

## Source, Distribution, Toxicity and Remediation of Arsenic in the Environment – A review

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### Abstract

Arsenic (As), a mobilizing metalloid, is found in almost every fraction of the environment. Arsenic levels in the environment have become a global concern due to its toxicity and adverse effects on human health; even at low concentrations, it is highly toxic and classified as a carcinogen. Although it often exists in soils and plants from natural sources such as igneous and sedimentary rocks, the largest anthropogenic source of arsenic is the use of chromated copper arsenate (CCA)-treated wood. As the wood comes in contact with both soil and water, arsenic can be released into the environment. Atmospheric releases of arsenic may also occur when mining, smelting and refining, industrial processes, coal combustion, and waste incineration take place. Once released, it may undergo cycling processes in the environment, depending upon its oxidation state, speciation, concentrations, and the presence of organic matter, competing ions, and other environmental factors (e.g., pH, redox). This paper reviews the fundamentals of managing arsenic contamination in the environment, including identifying the sources, uses, and cycling of arsenic; understanding the behavior pattern of arsenic in media; and summarizing toxicity in natural and anthropogenic occurrence of arsenic in the environment. In addition, this paper summarizes currently available remediation technologies from arsenic-contaminated water and soils.

**Keywords:** Arsenic, Cycling, Chromated Copper Arsenate, Toxicity, Remediation, Soil pollution.

## Introduction

Arsenic, a ubiquitous metalloid, is naturally present in the lithosphere (earth crusts, soil, rock and sediment), hydrosphere (surface water, aquifers, deep wells and oceans), atmosphere and biosphere (food chain and ecosystems) [1, 2]. It can exist in both organic and inorganic forms. Organic forms of arsenic are associated with carbon and hydrogen, while inorganic forms are associated with iron, cobalt or nickel coupled with sulfide minerals [3].

Arsenic is one of the top five toxic chemicals that were listed in the US Comprehensive Environment Response, Compensation, and Liability (CERCLA) Act of hazardous substances [4, 5]. Among the four oxidation states of arsenic such as arsines and methyl arsines ( $\text{As}^{-3}$ ), elemental arsenic ( $\text{As}^0$ ), arsenite ( $\text{As}^{3+}$ ) and arsenate ( $\text{As}^{5+}$ ), the inorganic form ( $\text{As}^{3+}$  or  $\text{As}^{5+}$ ) of arsenic is highly toxic and mobile in the environment compared to the organic form ( $\text{As}^{3-}$  or  $\text{As}^{5-}$ ). In specific, arsenite ( $\text{As}^{3+}$ ) is found to be 10 times more toxic than arsenate ( $\text{As}^{5+}$ ) [6, 7, 8, 9].

The widespread contamination of the inorganic form of arsenic and its level of toxicity is an alarming issue as the metalloid does not degrade, nor can it be destroyed in the environment. Instead, it circulates around the earth; therefore, arsenic toxicity has received increasing international attention. In more than 42 nations including China, Australia, Cambodia, Vietnam, Bangladesh and India, the observed arsenic levels in the drinking water often exceed the WHO standard guideline ( $10\mu\text{g/l}$ ) [1, 9]. Approximately 150 million people have been affected by drinking arsenic contaminated water. In addition, arsenic can enter the human body via inhalation, direct ingestion, or dermal contacts. Arsenic, a known human carcinogen can adversely affect human health even at low concentrations ( $0.002\text{mg/l}$ ) [10]. Associated effects of acute toxic exposure include intestinal distress followed by vomiting and diarrhea, while exposure to arsenic in chronic concentration leads to inflammation of the kidney or liver [11].

As the mobilization and contamination of arsenic in the environment (especially in drinking water) is becoming a serious global issue, a number of simple, sustainable and sophisticated technologies have been developed to remediate arsenic in water and soil. Several physical, chemical, and biological methods have been made available to remediate arsenic in water and soil [9, 10] Although a number of researchers have published case studies on acute and chronic health disorders pertaining to arsenic contamination [1, 2, 9, 10], there is a need to review a systematic and extensive study from sources to removal technologies of arsenic in various environmental media. This paper reviews the sources, uses, cycling, behavior (chemistry, speciation and mobilization) and toxicity of arsenic in the environment and summarizes currently available remediation technologies for effective management of arsenic in soil and water.

## Sources and Use of Arsenic

### Sources

The Earth's crust is naturally comprised of approximately  $4.0 \times 10^{16}$  kg of arsenic [12]. Arsenic associated with arsenide of copper, lead, gold, iron hydroxides and sulfides is

stored in geological bedrocks (sedimentary rocks) or in the arsenic-rich aquifer matrices in many regions of the world such as Bangladesh, Australia, Canada, India, Vietnam, and Latin America [1]. In Australia, arsenic is associated with pyrite as arsenian pyrite clusters [13]. Deposited arsenic evolves and translocates through natural processes either by volcanic eruptions, weathering (physical and biological) or by geochemical reactions [2]. For example, arsenic from the aquifers of Australia is derived from erosion of arsenic-rich stibnite ( $\text{Sb}_2\text{S}_3$ ) mineralization present in the hinterland [13].

Another major source of concern for arsenic is anthropogenic sources, which account for 82,000 metric tons/yr worldwide [12]. Arsenic is generally associated with other metals; when mined or smelted for industrial purposes, it is released into the environment. Some of the anthropogenic industrial sources that release arsenic directly or indirectly into the environment include wood preservatives (chromated copper arsenate [CCA] chemicals), mining of arsenopyrite, electrical waste (semiconductors), insecticides, pesticides, weed controller, disposal of industrial and sewage materials, and paint products [6].

### **Uses**

Arsenic has been used throughout history for purposes ranging from medicines to poisons. The first usage of arsenic compounds dates back to 315 B.C. It is believed that arsenic was used to increase the shininess of bronze [14]. These copper and arsenic alloys were used in the manufacturing of tools and ornaments. In addition to the alloys, orpiment and realgar were used as dyes in cosmetics [15]. In Egypt, arsenic was used to create mirrors. Medicinal solutions such as potassium arsenite, arsenic iodide and arsphenamine were touted as a cure for a variety of diseases such as rheumatism, arthritis, asthma, malaria, trypanosome infection, tuberculosis and diabetes [16]. In early 1900s, arsphenamine (sold under the name salvarsan) was used as a treatment for syphilis until antibiotics were discovered; it was also used to treat ailments such as trypanosomiasis and amoebic dysentery.

