

Arsenic: Source, Occurrence, Cycle, and Detection

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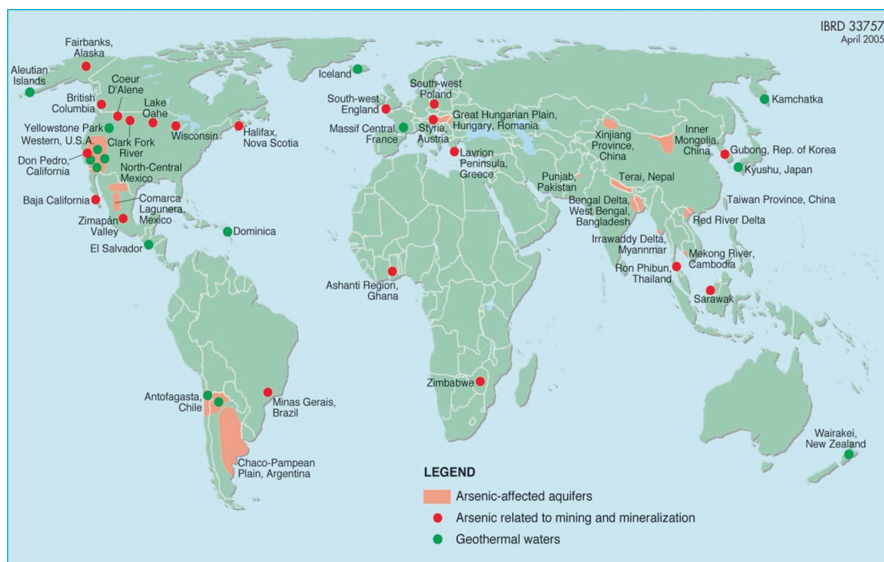


Fig. 1 Arsenic distribution in groundwater and in the environment worldwide. [Photo downloaded from <http://web.worldbank.org/WBSITE/EXTERNAL/COUNTRIES/SOUTHASIAEXT/0,,contntMDK:22392781~pagePK:146736~piPK:146830~theSitePK:223547,00.html> (Downloaded on 27.04.2016)]

1 Introduction to Arsenic: Its Sources and Occurrence in the Environment

Worldwide, arsenic exposure is one of the most dreaded public health crises with millions of people exposed to drinking water with arsenic concentrations that surpass the recommended limit of $10 \mu\text{g L}^{-1}$ (George et al. 2014). Most affected individuals live in southern Asian countries such as Bangladesh, India, Cambodia, Nepal, and Vietnam, and many countries in the world are affected by arsenic, including the United States, Argentina, Bolivia, Chile, Peru, and Mexico (George et al. 2014; Shibata et al. 2016; Yunus et al. 2016) (Fig. 1). The extent of the difficulty is very severe in Bangladesh, with nearly 85 million people (of a total population of ca. 125 million people) are affected by this curse. The adjoining state of West Bengal (India), with more than 6 million people, is also affected. Therefore, arsenic poisoning of groundwater affects about one third of the people in the Bengal basin (Sen 2013). In India, the Ministry report (2014; downloaded from: http://wrmin.nic.in/writereaddata/16_Estimates_on_arsenic.pdf) suggests 10 affected states: West Bengal, Bihar, Assam, Chhattisgarh, Manipur, Punjab, Haryana, Karnataka, Jharkhand, Uttar Pradesh.

Arsenic (As, with atomic number 33) is an element that naturally occurs in many minerals and can exist in various allotropes. More than 200 species of minerals contain arsenic, among which arsenopyrite (FeS) is most common. It is predicted

that about one third of the atmospheric flux of arsenic is naturally derived, with volcanic eruption the most significant source. The geological origin of inorganic arsenic (iAs) has also become a considerably important source as it is found to be associated with groundwater. Arsenates present in the soil can dissolve easily in groundwater, which becomes the source of contaminated water flowing in rivers to the sea (Wang et al. 2014; Kim et al. 2015). The typical richness of As in the Earth's crust is between approximately 2 and 5 mg kg⁻¹. However, an enriched amount may be found in shale and coal deposits of sedimentary and igneous rocks (Smedley and Kinniburgh 2002). The occurrence of iAs with other metals such as iron (Fe), cobalt (Co), copper (Cu), nickel (Ni), silver (Ag), and gold (Au) is common (Tamaki and Frankenberger 1992). Direct mixing of arsenic into the aquatic environment may also be occurring through geothermal water, for example, the hot springs in Hot Creek, Nevada (Wilkie and Hering 1998). Arsenic adsorption to mineral surfaces (including Fe-, Mn-, and Al-rich soil and sediments) act as an important sink. This kind of mineral association is thought to be one of the important reasons for arsenic toxicity in groundwater, especially in the case of the Bengal delta aquifer, where Fe(III) oxide coatings on weathered alluvial sediments helping in release of arsenic into groundwater upon reductive dissolution of the Fe(III) oxide coating (Nickson et al. 1998; Nickson et al. 2000; Chowdhury et al. 2000; Acharya 2002; McArthur et al. 2004; Khalequzzaman et al. 2005; Ahuja 2008).

2 Properties of Arsenic and Its Different Species

Arsenic and its compounds occur naturally in trace quantities in all rock, soil, water, and air in various forms including crystalline, amorphous, powder, and vitreous. However, concentrations and the specific nature of species may vary due to a number of factors such as weathering, pH and Eh of the ambience, physical, chemical, biological (microbial), and anthropogenic activities, among others. Typically, arsenite compounds predominantly present under reducing or anoxic and waterlogged conditions (<200 mV) whereas arsenate species dominate in oxidizing and aerated conditions. The identity of chemical arsenic is represented in Table 1. In addition, naturally occurring and environmentally important arsenic species are presented in Table 2.

