# Chapter 5
# Arsenic Contamination of Groundwater and Its Mitigation Strategies

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## 5.1 Introduction

Contamination of arsenic (As) in groundwater and their resources globally affects human health. The problem of As contamination is becoming more worsen due to day by day increasing concentration of As and discovery of new As-contaminated areas. In recent years, many As-contaminated regions have been identified, but still systematic evaluation and monitoring of some areas that are at high risk remains to be carried out. Contamination of groundwater through geogenic and anthropogenic activities is the main concern for environment and human health (Fig. 5.1). Across the world in several countries including India, millions of people are using As-contaminated water beyond the permissible limit (10 μg/L). Many countries such as Bangladesh, Hungary, Taiwan, Argentina, China, Chile, Mexico, USA, Nepal, and India have crossed the safe limit of As in drinking water guided by WHO (IWA 2016; Singh 2017). Various standards of As have been accepted in several countries ranging from 5 mg/L in the United States to 50 mg/L in most developing countries (Ahmed 2003; Singh and Stern 2017). Ravenscroft et al. (2009) reported that millions of inhabitants are consuming contaminated drinking water having As more than the permissible limit, i.e., 10 μg/L.

Arsenic is a naturally occurring toxic metalloid with atomic number 33, atomic mass 75, and four oxidation states (−3, 0, +3, and + 5) (Awasthi et al. 2017). Arsenic

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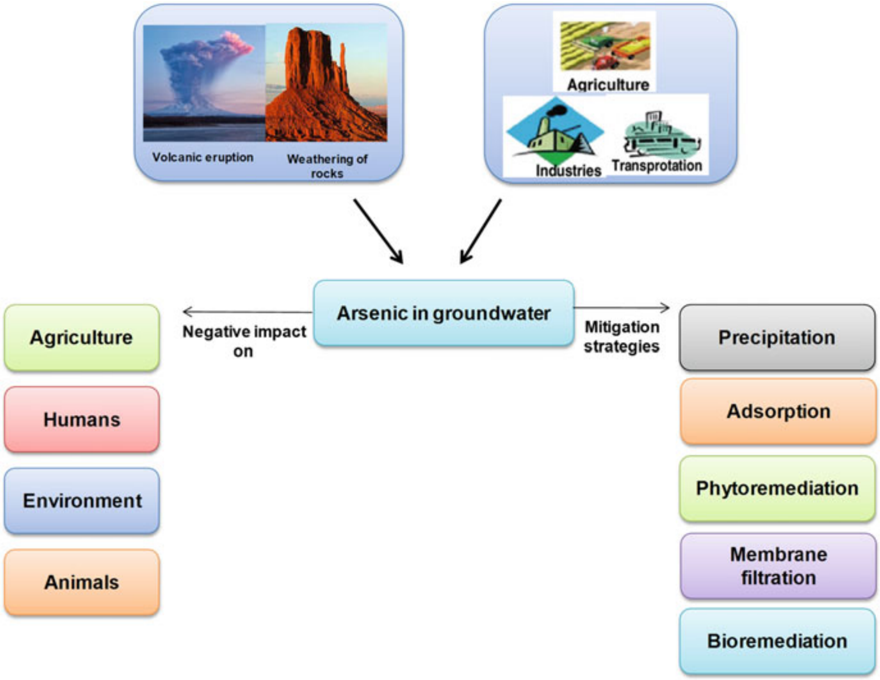