Inorganic forms of arsenic such as calcium arsenate, lead arsenate and sodium arsenate were used as insecticides, pesticides, wood preservatives, aquatic weed controller, and glass and electronics manufacturing [2, 17]. Arsenic was introduced into livestock (sheep, cattle) through such practices as the dipping of sheep and cattle into vats filled with an arsenic solution to prevent insect borne disease. Prior to the advent of DDT in 1940s, arsenic-based pesticides were the predominant forms used in both farms and cotton orchards [1]. Large amounts of arsenic that was mined were used in the form of monosodium methyl arsenate (MSMA), disodium methyl arsenate (DSMA), dimethyl arsenic acid (cacodylic acid—used as a defoliant in cotton fields) and arsenic acid. Recently, anthropogenic forms of arsenic have been widely used in many modern purposes, such as the electronics industry (semiconductor materials in computers), lead acid batteries and corrosion resistant materials. Another major compound of arsenic, arsenic trioxide has been widely used in paints, wood preservatives, and pharmaceuticals. A summary of the main uses and chemical types of arsenic in our modern society is presented in Table 1.

**Table 1:** Sources and uses of arsenic compounds

<i>Sector</i>	<i>Uses</i>	<i>Chemical Type</i>	<i>Formula</i>
Agriculture	Insecticides, Herbicides, larvicides	Monosodium arsenate, disodium arsenate And diethyl arsenic acid	(NaCH <sub>3</sub> HAsO <sub>3</sub> ) <sub>3</sub> (Na <sub>2</sub> CH <sub>3</sub> AsO <sub>3</sub> ) <sub>3</sub> ((CH <sub>3</sub> ) <sub>2</sub> AsOCOH)
Wood Preservative	Chromated copper arsenate (CCA) wood preservative, decolorized glass	Arsenic trioxide	As <sub>2</sub> O <sub>3</sub>
Livestock	Feed additives, disease prevention (swine dysentery, heartworm infection), aquatic weed, cattle dips and sheep dips, algacides	Sodium arsenite	NaH <sub>2</sub> AsO <sub>4</sub>
Medicine	Antisymphilitic drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness	Arsine and Arsenic acid	H <sub>3</sub> AsO <sub>4</sub>
Electronics	Solar cells, optoelectronic devices, semiconductor application, light-emitting diodes (digital watches)	Gallium arsenide (GaAs)	
Industry	Glassware, electro photography, catalysts, pyrotechnics, antifouling paints, dyes and soaps, ceramics, pharmaceutical substances, defoliated cotton balls	Arsenic acid	H <sub>3</sub> AsO <sub>4</sub>
Metallurgy	Alloys (automotive body solder and radiators), battery plates (hardening agents)	Arsine	AsH <sub>3</sub>

### **Arsenic Cycling in the Environment**

Arsenic is introduced into the environment either naturally or anthropogenically; once released, it cannot be degraded or destroyed, and therefore it cycles in the environment. Arsenic cycling and mobility depends on the availability of arsenic in the geological source, in addition to the oxidation state, speciation and other environmental factors (e.g., pH and redox potential) [4, 17, 19]. There is limited information regarding the rate of mobilization in the environment (lithosphere, hydrosphere, atmosphere and biosphere). Arsenic cycling in the environment is summarized in Figure 1.

In the lithosphere, arsenic is generally associated with pyrite (ferrous and sulphur ligand) and other metals such as gold, lead, nickel, cobalt and copper. Figure 1(A) illustrates the anthropogenic process of mining these metals for industrial purposes. Arsenic can be released into the atmosphere in the form of arsenic gas (As<sub>2</sub>SO<sub>3</sub>) or as dust particles. Smelting of coal for fuel, burning fossil fuels and waste materials

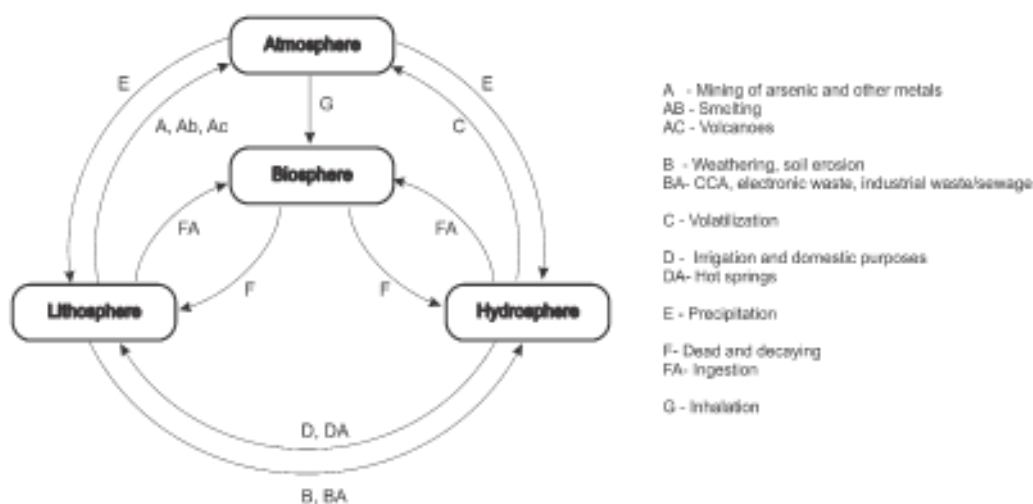
containing arsenic also contributes to the emission of arsenic into the atmosphere [3] (see Figure 1(AB)). Natural sources such as volcanoes can contribute to the release of arsenic into the atmosphere (Figure 1(AC)).

Natural processes such as weathering of oceanic rocks containing arsenic and submarine volcanoes can liberate arsenic into the hydrosphere. Indirect natural sources such as weathering of sedimentary rocks or mining is generally followed by soil erosion (Figure 1(B)). Anthropogenic sources such as the addition of pesticides containing arsenic, CCA-treated woods, landfilling of electronic waste or disposal of industrial wastewater and sewage are responsible for contamination of soil and water (Figure 1(BA)). Even after the United States and many other countries banned the use of arsenic in agricultural products in the 1960s, the soils at these farms and orchards still contain residue of arsenic, which further contaminates the soil and groundwater [19].

