the top soil (Meharg and Rahman 2003; Norra et al. 2005; Williams et al. 2006; Roychowdhury et al. 2002). Studies from Argentina, Chile, and Taiwan (Chen et al. 2002; Tu and Ma 2004) also reported that As contents in agricultural soils are significantly higher than the normal levels due to irrigation with As-rich groundwater.

There are a number of studies that investigated the impact of irrigation with As-rich groundwater on soil and its subsequent impact on rice grains (Mehrag and Rahman 2003; Williams et al. 2006; Dittmar et al. 2010). Meharg and Rahman (2003) reported the positive relations among As in irrigation water, soil, and rice from Bangladesh. Williams et al. (2006) did an extensive sampling of rice throughout Bangladesh, and found that high As concentration in rice is associated with As contaminated irrigation water. In another study from Murshidabad district of Bangladesh, Roychowdhury et al. (2005) reported the positive relations among As concentrations in irrigated water, soil, and plants. Recently, Singh et al. (2010) observed the positive relations between irrigation water and rice. However, this relationship is conflicting in some cases. Norra et al. (2005) found no significant relationship between rice grains from West Bengal, India, where plants are irrigated with low and high concentrations of As containing water. Van Geen et al. (2006) reported that there was no evidence of a proportional transfer As from soil to rice grains, despite the soil irrigated with As rich-groundwater. Furthermore, Williams et al. (2007a) reported elevated As concentration in rice grains in background paddy soil. These observations indicate that As content in rice is not directly dependent on total concentration of As in soil and irrigation water, but may be with other factors in the soil-rhizosphere-plant system, which are relevant.

5 Arsenic Behavior in Soil–Plant System

5.1 Soil

Arsenic is naturally present in soil. Its average concentration in non-contaminated soils is ~ 5 mg/kg; however, the concentration can increase up to 27,000 mg/kg or more than that in contaminated soil (McLaren et al. 1996). The solubility and bio-availability of As in soil is influenced by various factors (Fitz and Wenzel 2002; Zhao et al. 2009), which are discussed below.

As Speciation

Arsenic in soil exists in both inorganic and organic forms. The most common inorganic As species in soil are As(V) and As(III), while organic forms are MMA and DMA (Zhao et al. 2009). As(III) is more toxic than As(V), and also much more toxic than MMA or DMA (Zhao et al. 2010). Inorganic As species are dominating in paddy soils, whereas organic species are in low quantities (Fitz and Wenzel 2002). Inorganic species can be converted to organic form by methylation linked with microbial action in paddy soil (Takamatsu et al. 1982). Each species has different solubility and bioavailability. Marine et al. (1992) reported that the As availability to rice plants followed the order $\text{As(III)} > \text{MMA} > \text{As(V)} > \text{DMA}$. Meharg and Whitaker (2002) also observed that both As(III) and MMA are more available to rice plants. This indicates that speciation of As in soil environment is essential to assess As toxicity to plants.

Redox Potential

The balance of reducing and oxidizing condition (redox status) in the soil is important because it controls arsenic mobility and speciation (Fitz and Wenzel 2002). Under oxidizing conditions (aerobic), As(V) usually dominates, which has strong affinity for soil minerals such as Fe-oxhydroxides, leading to decrease As solubility and bioavailability to plants (Takahashi et al. 2004; Xu et al. 2008). However, under reducing conditions, such as soil flooding, As(III) is the most common inorganic species, and its mobility is sharply increased in the soil-rhizosphere (Takahashi et al. 2004). This is due to the reductive dissolution of Fe-oxhydroxides, and relatively high abundance of Fe reducing bacteria and algae in reduced soil, which help in As solubility via reduction of As(V) and methyl As species to more soluble As(III) species (Horneman et al. 2004; Mahimairaja et al. 2005). Therefore, in flooded soil, As is readily available for plant uptake. This may be the cause for higher As content in lowland crops usually growing in a reducing environment, such as paddy rice, than upland cereal crops (Williams et al. 2007a). However, changing irrigation practice can manage As uptake in plants (Das et al. 2008). Somennahally et al. (2011) con-

ducted an experiment by changing the irrigation process, and found that rice takes up less As in intermittently flooding than continuous flooding. Other studies also supported that irrigation practice can significantly control As accumulation in plants (Arao et al. 2009; Roberts et al. 2011; Rahaman et al. 2011; Talukdar et al. 2011).

pH

The sorption of As to metal-oxyhydroxides is generally affected by soil pH (Fitz and Wenzel 2002; Quazi et al. 2011), but there is not any universal agreement on this issue. Arsenic (AsV) tends to be sorbed by Fe–Al oxyhydroxides at near neutral to acidic pH (Mukherjee et al. 2009). However, at extremely acidic pH ($\text{pH} < 3$), arsenic mobility can increase due to the dissolution of arsenic binding species, such as Fe and Al oxycompounds (Signes-Pastor et al. 2007). Furthermore, the mobility of As in soil can increase at higher soil pH, above pH 8.5, because at high pH, mineral surfaces (mainly Fe-oxides) become progressively negatively charged that facilitate desorption of As from Fe-oxides (Marine et al. 1992; Streat et al. 2008), and increases labile As in the rhizosphere, leading to more As accumulation in plants (Fitz and Wenzel 2002). Campbell et al. (1985) observed that uptake of arsenic in plants increases at higher soil pH. In a recent work, Ahmed et al. (2011) also observed the positive relationship between grain As and soil pH.

Organic Matter

Organic matter (OM) can have a profound effect on As solubility in the soil since it tends to form insoluble and soluble complexes with As (Mukhaopadhyay and Sanyal 2004). Pikaray et al. (2005) reported that organic matter has a greater potential for As sorption due to formation of organo-As complex. Thus, high OM containing soil can reduce As availability to plants. Considering this effect, Rahaman et al. (2011) conducted an experiment, and observed that organic amendments significantly reduce arsenic content in rice grains. This can be supported by Fu et al. (2011) who found the negative correlation between As concentration in rice grain and soil OM.

On the contrary, organic matter can increase arsenic mobility in soil by forming water-soluble complexes with As, leading to inhibit As sorption on mineral surfaces (Bauer and Blodau 2006). Dissolved organic matter contains negative charge, which has high potential to compete with As for sorption sites in the soil, thus, it can increase As mobility (Lin et al. 2008). Furthermore, dissolved organic matter can promote As release by changing the redox chemistry of site surfaces and As species (Wang and Mulligan 2006). Selim Reza et al. (2010) reported that As is released by the reductive dissolution of Fe-Ox hydroxides linked to organic matter. Others studies also supported that As solubility in soil is positively related with organic matter (Hunag et al. 2006; Harvey et al. 2002; Rowland et al. 2006). This may be the cause for the positive relationship between rice and OM reported by Bhattacharya et al. (2010a), and elevated grain As in paddy soil even at background soil (Williams et al. 2011).