**Fig. 5.1** Geogenic and anthropogenic contamination of arsenic in groundwater and its mitigation strategies

exists in >200 mineral forms, including arsenites, arsenates, arsenides, sulfides, sulfosalts, metal alloys, and native elements. Among these, arsenate minerals are scorodite, beudantite, yukonite, and sulfide viz., arsenopyrite, pyrite, loellingite, and realgar (Srivastava et al. 2015). Arsenite (AsIII) and arsenate (AsV) are the most prevalent and more toxic inorganic forms, while monomethylarsine (MMA), dimethylarsine (DMA), and trimethylarsine (TMA) are less toxic organic forms of As (Srivastava et al. 2015; Awasthi et al. 2017). Other organic forms of As include arsenosugars, arsenobetaine, and arsenocholine, which are less toxic or non-toxic and also found in seafood (Srivastava et al. 2015). Drinking of As-polluted water and its utilization for cooking and irrigation of crops poses severe threat to public health. Long-term human exposure of As from food and drinking water resulted in several skin diseases, diabetes, increased blood pressure, and cancer of lung, skin, bladder, and kidney (WHO 2011; USEPA 2013; Santra et al. 2013). To avoid the human exposure of As contamination, the hand pumps polluted with >50 mg/L of As were colored red in India and Bangladesh and the hand pumps with less contamination >50 μg/L were colored blue in India and with green color in Bangladesh (Nickson et al. 2007; Milton et al. 2007). Besides this precaution, several people still have to depend on As-contaminated drinking water (red-painted hand pumps) because of the water scarcity (Singh and Vedwan 2015; Singh and Stern 2017). The concentration of As is also increasing in groundwater due to the geochemical and physical conditions of aquifers and the water–rock interactions for the mobilization and accumulation of As in water. The order of As minerals dissolution in groundwater observed in the series of arsenics >arsenolite>orpiment>realgar>arsenopyrite>tennantite (Islam et al. 2013). The present chapter summarizes the possible sources of As contamination in groundwater and presents an overview of strategies for mitigation of As toxicity and to reduce the As level in drinking water and groundwater.

## 5.2 Global Arsenic Contamination of Groundwater

Contamination of As in groundwater and drinking water is a public health issue and adversely affects millions of people globally. This leads to a marked increase in cancer risk (Chakraborti et al. 2017). The International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA) declared As and its compounds as class 1 human carcinogen (WHO 2004). The Agency of Toxic Substances and Disease Registry (ATSDR) marked As at number 1 position among 20 top hazardous substances. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) analyzed the impact of As on human health and reported exceeded concentration of As (50–100 μg/L) in drinking water of many regions of the world (WHO 2019). Across the world, highly As-contaminated areas have been reported mainly in large deltas, e.g., Bengal delta (Chakraborti et al. 2010) and along river basins (Table 5.1) such as Duero Cenozoic Basin in Spain, Danube river basin in Hungry, Zenne river basin in Belgium Hetao river basin in Mongolia, Tulare Lake in the USA, and Paraiba do Sul delta in Brazil (Gómez et al. 2006; Nriagu et al. 2007; Khan and Ho 2011; Cutler et al. 2013; Mirlean et al. 2014). For technical and financial support in many states, a large number of National Rural Drinking Water Programmes (NRDWP) have been sponsored by the government (Ministry of Drinking Water and Sanitation) for safe drinking water. Up to 67% of fund was provided under NRDWP with priority to As- and fluoride-contaminated areas to tackle water quality problems. Advances have been made to the reduction of As exposure, e.g., by removal of As from drinking water and by providing residents with other resource of drinking water.

## 5.3 Sources of As and Its Impact on Human Health

Several geogenic and anthropogenic activities are being reported for increased As pollution in groundwater. Himalayan mountains and Shillong plateau are considered as main sources of As contamination in Gangetic river basin and delta sediments. Additionally, the Gondwana coal region, Bihar mica belt, the pyrite-bearing region in Vindhyan range, Sone river valley gold belt, and sulfide regions of eastern

**Table 5.1** Arsenic contamination of groundwater in different countries

| Country | As concentration (μg/L) | References |
|---|---|---|
| Bangladesh | ≥1-5500 | Ahmad et al. (2018) |
| Vietnam | 1-3050 | Rahman et al. (2009) |
| Thailand | 1-5000 | Jones et al. (2009) |
| Chile | 1-900 | Ferreccio and Sancha (2006) |
| Afghanistan | 10-500 | Nriagu et al. (2007) |
| West Bengal, India<br>West Bengal, India<br>Chhattisgarh, India | 10-3200<br>> 3600<br>> 4500 | Chakraborti et al. (2010)<br>Mishra et al. (2016) |
| Mekong Delta, Cambodia | 1-900 | Sthiannopkao et al. (2008) |
| Brazil | 0.4-350 | Khan and Ho, (2011) |
| China | 52-4440 | Rahman et al. (2009) |
| Pakistan | ≥906 | Mukherjee et al. (2006), Khan and Ho (2011) |
| Taiwan | 10-1820 | Nriagu et al. (2007) |
| USA | 10-2600 | Cutler et al.(2013) |
| Argentina | 4-5300 | Smedley et al. (2005) |
| Nepal | 10-2620 | Shrestha (2012) |