Through natural calamities such as heavy rain, floods and landslides, arsenic can enter surface water through soil washing and runoffs or sink into the soil and/or enter a groundwater source (hydrosphere) through seepage/leaching [18]. Arsenic concentrations in this process can vary depending on the source and mode of contamination. Microbial volatilization of methylated arsenic compounds contributes to the arsenic contamination of the atmosphere at low temperatures (Figure 1(C)). Arsenic in contaminated water enters the lithosphere through volatilization, irrigation and other domestic uses (Figure 1(D)). In addition, arsenic can be directly released into the aquatic and soil environment through geothermal water sources such as hot springs (Figure 1(DA)) [20].

Arsenic mostly in the form of dust with a residence time of between 7 and 10 days can be precipitated back into the lithosphere and hydrosphere after rainfall (Figure 1(E)). People residing at the delta of arsenic contaminated water and soil, smelting industries, pesticides and wood preservative manufacturing units can be highly exposed to arsenic. Arsenic in the atmosphere ranges from 0.5 to 15 ng/m<sup>3</sup>, depending on the amount of polluted and non-polluted areas. Smelting and coal combustion contribute to approximately 60% of the anthropogenic arsenic concentrations in the atmosphere [3].

Arsenic is often present in organic top soils. Under aerobic conditions, it usually occurs as arsenates that are taken up by plants and therefore enter the biosphere [21]. Further, it is introduced into the human body either through dermal contact (hand-to-mouth) or through the ingestion of arsenic-contaminated vegetables or fruits. The majority of the risks associated with arsenic contamination are due to ingestion of contaminated water and the intake of aquatic organisms (Figure 1(FA)). Another mode of arsenic entry into the biosphere is irrigation of agricultural crops with arsenic-contaminated water (e.g., rice), which affects biological users (human, plant and aquatic animals). Arsenic also enters the biosphere through inhaling arsenic dust (Figure 1(G)).



**Figure 1:** Arsenic cycling in the environment

## Behavior of Arsenic in the Environment

### Arsenic in geological formations

Arsenic levels in natural soils and rocks vary ranging from 1 to 150 mg/kg [8]. Arsenic occurs in both igneous and sedimentary rocks. The concentrations of arsenic in these rocks are dependent on the type of rock, chemical and structural aspects such as pH, and organic and inorganic components. Redox potentials also affect the quantity of arsenic present in a soil matrix [1, 4]. The average arsenic levels found in igneous, sandstone, and shale are reported as 1.5, 2.6 and 14.5 mg/kg, respectively [14].

### Arsenic in soils

Arsenic in soil can be present in three predominant forms; arsenite ( $\text{As}^{3+}$ ), arsenate ( $\text{As}^{5+}$ ) and organic arsenic. In general, naturally occurring arsenic in soil exists as a form of amorphous iron and aluminum oxides. Only a small portion of arsenic is found in its natural form [22]. The concentrations of arsenic in Canadian sediments range from 6 to 100 mg/kg [8]. Naturally, 4.8 to 13.6 mg/kg of arsenic was found in agricultural soils in Canada [8]. Arsenic in soil concentrations was estimated to be 7.5 mg/kg in the US [23].

Soil texture is an important characteristic that affects arsenic chemistry. Arsenic levels in soil depend on climate, pH and redox potential [12]. For example, during the wet season, redox condition in soil becomes reduced and results in releasing arsenic from arsenic containing iron hydroxide. In the presence of sulfide, arsenic may be precipitated as a form of arsenic sulfide, but excessive arsenic may be released to the environment [25]. In the dry season, arsenic remains fixed in the soil matrix and therefore the arsenic content in these soils tends to be higher [24, 25]. In addition to the above factors, larger concentrations of arsenic were observed in alluvial and

organic soils, while lower concentrations of arsenic were found in sandy soil [1]. Organic soils act as a trap for arsenic and other trace metals and therefore act as a barrier in preventing their movement in soil. The arsenic level in soil is often related to the amount of clay found in the soil [26]. Hence, clay plays an important factor in arsenic fixation. Arsenate is mainly sorbed to clay particles in soils at neutral pH.

Arsenic can be chemically transformed in soils through several mechanisms. These include oxidation, reduction, adsorption, dissolution, precipitation, and volatilization. The trivalent form ( $\text{As}^{3+}$ ) is easily absorbed to ferric and aluminum oxides in the soil environment and oxidized to the pentavalent form in aerobic condition and reduced back to the trivalent form on reduction with ArsC protein [27]. Under aerobic environment, the inorganic form of arsenic can easily bind to inorganic and organic materials in soil such as clay, iron and manganese dioxide, and exists in the pentavalent state (arsenate  $\text{AsO}_4^{3-}$ ). Under anaerobic environment, anaerobic bacteria degrade into less toxic volatile forms such as dimethyl arsenic acid (DMAA) and monomethyl arsenic acid (MMAA) [12]. Oxidation and reduction of arsenic species are carried out both biologically and chemically in soil and water [28, 29].

Aluminum, magnesium and iron oxides, as well as soil mineralogy and organic content are the components of soil that contribute to the sorption and mobility of arsenic. Chloride, nitrate and sulfate ions have no relation to arsenic concentration variations, but the presence of phosphate from fertilizers or waste products inhibits the mobility of arsenical compounds [30, 31]. The acid/base chemistry also plays a major role in the types of arsenical compounds present in the soils. Under acidic conditions, arsenic tends to form compounds with aluminum and iron ( $\text{AlAsO}_4$ ,  $\text{FeAsO}_4$ ), whereas under alkaline conditions (limestone soils) calcium arsenate ( $\text{Ca}_3(\text{AsO}_4)_2$ ) is the predominant compound.

Naturally, arsenic can be released into the soil environment by weathering and erosion (hydrolysis and oxidation process) of primary sulfide mineral (arsenopyrite). Thus, released arsenic is absorbed in ferric hydroxide. The amount of ferric hydroxide is proportional to arsenic availability in the soil. Bioavailability plays an important role in uptake of arsenic from soil to plants [32]. Anthropogenic releases of arsenic, especially due to pesticides and CCA-treated wood, result in higher levels of arsenic in soils than those in natural sources. Even after the ban of arsenic-containing pesticides, arsenic still persists in the soil [5, 19].

Iron oxides adsorb arsenic more strongly than manganese oxides. Ferric hydroxide plays an important role in controlling the concentration retention and mobilization of arsenic in soil as well as aqueous media [12]. Arsenic is attracted to iron oxides and under anoxic conditions is released in the groundwater. Phosphate is an important adsorbent in arsenic chemistry. The geochemical behaviors of arsenic and phosphate are similar as they form complexes with aluminum, iron and manganese [12]. When in solution with iron oxides, approximately 60% of the adsorbed pentavalent arsenic and 70% of the trivalent arsenic were displaced by  $\text{H}_2\text{PO}_4^-$  [34]. Other anions can displace iron oxides, but are less effective than phosphate; these include carbonate, sulfate and a variety of other anions [30].

