



Review article

Aquatic arsenic: Toxicity, speciation, transformations, and remediation

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ABSTRACT

This paper reviews the current knowledge on the toxicity, speciation and biogeochemistry of arsenic in aquatic environmental systems. The toxicity of arsenic is highly dependent on the chemical speciation. The effects of pH, E_h , adsorbing surfaces, biological mediation, organic matter, and key inorganic substances such as sulfide and phosphate combine in a complex and interwoven dynamic fashion to produce unique assemblages of arsenic species. The number of different arsenic species found in environmental samples and an understanding of the transformations between arsenic species has increased over the past few decades as a result of new and refined analytical methods. Changes in arsenic speciation and in total arsenic content of foods upon processing have suggested possible risks associated with processed and unprocessed food. Arsenic removal from water using adsorbents, chemical oxidation, photolysis and photocatalytic oxidation techniques is also reviewed.

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1. Introduction

Arsenic (As, atomic number = 33) is a ubiquitous element, which occurs naturally in the earth's crust. It ranks 20th in natural abundance, 14th in seawater, and 12th in the human body (Mandal

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Table 1
Some arsenic compounds of environmental interest.

Name	Formula or structure	Name	Formula or structure
Methylarsine	CH ₃ AsH ₂	Arsenobetaine	(CH ₃) ₃ As ⁺ CH ₂ COO ⁻ , AB
Dimethylarsine	(CH ₃) ₂ AsH	Arsenocholine	(CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH, AC
Trimethylarsine	(CH ₃) ₃ As	Dimethylarsinoylribosides	1–11
Monomethylarsonic acid	CH ₃ AsO(OH) ₂ , MMA ^V	Triaklylarsonioribosides	12, 13
Monomethylarsenous acid	CH ₃ As(OH) ₂ , MMA ^{III}	Dimethylarsonoutritol sulfate	14
Dimethylarsinic acid	(CH ₃) ₂ AsO(OH), DMA ^V	Glycerophosphorarsenocholine	15
Dimethylarsenous acid	(CH ₃) ₂ AsOH, DMA ^{III}	Glycerophosphatidylarsenocholine	16
Trimethylarsinic oxide	(CH ₃) ₃ AsO, TMAO		
Tetramethylarsonium ion	(CH ₃) ₄ As ⁺ , TMA ⁺		

and Suzuki, 2002). Since its isolation in 1250 A.D., it has been used in various fields such as medicine, electronics, agriculture and metallurgy (Nriagu and Azcue, 1990). More than 245 minerals contain arsenic and although the ultimate source of arsenic is geological, human activities such as mining, the burning of fossil fuels, and pesticide application, also cause arsenic pollution (Bissen and Frimmel, 2003a,b). Arsenic exists in four oxidation states, +V (arsenate), +III (arsenite), 0 (arsenic), and –III (arsine). In addition to arsenite, arsenate, and their methylated derivatives, there are “fish arsenic” (arsenobetaine, AB and arsenocholine, AC) and arsenosugar compounds of environmental interest (Ng, 2005). The molecular formulae of organic arsenic compounds are given in Table 1 and structures of arsenosugars are provided in Fig. 1.

Both inorganic and organic forms of arsenic have been determined in water (IPCS, 2001). Early work on the formation of methylated As species was reviewed several decades ago (Challenger, 1945). Methylated As species are formed through arsenic metabolism using S-adenosyl methionine (SAM) as a methyl donor and glutathione (GSH) as an essential co-factor (Vahter, 1994). This process is responsible for the reported presence of MMA^V and DMA^V (abbreviations and structures shown in Table 1) in human urine as well as in seashells and eggshells (Braman and Foreback, 1973). Most of the organic compounds given in Table 1 have been found in marine and terrestrial systems (Francesconi and Edmonds, 1997; Grotti et al., 2008). The occurrence of organoarsenic compounds in fish and other aquatic fauna and flora has been shown in several studies (Francesconi et al., 1994; Maeda, 1994; Geislinger et al., 2002; Schmeisser et al., 2004; Kahn et al., 2005; Meier et al., 2005; Soeroes et al., 2005; Schaeffer et al., 2006; Jankong et al., 2007; Grotti et al., 2008). It is noteworthy that arsenobetaine, which is the most commonly reported organoarsenic in marine animals, is virtually absent in the vertebrate and invertebrate freshwater organisms analyzed by Schaeffer et al. (2006). This represents the major difference in arsenic speciation between marine and freshwater organisms. Recently, arsenolipids have been found in cod fish oil; causing human health concerns (Rumpler et al., 2008).

In seawater, the concentration of arsenic is usually less than 2 µg L⁻¹ (Ng, 2005). The levels of arsenic in unpolluted surface water and groundwater vary typically from 1–10 µg L⁻¹. In freshwater, the variation is in the range of 0.15–0.45 µg L⁻¹ (Bissen and Frimmel, 2003a,b). In thermal waters, concentrations of upto 8.5 mg L⁻¹ and 1.8–6.4 mg L⁻¹ have been reported in New Zealand and Japan, respectively (Ritchie, 1961; Nakahara et al., 1978). Natural geological sources of As to drinking water are one of the most significant causes of arsenic contamination around the world. Arsenic contamination in different parts of the world is summarized in Table 2. The World Health Organization (WHO) has set a guideline of 10 µg L⁻¹ as the drinking water standard. As Table 2 suggests, arsenic imposes significant risks to the health of people of many different countries. As many as 60–100 million people globally may be at risk of exposure to excessive levels of arsenic (Ng et al., 2003).

This review presents a detailed summary of the current knowledge of arsenic biogeochemistry in natural water systems. Fairly current reviews on arsenic geochemistry of aquatic systems (Korte and

Fernando, 1991; Smedley and Kinniburgh, 2002) have focused on groundwater geochemistry because of the importance of groundwater as a source of drinking water and because some of the highest natural levels of aquatic arsenic are found in these waters. This review focuses on fresh and marine waters and describes concentrations and speciation of arsenic as affected by pH, E_h, organic matter, key inorganic substances such as phosphate and sulfide, and adsorbents. A thorough review of the knowledge of changes in arsenic speciation in food as a function of processing is also presented along with a thorough discussion of arsenic contaminated water remediation with a special focus on chemical, catalytic, and photocatalytic strategies.

2. Toxicity of inorganic and organic arsenic species

Arsenic is toxic to both plants and animals and inorganic arsenicals are proven carcinogens in humans (Ng, 2005). The toxicity of arsenic to human health ranges from skin lesions to cancer of the brain, liver, kidney, and stomach (Smith et al., 1992). A wide range of arsenic toxicity has been determined that depends on arsenic speciation. Generally inorganic arsenic species are more toxic than organic forms to living organisms, including humans and other animals (Goessler and Kuehnelt, 2002; Meharg and Hartley-Whitaker, 2002; Ng, 2005). The oral LD₅₀ for inorganic arsenic ranges from 15–293 mg (As) kg⁻¹ and 11–150 mg (As) kg⁻¹ bodyweight in rats and other laboratory animals respectively (Done and Peart, 1971; Ng, 2005). Exposure to arsenic trioxide by ingestion of 70–80 mg has been reported to be fatal for humans (Vallee et al., 1960). Arsenite (iAs^{III}) is usually more toxic than arsenate (iAs^V). Recent studies found that MMA^{III} and DMA^{III} are more acutely toxic and more genotoxic than their parent compounds (Mass et al., 2001; Petrick et al., 1993, 2000). These trivalent arsenicals are more toxic than iAs^V, MMA^V, and DMA^V in vitro (Styblo et al., 2000; Mass et al., 2001). This may be related to more efficient uptake of trivalent methylated arsenicals than of pentavalent arsenicals by microvessel endothelial cells and CHO (Chinese Hamster Ovary) cells (Hirano et al., 2003; Dopp et al., 2004). Recently, LC₅₀ values were calculated as 571, 843, 5.49, and 2.16 µM for iAs^V, DMA^V, iAs^{III}, and DMA^{III}, respectively, for human cells (Naranmandura et al., 2007). This study also showed that dimethylmonothioarsenic (DMMTA^V) is much more toxic than other pentavalent nonthiolated arsenicals (Naranmandura et al., 2007).