Himalayas are other geological sources for groundwater As contamination (Acharya et al. 1999; Bhattacharya et al. 2013). Mining, manufacturing, and processing of metallic ores using As-containing sulfides are main anthropogenic activities that contribute to groundwater As contamination. Anthropogenic activities that lead to As contamination affect the quality of surface water and discharge and runoff of groundwater (Khatri and Tyagi 2015). The excess As in groundwater is due to predominating sulfidic minerals of As such as pyrite and arsenopyrite and their association with other ore deposits (Borba et al. 2003). As-containing mineral, arsenopyrite (FeAsS), abundantly exists in anaerobic environments and in the other rock-forming minerals such as carbonate, phosphate, sulfide, silicate, and oxide (Smedley and Kinniburgh 2002). Arsenic in groundwater is attributed to many geochemical processes, including desorption of As from oxide and hydroxides, oxidation of As-bearing sulfides, dissolution of As (reductive)-bearing oxides and hydroxides, release of As from geothermal water as well as leaching of As. According to McArthur et al. (2001), the reductive dissolution of As-containing iron minerals in aquifer sediments chemically or with the help of microbes is the major cause of As release.

Drinking water contaminated with As severely affects human health and is a major environmental cause of cancer (Tripathi et al. 2007). In 1980, the International Agency for Research on Cancer (IARC) has listed As as a human carcinogen. Chronic exposure to As causes severe harm to internal organs such as digestive,

**Table 5.2** Impact of arsenic on human health

| | Symptoms | References |
|---|---|---|
| Respiratory | Laryngitis, tracheal bronchitis, rhinitis, pharyngitis, shortness of breath, perforation of nasal septum | Chakraborti et al. (2017) |
| Gastrointestinal | Heartburn, nausea, abdominal pain | Jain et al. (2016) |
| Dermal | Hyperpigmentation, abnormal skin thickening, narrowing of small arteries leading to numbness (Raynaud's disease), squamous and basal-cell cancer | Banerjee et al. (2011); Jain et al. (2016) |
| Cardiovascular | Heart attack, cardiac arrhythmias, thickening of blood vessels, loss of circulation leading to gangrene of extremities, hypertension | Wade et al. (2015) |
| Hematological | Anemia, low white-blood-cell count (leucopenia) | Correia et al. (2009) |
| Renal | Hematuria, proteinuria, shock, dehydration, cortical necrosis, cancer of kidneys and bladder | Zheng et al. (2014) |
| Reproductive | Spontaneous abortions, still-births, congenital malformations of fetus, low birth weight | Jain et al. (2016) |

respiratory, neural, circulatory, and renal systems (ATSDR 2000; WHO/IPCS 2001) (Table 5.2). Ferreccio et al. (2000) reported the positive correlation between ingestion of inorganic As and lung cancer in humans in Chile. Besides the exposure of As-contaminated water, the dietary consumption of As-contaminated crops, vegetables, and spices are another major source of As exposure (Upadhyay et al. 2018). Among As-contaminated cereal crops, rice is the widely consumed and staple food for the large population of the world. Rice accumulates relatively high amount of As than other cereals (Mitra et al. 2017). People regularly exposed to As for more than 5 years may suffer with cancers of the hepatic, pulmonary, hematological, cardiovascular, renal, immunological, and neurological systems (Mazumder 2000; Chakraborti et al. 2017). Exposure of As may also cause spontaneous abortion in pregnant women (Chakraborti et al. 2016, 2017) and infants as well as children are more sensitive for the adverse effects of As (Das et al. 2009).

## 5.4 Mitigation Strategies of Arsenic

The mitigation measures for As removal are ranging from decreasing the level of As within the aquifer and dilution of the As contaminants by artificial recharge, blending with As free water, etc. Installation of As treatment unit and other resources of As free water are the two major means for As mitigation in hotspots of As contamination (Bundschuh et al. 2010). The common strategies adopted for As removal are based on the principles of co-precipitation, adsorption, oxidation, coagulation, flocculation, and filtration (Bundschuh et al. 2010). Sorghum biomass, sedges, cellulose, milled bones, keratin-rich biomass lettuce biomass, and cysteine-rich biomass are also used for As removal. Pond sand filters and sono filters are cost-effective household technologies that have been developed for As removal.

Advanced technologies such as phytoremediation, bioremediation, and artificially constructed wetlands are also effective strategies for As remediation (Bundschuh et al. 2010). Apart from this, deep tube wells, artificial groundwater recharge, surface water sources, rainwater harvesting systems, and digging of wells gained a marked degree of success in As amelioration technologies (Kabir and Howard 2007; Shibasaki et al. 2007; Shafiquzzaman et al. 2009; Bundschuh et al. 2010; Mosler et al. 2010). In southern parts of Bangladesh and many states of India, the rainwater harvesting is still a common practice. In Mizoram, almost 90% households use rainwater for drinking and cooking as a potential strategy to minimize arsenic toxicity. Government agencies such as Central Groundwater Board-Mid Eastern Region (CGWB-MER), Public Health Engineering Department (PHED) as well as UNICEF have started As mitigation programs (CGWB and NIH 2010).