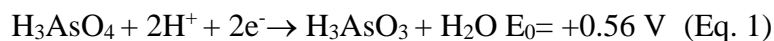
As with soils, organic content, iron and aluminum oxides, hydroxides and phosphate ion ( $\text{PO}_4$ ) play an important role in the speciation as well as mobility and sorption of

arsenic in sediments [34]. Arsenic retention in soil media is mainly dictated by adsorption and desorption reactions, presence of ligands and soil redox conditions [14, 24, 29]. Arsenic is more soluble under high or low pH values.

### Arsenic in water

Arsenic in water is either dissolved or in particulate form. In the US, approximately 10% of all groundwater was contaminated by arsenic mainly because of geothermal water, desorption and reductive dissolution of iron oxides and oxidation of sulfide minerals [12]. Arsenic drinking water standards throughout the world range from 0.01 mg/L to as much as 0.05 mg/L. Although inorganic and organic species of arsenic are present in the environment, inorganic forms are typically more abundant in freshwater systems [35]. Arsenic can be released into the environment naturally either by oxidation of arsenopyrite, or by reductive dissolution of arsenic rich ferrous oxyhydroxides in reducing aquifer environment [24].

The most common forms of arsenic in natural waters, as in soils, are arsenite and arsenate. Organic species are not commonly found in anthropogenic sources. Equilibrium constants ( $pK_a$ ) help in quantification, as shown in Table 2. As with soils, the principal species found in natural waters are forms of inorganic arsenic, namely  $H_2AsO_4^-$ ,  $H_3AsO_3$ ,  $HAsO_4^-$  and  $As_3O_4^{3-}$ . In terms of dissociation, precipitation, adsorption and ion exchange, the oxidized forms of arsenic react in a similar manner to orthophosphate ions. The redox reaction in a system containing  $As^{3+}$  and  $As^{5+}$  is shown in Eq. 1:



**Table 2:**  $pK_a$  Values for  $As^{3+}$  and  $As^{5+}$

Arsenic Species	$pK_{a1}$	$pK_{a2}$	$pK_{a3}$
$H_3AsO_4$	2.19	6.94	11.5
$H_3AsO_3$	9.20	----	

Using the Nernst equation, the oxidation of  $As^{3+}$  to  $As^{5+}$  is easily accomplished with dissolved oxygen. With those relationships, types of arsenic species that are thermodynamically formed at given electron concentrations and pH can be illustrated on the pe-pH diagram (Figure 2). If kinetics is taken into account, oxidation of  $As^{3+}$  by air (without additional oxidant) proceeds very slowly; only a small fraction of  $As^{3+}$  was oxidized within a week [4].

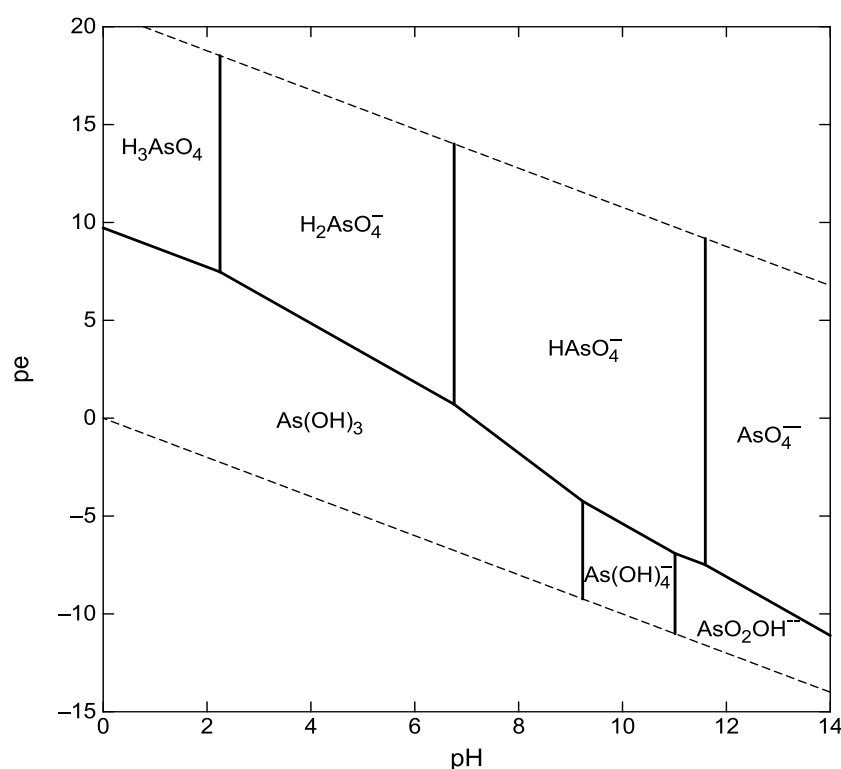
Change in arsenic solubility in sulfidic water is noticeable. In reduced condition, sulfur is dissolved as a form of sulfide ( $S^{2-}$ ) that may easily bind with metals and forms amorphous metal-sulfide complex. However, water solubility of As-sulfide complex, sometimes, may increase as a result of thioarsenic compounds formation [36]. As shown in the pe-pH diagram (Figure 3), both  $As^{5+}$  and  $As^{3+}$  would be able to form a complex with sulfide, and types of thioarsenic species are mainly dictated by pH and oxidation condition [37]. The molar ratio of total sulfide to arsenic in water is also involved in transforming thioarsenic species [38]. For example, monoarsenate