The toxicity of trivalent arsenic is related to its high affinity for the sulfhydryl groups of biomolecules such as glutathione (GSH) and lipoic acid and the cysteinyl residues of many enzymes (Aposhian and Aposhian, 2006). The formation of As(III)–sulfur bonds results in various harmful effects by inhibiting the activities of enzymes such as glutathione reductase, glutathione peroxidases, thioredoxin reductase, and thioredoxin peroxidase (Schuliga et al., 2002; Wang et al., 1997; Lin et al., 2001; Chang et al., 2003). An example of As^{III}–S bond formation is the 1:3 complex of As with Cys-containing tripeptide GSH, which has an unusually high stability constant (Rey et al., 2004). Such As^{III}–GSH conjugates have been detected in the bile of rats (Suzuki et al., 2001). Stable arsenic complexes with the common reductant, dithioerythritol, and other dithiols, are known

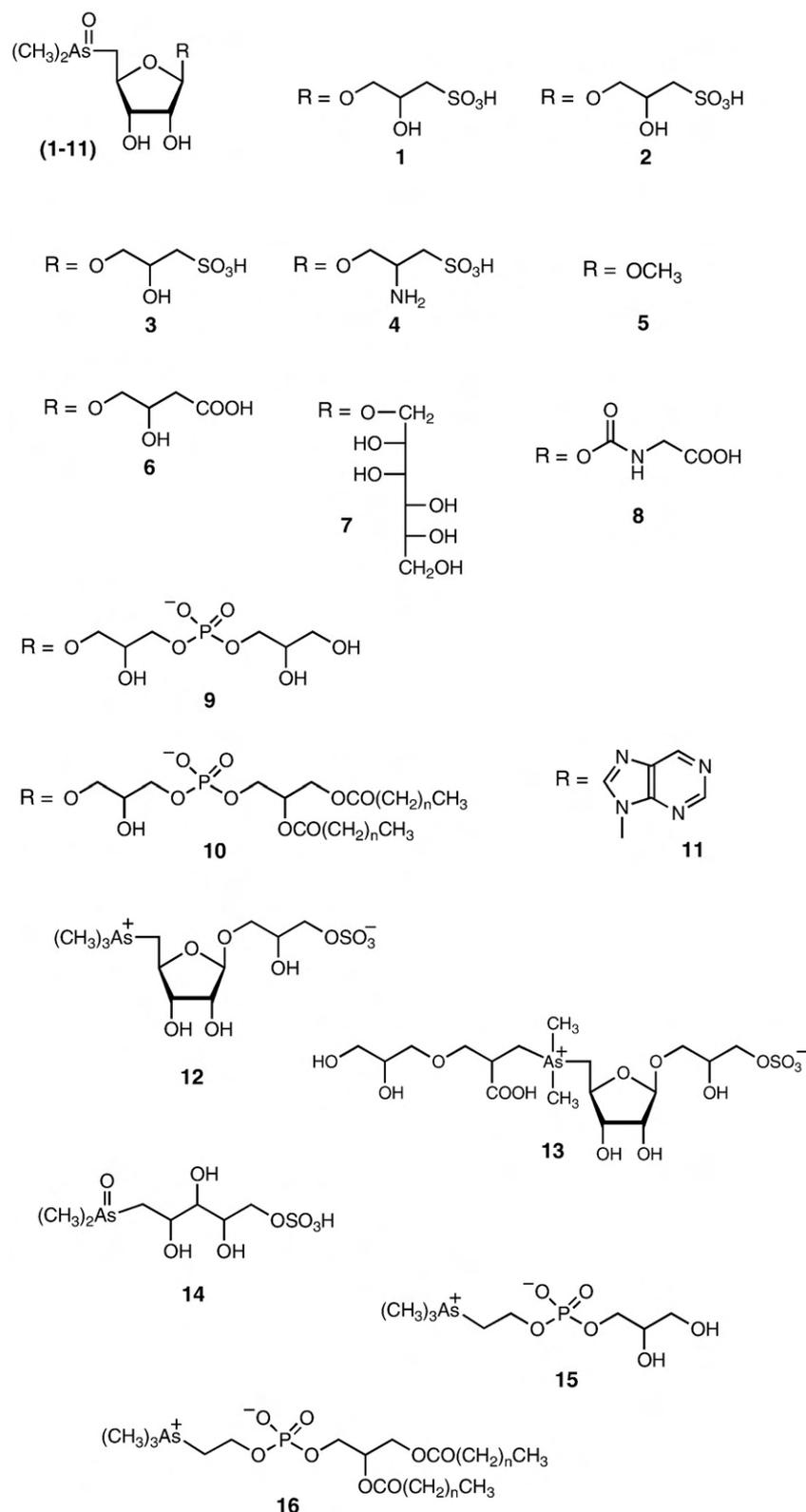


Fig. 1. Examples of structures of arsenosugars, 1–16 of Table 1 (modified from Ng, 2005 with permission of CSIRO).

to exist (Zahler and Cleland, 1968; Kolozsi et al., 2008). The higher toxicity of MMA^{III} than iAs^{III} may be caused by a higher affinity of MMA^{III} for thiol ligands in biological binding sites than As^{III} -thiolate complexes (Spuches et al., 2005). DMA^{III} also forms complexes with sulfur-rich proteins (Shiobara et al., 2001; Naranmandura et al., 2006).

It is generally accepted that pentavalent arsenicals do not directly bind to sulfhydryl groups to cause toxic effects (Suzuki et al., 2008). However, a recent study reported that sulfide-activated pentavalent arsenic could bind to the sulfhydryl group of GSH (Raab et al., 2007). An exposure of DMA^{V} to cabbage (*Brassica oleracea*) gave dimethylmonothioarsinic acid-GSH conjugate (DMMTA^{V} -GSH). DMMTA^{V} was

Table 2
Continent of arsenic in different parts of the world.

Continent	Location	Arsenic source	Conc. $\mu\text{g L}^{-1}$	Sampling period	Reference
Americas	Pampa, Cordoba, Argentina	2–15 m	100–3810	Not stated	Nicolli et al. (1989)
	Cordoba, Argentina		>100		Astolfi et al. (1981)
	Chile		470–770		United Nations (2001)
	Lagunera region, Mexico	Well waters	8–624	Not Sated	Razo et al. (1990)
	Peru	Drinking water	500	1984	Sancha and Castro (2001)
	Northeastern Ohio	Natural origin	<1–100	Not Stated	Matisoff et al. (1982)
	Western USA	Drinking water	1–48,000	1988	Welch et al. (1988)
Europe	Hungary	Deep groundwater	1–174	1974	Sancha and Castro (2001)
	Romania	Drinking water bores	1–176	2001	Gurzau and Gurzau (2001)
	South-west Finland	Well waters; natural origin	17–980	1993–1994	Kurttio et al. (1998)
Asia	Bangladesh	Well waters	<10–>1000	1996–1997	Dhar et al., 1997
	Calcutta, India	Near pesticide production plant	<50–23,080	1990–1997	Mandal et al. (1996)
	West Bengal, India	Arsenic-rich sediments	3–3700	1989–1996	Mandal et al. (1996)
	Nepal	Drinking water	8–2660	2001	Shrestha et al. (2003)
	Hanoi, Vietnam	Arsenic-rich sediments	1–3050	1999–2000	Berg et al. (2001)
	Xinjiang, PR China	Well water	0.05–850	1983	Yinlong (2001)
	Shanxi, PR China	Well water	0.03–1.41	Not Stated	Yinlong (2001)
	Inner Mongolia, China	Drinking water; bores	1–2400	1990s	Guo et al. (2001)
	Ronpibool, Thailand	Water contaminated by tin mining waste	1–5000	1980s	Choprapwon and Porapaktham (2001)
	Nakhon Si Thammarat Province, Thailand	Shallow (alluvial) groundwater, mining	1.25–5114	1994	Williams et al. (1996)
	Fukuoka, Japan	Natural origin	0.001–0.293	1994	Kondo et al. (1999)
Mekong River floodplain, Cambodia	Groundwater	1–1340	2004–2006	Buschmann et al. (2007)	

found in the urine of arsenic-exposed humans and animals (Raml et al., 2007; Naranmandura et al., 2007) and showed distinct behavior and toxicity *in vivo* and *in vitro* relative to those of the corresponding oxo acids (Suzuki et al., 2007; Naranmandura et al., 2007; Raml et al., 2007). Interestingly, DMMTA^V demonstrated a significantly higher cytotoxicity than nonthiolated DMA^V (Raab et al., 2007; Raml et al., 2007). Moreover, the toxicity of DMMTA^V is comparable to that of trivalent arsenicals. The toxicity of DMMTA^V may be caused by the production of reactive oxygen species (ROS) during its exposure, which may cause mutagenesis and DNA damage, initiating cancer (Kitchin, 2001). A mechanism has been proposed to suggest the production of ROS through the redox equilibrium between DMA^V and DMA^{III} in the presence of GSH (Naranmandura et al., 2007; Suzuki et al., 2008).