Soil Texture

Soil texture is another important factor that can influence arsenic mobility (Fitz and Wenzel 2002; Quazi et al. 2011). In general, clay or finer texture soils have much more surface area than coarse or sandy soils. In addition, Fe oxides are mainly present in the clay size soil fraction; therefore, clayey soils can have a higher As retention potential compared to sandy soils (Fitz and Wenzel 2002; Mahimairaja et al. 2005; Heikens et al. 2007), and soils with clayey texture are supposed to be less toxic of arsenic to plants compared to sandy soils (Heikens et al. 2007). Sheppard (1992) observed that phytotoxicity of As is five times more in sands and loams than clay soils. Similar studies have reported that plant uptake of As is high in loamy sand and low in silty clay loam (Woolson 1973; O'Neil 1995).

As Bound to Fe–Mn Oxides

Oxides of Fe and Mn are common in soils, and these phases are very efficient in sorbing As due to their high sorption capacity (Dudas 1987). However, their sorption property is strongly dependent on the environmental conditions (Mukherjee et al. 2009). Under aerobic conditions, the affinity of the oxyhydroxides is very high for As. However, under flooding conditions, oxyhydroxides release As from soil by the reductive dissolution of Fe oxyhydroxides, leading to more As available for plant uptake (Fitz and Wenzel 2002; Takahashi et al. 2004). Fu et al. (2011) found the positive relations between Fe–Mn bound As and grain As. Moreover, amorphous or poorly crystalline Fe oxides are much more readily dissolved than the crystalline Fe oxides under flooding conditions (Biswas et al. 2003). Ahmed et al. (2011) observed the significant positive relations between As in Fe-amorphous fraction and rice. This indicates that As content in amorphous/poorly crystalline Fe-oxides in soil can be an important factor for rice As.

Phosphate

Phosphate (PO_4) is an important parameter in agricultural field not only as an important nutrient, but also it controls As phytoavailability (Woolson et al. 1973; Peryea and Kammereck 1995; Bodgan and Schenk 2009). Generally, phosphate is a chemical analog of AsV (Fitz and Wenzel 2002); thus, it competes with As(V) to occupy the same sorption sites in soils, leading to increase As solubility (Smith et al. 2002; Fitz and Wenzel 2002). Many studies reported that addition of PO_4 increases As mobility in soil (Peryea and Kammereck 1995; Smith et al. 2002; Campos 2002; Cao et al. 2003; Signes-Pastor et al. 2007), which can subsequently increase As uptake by plants (Bogdan and Schenk 2009; Islam and Jahiruddin 2010). However, it is conflicting at some point, since, PO_4 also competes with As(V) at the same transport during uptake, and can reduce arsenate accumulation in plants (Fitz and Wenzel 2002). This is supported by several works (Abedin et al. 2002a; Tu and Ma 2003; Lihong and Guilan 2009).

Sulfur

Sulfate has a high sorption affinity for arsenic. Under reducing conditions, it forms insoluble As-sulphide minerals, thus less As in the soil–rhizosphere (Signes-Pastor et al. 2006). In addition, sulfur containing thiol (SH) compounds make chelation of As in plant roots, that can inhibit As transfer to grains (Raab et al. 2005). Zhang et al. (2011) highlights the important role of sulfur on arsenic accumulation in rice. They reported that increase of sulfur content reduced the As content in rice. Hu et al. (2007) in a pot experiment also found that the addition of sulfur to soil considerably decreased the As content of rice shoots. This result hypothesized that application of S fertilizers in paddy fields can obtain high yields, and additionally benefit of restricting As uptake by plants. However, this needs to be studied under field conditions.

Fe-Plaque

In flooded paddy fields, rice plants release oxygen to their root zones through aerenchyma, which leads to oxidized Fe(II) concentrations, and form Fe-oxhydroxide coating, termed as Fe-plaque, on the root surface (Fig. 2). This plaque is known to control As uptake by rice plants (Chen et al. 2005; Zhao et al. 2010). Numerous studies have reported that Fe-plaque scavenges significant amounts of As in root zones and decreases As uptake by plants (Hossain et al. 2009; Sefferth et al. 2010; Garnier et al. 2010). However, the formation of Fe-plaque is strongly influenced by soil properties. Hu et al. (2005) observed that the formation of Fe-plaque is decreased on the rice roots after the application of phosphate. Liu et al. (2004) found that phosphorous (P) sufficiency had little iron plaque on the rice roots while P-deprivation in solution enhanced the formation of iron plaque on the roots. This may be because the low P in plant tissue increases oxygen release from rice roots to the rhizosphere (Kirk and Du 1997), which stimulates the formation of iron plaque. Nitrate concentrations also affect Fe-plaque formation in the rhizosphere (Chen et al. 2008), because it is an oxidizer, which reduces Fe(II) concentration in soil solution leading to decrease Fe-plaque formation in the rhizosphere (Chen et al. 2008). However, in spite of decreasing Fe-plaque, it reduces As uptake by rice (Chen et al. 2008). This is due to NO_3^- stimulates Fe(II) oxidation and/or inhibits Fe(III) reduction, which sequesters mobile As on Fe(III) minerals in soil and subsequently make unavailable for plants. On the other hand, the amendment of NH_4 enhances Fe(III) reduction, which increases Fe(II) concentration in the rhizosphere, leading to more Fe-plaque formation on the root surface (Chen et al. 2008).

Nevertheless, accumulation of As on Fe plaque can be a source for As for plants (Voegelin et al. 2007) depending on the localized soil condition (Somennahally et al. 2011). Further, Seyfferth et al. (2010) found that Fe-plaque does not coat many of the young roots or the younger portion of mature roots, which are important for solute uptake. Thus, Fe-plaque does not directly prevent As supply and uptake by rice, but rather serves as a bulk scavenger of As at the root base.

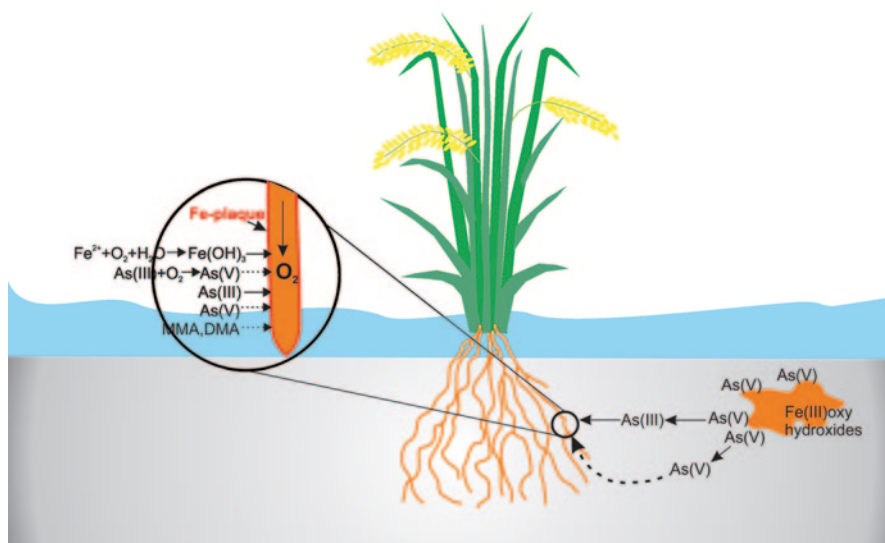


Fig. 2 Formation of Fe-plaque on rice roots in the soil–rhizosphere, and the arsenic uptake by rice plants. Arrows with solid and broken lines indicate major and minor processes, respectively. (Modified after Zhao et al. 2010)

5.2 Plants

The pathway of arsenic uptake, accumulation, and transformation can vary within and among species (Heikens 2006), which are discussed below.