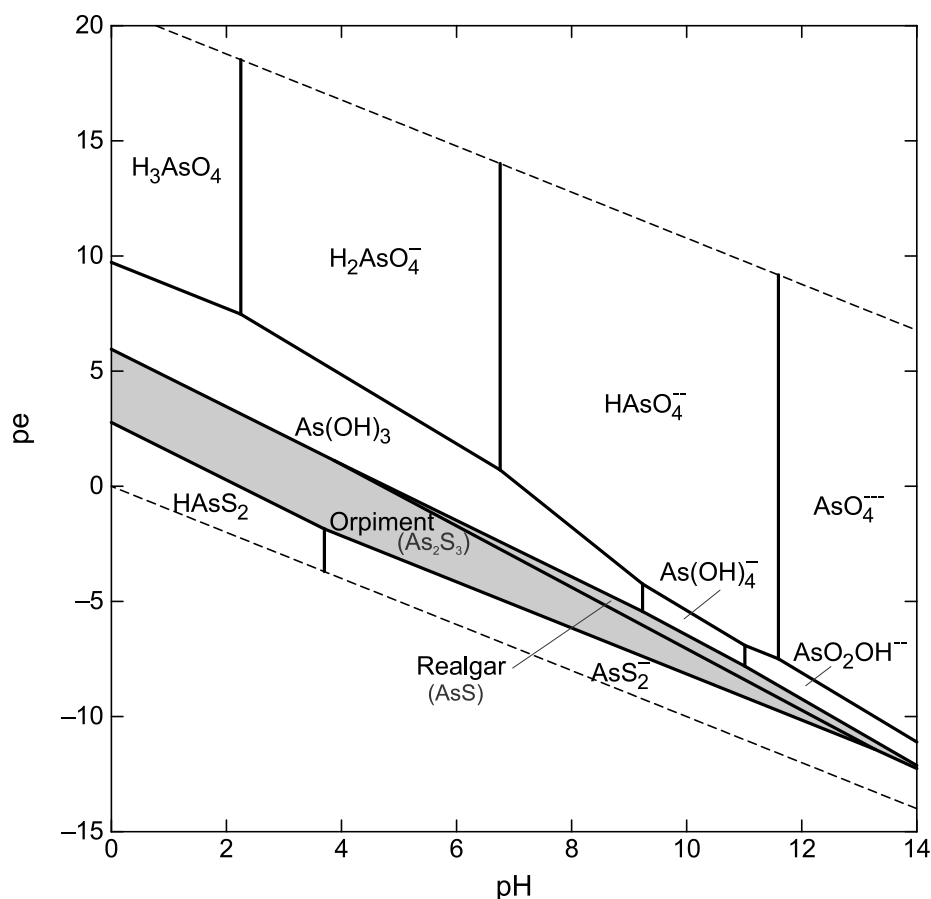
( $\text{AsSO}_3^{3-}$ ) and dithioarsenate ( $\text{AsS}_2\text{O}_2^{3-}$ ) are dominantly formed at equal molar ratios of sulfur and arsenic whereas the formation of trithioarsenate ( $\text{AsS}_3^{3-}$ ) and tetrathioarsenate ( $\text{AsS}_4^{3-}$ ) is more favorable at high As/S ratios (As:S = 1:50). In addition to those basic water chemistry parameters, Fisher [39] reported that microorganisms in water may play an important role in determining thioarsenic species.

Biomethylation of arsenic takes place with the help of various species of micro- and higher organisms. Biomethylation reduces  $\text{As}^{5+}$  to soluble  $\text{As}^{3+}$  species at anoxic condition [12]. The majority of arsenic found in freshwater organisms is the organic species such as dimethylarsenic compounds [40] and trimethylarsenic compounds (e.g., arsenobetaine) [41]. In aqueous plants such as algae, the organic arsenic species tend to be in the form of dimethylarsenic compounds, while in mollusks, crustaceans and fish the species tend to be in the form of trimethylarsenic compounds [42].

Arsenate is the predominant form of arsenic in seawater and total arsenic is present in the marine environment at a fairly uniform concentration of  $2 \mu\text{g/L}$ . Dimethyl arsenic acid (DMMA) and methylarsenic acid (MMA) are also present in seawater in small amounts [43]. Arsenite, DMMA and MMA are more prevalent in the photic zone, indicating that algae may be important in the biotransformation of inorganic arsenic. Because the determination of arsenic in saline waters requires the transformation of arsenic to arsine gas, the method does not measure arsenate compounds [14].



**Figure 2:** pe-pH diagram for the system As-H<sub>2</sub>O at 25 °C and 1 atm. Total activity of arsenic species is  $10^{-5}$



**Figure 3:** pe-pH diagram for the system As-H<sub>2</sub>O-sulfur at 25 °C and 1 atm. Total activities of arsenic and sulfur species are 10<sup>-5</sup> and 10<sup>-3</sup>, respectively

### Arsenic in the atmosphere

Atmospheric emissions of arsenic occur from natural and anthropogenic processes. Anthropogenic emission is higher than natural emission. It was estimated that the annual global atmospheric emission of arsenic is  $7.8 \times 10^7$  kg/yr. Natural sources contribute to  $1.2 \times 10^7$  kg/yr. Volcanoes emit  $8.9 \times 10^6$  kg /yr, while by microbial volatilization it is emitted to be around  $2.1 \times 10^7$  kg of arsenic/yr [12]. The amount of arsenic stored in the northern and southern hemispheres is not evenly distributed. Approximately five times more arsenic is stored in the northern hemisphere than in the southern hemisphere. This phenomenon is attributed to greater industrialization in the northern hemisphere. Other contributors of arsenic to the atmosphere include deforestation, burning of grasslands, the use of wood for fuel, and the deforestation of savanna and temperate woodlands [44]. Low temperature volatilization from soil and volcanoes contributes to 60% and 40% of atmospheric emissions from natural sources, respectively. Volcanoes and volatilization through biomethylation of arsenic are the highest contributors to natural emission of arsenic to the atmosphere [44].

### Arsenic toxicity

Arsenic toxicity depends on the oxidation state (either as arsenite or arsenate), intake rate, frequency and route of intake, exposure time and bioavailability [5, 17, 27, 46]. Arsenic exposure to humans can affect internal organs such as the lung, kidney, urinary bladder and liver, causing cancerous effects. It can also cause non-carcinogenic effects such as keratosis, hyperpigmentation, hypopigmentation, peripheral vascular and cardiovascular disease, diabetes mellitus, and peripheral nervous and central nervous disorders [5, 35, 46, 47]. A summary of arsenic toxicity is presented in Table 3.

**Table 3:** Acute and chronic toxicity of arsenic by exposure route

<i>Acute or Chronic</i>	<i>Route</i>	<i>Toxicity</i>
Acute	Ingestion of water or accidental ingestion of insecticides or pesticides	Nausea, vomiting, diarrhea, cyanosis, cardiac arrhythmia, confusion and hallucinations
	Dermal via CCA contamination	Cell death associated with disruption of the cell membrane, and inhibition of DNA and protein syntheses
	Inhalation of arsenic gas	Cough, bronchitis, shortness of breath
Chronic (arsenicosis)	Ingestion of water	Keratosis, pigmentation (hyper pigmentation/hypo pigmentation) of feet, hands, fingers,
		central and peripheral vascular and cardiovascular disease, malignant diseases such as bladder, kidney and liver cancer, diabetic millets, low blood count, numbness
	Inhalation	Lung cancer, chronic bronchitis, chronic obstructive pulmonary disease and bronchiectasis.