3. Analysis of inorganic and organic arsenic species

Currently, HPLC-ICPMS (High Performance Liquid Chromatography – Inductively Coupled Plasma Mass Spectrometry) is the most commonly utilized technique for arsenic speciation analysis, which quantifies virtually all environmentally relevant forms of arsenic at appropriate concentration ranges. Atomic absorption by either hydride generation or heated graphite atomizer is also routinely used in many laboratories. One of the interesting developments in analytical methods for inorganic and organic As species is the inclusion of UV-irradiation of the sample prior to measurement of As, which overcomes the inability of some organoarsenic compounds to form volatile hydrides (Cullen and Dodd, 1988; Atallah and Kalman, 1991; De Bettencourt and Andrae, 1991; Howard and Hunt, 1993). An average 25% increase in the concentration of total dissolved As in coastal marine waters was found in analysis conducted by hydride generation atomic absorption spectrophotometry after sample UV-irradiation (Howard and Comber, 1989). This increase was attributed to arsenosugars and related breakdown products, which do not all form volatile species when reduced with borohydride. Average increases in MMA^V and DMA^V of 47% and 79%, respectively, were also found after UV-irradiation. Photooxidation is commonly coupled with liquid chromatographic separation, which allows for the analysis of complex environmental samples with separation of arsenicals including iAs^{III}, iAs^V, MMA^{III}, MMA^V, DMA^{III}, DMA^V, AB, AC, phenylarsonic acids and potentially most if not all organoarse-

nicals of environmental importance. Recent developments in the detection of hydrides have included atomic fluorescence spectroscopy (Ouyang et al., 1999; Gomez-Ariza et al., 2000; Simon et al., 2004; Schaeffer et al., 2005) and ICP or ICP/MS (Rubio et al., 1993a; Gomez-Ariza et al., 2000; Nakazato and Tao, 2006) for the detection of arsenohydrides. The use of a high efficiency photo-oxidation (HEPO) reactor which was able to oxidize organoarsenicals such as AB to iAs^V with as little as 3.5 s of irradiation with 185 nm vacuum UV light without the addition of a chemical oxidizing agent has been described (Nakazato and Tao, 2006). Other studies applied potassium persulfate to oxidize organoarsenicals by UV irradiation (Atallah and Kalman, 1991; Rubio et al., 1993b; Howard and Hunt, 1993; Willie, 1996). The determination of iAs^{III}, iAs^V, mono-, di- and trimethyl arsine, MMA^{III}, MMA^V, DMA^{III}, DMA^V, and TMAO in natural waters with detection limits of several ng L⁻¹ was carried out using gas stripping, selective reduction and cold trap cooling, followed by trap warming or gas chromatography and detection by atomic absorption, flame ionization (FID) or electron capture (ECD) (Andrae, 1977).

A comprehensive review on current analytical methods for arsenic has been recently written (Francesconi and Kuehnelt, 2004) and the reader is referred to that work for a detailed comparison of analytical methods. Schaeffer et al. (2006) describe the development of a cation- and anion-exchange HPLC separation coupled to electrospray selected reaction monitoring (HPLC/ES-SRM) method for the analysis of fifteen different organoarsenic compounds found in marine and freshwater samples. The advantage of this method stems partially from the fact that it is a relatively soft ionization method (avoids the high temperatures required for ICP and thus the atomization process) and produces a molecular ion, which allows for species identification from the molecular ion and fragmentation patterns with greater certainty due to tandem mass spectrometry (MS/MS). Importantly, the identification of species could be carried out, which were undetected by ICP/MS. ICP/MS ultimately atomizes all As species and relies on retention times for species identification.

4. Dependence of arsenic speciation on environmental parameters

4.1. Effect of pH

Of the several forms of arsenic, As(III), As(V), MMA^V, and DMA^V undergo acid–base equilibria, thus different major and minor species

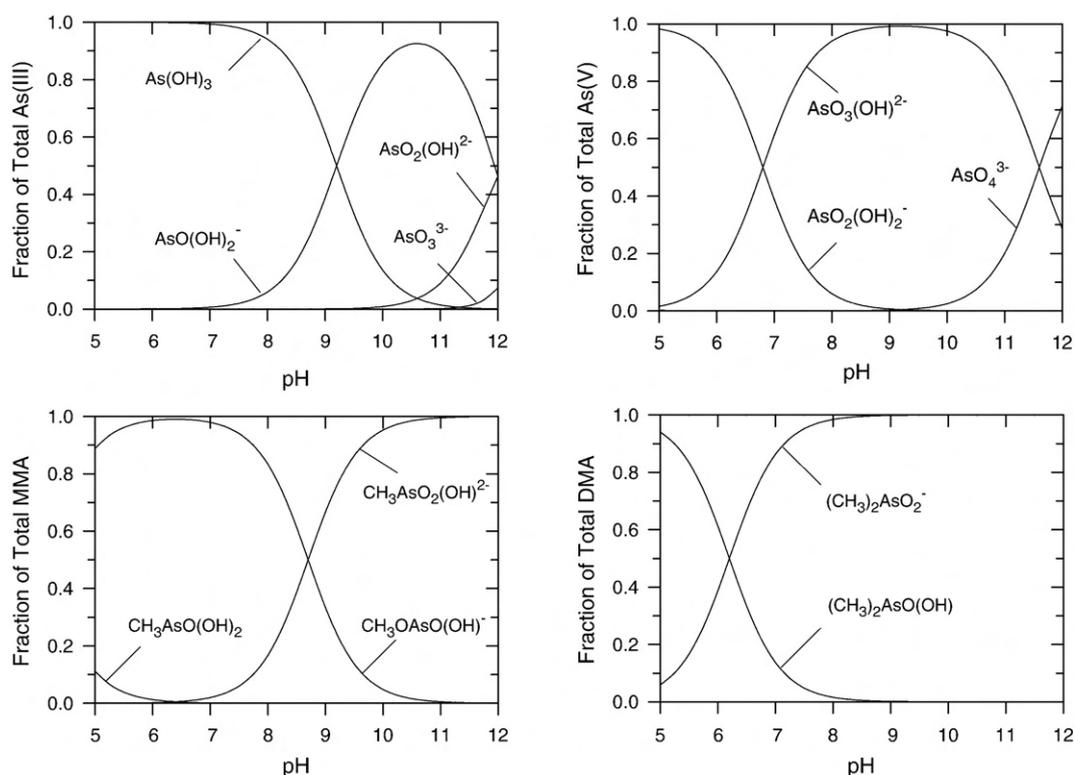


Fig. 2. Distribution of As(III), As(V), MMA, and DMA hydroxide species as a function of pH at 25 °C.

will be present depending on the pH. As(OH)₃ dissociates sequentially in water according to Eqs. (1)–(3) (Pierce and Moore, 1982).

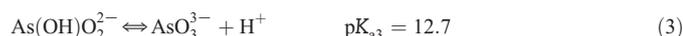
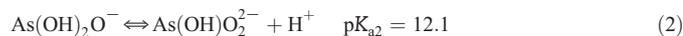
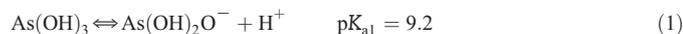
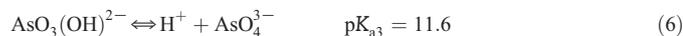
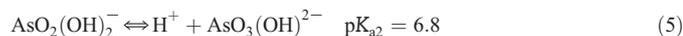
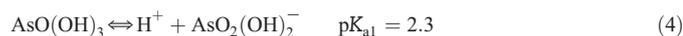
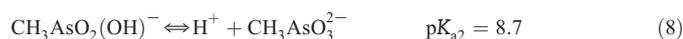


Fig. 2 shows that at neutral pH, As(OH)₃ is the dominant species while As(OH)₂O⁻ represents a small fraction (<1.0%) and the contribution of As(OH)O₂²⁻ and AsO₃³⁻ is insignificant. As(V) is a triprotic acid (Goldberg and Johnston, 2001) (Eqs. (4)–(6)).



At pH 7, almost equal concentrations of AsO₂(OH)₂⁻ and AsO₃(OH)²⁻ will be present (Fig. 2). MMA and DMA are diprotic acids, respectively (Eqs. (7)–(9)) (Cox and Ghosh, 1994).



The major species of MMA^V is CH₃AsO₂(OH)⁻ at a neutral pH, but the minor species, CH₃AsO₃²⁻ will also be present (Fig. 2). In the case of DMA^V, both (CH₃)₂AsO(OH) and (CH₃)₂AsO₂⁻ exist at pH 7 (Fig. 2).

4.2. Effect of E_h

Both redox potential (E_h) and pH impose important controls on arsenic speciation in the natural environment (Ferguson and Gavis, 1972). Fig. 3 shows the E_h–pH diagram for inorganic As compounds in the natural environment. Under oxidizing conditions (high E_h values), inorganic arsenic occurs primarily as H₃AsO₄ (iAs^V) at pH < 2, and both H₂AsO₄⁻ and HAsO₄²⁻ species exist in the pH range from 2–11. At low E_h values, H₃AsO₃ is the predominant inorganic arsenic species (iAs^{III}) under reducing conditions (Fig. 3). If E_h values below –250 mV exist in the environment, arsenic compounds such as As₂S₃ in the presence of sulfur or hydrogen sulfide can be formed (Fig. 3) but these conditions are not environmentally relevant. The solubility of these compounds is very limited under neutral and acidic conditions (Ferguson and Gavis, 1972). Under very strong reducing conditions, arsine and elemental arsenic are formed (Fig. 3) but again, only rarely, if ever in the natural environment.

An example of the effect of redox conditions on As speciation is illustrated in the levels of inorganic arsenic species in the water column of the stratified Lake Pavin (France) (Seyler and Martin, 1989). In well oxidized surface waters of Lake Pavin, iAs^V dominates with % iAs^{III}/As(tot) varying from 7–12% above the redoxcline. At depth, below the redoxcline, in waters characterized by a total depletion of dissolved oxygen, acidic pH and the presence of hydrogen sulfide and high turbidity, as expected iAs^{III} becomes the dominant form of inorganic As in which % iAs^{III}/As(tot) values increased from 51 to 90% with increasing depth. Low levels of MMA^V and DMA^V were also detected in samples. Importantly, iAs^{III} was consistently detected in highly oxygenated surface waters and at the redoxcline of Lake Pavin the data yielded a ratio of iAs^{III}/As(V) close to one (Seyler and Martin, 1989). However, the calculated ratios were determined to be 10¹⁰. This suggests that there are other processes such as sorption, adsorption, precipitation, and biological mediation besides oxidizing versus reducing conditions playing a role in distributions of inorganic arsenic in natural waters (Fig. 4).