Rice Varieties

Arsenic uptake by plants is varied with respect to rice varieties (Table 3). Meharg and Rehman (2003) found the significant variation of As accumulation among the rice varieties; BR11 was the highest accumulator, collected from Bangladesh. In a study from West Bengal, Bhattacharya et al. (2010b) reported that among the rice varieties, IR 50, White Minikit, and Red Minikit were the higher accumulators of As compared to Nayanmani, Jaya, Ratna, Ganga-kaveri, and Lal Sanna. Ahmed et al. (2011) also recently reported the As variation among the rice varieties. Though, there are a number of factors that can influence this variation, Zhang and Duan (2008) stated that rice genotype is the one of the dominating ones. In this regard, Norton et al. (2009a) conducted a field based experiment in Bangladesh by selecting 76 cultivars, and noticed 4–5-fold variations in grain As among genotypes, higher accumulation in landraces cultivars compared to BRRI. The same authors conducted another study in a multiple environment (Norton et al. 2009b). They cultivated 13 cultivars at 2 field sites each in Bangladesh, India, and China, and found 4–5-fold variations in grain As concentration among 7 rice cultivars grown

Table 3 Arsenic variations in rice grains (mg/kg) with respect to rice varieties

Bangladesh (Meharg et al. 2003)	
Rice variety	Grain As (mg/kg)
Khatobada	0.058
Pajam	0.082
Swarna	0.096
BR11	0.203
BR11	1.830
BR11	1.740
BR11	1.770
BR8	0.078
BR11	0.185
Gocha	0.075
Kalla	0.117
Swarna	0.096
<i>WB, India (Bhattacharya et al. 2010b)</i>	
IR 50	0.29
Ratna	0.20
Red minikit	0.24
White minikit	0.31
Ganga-kaveri	0.19
Jaya	0.14
Lal Sanna	0.20
Nayanmani	0.16
<i>Barisal, Bangladesh (Ahmed et al. 2011)</i>	
BR3	0.078
BR4	0.068
BR5	0.091
BR10	0.095
BR11	0.086
BR22	0.105
BR23	0.068
BR25	0.130
BR32	0.140
BR33	0.215
BR34	0.110
BR39	0.139
BR40	0.109
BR41	0.124

in 2 paddy fields in Bangladesh, and a significant correlation between 2 different As contamination sites in Bangladesh and India among the common genotypes. Chaturvedi (2006) and Ahmed et al. (2011) also reported that genotype is one of the major causes for As variation in rice plants. This is may be because genotype controls the physiological or morphological attributes of the root systems, which influence the root aeration capacity to form iron plaque on roots (Wu et al. 2011;

Dwivedi et al. 2011). Therefore, selection of suitable rice genotype based on root aeration capacity is one of the important factors to control As uptake in rice.

Uptake Mechanisms

All As species can be taken up by rice roots; however, inorganic species are taken up in a much higher rate than organic species (Abedin et al. 2002a). In inorganic As, As(V) takes up in the plasma membrane via phosphate transport pathway (Meharg 2004). This mechanism involves cotransport of phosphate or arsenate and protons, with stoichiometry of at least 2H^+ for each H_2PO_4^- or H_2AsO_4^- (Ullrich-Ebrius et al. 1989). Plants contain a number of phosphate transporters, most of are in roots (Zhao et al. 2009). Due to the competition of both ions in the same transport, it has been hypothesized that increasing phosphate supply can decrease As uptake (Zhao et al. 2009). This is supported by several studies (Abedin et al. 2002a; Tu and Ma 2003; Lihong and Guilan 2009). However, phosphate is not an analog of As(III), thus the presence of phosphate in anaerobic soils is probably less relevant in terms of As behavior (Takahashi et al. 2004). In a pot experiment, Abedin et al. (2002b) observed that no response of the effect phosphate application on As uptake in rice under flooding condition. This may be due to the conversion of soil As(V) to As(III) in reducing environment, and subsequent uptake of As(III) by plant, which leads to lack of effect of phosphate. This is consistent with other studies (Wang et al. 2002; Hu et al. 2005). However, there are conflicts in certain cases since some studies showed that addition of phosphorus enhances the As accumulation in the grains of rice in flooded condition (Jahiruddin et al. 2004; Hossain et al. 2009). In addition, it is not known if arsenite can be oxidized to arsenate in the root rhizosphere, since the rice root is known to develop oxidized conditions proximal to the root zones (Armstrong 1967), and competing with phosphate for plant uptake. Therefore, it cannot be excluded that phosphate does not influence arsenite behavior in the rhizosphere where aerobic conditions can occur under flooded conditions. However, a detail investigation is still required in this aspect.

As(III) is actively taken up by roots via aquaporin channels, which is used for silica transport in the roots (Ma et al. 2008). Since both ions compete during uptake at the same transport (Zhao et al. 2009), the high silica availability in the soil solution reduced the arsenite uptake by rice (Bogdan and Schenk 2008; Guo et al. 2007, 2009). This implies that Si amendment of paddy soils could possibly reduce As(III) uptake in rice plants. Reason for the inhibiting effect of Si is probably because the supply of Si reduces the expression of Si transporters, Lsi1 and Lsi2, which mediate arsenite uptake as well (Ma et al. 2006, 2007, 2008). However, these mechanisms need to be studied further. The ratio of the plant-available Si to arsenite in pore-water may be useful to predict the arsenic acumination in rice.

Translocation and Accumulation of As

Several studies (Table 4) reported that the translocation of As from the roots to the above-ground parts is significantly limited. Bhattacharya et al. (2009) conducted a micro level study from West Bengal, India, and noticed the As concentration decreasing in plant parts following the order: root>stem>leaves>grain, regardless of the sampling locations (Table 4). Similar observations were made by Bhattacharya et al. (2010b) and Biswas and Santra (2011) from the Gangetic West Bengal, India (Table 4). Das et al. (2004) reported that in rice plant, 73% of total As is deposited in roots, while in stems and grain, it is reduced to 22 and 4%, respectively. This decrease in As transfer may be influenced by the plant physiological processes (Abedin et al. 2002b; Williams et al. 2007a).

Among all species, organic As is more readily translocated, but, its uptake is very lower compared to inorganic As (Carbonell et al. 1998). Therefore, inorganic As dominates in rice grains (Zavala et al. 2008). According to Heikens (2006), about 50% of the total As in grains is inorganic, though it is varied from 10 to 90%. Compared to various countries, rice from India and Bangladesh contains highest percentage of inorganic As (Adomako et al. 2009), implying rice from these regions are at a higher risk than other parts of world, as this is the main carcinogenic component (NRC 2001). William et al. (2005) reported that the average percentage of inorganic As is near about 80% in Dhaka. With the information on As speciation in rice, the potential risk of the rice to the human diet can be estimated.