Exposure routes of arsenic in humans commonly include ingestion, inhalation and dermal contact. It is important to know the level of toxicity as even at low exposure arsenic has a great effect on human health. The two major potential exposure routes of arsenic to humans are ingestion and inhalation. Ingestion through water, food, soil (hand to mouth) and inhalation of dust containing arsenic have commonly been reported. Another potential route of concern is through drinking water [35]. In the early 1990s, the water quality problems that surfaced in India and Bangladesh were mainly due to ingestion of arsenic; likely through the consumption of fish and shellfish in arsenic contaminated water. A previous study showed arsenic level of up to 30 µg/g in shellfish. Arsenic in shellfish was found to be organic arsenic, which is less toxic than inorganic arsenic [48]. In 1993, the World Health Organization (WHO) developed a new guideline for drinking water quality for arsenic in which the “safe”

level for the consumption of arsenic was lowered from 0.05 mg/L to 0.01 mg/L. However, because the new arsenic level is only a suggested guideline by the WHO; many countries have not changed their national guidelines for water quality to reflect the lower limit for drinking water. The other source of arsenic exposure is inhalation of arsenic gas or arsine through industrial processes and smelting or refining of metals. The gaseous phase of arsenic occurs usually through the mixture of acids and crude metals. Inhalation of gas containing arsenic for a prolonged period can be potentially toxic and carcinogenic to humans. Inhalation of gas containing arsenic can cause acute and chronic effects. Acute exposure can lead to gastrointestinal effects such as nausea, diarrhea and abdominal pain, central and peripheral nerve disorder whereas, chronic exposure can cause gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, liver or kidney damage in humans, lung cancer, bladder and liver cancer [49]. In recent years, there has also been an increasing concern regarding the direct and indirect exposure to arsenic in CCA-treated wood playground sets on children around the world. Children's exposure to inorganic arsenic from playground sets and tables treated with CCA was studied to evaluate their potential health risk [50, 51, 52, 53].

Symptoms of arsenic toxicity/poisoning include weakness, loss of appetite, weight loss, anemia, leucopenia and dementia. Arsenicosis or chronic arsenic exposure has been linked to lung, skin, liver, bladder, and kidney cancer [47, 48]. Dermal absorption of arsenic does not take place, but keratosis or pigmentation is a common chronic disease due to ingestion of water. Hyperpigmentation and hypopigmentation due to chronic poisoning of arsenic can lead to wart like pigmentation on feet, hands and fingers. Chronic arsenic exposure also leads to impairment of central and peripheral vascular systems and cardiovascular disease. Peripheral nervous and central nervous disorders and diabetes mellitus have been associated with arsenic exposure. Cardiovascular diseases such as "black foot disease" generally affect the legs; the effects can be severe with a slow recovery [47].

Trivalent arsenic is known to be more toxic than pentavalent arsenic due to its strong affinity for sulfhydryl groups of biomolecules (e.g., thiol groups in enzymes). Pentavalent arsenic toxicity is due to its interference with oxidative phosphorylation in cells by substituting for P (phosphate) in adenosine triphosphate (ATP) synthesis, essentially deactivating intracellular energy storage. Another problem with the toxicity of arsenic is the byproducts of oxidation of arsenate, which are arsenite, monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA). The methylation of arsenate helps in the removal of arsenic from the body; at the same time, it has been shown to increase the levels of these three toxicants. Oral LD<sub>50</sub> ranged from 15 to 293 mg/kg of inorganic arsenic in most laboratory animals such as rats. Approximately 70~80 mg of arsenic trioxide was reported to be fatal to humans [54]. These forms of arsenic gain entry through one of the above mentioned routes and interfere with the enzymatic action, DNA transcription and metabolism, further spificating human cells and organs. Once arsenic enters the body through ingestion, it is well absorbed by the digestive tract to the blood stream. Arsenic in blood binds

with oxyhemoglobin and causes the extensive destruction of red blood cells, reducing the blood's ability to carry oxygen to the vital organs and causing problems with the ability of the kidney and liver to function properly [55].

The breakdown of arsenic by the human body is accomplished through the process of methylation. The liver is the primary site for methylation of both  $\text{As}^{5+}$  and  $\text{As}^{3+}$ . Enzymes convert  $\text{As}^{5+}$  into  $\text{As}^{3+}$  and then  $\text{As}^{3+}$  is further converted into both DMAA and MMAA [56]. The new arsenic metabolites that are formed are less reactive with internal tissue but can be as damaging to the body if they are allowed to build up in sufficient quantities.  $\text{As}^{3+}$  tends to accumulate in organs that help in methylation while  $\text{As}^{5+}$  is removed from the blood stream via the kidneys [57]. Ingested arsenic is excreted through urine, which will show high levels of arsenic but as much as 95% of the arsenic is converted over to DMAA and/or MMAA (Aposhian et al., 2000). In a recent study, DMAA (60~80%) and MMAA (20%) were found in urine. The results showed that DMAA is more toxic than  $\text{As}^{3+}$  and  $\text{As}^{5+}$  [2]. Organic arsenic is believed to be less toxic than inorganic arsenic, which may explain why consuming food contaminated with arsenic is not as harmful to humans as consuming water with the same amount of inorganic arsenic.

Research has shown that all four forms of arsenic ( $\text{As}^{3+}$ ,  $\text{As}^{5+}$ , DMAA, MMAA) have adverse effects at the cell metabolism level, but there is a problem with correlating data obtained from animal studies to actual human effects. There is not a clear dose-response curve for arsenic because of the different metabolites that are formed from arsenic poisoning. Arsenic and its metabolites are believed to have adverse influences at the cell level by damaging cell DNA or by reacting with critical sulfhydryl-containing enzymes. Arsenic alone does not cause mutation of DNA in mammalian cells; damage to DNA occurs by the release of iron bound inside the cell. The release of iron induces an oxidative stress within the cell that can lead to a combination of mutations and/or carcinogenesis [58]. By damaging DNA, arsenic directly causes changes to occur in the formation of proteins and enzymes. While arsenic is not believed to cause point mutations in cells, it was known to cause sister chromatid exchanges (SCEs), chromatid aberrations, aneuploidy, polyploidy, DNA amplification and morphological transformations [59].