3 Organic Arsenic Compounds

There is a range of organic arsenic (oAs) compounds present, according to the metabolism and transformation of iAs into a less toxic form within the body of organisms. In marine creatures these oAs include arsenobetaine, tetramethylarsonium salts, arsenocholine, lipids (arsenolipids), and arsenic containing sugars (arsenosugars), even though some of these compounds have also been found in

Table 1 Identity of elemental arsenic

Periodic table:	Group 15 element
Atomic number:	33
Atomic mass:	74.91
Valence states:	-3, 0, +3, and +5
Chemical Abstract Service (CAS):	7440-38-2
National Institute for Occupational Safety	HSB 509
Health Registry of Toxic Effects of Chemicals (RTECS):	CG 05235 000
Hazardous Substances Data Bank (HSDB):	03300100X
UN transport class numbers:	UN 1558

terrestrial species (Table 3). The major sources of anthropogenic arsenic contamination of water, soil, and air are mining and smelting of nonferrous metals, burning of fossil fuels, coal-fired power generation plants, and indiscriminate use of arsenic-containing products (Carlin et al. 2016). Approximately 70% of the world arsenic production is used in manufacturing copper chrome arsenate (CCA) for wood/timber treatment and 22% in making a variety of herbicides, pesticide-like agricultural chemicals. Arsenic (As_2O_3) in the atmosphere mainly exists as adsorbed on particulate matter, which circulates and is returned to the Earth by wet or dry deposition and simultaneous oxidation and reconversion of arsenic to nonvolatile forms. In anoxic/reducing conditions, As(III) is thermodynamically stable, whereas As(V) is stable under more aerobic conditions, but they often co-occur in both anoxic and oxic soils and water (Anderson and Bruland 1991; Dowdle et al. 1996). Depending on the pH, redox potential (Eh), oxygen enrichment status, organic and other dissolved matter contents, clay particle composition, and biological processes (bacterial action), oxidation interchange may be effective between arsenate and arsenite species and can lead to potential arsenic release.

4 Arsenic Sinks and Iron Oxides

Abundantly present natural Fe(III) oxides (Fe(III) oxyhydroxides, Fe(III) hydroxides, and Fe(III) oxides) also play an important role as an arsenic sink (Hering and Kneebone 2001; Aide et al. 2016). Again, predominant biotransformations of arsenic species include interconversion between arsenite and arsenate, reduction and arsenic methylation, and organoarsenic biosynthesis. Because of relatively neutral pH, mobility of organoarsenicals is greater in sediment environments, generally contributing approximately 10% of the total arsenic in water (NRC 2001; Newman 2000). A schematic of configurations for the arsenic adsorbed on iron oxide surfaces follows (adopted from Cornell and Schwertmann 1996).

Table 2 Naturally occurring and environmentally important inorganic arsenic species (after Gomez-Camintero et al. 2001; WHO 2011)

	Name	CAS No.	Structure	
Naturally occurring arsenic species	Arsenate		AsO ₄ ³⁻	
	Arsenite		(different arsenite anions are known) AsO ₃ ³⁻ orthorsenite, [AsO ⁻²] ⁿ metarsenite, As ₂ O ₅ ⁴⁻ pyrorsenite, As ₃ O ₇ ⁵⁻ polyarsenite, As ₄ O ₉ ⁶⁻ polyarsenite, [As ₆ O ₁₁ ⁴⁻] ⁿ , polymeric anion	
	Methylarsonic acid/ monomethylarsonic acid/MMA	124-58-3	CH ₃ AsO ₃	
	Dimethylarsinic acid/cacodylic acid/DMA	75-60-5	C ₂ H ₇ AsO ₂	
	Trimethylarsine oxide	4964-14-1	C ₃ H ₉ AsO	
	Tetramethylarsonium ion	27742-38-7	C ₄ H ₁₂ As ⁺	
	Arsenobetaine	64436-13-1	C ₅ H ₁₁ AsO ₂	
	Arsenocholine	39895-81-3	C ₅ H ₁₄ AsO ⁺	
	Lead arsenate	10102-48-4	PbHAsO ₄	
	Potassium arsenate	7784-41-0	KH ₂ AsO ₄	
	Potassium arsenite	10124-50-2	KAsO ₂ HAsO ₂	
	Dimethylarsinoylribosides			
	Trialkylarsonioribosides			
	Dimethylarsinoylribitolsulfate			
Inorganic As, trivalent	As(III) oxide/As trioxide/ arsenous oxide/white As	1327-53-3	As ₂ O ₃ (or As ₄ O ₆)	
	Arsenenous acid/arsenious acid	13768-07-5	HAsO ₂	
	As(III) chloride/As trichloride/ arsenoustrichloride	7784-34-1	AsCl ₃	
	As(III) sulfide/As trisulfide orpiment/Auripigment	1303-33-9	As ₂ S ₃	
Inorganic As, pentavalent	As(V) oxide/As pentoxide	1303-28-2	As ₂ O ₅	
	Arsenic acid/ <i>ortho</i> arsenic acid		H ₃ AsO ₄	
	Arsenenic acid/ <i>meta</i> arsenic acid	10102-53-1	HAsO ₃	
	Arsenates/salts of <i>ortho</i> arsenic acid		H ₂ AsO ₄ ⁻ , HAsO ₄ ²⁻ , AsO ₄ ³⁻	
Mononuclear monodentate:		Fe	—O—	As
Mononuclear bidentate:		Fe<	O O>	As
Binonuclear bidentate:		Fe	—O—	As
		Fe	—O>	