Phytotoxicity

The As exposure to rice plants leads to phytotoxicity, often resulting in straighthead disease, which is a physiological disorder of rice (Zhao et al. 2009; Van Geen et al. 2006). Yan et al. (2005) and Williams (2003) reported “straighthead” disease is considered to be an indicator of As toxicity in the USA and Australia. Recently, this disease has been noticed in rice from Faridpur, Bangladesh (Duxbury and Panaulah 2007). The symptom of this disease includes shortened plant height, delayed heading, reduction of panicle formation and panicle length, sterile florets, and reduced grain yields (Williams 2003; Rahman et al. 2008). However, this disease may be influenced by soil type and cultivation practices. Frans et al. (1988) found that straighthead disease is frequently noticed on sandy loam soils but rarely on clay soils, and often in fields where undecayed vegetation had been ploughed into soils just before planting rice. Williams (2003) reported that though straighthead disease was observed over a wide range of Australian soils, the toxicity was worse in soils with low nitrogen, and in those after pasture or where previous crop stubble had been incorporated in soils.

Table 4 Arsenic accumulation (mg/kg) in different parts of the rice plant

Bhattacharya et al. (2009)					
Regions	No. of samples	Root	Straw	Husk	Grain
Tatla-1	3	8.32	3.58	0.96	0.52
Tatla-2	3	10.48	1.9	0.94	0.59
Ghetugachi	4	7.74	1.88	0.74	0.41
Dubra	3	10.42	2.96	1.35	0.73
Dewli	4	9.02	1.17	0.67	0.25
Hingrara	4	8.93	3.05	0.56	0.47
Shilinda-1	4	12.22	1.94	0.71	0.58
Shilinda-2	3	7.19	2.62	0.79	0.3
Chanduria-1	4	10.09	1.47	0.89	0.72
Chanduria-2	3	18.63	1.41	1.34	0.6
Madanpur-1	3	10.89	1.17	0.99	0.66
Madanpur-2	3	16.83	3.09	1.28	0.69
Sarati	4	11.85	3.35	0.91	0.42
Saguna	4	9.5	1.79	0.74	0.34
Simurali	3	17.06	4.15	0.74	0.48
Routari	3	14.09	1.17	1.05	0.54
Kancharpara	3	9.33	2.13	0.78	0.65
Bhattacharya et al. (2010a) (Boro rice)					
Chakdaha	18	10.45	1.41	0.67	0.23
Ranaghat-I	12	18.93	1.47	0.79	0.3
Shantipur	12	28.63	2.13	0.99	0.4
Krishnagar	12	11.85	1.79	0.74	0.24
Haringhata	9	14.09	1.34	1.05	0.54
Contai	5	0.44	0.08	0.07	0.05
Biswas and Santra (2011)					
Chakdah	105	11.07	5.24	0.96	0.59
Haringhata	105	15.01	3.82	1.67	0.81
Ranaghat	105	17.61	4.24	0.71	0.49
Tehatta	105	13.01	5.98	1.13	0.4
Karimpur	105	11.92	3.57	1.79	0.52
Krisnanagar	105	9.79	2.52	0.97	0.1
Hanskhali	105	13.67	5.97	0.72	0.51
Control	105	2.39	1.9	0.02	0.03

6 Conclusions

Arsenic contaminated groundwater is not only posing a risk via drinking of water but also a serious threat to sustainable agriculture. This chapter discussed the As levels in rice in several countries, effect of As-rich groundwater on paddy soils and rice grains, and the factors controlling As mobilization and uptake in the soil–rhizosphere system, along with the toxic effects of As on rice plants.

Arsenic levels in rice significantly varied among countries; higher enrichment in Asian rice, particularly in Bangladesh. Therefore, rice from this region could add significant levels of As in the food stuffs. Arsenic contamination in rice is caused

due to irrigation with As-rich groundwater, and subsequent contamination of soil. However, arsenic risk assessment in rice based on the total As concentration in soil and irrigation water can be misleading, since As accumulation in plants is controlled by a number of factors within the soil–rhizosphere–plant system. Soil parameters such as soil pH, Eh, texture and concentrations of P, Si, S and Fe and arsenic speciations should be considered in the assessment of soil As for potential rice toxicity. Environmental factors such as soil flooding is also one of the potential factors influencing arsenic accumulation in rice by increasing As mobility in the soil–rhizosphere. Therefore, growing rice in aerobic conditions may be a feasible strategy to mitigate this problem. In addition, rice genotype, which controls the root aeration, is significant in affecting the accumulation of As. Therefore, selection of suitable rice genotype is important to minimize As accumulation in rice.

Arsenic is taken up by roots, and then transferred to the edible portion of plant, which leads to phytotoxicity, often resulting straighthead disease in rice plants. However, the translocation of As from the roots to the above parts is significantly limited. Among all species, organic As is more readily translocated, but, its uptake is very low compared to inorganic As; thus, inorganic As predominates in grains. Uptake of arsenite in rice occurs through the silicon transport pathway; therefore, application of silica fertilizers in soil is suggested to decrease the transfer of arsenic from soil to rice. Further, phosphate fertilization is also suggested to lower the arsenate uptake in plants, since both enter to rice through the same transporter. However, there are arguments in certain cases, since in the flooding condition As is present as arsenite which cannot compete phosphate, and further, phosphate increases As mobility since it competes with arsenate for adsorption site on Fe-oxides/hydroxides. In addition, accumulation of As in the presence Fe-plaque and other soil parameters is still confusing. More work needed, especially on a close monitoring of soil, irrigation water, and rice in both lab and field based experiments to understand the role of Fe-plaque, phosphorous, silica, and sulfur in influencing As mobility and solubility in soil-rhizosphere and its uptake mechanisms by plants.

References

- Abedin MJ, Feldmann J, Mehrag AA (2002a) Uptake kinetics of arsenic species in rice plants. *Plant Physiol* 128(3):1120–1128
- Abedin MJ, Howells JC, Mehrag AA (2002b) Arsenic uptake and accumulation in rice (*Oryza sativa* L.) irrigated with contaminated water. *Plant Soil* 240:311–319
- Adomako EE, Solaiman ARM, Williams PN, Deacon C, Rahman GKMM, Mehrag AA (2009) Enhanced transfer of arsenic to grain for Bangladesh grown rice compared to US and EU. *Environ Int* 35:476–479
- Adomako EE, Williams PN, Deacon C, Mehrag AA (2011) Inorganic arsenic and trace elements in Ghanaian grain staples. *Environ pollut* 159:2435–2442
- Ahmed UZ, Panaullah GM, Jr HG, McCouch SR, Tyagi W, Kabir MS, Duxbury JM (2011) Genotype and environment effect rice (*Oryza sativa* L.) grain arsenic concentration in Bangladesh. *Plant Soil* 338:367–382