## **Remediation**

Removal of arsenic from contaminated soil or water is important as arsenic has been recognized as a toxic element that causes potential health risks. Arsenic form in the environment varies depending on the pH and redox potential. At normal pH values, the oxidation states of inorganic arsenic are  $\text{As}^{3+}$  and  $\text{As}^{5+}$  [18]. Remediation or removal of these two oxidation states from a particular source involves commuting arsenic from  $\text{As}^{3+}$  to  $\text{As}^{5+}$  in a less toxic form. Remediation of arsenic from soil or water can involve a range of simple to sophisticated technologies, each of which has its own advantages and disadvantages. Comprehensive studies on these technologies have been conducted in order to reduce potential health risks in most arsenic

contaminated areas. Implementation of the appropriate technology depends on the source and levels, route and distribution, and chemical form of arsenic [9, 12, 18]. The common methods used for remediating arsenic from soil and water are summarized in Table 4. The following section discusses some of the methods in more details.

**Table 4:** Remediation methods of arsenic in soil and water

<i>Media</i>	<i>Method</i>	<i>Principle and characteristics</i>
Soil	Chemical fixation	Executed by the addition of chemical additives, an effective and low-cost treatment method
	Soil washing	Mixed with washing solution of acids or chelating agents, short reaction time and large size treatment, but waste disposal required
	Electro remediation	Executed by using direct current, simple to operate and low cost
	Biological users-fungi and microorganisms	Biotransformation/biomethylation Bioremediation has a positive effect on the removal of arsenic.
Water	Oxidation	Oxidization of contaminated water with oxygen, hypochlorite, and sustainable way of storage, simple and low cost method
	Chemical precipitation	Treatment of contaminated water with a good coagulant, use of simple chemicals, low capital cost but requires pretreatment
	Adsorption	Adsorption of arsenic using natural and synthetic filters, effective removal of arsenic
	Ion exchange	Treatment of contaminated water using electric current (EC), simple and cost effective hence suitable for rural areas but requires change of the electrodes; applicable for small treatment systems
	Phytoremediation	Treatment using plants to detoxify arsenic present in water, often followed by electrochemical technology. This technique has relatively low capital, operating, and maintenance costs as it depends on growth of plants but it is less robust
	Reverse osmosis, nanofiltration, ultrafiltration and electro dialysis	Use of membrane process technologies in treating arsenic-contaminated water, This method is relatively expensive, requires high operation and maintenance, and produces toxic wastewater

### Soil remediation technologies

Arsenic in soil can be due to natural or anthropogenic sources. Remediation of arsenic from soil can be achieved mainly by chemical fixation, soil washing, electroremediation, bioremediation, or phytoremediation. Chemical fixation is viewed

as one of the best remediation methods, as it suspends the mobilization of arsenic in soil. Chemical fixation of soil containing arsenic can be executed by the addition of chemical additives such as ferric hydroxide, ferrous sulphate and lime; arsenic in soil binds well with ferrous compounds to produce ferric arsenate. Soil washing is also commonly used for arsenic removal from metal-contaminated soils due to shorter time and relatively simple technique. During soil washing, arsenic-contaminated soil is mixed and agitated with a washing solution of neutral phosphate or acids (e.g., hydrochloric acid, phosphoric acid) [60] and chelating agents and humic substances [61]. The performance of the washing solution may be influenced by the characteristics of soils, the concentration and chemical form of arsenic in soils, and washing condition [60].

Electroremediation is removal of arsenic physically using direct current (DC) either by electromigration, electroosmosis or electrophoresis. The rule of thumb is movement of charged particles and dissolved ions to cathode or anode tubes at low level DC. Bioremediation or conversion of inorganic arsenic to organic arsenic compounds with the application of microorganisms (molds and fungi) is the simplest and most readily available remediation method [12]. Extensive work on bioremediation has been done by many researchers [4, 9, 12, 17, 62]. Fungi such as *Scopulariopsis brevicaulis*, *Pencillium* sp., *Candida humicola*, *Gliocladium roseum* and *Aspergillus niger* and bacteria such as *Bacillus arsenoxydans* and *Pseudomonas putida* are known bioremediators [7, 63]. Microorganisms can uptake inorganic arsenic and convert to methylarsenic and dimethylarsenic and further to trimethylarsine (gaseous arsines as a volatile form) under anaerobic conditions; this causes the immobilization of arsenic metal. This can be achieved either by biotransformation, biooxidation or biomethylation [7, 12]. Fungi such as *Trichoderma* sp., *Neocosmospora* sp., *Pencillium* sp. and *Rhizopus* sp. showed metal tolerance and enhanced growth in sodium arsenate solution at 10,000mg/l, indicating that they can be effective strains in bioremediation of arsenic-contaminated soil [7]. Microorganisms undergo redox cycling of arsenic from  $As^{5+}$  to  $As^{3+}$  and vice versa at anoxic and oxidation conditions, making the chemical behavior of arsenic less mobile and toxic [62]. Apart from bacteria and fungi, earthworms are also able to withstand in high arsenic-contaminated soils. Earthworms as an environmental indicator showed enhanced growth in arsenic-contaminated ferrous soil [17].

Phytoremediation is an inexpensive technology used in remediating heavy metals. Phosphorous is commonly used in fertilizer and behaves as a mobilizing agent in enhancing arsenic uptake by plants such as sunflower (*Helianthus annuus*, L., San Luca), marsh fern (*Thelypteris palustris*) and mesquite (desert plant), reducing arsenic toxicity in soil [4, 12]. Few species of plants have the ability to remediate arsenic from contaminated soil and water due to the presence of anti-oxidant defense system. Sunflower can withstand arsenic concentration up to 250mg As/kg [4]. Fern's belonging to the family Pteridaceae (*Pteris vittata* Linn (hyper accumulator of arsenic), *Pteris cretica*), *Adiantum capillus-veneris* and *Nephrolepis exaltata* are known to tolerate and accumulate arsenic from root and then translocate to shoot and leaves. According to a study conducted by Singh [64], *Adiantum capillus-veneris* was

detected to have a high tolerance of 500mg As/kg of soil whereas *Pteris vittata* Linn has a tolerance level up to 22,600mg As/kg at the lower ground tissue [65].