Government of India (GoI) initiated As mitigation technologies include arsenic removal plants (ARP), new hand pumps (NHP), arsenic treatment units (ATU), and new tube wells with stand post (NTWSP) (CGWB and NIH 2010). Phytoremediation is also an effective strategy for As and fluoride removal. Plants have evolved an extraordinary potential to remediate As through strategies including uptake, repression, sequestration into vacuoles or extrusion. Arsenic removal plants will not be effective until they are not managed and maintained properly and there is an urgent need of political and people's participation. These proposed arsenic mitigation interventions will benefit millions of people, whether directly or indirectly (CGWB and NIH 2010).

### *5.4.1 Precipitation Processes*

For As removal, precipitation is an effective method. Precipitation involves coagulation, coagulation-assisted microfiltration, filtration, and enhanced lime softening. Coagulation of As with salts of iron and aluminum and softening with lime is the most effective treatment. Adsorption co-precipitation with hydrolyzing metals such as iron and aluminum is the effective technique for groundwater As removal. Sedimentation is followed by rapid sand filtration or microfiltration to remove the precipitates (Mishra et al. 2016). In this method of As removal, oxidation of AsIII to AsV is necessary to improve the efficiency of this method. Hypochlorite and permanganate are commonly used for the oxidation of As. The examples of major techniques used for As removal based on precipitation process are fill and draw treatment unit, bucket treatment unit, iron As treatment unit, and tube well-attached As treatment.

#### 5.4.1.1 Fill and Draw Units

This treatment unit is based on the precipitation method. Fill and draw treatment unit has good capacity to store water with slightly tapered bottom. The water contaminated with As is filled in the container along with addition of oxidant and coagulant. The water is mixed with the help of a manually operable mixer and then the unit is left overnight for sedimentation of precipitated As to occur. Then, next day settled water is taken out with the help of a pipe near bottom and is passed through sand bed before using this as drinking water (Ahmed 2001).

#### 5.4.1.2 Bucket Treatment Unit

The bucket treatment unit operates on the principle of coagulation, co-precipitation, and adsorption. In this technique, one bucket serves the purpose of mixing As-contaminated water with chemicals like potassium permanganate and aluminum sulfate, and coagulation is promoted to enhance the sedimentation rate. The second bucket collects settled water. The water is finally filtered with a cloth and passed through another bucket containing sand filters and water is then used for drinking (Tahura et al. 2001).

#### 5.4.1.3 Iron As Treatment Unit

This process involves the oxidation of soluble As forms into the insoluble forms followed by removal through filtration. Arsenic, which is usually present in reduced arsenite ($As^{+3}$) form, is oxidized to arsenate ($As^{+5}$) along with the oxidation of ferrous ions to ferric ions. The $As^{+5}$ is adsorbed onto iron hydroxide and the precipitated As is then removed from the water through filteration (Akhter et al. 2015).

#### 5.4.1.4 Tube Well-Attached As Treatment Unit

In this method, the arsenic removal plant is attached directly to the tube well. Arsenic removal in this technique utilizes principles of coagulation, sedimentation, and filtration. For the coagulation and sedimentation, sodium hypochlorite and aluminum alum are commonly used. This method has been found to remove As up to about 90% in the villages of West Bengal, India.

### *5.4.2 Adsorptive Processes*

Adsorption involves the removal of As by surface chemical reaction that includes passage of water through a contact bed. In India and Bangladesh where the problem of groundwater As contamination is severe, sorptive media based on activated alumina are being extensively used for adsorption process for water treatment of As. In adsorption treatment no chemicals are used and the process based solely adsorption on the active surface of the media. The removal of As from natural water by adsorption method, and the use of granular ferric hydroxide as an adsorbent are highly effective (Mohan and Pittman 2007). Sono 3-Kolshi filter containing sand, brick chips, zero valent iron fillings, and wood coke are also good example of adsorbent used for As removal.