Table 3 Naturally occurring and environmentally important organic arsenic species (after Gomez-Camirero et al. 2001)

	Name	CAS No.	Structure
Organic arsenic	Methylarsine	593-52-2	CH_3AsH_2
	Dimethylarsine	593-57-7	$(\text{CH}_3)_2\text{AsH}$
	Trimethylarsine	593-88-4	$(\text{CH}_3)_3\text{As}$
	(4aminophenyl) arsonic Acid/arsanilic acid/ <i>p</i> aminobenzenearsonic acid	98-50-0	
	4,4arsenobis(2aminophenol) Dihydrochloride/arsphenamine/salvarsan	139-93-5	
	[4[aminocarbonylamino]Phenyl] arsonic acid/ Carbarsone/ <i>nc</i> carbamoylearsanilic acid	121-59-5	
	[4[2amino2oxoethyl]amino]phenyl]arsonic acid/ tryparsamide	554-72-3	
	3nitro4hydroxyphenylarsonic acid	121-19-7	
	4nitrophenylarsonic acid/ <i>p</i> nitrophenylarsonic acid	98-72-6	
	Dialkylchloroarsine		R_2AsCl
	Alkyldichloroarsine		RAsCl_2

5 Volatile Arsenicals

Approximately 20 As species are arsines (AsH_3 , monomethylarsine- $((\text{CH}_3)\text{AsH}_2)$, dimethylarsine- $(\text{CH}_3)_2\text{AsH}$, trimethylarsine- $(\text{CH}_3)_3\text{As}$, and diarsine (As_2H_4) (bp:) with their boiling points -62.5 , -2 , $+36$, $+52$, and $+100^\circ\text{C}$, respectively (Planer-Friedrich et al. 2006). The complete methylated arsines constitute a volatile group of trivalent arsenic compounds that are partitioned into the atmosphere from aqueous solutions due to low (below 150°C) boiling points (Gong et al. 2002; Mestrot et al. 2013). Interestingly, arsine formation could well alleviate As poisoning. Global arsenic volatilization from land surfaces to the atmosphere has been estimated about 2.1×10^7 kg (Srivastava et al. 2011). Several microorganisms (bacteria, fungi, and algae) are capable of reducing intercellular As to form arsines (Mestrot et al. 2013; Yin et al. 2011a, b; Jia et al. 2012, 2013). In contact with HCl vapor, arsine can form volatile chloroarsine (AsCl_3), monomethylchloroarsine (CH_3) AsCl_2 , and dimethylchloroarsine $(\text{CH}_3)_2\text{AsCl}$ (Mester and Sturgeon 2001). Furthermore, volatile As-S and As-Cl species $((\text{CH}_3)_2\text{AsCl}$, $(\text{CH}_3)_2\text{AsSCH}_3$, and CH_3AsCl_2) have also been identified as some degree of microbial interaction for volatilization (Planer-Friedrich et al. 2006). Studies have shown that the toxicity of soluble inorganic and organic arsenic species in the order dimethylarsenite (DMAs(III)) and monomethylarsenite (MMAs(III)) $>$ As(III) $>$ As(V) $>$ dimethylarsenate, (DMAs(V)), monomethylarsenate (MMAs(V)) $>$ trimethylarsine (TMAs), trimethylarsine oxide (TMAsO) (Akter et al. 2005; Wang et al. 2014).

6 Arsenic Biogeochemical Cycle

Between organic and inorganic arsenic, iAs is of more interest due to its contribution to the biogeochemical cycle (Fig. 2), although involvement of organoarsenicals is insignificant. The iAs present in four oxidation states: As(III), As(0), As(III), and As(V). Microorganisms play a key role in the arsenic geocycle (Mukhopadhyay et al. 2002) by the processes of oxidation, reduction, methylation, and demethylation of arsenic species. However, microbial transformations between 3 and 5 oxidation states affect its mobility and speciation in the environment. To date various species belongs to different genera have been reported to be involved in arsenic chemistry. Some bacteria such as sulphate reducers and iron oxidizers are reported to precipitate As with their metabolic product out of the cell resulting in an insoluble form (Keimowitz et al. 2007; Battaglia-Brunet et al. 2012). Bacteria mediating Fe(II) oxidation through nitrate reduction in anoxic conditions have been shown to play a key role in arsenic cycling by forming solid hydrous ferric oxide on which As(V) (Senn and Hemond 2002; Hohmann et al. 2009) or As(III) (Gibney and Nusslein 2007; Hohmann et al. 2009) sorbs. As(III) can also be trapped with Fe(III), tightly bound to extracellular polymeric substances. Prokaryote metabolisms actively participated in mobilization of arsenic from the solid phase into the aqueous phase in a subsurface drinking water aquifer. Some fungi biotransform arsenic into volatile As gas (Pakulska and Czerczak 2006).