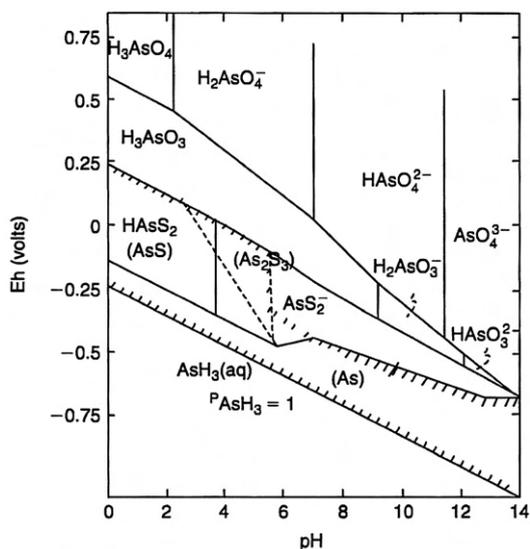


Fig. 3. The Eh–pH diagram for arsenic at 25 °C and 1 atmosphere with total arsenic 10^{-5} mol L $^{-1}$ and total sulfur 10^{-3} mol L $^{-1}$. Solid species are enclosed in parentheses in the cross-hatched area, which indicates a solubility of less than $10^{-5.3}$ mol L $^{-1}$ (reproduced from Ferguson and Gavis, 1972 with permission from Elsevier).

The importance of biological processes in affecting the speciation of As in natural waters was illustrated in a study of seawater samples from the coast of Southern California with surface concentrations hovering at around 2.0 $\mu\text{g L}^{-1}$ total As (Andreae, 1978). While $i\text{As}^{\text{V}}$ was the most abundant As species in the photic zone, $i\text{As}^{\text{III}}$, DMA^{V} and MMA^{V} were found to positively correlate with both chlorophyll concentrations and C^{14} uptake, indicating that reduction of $i\text{As}^{\text{V}}$ to $i\text{As}^{\text{III}}$ and methylation of $i\text{As}^{\text{V}}$ were likely associated with biological activities. The occurrence of MMA^{V} and DMA^{V} in marine macroalgae and the correlation of arsenate with phosphate concentrations in the photic zone pointed to reduction and methylation of $i\text{As}^{\text{V}}$ as a mechanism to assist marine primary producers with overcoming the inhibition of phosphate uptake by $i\text{As}^{\text{V}}$. The phenomenon of phosphate uptake inhibition by $i\text{As}^{\text{V}}$ has also been demonstrated for algae (Blum, 1966). Competitive binding between arsenate and phosphate onto nonbiological substrates is discussed in the next section.

4.3. Effect of adsorption

Adsorption of dissolved arsenic onto particulate phases has been actively studied not only because of its pivotal role in determining As concentrations and speciation in natural waters but as an important remediation tool for arsenic removal in contaminated drinking water. Iron oxides and hydroxides of a variety of composition and degree of crystallinity are virtually ubiquitous in natural aqueous systems and are known to play a major role in As geochemistry. Ferrihydrite (approximately $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), formed from the rapid precipitation of Fe(III) from aqueous solution, is largely amorphous with a high adsorptive surface area and is often used to simulate solid adsorption surfaces in aquifers (Stollenwerk, 2003). While earlier studies of As adsorption onto iron and aluminum oxyhydroxides found behavior conforming to Langmuir isotherms (Ferguson and Anderson, 1974; Anderson et al., 1976; Gupta and Chen, 1978), later work distinguished between the adherence of both arsenite and arsenate to a Langmuir isotherm at lower As concentrations (0.667–13.3 μM), while at higher As concentrations (33.4–667 μM), linear adsorption isotherms for arsenite and arsenate adsorption onto amorphous iron hydroxide were found (Pierce and Moore, 1982). The observed change in isotherm adherence with change in As concentration range

was most likely due to the variability of adsorption sites on the solid surface. Initial As adsorption at low As levels involves sorption to the strongest surface sites and this results in Langmuir behavior as those sites become filled. Henceforth, adsorption continues onto weaker surface sites, which may be more numerous than the stronger sites and may involve penetration of As onto sites of a permeable amorphous solid, and adsorption proceeds with a linear relationship (constant adsorption constant). The oxidation state of As and pH of the system are crucial to adsorptive behavior as is the presence of competing ions. For example, Maximum $i\text{As}^{\text{III}}$ adsorption occurred on amorphous hydroxide at around pH 7 while $i\text{As}^{\text{V}}$ adsorption was fairly independent of pH at low As concentrations but increased with pH decrease (pH 9–4) at higher As concentrations (Pierce and Moore, 1982). While some adsorption studies have shown that $i\text{As}^{\text{V}}$ adsorbs more strongly than does arsenite at concentration ranges typical of natural systems (Pierce and Moore, 1982), higher adsorptive capacities of goethite and amorphous iron hydroxide at pH < 9 for arsenite compared to arsenate have been found (Lenoble et al., 2002).

The effects of oxyanions such as phosphate, sulfate, carbonate and silicate on As adsorption onto solid phases is complicated by not only competition for active sites but by redox processes and co-precipitation (Han et al., 2007; Ciardelli et al., 2008). Recent studies point to a solubilization of arsenic from sediment and iron oxyhydroxide surfaces by carbonate and bicarbonate under environmentally relevant conditions (Kim et al., 2000; Appelo et al., 2002; Anawar et al., 2004; Arai et al., 2004; Stachowicz et al., 2007). Clays and oxides/oxyhydroxides of aluminum and manganese are also important adsorbents of As, especially in iron deficient systems (O'Day, 2006). The oxidation of $i\text{As}^{\text{III}}$ to $i\text{As}^{\text{V}}$ upon adsorption onto clay minerals such as illite and kaolinite has also been described (pH range 4–10) (Manning and Goldberg, 1997). This study observed $i\text{As}^{\text{III}}$ oxidation in the absence of clay mineral surfaces at pH > 9. Studies of the extent of adsorption of arsenic onto different clays have shown, that as has been often reported with iron oxyhydroxides, $i\text{As}^{\text{V}}$ adsorbs to a greater extent than does $i\text{As}^{\text{III}}$, specifically at pH < 7. At higher pH values, the extent of $i\text{As}^{\text{III}}$ and $i\text{As}^{\text{V}}$ adsorption is more similar (Frost and Griffin, 1977; Lin and Puls, 2000).

The effects of carbonate species on arsenic adsorption are complex. Different adsorbed carbonate concentrations due to different $p\text{CO}_2$ conditions resulted in enhanced/suppressed $i\text{As}^{\text{V}}$ adsorption onto hematite (pH 4–8) (Arai et al., 2004). Bicarbonate adsorption may decrease the ability of sediments to adsorb $i\text{As}$ under conditions similar to those of Bangladesh groundwater (Arai et al., 2004). Bicarbonate is an effective competitor with $i\text{As}^{\text{III}}$ and $i\text{As}^{\text{V}}$ for adsorption onto goethite under field conditions with the largest effect seen at the lowest experimental pH (~6.5). (Stachowicz et al., 2007).

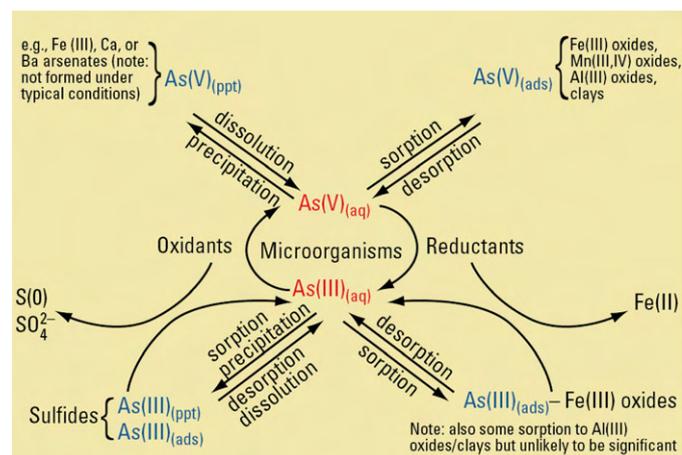


Fig. 4. Possible processes in biogeochemical cycling of arsenic (reproduced from Reisinger et al., 2005 with permission of the American Chemical Society).

Although the charge distribution model was effective in modelling the bicarbonate interaction, comparison with field conditions indicated that bicarbonate alone could not account for As loading of aquifer materials and other species such as phosphate and the effect of organic matter may also play important roles.