- Ahsan DA, DelValls TA (2011) Impact of arsenic contaminated irrigation water in food chain: an overview from Bangladesh. *Int J Environ Res* 5(3):627–638
- Arao T, Kawasaki A, Baba K, Mori S, Matsumoto S (2009) Effects of water management on cadmium and arsenic accumulation and dimethyl arsenic acid concentrations in Japanese rice. *Environ Sci Technol* 43:9361–9367
- Armstrong W (1967) The use of polarography in the assay of oxygen diffusing from roots in anaerobic media. *Physiol Plant* 20:540–553
- Baig JA, Kazi TG, Shah AQ, Afridi HI, Kandhro GA, Khan S, Kolachi NF, Wadhwa SK, Shah F, Arain MB, Jamali MK (2011) Evaluation of arsenic levels in grain crops samples, irrigated by tube well and canal water. *Food Chem Toxicol* 49:265–270
- Bauer M, Blodau C (2006) Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediment. *Sci Total Environ* 354:179–190
- Bhattacharya P, Chatterjee D, Jacks G (1997) Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, eastern India: options for safe drinking water supply. *Int J Water Resour Dev* 13(1):79–92
- Bhattacharya P, Claesson M, Bundschuh J, Sracek O, Fagerberg J, Jacks G, Martin RA, Storniolo AR, Thir JM (2006) Distribution and mobility of arsenic in the Río Dulce alluvial aquifers in Santiago del Estero Province, Argentina. *Sci Total Environ* 358:97–120
- Bhattacharyya P, Tripathy S, Kim K, Kim SH (2008) Arsenic fractions and enzyme activities in arsenic-contaminated soils by groundwater irrigation in West Bengal. *Ecotoxicol Environ Saf* 71:149–156
- Bhattacharya P, Samal AC, Majumdar J, Santra SC (2009) Transfer of arsenic from groundwater and paddy soil to rice plant (*Oryza sativa* L.): a micro level study in West bengal, India. *World J Agric Sci* 5(4):425–431
- Bhattacharya P, Samal AC, Majumdar J, Santra SC (2010a) Accumulation of arsenic and its distribution in rice plant (*Oryza sativa* L.) in Gangetic West Bengal, India. *Paddy Water Environ* 8:63–70
- Bhattacharya P, Samal AC, Majumdar J, Santra SC (2010b) Uptake of arsenic in rice plant varieties cultivated with arsenic rich groundwater. *Environ Asia* 3:34–37
- Bibi MH, Ahmed F, Ishiga H (2008) Geochemical study of arsenic concentrations in groundwater of the Meghna River Delta, Bangladesh. *J Geochem Explor* 97:43–58
- Biswas A, Santra SC (2011) Arsenic distribution in winter rice and vegetable crops-in vivo micro level study in a contaminated region. *Int Res J Agric Sci Soil Sci* 1(6):205–210
- Biswas BK, Loeppert RH, Hossain MB, Rahman GKMM, Jahiruddin M, Miah MAM, Farid TM, Panaullah GM, Meisner CM, Duxbury JM (2003) Impact of soil oxides on retention of arsenic in Bangladesh rice-producing soils. In: Proceedings of 7th international conference on the biogeochemistry of trace elements, Uppasala, Sweden, June 15–19, 2003.
- Bogdan K, Schenk MK (2008) Arsenic in rice (*Oryza sativa* L.) related to dynamic of arsenic and silicic acid in paddy soils. *Environ Sci Technol* 42:7885–7890
- Bogdan K, Schenk MK (2009) Evaluation of soil characteristics potentially affecting arsenic concentration in paddy rice (*Oryza sativa* L.). *Environ Pollut* 157:2617–2621
- Campbell JA, Stark JH, Carlton-Smith CH (1985) International symposium on heavy metals in the environment (vol 1). CEP Consultants, Athens
- Campos V (2002) Arsenic in groundwater affected by phosphate fertilizers at São Paulo, Brazil. *Environ Geol* 42:83–87
- Cao X, Ma LQ, Shiralipour AS (2003) Effect of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyperaccumulator, *Pteris vittata* L. *Environ Pollut* 126:157–167
- Carbonell AA, Aarabi MA, DeLaune RD, Gambrell RP, Patrick JWH (1998) Arsenic in wetland vegetation: availability, phytotoxicity, uptake and effects on plant growth and nutrition. *Sci Total Environ* 217:189–199
- Chakraborti D, Basu GK, Biswas BK (2001) Characterization of arsenic-bearing sediments in the Gangetic delta of West Bengal, India. In: Chappell WR, Abernathy CO, Calderon RL (eds) Arsenic exposure and health effects IV. Elsevier, Oxford

- Chaturvedi I (2006) Effect of arsenic concentrations on growth and arsenic uptake and accumulation by rice (*Oryza Sativa* L.) genotype. *Electron J Environ Agric Food Chem* 5:1546–1552
- Chen KY, Liu TK (2007) Major factors controlling arsenic occurrence in the groundwater and sediments of the Chianan coastal plain, SW Taiwan. *Terr Atmos Ocean Sci* 18:975–994
- Chen TB, Fan ZL, Lei MEI (2002) Effect of phosphorus on arsenic accumulation in As-hyperaccumulator: *Pteris vittata* L. and its implication. *Chin Sci Bull* 47:1876–1879
- Chen Z, Zhu YG, Liu WJ, Meharg AA (2005) Direct evidence showing the effect of root surface iron plaque on arsenite and arsenate uptake into rice (*Oryza sativa*). *New Phytol* 165:91–97
- Chen XP, Zhu YG, Hong MN, Kappler A, Xu YX (2008) Effects of different forms of nitrogen fertilizers on arsenic uptake by rice plants. *Environ Toxicol Chem* 27:881–887
- Cullen WR, Reimer KJ (1989) Arsenic speciation in the environment. *Chem Rev* 89:173–764
- Das HK, Mitra AK, Sengupta PK, Hossain A, Islam F, Rabbani GH (2004) Arsenic concentrations in rice, vegetables and fish in Bangladesh: a preliminary study. *Environ Int* 30(3):383–387
- Das DK, Sur P, Das K (2008) Mobilization of arsenic in soils and in rice (*Oryza sativa* L.) plants affected by organic matter and zinc application in irrigation water contaminated with arsenic. *Plant Soil Environ* 54:30–37
- Dittmar J, Voegelin A, Maurer F, Roberts LC, Hug SJ, Saha GC, Ali MA, Badruzzaman ABM, Kretzschmar R (2010a) Arsenic in soil and irrigation water affects arsenic uptake by rice: complementary insights from field and pot studies. *Environ Sci Technol* 44:8842–8848
- Dowling CB, Poreda RJ, Basu AR et al (2002) Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. *Water Resour Res* 38(9):12.1–12.18
- Dudas MJ (1987) Accumulation of native arsenic in acid sulphate soils in Alberta. *Can J Soil Sci* 67:317–331
- Duxbury JM, Panaullah G (2007) Remediation of arsenic for agriculture sustainability, food security and health in Bangladesh. Working paper, Water Service, FAO (2007), Rome. http://www.fao.org/nr/water/docs/FAOWATER_ARSENIC.pdf
- Dwivedi S, Tripathi RD, Srivastava S, Singh R, Kumar A, Tripathi P, Dave R, Rai UN, Chakrabarty D, Trivedi PK, Tuli R, Adhikari B, Bag MK (2010) Arsenic affects mineral nutrients in grain of various Indian rice (*Oryza sativa* L.) genotypes grown on arsenic-contaminated soils of West Bengal. *Protoplasma* 245:113–124
- Fitz WJ, Wenzel WW (2002) Arsenic transformations in the soil–rhizosphere–plant system: fundamentals and potential application to phytoremediation. *J Biotechnol* 99:259–278
- Frans R, Horton D, Burdette L (1988) Influence of MSMA on straight-head, arsenic uptake and growth responsible in rice. *Res Ser* 302: 1–12, Univ of Arkansas Agri Exp Sta, Fayetteville
- Francesconi KA (2007) Toxic metal species and food regulations—making a healthy choice. *Analyst* 132:17–20
- Fu Y, Chen M, Bi X, He Y, Ren L, Xiang W, Qiao S, Yan S, Li Z, Ma Z (2011) Occurrence of arsenic in brown rice and its relationship to soil properties from Hainan Island, China. *Environ Pollut* 159:1757–1762
- Garelick H, Jones H (2008) Mitigating arsenic pollution: bridging the gap between knowledge and practice. *Chem Int* 30(4):7–12. (ISSN 0193–6484)
- Garnier JM, Travassac F, Lenoble V, Rose J, Zheng Y, Hossain MS, Chowdhury SH, Biswas AK, Ahmed KM, Cheng Z, Geen A (2010) Temporal variations in arsenic uptake by rice plants in Bangladesh: the role of iron plaque in paddy fields irrigated with groundwater. *Sci Total Environ* 408:4185–4193
- 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
- Guo H, Yang S, Tang X, Li Y, Shen Z (2008) Groundwater geochemistry and its implications for arsenic mobilization in shallow aquifers of the Hetao Basin, Inner Mongolia. *Sci Total Environ* 393:131–144
- Guo W, Zhang J, Teng M, Wang LH (2009) Arsenic uptake is suppressed in a rice mutant defective in silicon uptake. *J Plant Nutr Soil Sci* 172:867–874