7 Environmental Transport and Distribution

The emission of arsenic into the atmosphere is either related to high-temperature processes (such as volcanic eruptions, coal-fired power generation plants, burning contaminated vegetation, etc.) or normal release through reduction and biomethylation to arsines (Mukhopadhyay et al. 2002). Arsenic (as As_2O_3) is primarily released into the atmosphere, adsorbed on particulate matter, circulated by the wind, and released to the Earth by dry or wet deposition. Similarly, the oxidation process in the air reconverts volatile arsines into the nonvolatile forms that settle back to the Earth. Arsenic species including arsenate, arsenite, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) are usually reported in water, with the thermodynamically more stable pentavalent state (arsenate) predominating in oxygenated water and sediments (Gomez-Caminero et al. 2001; David and Hemond 2002; Chen G et al. 2015; Chen Y et al. 2015). The interchange in oxidation and solubility of arsenic species depend upon various factors such as Eh, pH, soluble arsenic concentration, organic content, and biological activities. These factors further affect the environmental behavior of many arsenic species and subsequent transportation either by wind or by water (Gomez-Caminero et al. 2001). As discussed, the concentration of the arsenic level in the environment depends upon various factors. Mean total arsenic concentrations in air, water, soil, sediments, and marine water are represented in Table 4.

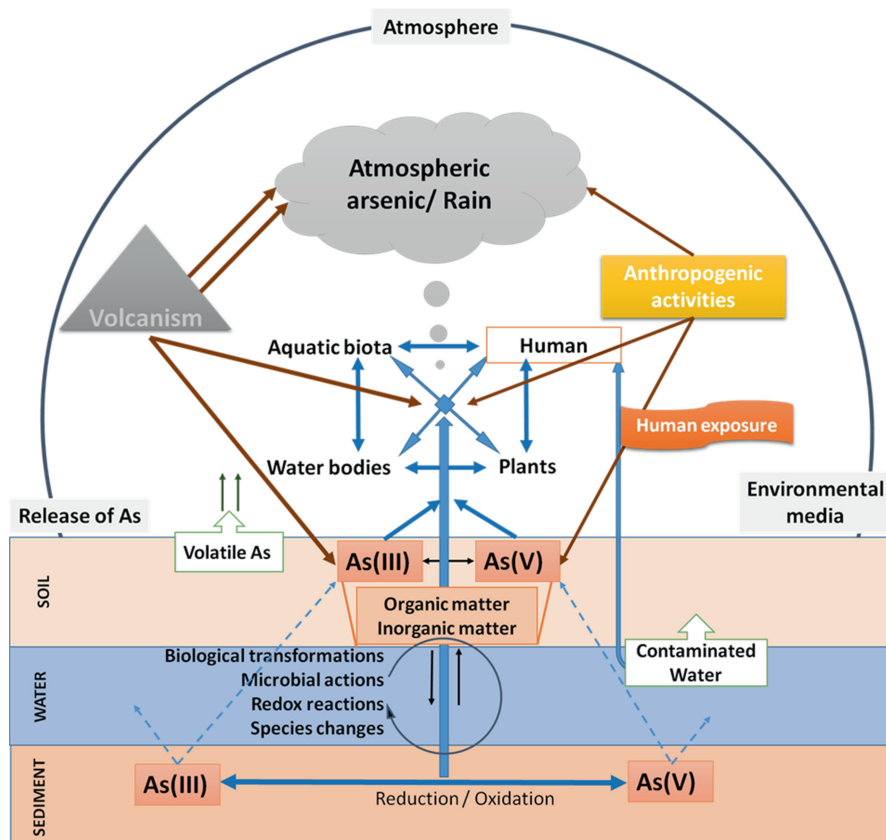


Fig. 2 Schematic representation of the biogeochemical cycle of arsenic

Arsenic concentrations in biota vary widely and depend upon exposure (higher in places with geothermal or anthropogenic sources) to arsenic. Bioconcentration factors (BCFs) in freshwater fish and invertebrates are less than for marine organisms regarding arsenic compounds (Chen G et al. 2015; Chen Y et al. 2015). Background arsenic concentrations in freshwater and terrestrial biota are usually less than 1 mg kg^{-1} (fresh weight). Root uptake or leaf-deposited arsenic and its subsequent adsorption leads to accumulations in terrestrial plants. Less than 1 mg kg^{-1} to more than 100 mg kg^{-1} arsenic compounds are reported to be present in marine biota with common compounds: arsenosugars (macroalgae) and arsenobetaine (invertebrates and fish; Gomez-Caminero et al. 2001; López-Serrano Oliver et al. 2011; Duan et al. 2015).

Human exposure to arsenic can either be occupational (industrial and other activities) or nonoccupational (contaminated water and food ingestion). There is hardly any limit for occupational exposure in small-scale unorganized industrial sectors, however, in workplaces with advanced occupational hygiene practices,

Table 4 Mean total arsenic concentrations in different components of environment

Components	Areas	Mean total arsenic concentrations
Air	Remote and rural areas	0.02–4 ng/m ³
	Urban areas	3–200 ng/m ³
	Vicinity of industrial sources	> 1000 ng/m ³
Freshwater	Rivers and lakes	<10 µg L ⁻¹ (vary widely)
	Groundwater	1–2 µg L ⁻¹
	Groundwater (areas with volcanic rock and sulfide mineral deposits)	3 mg L ⁻¹
Sediment	Natural	5–3000 mg kg ⁻¹
Soil	Natural	1–40 mg kg ⁻¹ , (mean ~ 5 mg kg ⁻¹)
	Contaminated due to human activities	Up to several grams per 100 ml
Ocean	Seawater	1–2 µg L ⁻¹