Because of the chemical similarities between phosphate and iAs^V , competitive binding to solids is expected and well documented on surfaces such as goethite (Gao and Mucci, 2001), and ferrihydrite (Jain and Loeppert, 2000; Dixit and Hering, 2003). Leaching of arsenic by phosphate solutions has been found to occur from lead arsenate contaminated soils (Peryea, 1991). Phosphate inhibition of iAs^V adsorption onto ferrihydrite was found to be significant over the entire pH range studied (3–10) by Jain and Loeppert (2000) with a strong dependence on pH and phosphate concentration. For iAs^V , the effect was greatest at high pH while the opposite was true for arsenite. The results suggested that iAs^V and iAs^{III} compete for the same surface sites on ferrihydrite, with a mild preference for iAs^V . Sites with a much higher affinity for iAs^{III} than for phosphate were also suggested (Jain and Loeppert, 2000). A lack of any effect of sulfate on iAs^V adsorption was observed, however, sulfate was found to reduce iAs^{III} adsorption at acidic pH with the effect increasing as pH was lowered (Jain and Loeppert, 2000). In contrast to the lack of effect of sulfate on iAs^V adsorption onto ferrihydrite, (Jain and Loeppert, 2000), sulfate was found to reduce the adsorption of iAs^V onto hematite (Xu et al., 1988). The anionic species of silicic acid (H_4SiO_4) have been shown to compete effectively with iAs^V and iAs^{III} for adsorption sites on iron oxyhydroxides (Swedlund and Webster, 1999; Davis et al., 2001), and, as was true for phosphate, the behavior was pH dependent.

4.3.1. Effect of organic matter

The effect of organic matter (OM) on As adsorption, speciation, and mobility is also a topic of keen interest because of the ubiquitous nature of natural organic matter in aqueous systems. OM consisting of relatively high molecular weight humic substances and distinct molecules of lower molecular weight, contain unique assemblages of reactive functional groups including but not limited to phenol and carboxylic acid which are negative at neutral pH (Macalady and Ranville, 1998). Functional groups associated with OM can be involved in As speciation due to (i) possible redox reactions of As, (ii) organic matter coatings on inorganic adsorbents and (iii) aqueous complexation of As species (Redman et al., 2002). The pH dependent charges associated with OM and arsenic species are key considerations when evaluating interactions between OM and arsenic.

The effects of OM on arsenic adsorption/mobility depend partly on the solubility of the OM itself under aqueous system conditions (e.g. pH and ionic strength). Fulvic acid (FA) and natural organic matter (NOM) have lower average molecular weights and greater pH solubility ranges than humic acid (HA), which is base soluble but acid insoluble. When FA or NOM is used to model OM, adsorption of As species onto a solid phase such as goethite or ferrihydrite, its presence tends to inhibit As adsorption due to competition for adsorption sites with DOM and due to complexation of As by DOM, increasing the mobility of arsenic. The complexation of iAs^{III} by aqueous solutions of Suwannee River NOM (SRNOM) was analyzed by capillary electrophoresis (Lenhart and Yang, 2004). The intensity of iAs^{III} peak decreased and changes occurred in NOM peaks (splitting of peaks) upon mixing solutions of iAs^{III} and NOM, indicating the formation of As^{III} –NOM complexes. When HA is used to model OM, a significant amount of the HA is present as solid phase (depending mainly on pH and ionic strength conditions) or exists as a solid coating on a mineral phase. This tends to remove As from the aqueous phase, enhancing As adsorption and immobilization (Stollenwerk, 2003). The pH effects on As speciation, and the charge on the solid surface, were found to be the major parameters affecting sorption behavior for systems containing iAs^V , FA, and inorganic solid phases (iron and aluminum oxides, quartz and kaolinite (Xu et al., 1988)). When the pH was less than

the IEP (isoelectric point; the pH at which the charge on a surface is zero), the solid surface adsorbs H^+ , increasing positive charge, which facilitates anionic adsorption. The differences in pH dependent adsorption of iAs^{III} and iAs^V have been discussed in detail (Stollenwerk, 2003).

The effects of NOM on arsenic adsorption have recently been reviewed (Wang and Mulligan, 2006a,b), with emphasis on the importance of competitive binding onto available adsorption sites, the mobilization of As by DOM and the immobilization of As by POM. Redman et al. (2002) used six different NOM samples from diverse sources of origin to study the effects of NOM on the adsorption of iAs^{III} and iAs^V onto hematite under natural freshwater conditions. All NOM samples effectively competed with both iAs^{III} and iAs^V for adsorption sites on hematite, and consequently diminished As adsorption onto hematite. Four of the six NOM samples were found to form soluble complexes with iAs^{III} and iAs^V . The extent of aqueous complexation of As species increased with the Fe content of the NOM samples and thus the complexation of anionic As species by anionic NOM (carboxylate and phenolate functional groups) was explained by complexation through metal ions such as Fe^{III} . An intuitive structure for a possible NOM–Fe–As complex has recently been proposed (Fig. 5) (Wang and Mulligan, 2006a,b). Sorption onto aquifer solids and/or precipitation of solids incorporating arsenic as a major or trace element can immobilize arsenic. Arsenic mobility (leaching/desorption) correlated well with concentrations of DOM for soils contaminated with As (Kalbitz and Wennrich, 1998).

Redox effects on As adsorption have been emphasized by Wang and Mulligan (2006a,b). For example, a rapid facilitated oxidation of iAs^{III} to iAs^V by six NOM samples upon incubation in darkness with no relationship to sample metal content was observed by Redman et al. (2002). SRFA (Suwannee River FA) promoted the reduction of iAs^V to iAs^{III} under both light and dark conditions while the oxidation of iAs^{III} to iAs^V was promoted to a greater extent at pH 2 than at pH 6 (Tongesay and Smart, 2005, 2007). An enhancement of iAs^{III} oxidation to iAs^V for adsorption onto TiO_2 (a semiconductor often used to catalyze redox reactions) in the presence of DOM from various sources under alkaline conditions and in the absence of both light and O_2 , was reported by Liu et al. (2008, in press).

The important role of pH in affecting the adsorption of arsenic onto solid surfaces in the presence of OM is well documented. The pH dependent inhibition of As uptake by the surface of TiO_2 in the presence of NOM was observed by Liu et al. (2008, in press). Shi et al. (2008) looked at the effects of low molecular weight organic acids and pH on iAs^V adsorption onto goethite and observed that citrate was most effective at inhibiting arsenate adsorption, especially at lower pH values (pH = 4.0), although oxalate dissolved more goethite than did citrate, suggesting that competition for binding sites, rather than goethite dissolution, was the key reason for arsenic mobilization. The effects of SRFA and a peat HA on iAs^{III} and iAs^V adsorption onto goethite also showed significant pH effects (Grafe et al., 2001). HA reduced iAs^V adsorption between pH 6–9 while SRFA reduced iAs^V adsorption between pH 3–8 and both inhibited iAs^{III} adsorption at pH

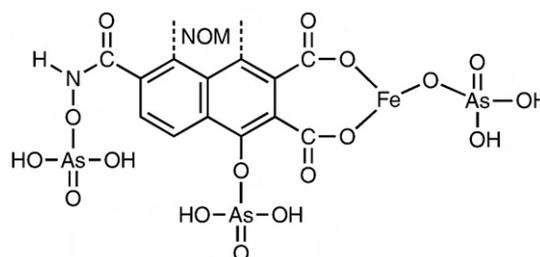


Fig. 5. Model structure of As–NOM complex (reproduced from Wang and Mulligan, 2006a,b).

3–8, suggesting that more than one OM functional group was involved. A similar study using ferrihydrite as the solid phase, yielded very different results: iAs^V adsorption onto ferrihydrite was not decreased by either SRFA or the HA while iAs^{III} adsorption was reduced by SRFA and HA had no effect (Grafe et al., 2002).

As noted above, the effects of POM on arsenic adsorption have been most commonly studied by introducing the less water-soluble fraction of humic substances, humic acid, into the reaction suspension. In an early study, two further purified commercially available humic acids (Fluka AG and Aldrich) were used to study pH and ionic competition effects on the adsorption of iAs^{III} and iAs^V onto solid HA (Thanabalasingama and Pickering, 1986). The adsorption experiments yielded Langmuir isotherms with maximum uptake at pH 5.5 with maximum remobilization of pre-sorbed As by phosphate species and lesser effects from sulfate and carbonate. This study suggested that the HA surface is acting like an anion exchanger, possibly employing amino groups as the active site (Thanabalasingama and Pickering, 1986). The adsorption of iAs onto kaolinite was enhanced upon coating kaolinite with Fluka HA and the observed behavior reinforced the possibility of HA amino group participation in iAs adsorption reactions (Cornu et al., 1999). A later study further examined the possible role of HA amino groups by measuring iAs^V adsorption onto HA coated kaolinite using two humic acids of different nitrogen content and found that the HA with the higher N/C content adsorbed more arsenate as a kaolinite coating (Saada et al., 2003). The experiments were done at pH 7, as were those by Cornu et al. (1999) and the authors hypothesize a pivotal role by amino groups which would be positively charged at pH 7 and could act as important anion exchangers. The effect of Aldrich HA coating on the rate of As adsorption onto hematite was also carried out in which HA coated hematite was characterized by slower adsorption kinetics and a lower adsorption capacity than the uncoated hematite (Ko et al., 2004). This work described the oxidation of iAs^{III} to iAs^V as the dominant redox reaction (Ko et al., 2004). An unusual source of OM (mixture of peat moss and poultry manure) was used to determine the influence of OM on arsenic speciation and mobilization in synthetic chromated copper arsenate (CCA) contaminated soils for long periods of exposure (upto 40 days) (Dobran and Zagury, 2006). This study found that while iAs^V was the predominant dissolved and sorbed form of As at high OM contents, formation of adsorbed iAs^{III} was significant and both arsenate and arsenite mobilization was enhanced with a noted persistence of soluble iAs^V .