- 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
- Harvey CF, Swartz CH, Badruzzaman ABM, Keon-Blute N, Yu W, Ali MA, Jay J, Beckie R, Niedan V, Brabander D, Oates PM, Ashfaque KN, Islam S, Hemond HF, Ahmed MF (2002) Arsenic mobility and groundwater extraction in Bangladesh. *Science* 298:1602–1606
- Heikens A (2006) Arsenic contamination of irrigation water, soil and crops in Bangladesh: risk implications for sustainable agriculture and food safety in Asia. Food and Agricultural Organization of the United Nations, Regional Office for Asia and the Pacific, Bangkok
- Heikens A, Panaullah GM, Meharg AA (2007) Arsenic behavior from groundwater and soil to crops: impacts on agriculture and food safety. *Rev Environ Contam Toxicol* 189:43–87
- Horneman A, VanGeen A, Kent DV, Mathe PE, Zheng Y, Dhar RK, O'Connell S, Hoque MA, Aziz Z, Shamsudduha M, Seddique AA, Ahmed KM (2004) Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part1: evidence from sediment profiles. *Geochim et Cosmochim Acta* 68:3459–3473
- Hossain MB, Jahiruddin M, Panaullah GM, Loeppert RH, Islam MR, Duxbury JM (2008) Spatial variability of arsenic concentration in soils and plants, and its relationship with iron, manganese and phosphorus. *Environ Pollut* 56:739–744
- Hossain MB, Jahiruddin M, Loeppert RH, Panaullah GM, Islam MR, Duxbury JM (2009) The effect of iron plaque and phosphorus on yield and arsenic accumulation in rice. *Plant Soil* 317:167–176
- Hu Y, Li JH, Zhu YG, Huang YZ, Hu HQ, Christie P (2005) Sequestration of As by iron plaque on the roots of three rice (*Oryza sativa* L.) cultivars in a low-P soil with or without P fertilizer. *Environ Geochem Health* 27:169–176
- Hu ZY, Zhu YG, Li M, Zhang LG, Cao ZH, Smith FA (2007) Sulphur(S)-induced enhancement of iron plaque formation in the rhizosphere reduces arsenic accumulation in rice (*Oryza sativa* L.) seedlings. *Environ Pollut* 147(17):387–393
- Hunag RQ, Gao SF, Wang WL, 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
- Islam MR, Jahiruddin M (2010) Effect of arsenic and its interaction with phosphorus on yield and arsenic accumulation in rice. 19th world congress of soil science, soil solutions for changing world, Brisbane, 1–6 Aug 2010
- Jahiruddin M, Islam MA, Islam MR, Islam S (2004) Effects of arsenic contamination on rice crop. *Environ tropica* 1:204–210
- Kar S, Maity JP, Jean JS, Liu CC, Nath B, Yang HJ, Bundschuh J (2010) Arsenic-enriched aquifers: occurrences and mobilization of arsenic in groundwater of Ganges Delta Plain, Barasat, West Bengal, India. *Appl Geochem* 25(12):1805–1814
- Kim K, Moon JT, Kim SH, Ko KS (2009) Importance of surface geologic condition in regulating As concentration of groundwater in the alluvial plain. *Chemosphere* 77:478–484
- Kim K, Kim SH, Jeong GY, Kim RH (2012) Relations of As concentrations among groundwater, soil, and bedrock in Chungam, Korea: implications for As mobilization in groundwater according to the As-hosting mineral change. *J Hazard Mater* 15:25–35
- Kirk GJD, Du VL (1997) Change in rice root architecture, porosity, and oxygen and proton release under phosphorus deficiency. *New Phytol* 135:191–200
- Lee JS, Lee SW, Chon HT, Kim KW (2008) Evaluation of human exposure to arsenic due to rice ingestion in the vicinity abandoned Myungbong Au-Ag mine site, Korea. *J Geochem Explor* 96:231–235
- Lihong W, Guilan D (2009) Effect of external and internal phosphate status on arsenic toxicity and accumulation in rice seedlings. *J Environ Sci* 21:346–351
- Lin HT, Wong SS, Li GC (2004) Heavy metal content of rice and shell fish in Taiwan. *J Food Drug Anal* 12:67–74
- Lin CF, Wu CH, Lai HT (2008) Dissolved organic matter and arsenic removal with coupled chitosan/UF operation. *Sep Purif Technol* 60:292–298