Adopted from, WHO 1987, 2011; USNRC 1999, 2001; Gomez-Caminero et al. 2001

exposure generally does not exceed 10 µg/m³ 8 h TWA (time-weighted average; Gomez-Caminero et al. 2001; Daria and Czerczak 2006; Rahman et al. 2013; Meliker et al. 2010). In nonoccupational exposures, ingestion and inhalation are the primary route of exposure. Although varying according to food stuff, approximately between 20 and 300 µg per person of total arsenic are being ingested daily (with 25% inorganic arsenic). Inorganic arsenic in cereals, poultry, meat, and dairy products is usually high, whereas in fish and shellfish is low. A smoker may be exposed to arsenic of approximately 10 µg day⁻¹ and a nonsmoker about 1 µg day⁻¹. The pulmonary exposure of arsenic may also vary according to the air quality of the ambience. Inorganic arsenic and its metabolite (MMA and DMA) concentration in individual urine usually ranges from 5 to 20 µg As L⁻¹, but may even exceed 1000 µg L⁻¹ (Gomez-Caminero et al. 2001; Rahman et al. 2013; Meliker et al. 2010).

8 Arsenic Kinetics and Metabolism

In general, the exposure route of arsenic in humans is ingestion, that is, oral intake of contaminated drinking water and food. Individuals who are occupationally exposed to arsenic are more prone to arsenic-related diseases. Typically less than 10 µg of arsenic is the standard for mean daily intake from drinking water. However, elevated arsenic concentrations in drinking water become a considerable source of inorganic arsenic within the body. Similarly, food stuffs are also important sources. In some circumstances where the drinking water requirement for preparation of food (such as rice, soups, or similar dishes) is obligatory, total arsenic ingestion occurs in even greater amounts (WHO 2011).

Ingested elemental arsenic is largely eliminated unchanged as it is poorly absorbed in the gut; however, soluble arsenic compounds are rapidly absorbed (Hindmarsh and McCurdy 1986), enter into the blood, and are rapidly and almost completely eliminated via kidney (especially arsenic(V) and organic arsenic; Buchet et al. 1981b; Luten et al. 1982; WHO 2011). Excess iAs is accumulated in the skin, liver, kidney, bone, and muscle (WHO 2011). Both the trivalent and pentavalent forms of arsenic are subjected to urinary excretion (half-life in humans is between 2 and 40 days; Pomroy et al. 1980). Sequential methylation to MMA and DMA in both As(III) and As(V) also takes place, but if daily intake exceeding more than 0.5 mg, saturates the process (Buchet et al. 1981b). Measuring the arsenic species in urine is the common technique to estimate the inner quantity of inorganic arsenic in individuals. Nonexposed individuals are reported generally having lower than 10 $\mu\text{g L}^{-1}$ arsenic in urine, whereas in highly exposed individuals from areas such as West Bengal, India, and Bangladesh, urinary arsenic concentrations above 1 mg-L^{-1} have been observed (IPCS 2001; WHO 2011)

9 Arsenic Volatilization by Microorganisms

Several microorganisms including bacteria, archaea, fungi, and a couple of eukaryotes are capable of volatilizing arsenic (Table 5).

9.1 Fungi

A number of fungi are known to metabolize arsenicals into its volatile forms. The involvement of fungi and arsenical poisoning came into the picture after severe cases were reported in Germany and other parts of Europe as early as 1815 (Challenger 1945; Bartrip 1994). At that time, arsenical pigments (including Scheele's green (copper arsenite), Schweinfurt green (Paris green), Emerald green (copper acetoarsenite), and Vienna green contained in paints and wallpapers (because arsenic has an insecticidal property) were widely used in houses (Meharg 2003). In damp conditions, these arsenicals usually produce toxic compounds as fungi develop. The Italian physician, Bartolomeo Gosio, first reported the involvement of certain fungi (*Mucormucedo* [sic] and subsequent report of *Penicillium brevicaulis*) in converting iAs into garlic-smelling volatile arsenicals (Gosio 1892a, b, 1893). This volatile garlic-odor toxic gas was called Gosio gas and identified as TMA (Challenger et al. 1933). Different studies have identified a long list of fungal species, including *Aspergillus glaucus*, *A. virens*, *A. niger*, *A. clavatus*, *Neosartorya fischeri*, *Mucor ramosus*, *Gliocladium roseum*, *Penicillium* sp., *Fusarium oxysporum*, *Trichoderma asperellum*, *Cephalothecium roseum*, *Trichoderma* sp., *Neocosmospora* sp., *Rhizopus* sp., and *Sterigmatocystis ochracea*, having the capability to volatilize arsenic (Bentley and Chasteen 2002; Urik et al. 2007; Cernansky

et al. 2009; Su et al. 2010; Srivastava et al. 2011; Wang et al. 2014). The efficiency of arsenic volatilization of these fungi may vary with species and the conditions of the ambience, with a mean from 3 to 30% (Srivastava et al. 2011; Wang et al. 2014).