### *5.4.3 Membrane Processes*

Membrane processes for As removal include nano-filtration, ultra-filtration, electro-dialysis, and reverse osmosis which use synthetic membranes for removal of many contaminants including As. The dramatic improvement in membrane technologies for water purification and treatment is due to its low energy cost, ease of scaling up, and high efficiency and stability over the past two decades. Membranes remove As through electric repulsion, filtration, and adsorption of arsenic-bearing compounds. Several cost-effective As removal filters have been developed by different national research organizations of India. The Indian Institute of Technology, Bombay (IITB) has developed a cost-effective, robust, iron-based As removal filter. Defence Research and Development Organization (DRDO) developed an As removal filter based on co-precipitation and adsorption. The Indian Institute of Technology, Kharagpur has developed a laterite-based As filter which is eco-friendly and ultra-low cost-effective. Agharkar Research Institute (ARI), Pune has developed a plant for As treatment. These As removal tools are efficient for As removal in lab conditions as well as in As-contaminated fields (Mishra et al. 2016). The use of membranes for the removal of contaminant like As has attracted attention as this possesses potential to be easily applicable even at personal home level. The membranes can also utilize biological functional components like specific transporter proteins to enhance the rate and efficiency of filtration (Werber et al. 2016; Ling et al. 2017).

### *5.4.4 Phytoremediation*

The biological methods that include phytoremediation and bioremediation are ecofriendly and cost-effective for protecting human health and environment from toxic metal contamination. Phytoremediation involves the use of green plants for removal of contaminants. In phytoremediation, plant removes heavy metals by using one of these mechanisms, such as phytodegradation, phytoextraction, rhizofiltration, phytostabilization, and phytovolatilization (Kumar et al. 2020). There is an immense natural diversity in the As response among different plant species. Few plant species have a great potential of phytoremediation strategies as they are enriched with mechanisms for As detoxification and hyperaccumulation. A plant species is recognized as As hyperaccumulator if it accumulates more than 1000 μg/g As. Several aquatic macrophytes and wetland plants grown in As-contaminated areas are reported to hyperaccumulate As (Robinson et al. 2006). *Pteris vittata* is an excellent As hyperaccumulator and reported to accumulate As up to 22,630 μg $g^{-1}$in 6 weeks (Ye et al. 2011). Aldrich et al. (2007) reported that mesquite plant is a potential candidate for the phytoremediation of As-contaminated regions.

### *5.4.5 Bioremediation*

Potential of living organisms to mitigate As contamination is known as bioremediation. Microorganisms have ability to grow and survive in the heavy metal (As)-contaminated areas. Some autotrophs and heterotrophs are reported to use As as their source of energy (Oremland 2009). Microbes methylate or biotransform the toxic form of As into less toxic form of As and thus can be used to amelioration of As from the contaminated environments. That microorganisms play an important role in the biogeochemical cycling of metal(oid) in the aquatic environment and have potential applications in bioremediation. It is also hypothesized that microorganisms are able to produce As-containing minerals or arsenosugars and thus can transform As into its less toxic form. Another important strategy of As removal includes plant-microbe interaction (Awasthi et al. 2018). The rhizospheric As-resistant microbes have been reported to play a vital role in plant growth promotion and phytoextraction of As from contaminated sites. Additionally, the ecological and socio-behavioral factors of As-affected areas, awareness about As-induced toxicity, and health risks should be of prime concern before design and implementation of any As mitigation proposals/policies. We must understand that so far there is no available treatment for As toxicity. The only solution to this ailment is non-As-contaminated drinking water, food, and essential vitamins and minerals. People living in the villages should be encouraged to include fresh fruits and vegetables in their diets due to their high nutritive value. They should be aware about the right cooking methods as over cooking can demolish essential nutrients in fruits and vegetables. In this reference, government should recruit food technologists, nutritionist, or medical personnel to aware villagers.

## 5.5 Conclusions and Future Prospects

Day by day, the addition of new As-affected areas due to the geogenic and anthropogenic activities has changed the present scenario of groundwater As contamination in India. Thus, it is of prime concern to explore the real picture of As contamination and its mitigation strategies to overcome the problem. In recent years, several As removal devices have been developed by different organizations that are proved to be efficient tools for As removal from groundwater. Deeper aquifers with no future risk of As contamination are helpful to supply As-free groundwater, thus exploration of deeper aquifers can provide a sound solution. Training and awareness program for As hazards and use of As removal tools to the user community would be helpful to minimize the exposure of As to human health. Considering the severity of the problem on a global scale, the awareness of population and implementation of facilities by setting proper guidelines is important for maintenance and mitigation of As problem. The government should monitor industrial and agriculture activities which contribute majorly in As pollution.

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