One weakness of many of the humic acid studies, is the use of commercially obtained humic acids. There are significant differences in functional group contents between commercial humic acids and those extracted and purified by International Humic Substances Society (IHSS) methods (Malcolm and MacCarthy, 1986). There is a clear need for research on the effects of noncommercial humic acids on adsorption and speciation of As in aqueous systems.

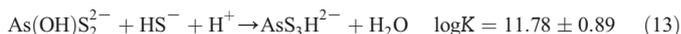
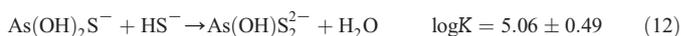
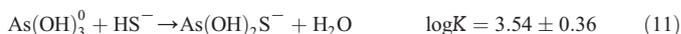
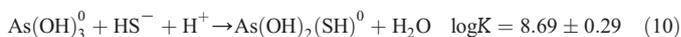
Studies on adsorption of organic forms of arsenic are limited mainly to MMA^V and DMA^V . Adsorption of MMA^V and DMA^V onto ferrihydrite and activated alumina while varying pH, ionic strength, and sorbate-sorbent ratio have been measured (Cox and Ghosh, 1994). A decrease of adsorption with increasing pH was observed. Adsorption decreases significantly at pH values above 7, but ionic strength showed only a weak dependence (Cox and Ghosh, 1994). The triple-layer surface complexation model was used to interpret results, which suggested two different types of active sites, while modelling a homogeneous surface gave inconsistent results (Cox and Ghosh, 1994). Similar adsorption behavior for MMA^V and iAs^V for adsorption onto hydrous Al_2O_3 was observed (Ghosh and Yuan, 1987). An adsorption study using goethite, hematite and lepidocrocite found that sorption decreased in the order $iAs^V > DMA^V = MMA^V > iAs^{III}$ below pH 7 and $iAs^V > iAs^{III} > MMA^V = DMA^V$ above pH 7 (Bowell, 1994).

In many instances, high concentrations of organic matter in natural waters coincide with reducing and/or highly sulfidic conditions. These

conditions are often found in ground water and thus their effects on As speciation may be critical with respect to the potability of water supplies.

4.4. Sulfidic waters

Arsenic chemistry in sulfidic environments may be controlled by the formation of thioarsenic species (thioarsenite and/or thioarsenate) (Wilkin et al., 2003; Hollibaugh et al., 2005). The formations of some thioarsenite species are described by the following reactions in sulfidic waters (Eqs. (10)–(15)) (Wilkin et al., 2003).



Visible–UV absorption spectra of thioarsenite and thioarsenates have been calculated from structural components (Tossell, 2003). Raman and X-ray absorption spectroscopic methods have also been applied to study thioarsenic speciation (Mikenda et al., 1982; Wood et al., 2002; Bostick and Fendorf, 2005; Beak et al., 2008). HPLC-ICPMS has also been used to study the speciation of arsenic in sulfidic solutions (Hollibaugh et al., 2005; Rochette et al., 2000; Wilkin et al., 2003; Stauder et al., 2005). Interpretation of the results from both spectroscopic and chromatographic methods agrees on monomeric species, but differs on the possible presence of polymeric species. The drawback of spectroscopic methods is that they usually use As and sulfide concentrations in the As–S–H₂O system, which are much higher than those present in natural environments. In addition, spectroscopic methods provide data on composite speciation of solutions rather than on individual arsenic species. Chromatographic methods have an advantage in this regard, but they have difficulties in detecting polymeric species. This may be the cause of differences reported in the literature for thioarsenic species, i.e. whether thioarsenites (Wilkin et al., 2003) or thioarsenates (Stauder et al., 2005) are present in sulfidic waters. This indicates a limitation of chromatographic methods in that the oxidation state of arsenic is inferred rather than measured (Beak et al., 2008).

There may be as many as eight different arsenosulfur species present in arsenite- and sulfide-containing solutions (Wood et al., 2002). Analysis of laboratory and environmental samples suggest that arsenic-thio compounds comprised $\geq 50\%$ of the total arsenic in sulfidic environments (Hollibaugh et al., 2005; Stauder et al., 2005; Planer-Friedrich et al., 2007). Spectroscopic measurements as well as solubility studies of As_2S_3 in hydrogen sulfide solutions suggest that HAs_2O^- and HAs_3^- are present in sulfidic waters undersaturated with respect to As_2S_3 (Helz et al., 1995). Under nearly saturated conditions, the trimer $As_3S_6^{3-}$ dominates (Webster, 1990; Eary, 1992; Helz et al., 1995). Four arsenic–sulfur species with As:S ratios from 1:1 to 1:4 have been identified by Wilkin et al. (2003). The proposed formula for the As:S ratio of 1:4 was $H_4AsS_4^-$ while the suggested species with ratios, 1:1, 1:2, and 1:3 were equivalent to thioarsenites (Wilkin et al., 2003). Monomeric and trimeric thioarsenite species have been suggested as the most probable arsenic–sulfur complexes in sulfidic waters (Nordstrom and Archer, 2003).

In sulfidic groundwaters and artificial arsenite/hydrogen sulfide solutions, thioarsenates are formed (Stauder et al., 2005). The high affinity between As(III) and sulfur results in the addition of the free

electron pair of As^{III} to form As^V in thioarsenates. Mono-, di-, tri-, and tetrathioarsenates have also been determined in geothermal waters of Yellowstone National Park (Planer-Friedrich et al., 2007). Determination of (oxy)thioarsenates in sulfidic waters has been carried out by Wallschläger and Stadey (2007) using anion exchange chromatography/ICPMS. A recent examination of arsenic speciation of sulfidic solutions using X-ray absorption spectroscopy raised doubts on the validity of thioarsenate analysis using chromatographic methods because thioarsenate chromatographic peaks may appear at positions identical to those of thioarsenites in undiluted sulfidic water samples (Beak et al., 2008). This study demonstrated that dilution prior to chromatographic analysis changes the speciation distribution in samples (Beak et al., 2008). It may be possible that natural sulfidic systems are characterized by complex nonequilibrium distributions of arsenic oxyanions, thioarsenites, and thioarsenates. Biochemical processes also play a major role in arsenic speciation in sulfidic waters as described by Fisher et al. (2008).

5. Transformation of arsenosugars

Arsenosugars are commonly found in marine algae including those species used in human food consumption (Francesconi et al., 2002a, b). Arsenosugars can also be found in marine animals feeding on algae such as scallops (Lai et al., 1999) and have also been identified in marine and freshwater fish and mussel samples (Schmeisser et al., 2004; Šlejkovec et al., 2006; Soeroes et al., 2005b). Although AB is the most commonly reported arsenosugar in marine organisms, it is virtually absent in freshwater organisms (Schaeffer, 2006b). High concentrations of arsenosugars were found in seaweed in which the concentration of arsenic was as high as 100 µg g⁻¹ (Castlehouse et al., 2003). Arsenosugars are assumed to be relatively nontoxic to animals and humans relative to inorganic arsenic species (Kaise et al., 1996; Sakurai et al., 1997). However biotransformations of arsenosugars can result in toxic arsenicals (Francesconi et al., 2002a,b).

Biotransformation of arsenosugars in humans has been found to produce DMA^V as a major metabolite (67%) in urine (Francesconi et al., 2002a,b). Diethylarsinoylethanol (DMAE) and TMAO have been found as other minor constituents of arsenic metabolites (Francesconi et al., 2002a,b). Metabolism of arsenosugars yielded DMA^V in excreted urine samples of sheep fed with seaweed (Hansen et al., 2003). Other metabolites in minor amounts were DMAE, TMA⁺, iAs^V, and methylarsonic acid (MMA^V) (Hansen et al., 2003). Biotransformation of arsenic in soil amended with the seaweed species, *Laminaria digitata* and *Fucus vesiculosus*, containing 85% total As as arsenosugars, was studied in microcosm experiments (Castlehouse et al., 2003). The dominant species found in soil pore waters were DMA^V, iAs^V, and iAs^{III}. A mechanism for the decomposition of arsenosugars to form these species has been proposed (Fig. 6). Decomposition of *F. vesiculosus* was slow relative to the fast transformation of arsenosugars to DMA^V, hence low concentrations of arsenosugars in the water-extractable phase was expected (Castlehouse et al., 2003). The arsenosugars identified in the used seaweed species have a dimethyl arsinoyl moiety, which is still present in the main metabolite DMA^V (Fig. 6), indicating that the ribofuranoside moiety on the arsenic can be removed easily in soil to form DMA^V. Interestingly, MMA^V as an intermediate was not identified in the pore water samples, suggesting that either MMA^V strongly binds to the soil matrix or is not very stable under the experimental conditions (Castlehouse et al., 2003).