9.2 Bacteria

Woolson and Kearney (1973) first reported arsenic volatilization from soil under anaerobic flooded conditions. With the decrease in redox potential (Eh), soil arsenic methylation increases, signifying efficient arsenic volatilization in anaerobic conditions (Frohne et al. 2011). Reports indicate a number of intestinal microbiota, dominated by anaerobic bacteria and archaea thriving in different anaerobic conditions have the capability to volatilize arsenicals (Eckburg et al. 2005; Meyer et al. 2007; Sun et al. 2016). Michalke et al. (2008) reported that the arsines are produced in the human intestine ranging from a rate of $0.7\text{--}5\text{ }\mu\text{mol h}^{-1}\text{ kg}^{-1}$ (dry weight), and the total As content of the samples was about $1.3\text{ }\mu\text{mol kg}^{-1}$ (dry weight) (Michalke et al. 2008; Wang et al. 2014). In another study on a simulated in vitro gastrointestinal model SHIME (simulator of the human intestinal microbial ecosystem), it has been reported that the human gut microbiome has the capacity of volatilization of metal(loid)s including arsenic (Van de Wiele et al. 2010).

Furthermore, several aerobic bacteria were also reported to volatilize arsenic. Bacterium of the Flavobacterium–Cytophaga group have been shown to generate TMA in the gas phase from a medium containing As(III; Honschopp et al. 1996). Majumder et al. (2013) reported arsenic volatilizing native soil bacteria (aerobic, anaerobic, and facultative), having the capacity to volatilize more than 30% of iAs in three days. Cyanobacteria, the lifeforms especially abundant in freshwaters and soils play an important role in the biogeochemical cycling of arsenic in aquatic systems (Yin et al. 2011a). The reported bacterial species (Table 5) include *Corynebacterium* sp., *E. coli*, *Proteus* sp., *Achromobacter* sp., *Aeromonas* sp., *Alcaligenes* sp., *Flavobacterium* sp., *Pseudomonas* sp., *Nocardia* sp., *Clostridium collagenovorans*, *Desulfovibrio gigas*, *D. Vulgaris*, and *Staphylococcus aureus* (Shariatpanahi et al. 1981; Wickenheiser et al. 1998; Michalke et al. 2000; Wang et al. 2014).

9.3 Methanoarchaea

In strict anaerobic conditions (such as in human and animal gut, wetland mud, etc.), methanogens (archaea) and sulphate-reducing bacteria (SRB) are other groups that can volatilize arsenic (Michalke et al. 2000). Methanoarchaea have the innate characteristic of volatilizing arsenic, which is very similar to the production of methane, where methylcobalamin acts as a methyl donor (Thomas et al. 2011). Among other methanobacteria, *Methanobacterium formicum*, *Methanosphaera stadtmanae*,

Table 5 Different microbes and their activity for production of volatile arsenic species

Arsenic species (volatile)	Species	Substrate
<i>Bacteria</i>		
Dimethylarsine	<i>Corynebacterium</i> sp.	Arsenate
	<i>Escherichia coli</i>	
	<i>Proteus</i> sp.	
Mono-, di-, and trimethylarsine; arsine	<i>Pseudomonas</i> sp.	Methylarsonate, arsenate
	<i>Nocardia</i> sp.	Methylarsonate
Mono- and dimethylarsine	<i>Achromobacter</i> sp	
	<i>Aeromonas</i> sp.	
	<i>Alcaligenes</i> sp.	Arsenate, arsenite, methylarsonate
	<i>Flavobacterium</i> sp.	Methylarsonate
	<i>Enterobacter</i> sp.	
Trimethylarsine	<i>Veillonella alcalescens</i>	Trimethylarsine oxide
	<i>Streptococcus sanguis</i>	
	<i>Fusobacterium nucleatum</i>	
	<i>Bacillus subtilis</i>	
	<i>Staphylococcus aureus</i>	
	<i>Flavobacterium cytophaga</i>	Arsenite
	<i>Clostridium collagenovorans</i>	
	<i>Desulfovibrio gigas</i>	
	<i>Desulfovibrio vulgaris</i>	
	<i>Rhodopseudomonas palustris</i>	Arsenate or arsenite
<i>Methanoarchaea</i>		
Arsine	<i>Methanothermobacter thermautotrophicus</i>	Arsenate
	<i>Methanobacterium barkeri</i>	
Di- and trimethylarsine	<i>Methanosphaera stadtmanae</i>	
Mono-, di- and trimethylarsine	<i>Methanococcus vanniellii</i>	
	<i>Methanobacterium formicicum</i>	
	<i>Methanobrevibacter smithii</i>	
Trimethylarsine	<i>Methanoplanus limicola</i>	
	<i>Methanosarcina mazei</i>	
<i>Eukaryotic microorganisms</i>		
Trimethylarsine	<i>Cyanidioschyzon</i> sp.	Arsenite
	<i>Microcystis</i> sp.	
	<i>Nostoc</i> sp.	
	<i>Synechocystis</i> sp.	
Total volatile arsenic	<i>Tetrahymena pyriformis</i>	
<i>Fungi</i>		

(continued)

Table 5 (continued)

Arsenic species (volatile)	Species	Substrate
Trimethylarsine	<i>Penicillium brevicaula</i>	Arsenic acid, monomethylarsonic acid
	<i>Mucormucedo</i>	
	<i>Cephalothecium</i>	
	<i>Sterigmata cystis</i>	
	<i>Paecilomyces</i>	Methylarsonate, dimethylarsinate
	<i>Gliocladium roseum</i>	
	<i>Candida humicola</i>	Trimethylarsine arsenate, arsenite and methylarsonate, dimethylarsinate
	<i>Rhodotorula rubra</i>	Arsenic trioxide
	<i>Aspergillus glaucus</i>	
	<i>Aspergillus versicolor</i>	Monomethylarsonic acid
	<i>Penicillium chrysogenum</i>	
	<i>Penicillium notatum</i>	
	<i>Aspergillus fischeri</i>	
Total volatile arsenic	<i>Ulocladium</i> sp.	Arsenate
	<i>Neocosmospora</i> sp.	
	<i>Rhizopus</i> sp.	
	<i>Aspergillus clavatus</i>	Arsenic acid
	<i>Aspergillus niger</i>	
	<i>Trichoderma viride</i>	
	<i>Penicillium glabrum</i>	
	<i>Neosartorya fischeri</i>	Arsenate or arsenite
	<i>Fusarium oxysporum</i>	