- Liu WJ, Zhu YG, Smith FA, Smith SE (2004) Do phosphorus nutrition and iron plaque alter arsenate (As) uptake by rice seedlings in hydroponic culture? *New Phytol* 162:481–488
- Lombi E, Sletten RS, Wenzel WW (2000) Sequentially extracted arsenic from different size fractions of contaminated soils. *Water Air Soil Pollut* 124:319–32
- Ma JM, Tamai K, Yamaji N, Mitani N, Konishi S, Katsuhara M, Ishiguro M, Murata Y, Yano M (2006) A silicon transporter in rice. *Nature* 440:688–691
- Ma JF, Yamaji N, Mitani N, Tamai K, Konishi S, Fujiwara T, Katsuhara M, Yano M (2007) An efflux transporter of silicon in rice. *Nature* 448:209–212
- 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
- Mahimairaja S, Bolan NS, Adriano DC, Robinson B (2005) Arsenic contamination and its risk management in complex environmental settings. *Adv Agron* 86:1–82
- Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. *Talanta* 58(1):201–235
- Marine AR, Masscheleyn PH, Patric WH (1992) The influence of chemical form and concentration of As on rice growth and tissue As concentration. *Plant Soil* 139:175–183
- Martinez VD, Vucic EA, Becker-Santos DD, Gil L, Lam WL (2011) Arsenic exposure and the induction of human cancers. *J Toxicol* 2011:431287. doi:10.1155/2011/431287
- McArthur JM, Ravenscroft P, Safiulla S, Thirlwall MF (2001) Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour Res* 37(1):109–17
- Mclaren RG, Naidu R, Tiller KG (1996) Fractionation of arsenic in soils contaminated by cattle dip. 1st international conference: Contaminants and soil environment, Adelaide, pp 177–178, 1996
- Meharg AA (2004) Arsenic in rice—understanding a new disaster for South-East Asia. *Trends Plant Sci* 9:415–417
- Meharg AA, Rahman MDM (2003) Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption. *Environ Sci Technol* 37:229–234
- Meharg AA, Whitaker JH (2002) Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species—review. *New Phytol* 154:29–43
- Meharg AA, Adomako E, Lawgali Y, Deacon C, Williams Paul (2007) Arsenic in rice—a literature review. Food Standards Agency contract C101045
- 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
- Mukherjee A, Fryar A, O'shea BM (2009) Major occurrences of elevated arsenic in groundwater and other natural waters. In: Henke K (ed) *Arsenic: environment chemistry, health threats and waste treatment*, Ch. 6. Wiley, New York
- Mukhopadhyay D, Sanyal SK (2004) Complexation and release isotherm of arsenic in arsenic-humic/fulvic equilibrium study. *Aust J Soil Res* 42(7):815–24
- Naguyen KP, Itoi R (2009) Source and release mechanism of arsenic in aquifers of the Mekong Delta, Vietnam. *J Contam Hydrol* 103:58–69
- National Research Council (2001) *Arsenic in drinking water—2001 Update*. National Academy, Washington DC
- Ng JC, Wang J, Shraim A (2003) A global health problems caused by arsenic from natural sources. *Chemosphere* 52:1353–1359
- Norra S, Berner ZA, Agarwala P, Wagner F, Chandrasekharam D, Stuben D (2005) Impact of irrigation with As rich groundwater on soil and crops: geochemical case study in West Bengal Delta Plain, India. *Appl Geochem* 20:1890–1906
- Norton GJ, Islam MR, Deacon CM, Zhao FJ, Stroud JL, McGrath SP, Islam S, Jahiruddin M, Feldmann J, Price AH, Meharg AA (2009a) Identification of low inorganic and total grain arsenic rice cultivars from Bangladesh. *Environ Sci Technol* 43:6070–6075
- Norton GJ, Duan G, Dasgupta T, Islam MR, Lei M, Zhu Y, Deacon CM, Moran AC, Islam S, Zhao FJ, Stroud JL, McGrath SP, Feldmann J, Feldmann J, Price AH, Meharg AA (2009b) Environ-

- mental 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
- O'Neil P (1995) Heavy metals in soils. In: Alloway BJ (ed) *Arsenic*. Blackie Academic and Professional, London, pp 105–121
- Peryea FJ, Kammereck R (1995) Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated top soil and through uncontaminated sub soil. *Water Air Soil Pollut* 93:243–254
- Pikaray S, Banerjee S, Mukherji S (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) Effect of soil types and forms of arsenical pesticide on rice growth and development. *Int J Environ Sci Technol* 8:45–460
- 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
- Rahman MA, Hasegawa H, Rahman MM, Miah MAM, Tasmin A (2008) Straighthead disease of rice (*Oryza sativa* L.) induced by arsenic toxicity. *Environ Exp Bot* 62:54–59
- Rahaman S, Sinha AC, Mukhopadhyay D (2011) Effect of water regimes and organic matters on transport of arsenic in summer rice (*Oryza sativa* L.). *J Environ Sci* 23:633–639
- Roberts LC, Hug SJ, Voegelin A, Dittmar J, Kretzschmar R, Wehrli B, Saha GC, Badruzzaman ABM, Ali MA (2011) Arsenic dynamic in porewater of an intermittently irrigated paddy field in Bangladesh. *Environ Sci Technol* 45:971–976
- Rowland HAL, Polya DA, Lioyd JR, Pancost RD (2006) Characterisation of organic matter in shallow, reducing, arsenic-rich aquifer, West Bengal. *Org Geochem* 37:1101–1114
- 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* 40:1611–21
- Roychowdhury T, Tokunaga H, Uchino T, Ando M (2005) Effect of arsenic-contaminated irrigation water on agricultural land soil and plants in West Bengal, India. *Chemosphere* 58:799–810
- Sahoo PK, Zhu W, Kim SH, Jung MC, Kim K (2013) Relations of arsenic concentrations among groundwater, soil and paddy from an alluvial plain of Korea. *Geosci J* 3:363–370
- Schoof RA, Yost LJ, Crecelius E, Irgolic K, Goessler W, Guo HR, Greene H (1998) Dietary arsenic intake in Taiwanese districts with elevated arsenic in drinking water. *Hum Ecol Risk Assess* 4:117–135
- Schreiber ME, Simo JA, Freiberg PG (2000) Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. *Hydrogeol J* 8:161–176
- Selim Reza AHM, Jena JS, Yang HJ, Lee MK, Woodall B, Liu CC, Lee JF, Luo SD (2010) Occurrence of arsenic in core sediments and groundwater in the Chapai-nawabgang District, north-western Bangladesh. *Water Res* 44:2021–2037
- Seyffert AL, Webb SM, Andrews JC, Fendorf S (2010) Arsenic localization, speciation and co-occurrence with iron on rice (*Oryza sativa* L.) roots having variable Fe coatings. *Environ Sci Technol* 44:8108–8113
- Sheppard SC (1992) Summary of phytotoxic levels of soil arsenic. *Water Air Soil Pollut* 64:539–550
- Signes-Pastor A, Burló F, Mitra K, Carbonell-Barrachina AA (2006) Arsenic biogeochemistry as affected by phosphorus fertilizer addition, redox potential and pH in a west Bengal (India) soil. *Geoderma* 137(3–4):504–510
- Signes-Pastor A, Burló F, Mitra K, Carbonell-Barrachina AA (2007) Arsenic biogeochemistry as affected by phosphorus fertilizer addition, redox potential and pH in a West Bengal (India) soil. *Geoderma* 137:504–510
- Sikdar PK, Sarkar SS, Palchoudhury S (2001) Geochemical evolution of groundwater in the quaternary aquifer of Calcutta and Howrah, India. *J Asian Earth Sci* 19:579–94
- Singh V, Brar MS, Sharma P, Malhi SS (2010) Arsenic in water, soil, and rice plants in the Indo-Gangetic plains of Northwestern India. *Commun Soil Sci Plant Anal* 41:1350–1360
- Smedley PL, Kinniburgh DG (2002) A review of source, behavior and distribution of arsenic in natural water. *Appl Geochem* 17:517–568