6. Transformation of arsenic species during thermal treatment

An extensive survey of cooked Canadian foods elucidated an increase in total arsenic levels of cooked relative to uncooked food such as marine and freshwater fish, which was correlated with a decrease in the weight of the food, (Dabeka et al., 1993). Similarly, total arsenic contents of fresh sea bass fillets increased significantly

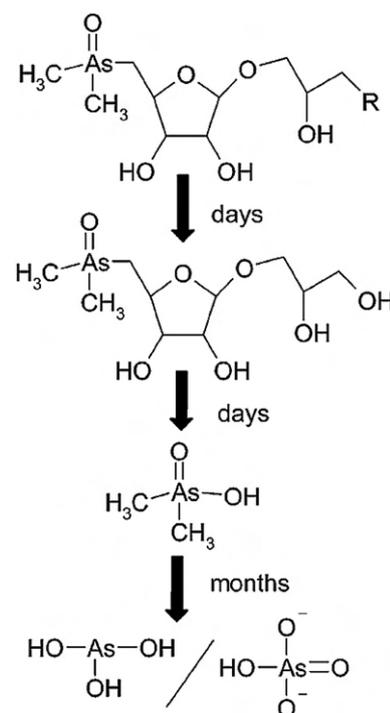


Fig. 6. Proposed mechanism of arsenosugars decomposition in top soil. R = -O-PO(OH)O-CH₂-CH(OH)CH₂(OH), -SO₂(OH), -O-SO₂(OH) (reproduced from Castlehouse et al., 2003 with the permission of the American Chemical Society).

upon microwave oven cooking of the fillets (Ersoy et al., 2006). The decrease in moisture content during cooking was suggested as the reason for the increase in arsenic content. However, another study on seafood samples reported both decreases and increases in total arsenic contents after cooking (Devesa et al., 2001a). The increase in arsenic levels could be due to loss of water, while solubilization or volatilization of arsenic compounds during the cooking may have caused a decrease in concentration of arsenic (Devesa et al., 2001a). In this study, the arsenobetaine (AB) content in water of cooked crustaceans and bivalves was determined (Devesa et al., 2008). Thermal treatment of mussels resulted in a lowering of the total arsenic level, which could be due to the loss of some arsenic species such as iAs^V, AB and other arsenosugars during the process (Lai et al., 2004). Decomposition of arsenic species upon baking at 160 °C has been observed (Van Elteren and Slejkovex, 1997).

Transformation of arsenic species during heat treatment has been studied in detail (Devesa et al., 2001a,b,c, 2005). Studies on seafood cooked by various means such as grilling, roasting, boiling, and microwaving reveals AB as the major species found, followed by DMA^V and TMA⁺ (Table 1) in the cooked seafood (Devesa et al., 2005) while minor species such as AC and MMA^V were also detected. Increases in DMA^V and TMA⁺ were observed during cooking. A kinetic study was carried out by heating AB at different temperatures (85–190 °C) and for different time periods. The effect of pH on the heating process was also studied by varying the pH from 4.5–8.0 (Devesa et al., 2001b). There was no effect of pH observed at 120 °C. However, with temperature increases of 150–180 °C, decomposition of AB to form TMAO and TMA⁺ were observed (Fig. 7). The kinetics of two reactions for the formation of these species were found to follow first-order kinetics for the degradation of AB (Devesa et al., 2001b). When heating at 160 °C was carried out for 24 h, the AB was fully degraded with the formation of 11% TMAO and 68% TMA⁺ of the transformed AB (Devesa et al., 2001b). Activation energy values were calculated as 108.6 kJ mol⁻¹ and 200.2 kJ mol⁻¹, respectively, for TMAO and TMA⁺. This indicates that generation of TMAO is faster than that of TMA⁺ from the thermal transformation of AB. Less than 1.1% transformation

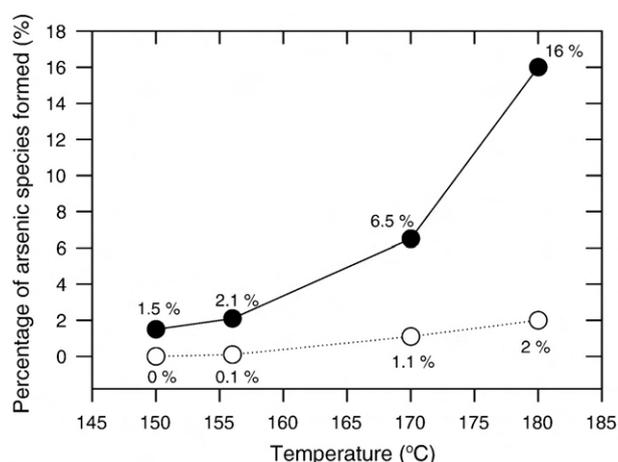


Fig. 7. Percentage of transformation of AB into TMAO (●) and TMA⁺ (○) at different temperatures. Time of application at each temperature was 44 min (reproduced from Devesa et al., 2001b with the permission of the American Chemical Society).

of AC into TMAO in the temperature range 150–180 °C was observed (Devesa et al., 2001b). Samples of sole, dory, sardine, and hake were subjected to different cooking processes (frying, baking, and grilling) at various temperatures (Devesa et al., 2001c). Similar results were obtained in another study (Hanaoka et al., 2001). Decarboxylation of AB yields TMA⁺ due to thermal treatment of seafood samples. Recently, concerns have also been raised on consumption of arsenic in cooked hijiki seaweed and rice (Laparra et al., 2005; Caumette et al., 2007; Nakamura et al., 2008; Torres-Escribano et al., 2008).

7. Remediation of arsenic contamination

7.1. Adsorbents

The most common method of arsenic removal from water and wastewater is the use of different adsorbents. In treatment of As contaminated water, adsorption of As by common coagulating agents (alum and ferric salts such as ferric chloride and ferric sulfate) have been studied extensively (EPA, 2000), revealing maximum As removal (over 95% of arsenate removed at levels of 10–50 mg/L at pH range 5.0–7.5) with ferric sulfate. An extensive review of the applications of different adsorbents with their advantages and disadvantages has recently been published (Mohan and Pittman, 2008). A review on recent developments in laboratory approaches for arsenic remediation of contaminated water has also been published (Mondal et al., 2006). Adsorption of arsenic by activated carbon has also been studied in detail (Gu et al., 2005; Chuang et al., 2005). This method removes only a few milligrams of arsenic per gram of activated carbon. There is also the problem of regeneration of spent adsorbent if activated carbon is used. There are several other adsorbents, which have equal or greater efficiency than activated carbon for removal of arsenic. These adsorbents include activated alumina, ion-exchange resins, sand, silica, clays, iron, iron compounds, and organic polymers (Goldberg and Johnston, 2001; Mohan and Pittman, 2008). Activated alumina requires low pH and oxidation of As^{III} for efficient As removal (Lin and Wu, 2001; Singh and Pant, 2004). Ion-exchange resins are less pH dependent, but other common constituents of natural waters such as sulfates and nitrates, reduce the efficiency (Bacocchi et al., 2005). Clays, sand, and silica are relatively less efficient than most other adsorbents (Manning and Goldberg, 1997; Goldberg, 2002). Iron-based adsorbents (IBS) appear to be an emerging treatment method for removal of arsenic. An advantage of IBS is that they have strong affinities for arsenic at neutral pH, hence no pH adjustment is needed (Mohan and Pittman, 2008).

7.2. Phytoremediation

Phytoremediation, plant based environmentally-friendly technology, for the remediation of sites contaminated with As, has been recently reviewed (Lasat, 2002; Cherian and Oliveira, 2005; Dickinson et al., 2009). The chinese brake fern, *Pteris vittata*, was found to be resistant to arsenic and capable of hyperaccumulating large amounts of As in its fronds (Ma et al., 2001) and the potential phytoremediation of As contaminated soil and water using *P. vittata* has been investigated (Huang et al., 2004; Elless et al., 2005; Wei and Chen, 2006; Anderson and Walsh, 2007). Other plants have also demonstrated the capacity to hyperaccumulate As (Francesconi et al., 2002a,b; Meharg, 2003; Du et al., 2005; Keller et al., 2007; Tripathi et al., 2007; Gonzaga et al., 2008; Zhang et al., 2008). Mechanisms for As tolerance deployed by plants vary. It is hypothesized that hyperaccumulation is associated with the interaction of As with high-affinity chelating molecules present in the cytoplasm of the plant. For example, an arsenate-activated glutaredoxin from the fern *P. vittata* L. regulates intracellular arsenite (Sundaram et al., 2008). Arsenic accumulation in the hyperaccumulating fern species (*P. vittata* and *P. multifida*) and in the non-hyperaccumulating species (*P. ensiformis* and *P. semipinnata*) may involve arsenic reductase and superoxide dismutase enzymes (Liu et al., 2008, in press). Various biological processes such as plant-microbe interactions can also affect phytoremediation efficiencies (Cherian and Oliveira, 2005). Recent molecular studies have shown that many gene products are involved in the process of hyperaccumulation of As (Dhankar et al., 2002), hence single genes and multigenic engineering approaches may be applied to enhance the efficiency of phytoremediation (Padmavathamma and Li, 2007; Tripathi et al., 2007).