Adopted from: Wang et al. 2014

Methanobrevibacter smithii, and *Methanococcus vannielii* are reported to produce volatile arsenic compounds, MeAsH_2 , Me_2AsH , and TMAs; *Methanobacterium barkeri*, *M. thermoautotrophicum*, and *M. formicicum* produce AsH_3 (Meyer et al. 2008; Wang et al. 2014).

9.4 Other Eukaryotic Microorganisms

The involvement of eukaryotic microorganisms, including aquatic alga and protozoans also has the capacity to volatilize arsenic. Qin et al. (2009) reported thermoacidophilic eukaryotic alga, *Cyanidioschyzon* sp., can reduce and methylate iAs to TMAs and DMAs at an optimal temperature of 60–70°C. There are other species such as marine green microalgae, *Ostreococcus tauri*, *Cyanidioschyzon* sp., that have the capacity through unique algal methyltransferases to methylate iAs

(Qin et al. 2009; Zhang et al. 2013). *Tetrahymena pyriformis*, a freshwater eukaryotic protozoan, is also capable of methylating iAs (Yin et al. 2011a, b; Zhang et al. 2012; Wang et al. 2014).

10 Analytical Methods for Arsenic Detection

Analysis for arsenic content of water and other environmental samples as well as food stuffs is an important issue as it is directly correlated with key decision making regarding the maximum contaminant level (MCL). Recently, the World Health Organization (WHO) recommended a guideline value of $10 \mu\text{g L}^{-1}$ (10 ppb) arsenic in drinking water and considers all dissimilar arsenic species irrespective of their toxicity. However, guidelines for other environmental samples such as soil, sludge, and foodstuffs vary widely. In the United Kingdom, the value of arsenic content in domestic gardens, allotments, and play areas is 10 mg kg^{-1} , whereas landscapes and building hardcovers have a threshold of 40 mg kg^{-1} . But in Canada, the minimum value for contaminated soil is 12 mg kg^{-1} , soil for agriculture use 20 mg kg^{-1} , parkland 30 mg kg^{-1} , and commercial and industrial land 50 mg kg^{-1} (CCME 2003; Francesconi 2007). Australia established a guideline value of foodstuffs as 1 mg kg^{-1} for total arsenic. In addition, some countries, such as China have incorporated import recommendations (for food items including rice) based on inorganic arsenic (Williams et al. 2005; Hossain et al. 2009; Garnier et al. 2010). Therefore, it is important to note that for any analytical instrument or analysis methodologies, performance parameters will vary according to the requirements. The qualitative and quantitative determination of arsenic in environmental samples (Table 6) should concentrate on maximum sensitivity, accuracy, user friendly, cost-effective technology with high throughput (Feldmann and Salaun 2008; Flora 2014).

10.1 Sample Preparation and Treatment

The collection of samples is the very first important step for appropriate measurement of arsenic present in the sample. Collection bottles must be cleaned properly before use to avoid contamination and avert speciation changes of the sample during transportation to the laboratory and storage before examination. (Freezing at -80°C is recommended.) Concentrated HCl may be added to biological fluid samples (such as urine) to prevent bacterial growth. Several types of filters (including polytetrafluoroethylene, glass microfiber, and cellulose ester) are used in sampling aerosol particles (Crecelius 1986; Tripathi et al. 1997; Gomez-Caminero et al. 2001; Hughes et al. 2011; Tripathi et al. 2012). Oxidative digestion (acid digestion, dry ashing, and microwave digestion) of samples is required before analysis (George and Roscoe 1951; George et al. 1973; Thomas et al. 1997).

A solvent extraction process may be followed for speciation study on arsenic (arsenite and arsenate). Several researchers have followed different techniques and

Table 6 Representing major methods used for analysis of different arsenic-containing samples

Method/instrument used	Samples for arsenic analysis
HGAAS	Blood, hair, urine, nails, food, water, air
NAA	Serum, urine, water
Colorimetric photometry	Urine, water/soil
XRF	Urine, soil, rock, sediments
GFAAS	Soft tissues, food, air
IEC-HGAAS	Urine
AES (direct current plasma)	Urine
HGAAS/TLC/ HRMS	Urine
GLC/ECD	Blood, tissue
HPLC/ICP-MS	Blood, tissue, urine, organism, food
HG-HCT/GC-MID	Water/soil
AAS	Water/soil
ICP-AES/ ICP-MS	Air/water/soil/ sediments/ solid wastes

Adopted from Gomez-Caminero et al. 2001; Feldmann and Salaun 2008

AAS atomic absorption spectrophotometry, AES atomic emission spectroscopy, GC-MID gas chromatography-multiple ion detection, GFAAS graphite furnace atomic absorption spectrometry, HGAAS hydride generation-atomic absorption spectroscopy, HG-HCT hydride generation-heptane cold trap, HPLC high-performance liquid chromatography, ICP-AES inductively coupled plasma-atomic emission spectrometry, ICP-MS inductively coupled plasma-mass spectrometry, IEC ion exchange chromatography, NAA neutron activation analysis, XRF X-ray fluorescence

chemicals to extract the arsenic compounds, which include chloroform, methanol-based extraction, extraction by ultrasonic treatment, selective chelation by sodium bis(trifluoroethyl) dithiocarbamate (NaFDDC), gas chromatograph (GC) detection, or supercritical fluid chromatography (SFC) detection (Hansen et al. 1992; Kuehnelt et al. 1997; Ng et al. 1998a, b).