### **Water remediation technologies**

Critical public concerns have been raised worldwide due to ingestion of arsenic-contaminated surface and groundwater. There are a number of water remediation technologies that aid in reducing high levels of arsenic to minimum detection of 1~2 µg/L of arsenic [66]. In recent years, sustainable, cost effective and efficient technologies have gained more attention. Commonly used remediation technologies for arsenic-contaminated water include oxidation, lime treatment, chemical precipitation/coagulation, ion exchange, adsorption, bioremediation, phytoremediation, hybrid membrane process (nanofiltration and ultrafiltration) and electro dialysis [12, 18, 67].

Oxidation is a simple method that converts arsenite to arsenic. This can be achieved by oxidizing arsenic contaminated water with oxygen, hypochlorite, free chlorine, hydrogen peroxide and permanganate. Other conventional oxidation methods include storage of water for about two weeks, reducing 50% of the arsenic concentration in water and solar oxidation [67]. Arsenic in subsurface water can also be removed by injecting oxygenated water and ferric chloride into an anaerobic aquifer [68]. Atmospheric air and chemical oxidation are simple and low cost technologies that aid in the removal of arsenic in rural areas.

Arsenic can be removed either by coagulation, coprecipitation or adsorption. Coagulation, a traditional way of treating arsenic-contaminated water, is practiced by the addition of ferric sulfates, ferric hydroxide, hydrated lime, alum or ferric chloride. Ferric salts are known to be good coagulants [18, 67].  $As^{5+}$  can be easily removed by the addition of coagulants and formation of aluminum or ferric floc. However,  $As^{3+}$  requires further treatment either by oxidation, filtration or the addition of bleaching powder (chlorine) or potassium permanganate. Alum with chlorine showed 90% removal efficiency of arsenic at pH 7 [69]. Changes in pH, phosphate and silicate levels affect coagulation [18]. Because coagulation involves the use of simple chemicals, only a low capital cost and pretreatment (oxidation) are required for complete removal of arsenic. Arsenic is generally associated with iron. Therefore, coprecipitation of arsenic with iron (ferric sulphate) serves as an excellent sustainable remediation technology [55, 69].

Adsorbents such as activated carbon, hydrous metal oxides, ion exchanger resin, activated red mud, zeolite and ferruginous manganese ore are used to remove smell, color and organic and inorganic pollutants [18]. Arsenic speciation is well determined by pH, which is an important indicator in arsenic removal by adsorption. Adsorptive filtration media such as activated alumina, activated carbon, kaolinite clay, hydrated ferric oxide, titanium oxide, indigenous filters and many other natural and synthetic filters are commercially available and have been reported for effective removal of arsenic [67].

Removal of arsenic-contaminated water electrolytically by injection of electric current (EC) into aqueous medium containing electrodes is also a practiced sustainable



method used to treat the contaminated water. The anode in the aqueous medium produces metal cations. Then the cations oxidize metal to oxides, creating flocculation, coagulation and settling. Electro-coagulation at 20V showed 75% of arsenic removal efficiency in a continuous flow reactor [70]. Electrocoagulation with iron and aluminum electrodes removes arsenic to the US EPA drinking water standard [71]. This method is suitable for rural areas as it does not involve any addition of chemicals. This is a simple and cost effective method, but requires frequent changes of the electrodes.

Phytoremediation of arsenic in water is done with the aid of water plants to detoxify arsenic present in water in combination with electrochemical technology. Plants such as *Eichornia crassipes* (water hyacinth) and *Rhaphidophyceae chattanello* have the capacity to absorb arsenic in their shoots, and arsenic metal can be extracted through an electrochemical method [12].

Reverse osmosis, nanofiltration, ultrafiltration and electrodialysis are the main membrane process technologies commonly used to treat arsenic-contaminated water. Reverse osmosis at low and high pressure removes dissolved solids. Higher removal efficiency of arsenic has been reported on hybrid membrane techniques than by conventional membrane techniques. It is highly expensive, requires high operation and maintenance, and produces toxic wastewater [17]. Research on the use of engineered magnetic nano-particles (NP) (nano zero-valent iron (NZVI), magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hydrous cerium oxide (HCO)) in remediating arsenic-contaminated water is gaining lot of interest due to their high removal efficiency, fast kinetics, reduction, adsorption and magnetic property. However, this technique is relatively expensive, while nano-particles with NZVI can be desorbed in the presence of phosphorus present in the ground water or by addition of phosphate into groundwater and reused [72, 73, 74, 75, 76].

## Conclusion

Arsenic is one of the most prevalent toxic chemicals found in various environmental media. Human exposure can occur from arsenic-contaminated water, soil, air, and as well as food contaminated with arsenic species via various exposure routes. Exposure of arsenic to the human body can be toxic at low concentrations. This study reviews the current available literature on the occurrence, behavior, cycling, toxicity, and removal technologies of arsenic present in environmental media. Understanding and knowledge of the sources, occurrence and distribution, cycling and chemistry of arsenic in the multimedia environment is needed because of its potential toxicity to human health and the environment as well as for its effective remediation of arsenic from contaminated water and soil. This study is compiled to provide a complete understanding of arsenic in the multimedia environment from source to removal. It is very important to raise awareness of the toxicity and the potential environmental impacts of arsenic exposure via various routes. A number of effective, promising and environmentally-sound removal technologies available for the treatment of arsenic-contaminated soil and water are also reviewed.

More and detailed studies are needed to focus on the mobility and cycling of arsenic species in the environment, as well as the effects of its exposure on human health at low levels. Behavior and mobility of arsenic species, both organic and inorganic, in the environment are influenced by a number of factors including, but not limited to pH, Eh, the presence of organic matter and complexing agent, and other competing ions. More research efforts are needed to examine on the interaction of these factors under relevant environmental conditions to determine the behavior and mobility of arsenic in the environment. Although many studies focused on the toxic effects of arsenic on human health, the detailed studies are required to examine arsenic exposure and its related effects via ingestion and inhalation pathways, based on different arsenic species, especially at low levels of arsenic. One of the major aspects of arsenic toxicity is the process of bioaccumulation of arsenic in plants. Since different plants have different genetic systems, there is a large variation of arsenic uptake by plants. The bioaccumulation and uptake of arsenic, along with other nutrients, in plants is very little known. Further studies must be devoted in this direction to understand fully the role of arsenic uptake and bioaccumulation in different plants. Arsenic contamination in water and soil is a serious environmental concern in many countries, which have led to a myriad of research on risk assessment and remediation of arsenic. However, more studies are still needed to understand the potential effects on human health and the effective removal mechanism in water and soil at both biochemical and molecular levels. Long-term field and economical studies of arsenic remediation are warranted to evaluate the efficiency and suitability of removal techniques for arsenic-contaminated water and soil.

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