- Smedley P, Kinniburgh DG (2005) Arsenic in groundwater and the environment. In: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley P (eds) Essentials of medical geology—impacts of the natural environment on public health. Academic, Waltham, pp 263–299
- Smith AH, Hopenhayn-Rich C, Bates MN, Goeden HM, Hertz-Picciotto I, Duggan HM, Wood R, Kosnett MJ, Smith MT (1992) Cancer risks from arsenic in drinking water. *Environ Health Perspect* 97:259–267
- Smith E, Naidu R, Alston AM (2002) Chemistry of arsenic in soils: II. Effect of phosphorous, sodium and calcium on arsenic sorption. *J Environ Qual* 31:557–563
- Somenahally AC, Hollister EB, Yan W, Gentry TJ, Loeppert RH (2011) Water management impacts on arsenic speciation and iron-reducing bacteria in contrasting rice-rhizosphere compartments. *Environ Sci Technol* 45(19):8328–8335. doi:10.1021/es2012403
- Streat M, Hellgardt K, Newton NLR (2008) Hydrous ferric oxide as an adsorbent in water treatment Part 3: Batch and mini-column adsorption of arsenic, phosphorus, fluorine and cadmium ions. *Process Saf Environ Prot* 86:21–30
- Sun GX, Williams PN, Carey AM, Zhu YG, Deacon C, Raab A, Feldmann J, Islam RM, Meharg AA (2008) Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain. *Environ Sci Technol* 42:7542–7546
- Takahashi Y, Minamikawa R, Hattori KH, Kurishima K, Kihou N, Yuita K (2004) Arsenic behaviour in paddy fields during the cycle of flooded and non-flooded periods. *Environ Sci Technol* 38:1038–1044
- Takamatsu T, Aoki H, Yoshida T (1982) Determination of arsenate, arsenite, monomethylarsenate, and dimethylarsinate in soil polluted with arsenic. *Soil Sci* 133:239–246
- 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
- Tu S, Ma LQ (2003) Interaction effect of pH, arsenic and phosphorous on uptake of As and P and growth of the arsenic hyperaccumulation *Pteris vittata* L. under hydroponic conditions. *Environ Exp Bot* 50:243–251
- Tu S, Ma LQ (2004) Comparison of arsenic and phosphate uptake and distribution in arsenic hyperaccumulating and nonhyperaccumulating Fern. *J Plant Nutr* 27:1227–1242
- Ullrich-Eberius CI, Sanz A, Novacky AJ (1989) Evaluation of arsenate and vandate-associated changes of electrical membrane potential and phosphate transport in *Lemna gibba* GI. *J Exp Bot* 40:119–128
- Van Geen A, Zheng Y, Cheng Z, He Y, Dhar RK, Garnier JM, Rose J, Siddique A, Hoque MA, Ahmed KM (2006) Impact of irrigating rice paddies with groundwater containing arsenic in Bangladesh. *Sci Total Environ* 367:769–777
- Voegelin A, Weber FA, Kretzschmar R (2007) Distribution and speciation of arsenic around roots in a contaminated riparian flood plain soil: micro-XRF element mapping and EXAFS spectroscopy. *Geochim et Cosmochim Acta* 71:5804–5820
- Walter JF, Wenzel WW (2002) Arsenic transformation in the soil–rhizosphere–plant system: fundamentals and potential application to phytoremediation. *J Biotechnol* 99:259–278
- Wang J, Zhao FJ, Meharg AA, Raab A, Feldmann J, McGrath P (2002) Mechanisms of arsenic hyperaccumulation in *Pteris vittata*. uptake kinetics, interactions with phosphate, and arsenic speciation. *Plant Physiol* 130:1552–1561
- Wang S, Mulligan CN (2006) Occurrence of arsenic contamination in Canada: sources, behavior, and distribution. *Sci Total Environ* 366:701–721
- Welch AH, Lico MS (1998) Factors controlling As and U in shallow ground water, southern Carson Desert, Nevada. *Appl Geochem* 13:521–539
- Williams P (2003) Investigating links between minerals in rice grain and straighthead. Final report. Leeton, Cooperative Research Centre for Sustainable Rice Production
- Williams M, Fordyce F, Pajitrapapon A, Charoenchaisri P (1996) Arsenic contamination in surface drainage and groundwater in part of the southeast Asian tin belt, Nakhon Si Thammarat Province, southern Thailand. *Environ Geol* 27:16–33

- 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, 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 groundwater. *Environ Sci Technol* 40:4903–4908
- Williams PN, Villada A, Deacon C, Raab A, Figuerola J, Green AJ, Feldmann J, Meharg AA (2007a) Greatly enhanced arsenic shoot assimilation in rice leads elevated grain levels compared to wheat and barley. *Environ Sci Technol* 41:6854–6859
- Williams PN, Raab A, Feldmann J, Meharg AA (2007b) Market basket survey shows elevated levels of As in South Central U.S. processed rice compared to California: consequences for human dietary exposure. *Environ Sci Technol* 41:2178–2183
- Williams PN, Zhang H, Davison W, Meharg AA, Hossain M, Norton G, Brammer H, Islam MR (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
- Woolson EA, Axley JH, Kearney PC (1973) The chemistry and phytotoxicity of arsenic in soils. II. Effects of time and phosphorus. *Proc Soil Sci Soc Am* 37(2):254–259
- Woolson EA (1973) Arsenic Phytotoxicity and Uptake in Six Vegetable Crops. *Weed Science*. 21(6):524–527
- World Bank (2005) Environment and social unit—South Asia region. Towards a more effective operational response. Arsenic contamination of groundwater in south and east Asian countries volume II technical report. Environmental Study (Report No 31303), The World Bank
- Wu C, Ye Z, Shu W, Zhu Y, Wong M (2011) Arsenic accumulation and speciation in rice are affected by root aeration and variation of genotypes. *J Exp Bot* 62(8):2889–2898. doi:10.1093/jxb/erq462
- Xu XY, McGrath SP, Meharg AA, Zhao FJ (2008) Growing rice aerobically decreases arsenic accumulation. *Environ Sci Technol* 42:5574–5579
- Yan W, Dilday RH, Tai TH, Gibbons JW, McNew RW, Rutger JN (2005) Differential response of rice germplasm to straighthead disease by arsenic. *Crop Sci* 45:1223–1228
- Zavala YJ, Gerads R, Gürleyük H, Duzbury JM (2008) Arsenic in rice: II. Arsenic speciation in USA and implications for human health. *Environ Sci Technol* 42:3861–3866
- Zhang J, Duan GL (2008) Genotypic difference in arsenic and cadmium accumulation by rice seedlings grown in hydroponics. *J Plant Nutr* 31:2168–2182
- Zhang J, Zhao QZ, Duan GL, Huang YC (2011) Influence of sulfur on arsenic accumulation and metabolism in rice seedlings. *Environ Exp Bot* 72:34–40
- 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
- Zhu YG, Williams PN, Meharg AA (2008) Exposure to inorganic arsenic from rice: a global health issue? *Environ Pollut* 154:167–171