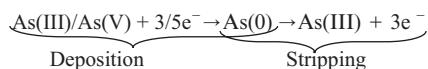
10.2 Atomic Spectrometry-Based Methods

Laboratory detection of total arsenic can be accomplished using atomic spectrometric techniques such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS). These techniques are highly sensitive and accurate and can be used in a quality assurance/quality control (QA/QC) system (detection limit: sub- $\mu\text{g L}^{-1}$ with $\pm 10\%$ accuracy) for detection of total arsenic, but are extremely expensive and require controlled laboratory practices including a skilled operator and stable power supplies (thus they are not suitable for field applications). Again, qualitative determination of contamination at the species level cannot be done unless coupled with other expensive instruments such as high-performance liquid chromatography (HPLC) or gas chromatography (GC; Feldmann and Salaun 2008; Duflou et al. 1987).

10.3 Electrochemical Detection

Stripping analysis is the basis of electroanalysis, where arsenic in samples accumulates on the surface of the working electrode (WE) by generating deposition potential (*E*_{dep}). The accumulated arsenic is then measured using potentiometric or voltammetry methods. This laboratory-based technique is a highly sensitive one (detection limit: sub- $\mu\text{g L}^{-1}$); cathodic stripping voltammetry (CSV) at a hanging mercury drop electrode (HMDE) is commonly used for arsenic detection (Holak 1980; Rasul et al. 2002; He et al. 2004; Muñoz and Palmero 2005). However, this technique consumes a high amount of mercury and is relatively complex and therefore not very acceptable for field conditions (Feldmann and Salaun 2008; Luong et al. 2014).

However, the use of solid electrodes is better for field conditions if anodic stripping voltammetry (ASV) or potentiometric stripping analysis (PSA; Muñoz and Palmero 2005) is utilized.



In both cases, arsenic is deposited at a negative potential (As 0) and stripped back into solution either by sweeping the potential anodically (ASV) or by enforcing a continuous anodic current (CCPSA). Stripping is generally done under high acidic conditions (HCl is the electrolyte; Muñoz and Palmero 2005; Salaün et al. 2007; Feldmann and Salaun 2008). But the deterioration of the electrode is common due to strong hydrogen and chlorine generation and the formation of gold–chloride complexes (Feldmann and Salaun 2008). A few studies reported arsenite detection only under neutral or alkaline conditions with comparatively low deposition potential (Salaün et al. 2007).

Interference by metals such as Fe, Bi, Cu, Ni, Se, Sb, Hg, and Zn is common, affecting the analysis of arsenic in natural samples. Electrodes are also affected by dissolved organic matter (humic acid, fulvic acid); surfactants form intermetallic compounds and interfere strongly by adsorbing on the electrode surface and obstructing the electron transfer reaction (Feldmann and Salaun 2008). Proper sample preparation to protect the electrode against adsorption is necessary for the accurate measurement of arsenic (Majid et al. 2006). There are different brands of electrochemical-based measurement systems available on the market that are potentially applicable for field measurement (Feldmann and Salaun 2008).

10.4 Radiochemical Methods

Neutron activation analysis (NAA) is a radiochemical method (first reported by Orvini et al. 1974) for determination of arsenic, zinc, selenium, cadmium, and mercury. A variety of samples and standard reference materials was analyzed by the

technique with a recovery of 98–100% (Chutke et al. 1994; Landsberger and Wu 1995; Gomez-Caminero et al. 2001; Calderon et al. 2013).

10.5 X-Ray Spectroscopy

PIXE (particle-induced X-ray emission) spectrometry and XRF (X-ray fluorescence) spectroscopy are important multielemental detection techniques. In PIXE, the sample (target) is bombarded with charged particles resulting in the emission of characteristic X-rays of the elements present with a detection limit of approximately $0.1 \mu\text{g As g}^{-1}$. PIXE is a nondestructive technique that requires small samples (1 mg or less) and can be used for a wide range of environmental samples (Maenhaut 1987). Similarly, XRF is also widely used for the determination of arsenite and arsenate with a detection limit of 3.1 ng g^{-1} (Hagiwara et al. 2015; Sánchez-Rodas et al. 2015). X-ray absorption fine structure (XAFS) spectroscopy is another technique capable of detecting speciation data at realistic concentrations of 10–100 mg kg^{-1} (Huffman et al. 1993; Gomez-Caminero et al. 2001; Wang et al. 2011; Rouff et al. 2016).

11 Conclusion

The problem of arsenic in drinking water, food stuffs, and so on is growing day by day. Chronic exposure and/or ingestion of arsenic can cause a range of diseases such as skin lesions, diseases of the respiratory system, nervous system, reproductive system, cancer, and painful death. Development of appropriate, cost-effective, user-friendly field technology for assessing arsenic in environmental samples, water, and biological samples such as urine and blood is urgently required. Only concerted efforts from different sectors, including engineers, scientists, social scientists, government, and nongovernmental organizations along with the political willingness to curb the grave problem by developing, implementing, and monitoring better technologies can save humanity from this mass poisoning.

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