Phytostabilization methods using plants can also be applied for long-term remediation of As. This method limits uptake and excludes mobilization of As. One of the major benefits of phytostabilization is that the above-ground vegetative biomass is not contaminated with As, thus reducing the risk of arsenic transfer through food chains (Madejon et al., 2002). Woody species have also been investigated with respect to photostabilization (French et al., 2006; Vazquez et al., 2006). More recently, four Eucalyptus species were used for photostabilization of As in gold mine tailings (King et al., 2008). Additionally, natural attenuation processes including many biological applications may transform As to less toxic species and this topic has been recently reviewed (Wang and Mulligan, 2006b).

7.3. Chemical oxidation

As shown in Fig. 3, under typical anoxic groundwater conditions, at a near neutral pH of 7, As^{III} is the predominant form of arsenic, while in oxic groundwater, As^V dominates (Masscheleyn et al., 1991). Arsenite has a low affinity to mineral surfaces, while arsenate adsorbs easily to solid surfaces. An oxidation/precipitation technology should thus be very effective for the removal of arsenic from water (Borho and Wilerer, 1996; Raven et al., 1998; Jain et al., 1999; Lin and Wu, 2001; Bissen and Frimmel, 2003b; Ghurye and Clifford, 2004; Leupin and Hug, 2005). Many studies have been published on the oxidation of As^{III} by traditional chemical oxidants (Ox) such as chlorine, chlorine dioxide (ClO₂), chloroamine (NH₂Cl), ozone, hydrogen peroxide, permanganate (MnO₄⁻), and ferrate (FeO₄²⁻) (Frank and Clifford, 1986; Kim and Nriagu, 1999; Pettine et al., 1999; Emmett and Khoe, 2001; Johnston and Heijnen, 2001; Bissen and Frimmel, 2003b; Lee et al., 2003; Ghurye and Clifford, 2004; Vasudevan et al., 2006; Dodd et al., 2006; Sharma et al., 2007). The kinetics of the reactions with O₃, Cl₂, H₂O₂, NH₂Cl, and ferrate are first-order with respect to both As^{III} and oxidants (Pettine et al., 1999; Lee et al., 2003; Dodd et al., 2006; Sharma et al., 2007). Fig. 8 shows the trend of the observed rate constants, *k*, for various oxidants as a function of pH. Chlorine and ozone react very rapidly, while NH₂Cl and H₂O₂ are sluggish in

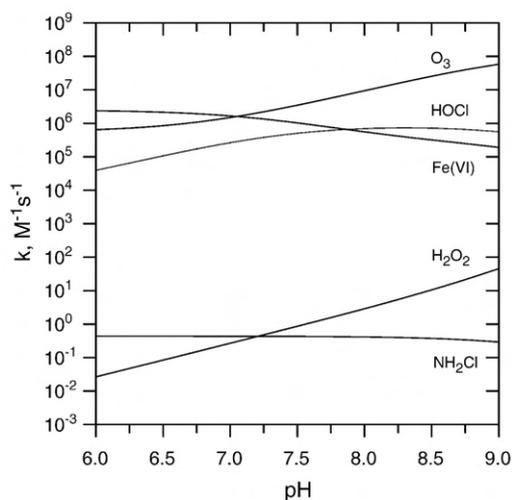
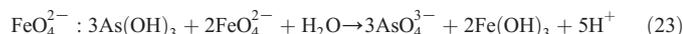
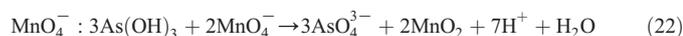
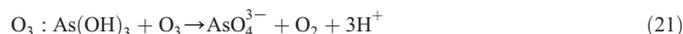
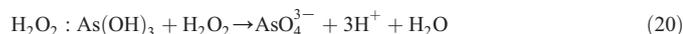
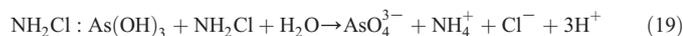
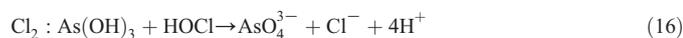


Fig. 8. Observed rate constants (k , $M^{-1} s^{-1}$) as a function of pH for the oxidation of As (III) by different oxidants (reproduced from Sharma et al., 2007 with the permission of Taylor and Francis).

reacting with As^{III} . Ozone reacts faster with As^{III} than with chlorine in the pH range 6.0–9.0. Though kinetic measurements have not been conducted for MnO_4^- oxidation, its reaction with As^{III} is fast (Ghurye and Clifford, 2004). Chlorine dioxide is a powerful oxidant but it is unable to completely oxidize As^{III} (Ghurye and Clifford, 2004). The reaction of Fe^{VI} with As^{III} is fast (Lee et al., 2003), however, the pH dependence of the Fe^{VI} reaction with As^{III} is opposite to that of other oxidants (see Fig. 8). This suggests that the reactivity of Fe^{VI} may be largely due to electrostatic interactions rather than to the nucleophilic behavior of As^{III} species (Sharma et al., 2007).

Stoichiometries of the oxidation reactions are expressed in the following equations.



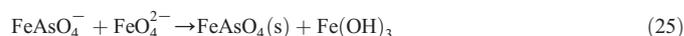
Oxidant amount requirements for the oxidation of As^{III} can be determined from these Eqs. (16)–(23). The reaction with ClO_2 , varies whether the reaction goes through a one-electron or five-electron transfer process (Eqs. (17) and (18)). The presence of interfering substances such as Fe^{II} , $Mn(II)$, sulfide (HS^- and S^{2-}), and total organic carbon (TOC) in water samples may interfere with the oxidant demand. For example, oxidation of As^{III} by ozone was significantly reduced in the presence of S^{2-} and TOC (Dodd et al., 2006).

Free chlorine or hypochlorite is effective for As^{III} oxidation, but chlorination creates and leaves disinfectant by-products (DBPs) in treated water. Trihalomethanes (THMs) are examples of DBPs that have been shown to be carcinogenic in rodents (Boorman et al., 1999). Ozone can reduce levels of THMs and halo acetic acids (HAAs), but it can form the potent carcinogenic bromate ion by reacting with bromide present in water (Gunten, 2003; Richardson, 2006). One

study suggests that treatment with NH_2Cl produced N-nitrosodimethylamine (NDMA), a suspected human carcinogen (Mitch and Sedlak, 2002). The use of ClO_2 is restricted to high quality water such as treated surface water (Gates, 1998). Dosing of ClO_2 must be kept low; for example, in the United States, dosages ranging from 1.0 to 1.4 $mg L^{-1}$ are used mainly for the preoxidation of surface water (Gates, 1998). Reduction of ClO_2 produces chlorite ion, which is considered a blood poison (Condie, 1986) and higher dosages of ClO_2 ($>1.4 mg L^{-1}$) are likely to produce chlorite levels that exceed the USEPA standard of 1 $mg L^{-1}$. Ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe^{VI}) can address some of the concerns related to the use of other chemical oxidants for removing arsenic (Sharma, 2007a). Interestingly, Fe^{VI} does not react with bromide ion and thus carcinogenic bromate ion would not be produced in the treatment of bromide-containing water (Sharma, 2007a). Moreover, a by-product of Fe^{VI} is non-toxic, Fe^{III} , which acts as a powerful coagulant (Sharma, 2002, 2004; Sharma et al., 2005a,b; Yngard et al., 2008) that is suitable for the removal of As^V , the oxidized product of As^{III} (reaction (23)), in water (Lee et al., 2003; Sharma et al., 2007). Thus Fe^{VI} acts as multifunctional chemical: oxidant, disinfectant, and coagulant in a single mixing (Sharma, 2007b).

Comparisons of rate constants and half-lives for the oxidation of As^{III} by different oxidants at pH 7.0 are given in Fig. 9. Chlorine, ozone, and ferrate would react instantaneously i.e. millisecond time scale with iAs^{III} . Comparatively, H_2O_2 and NH_2Cl oxidize As^{III} very slowly and removal of arsenic using these oxidants would take hours. It should be pointed out that scavenger substances present in water will affect the fast kinetics of iAs^{III} oxidation with chlorine, ozone, and ferrate. However, proper selection of oxidants can reduce the effect of scavengers on oxidant effectiveness. For example, it is better to use ozonation rather than chlorination in order to remove arsenic from water that contains excess ammonia because ozone reacts slowly with ammonia. On the other hand, if high levels of DOM are present, chlorination is a better choice due to a much slower reaction rate of free available chlorine (FAC) with DOM than that of ozone.

Interestingly, ion pairs between ferrous (a common constituent of groundwater) and As^{III} is known to react with Fe^{VI} in the removal of arsenic from water (Vogel and Johnson, 1988). Reaction of Fe^{VI} with this ion pair produces highly insoluble ferric arsenate, which immediately settles from solution (Eqs. (24) and (25)).



The optimum removal of arsenic (approximately $2 \mu g L^{-1}$) was obtained with a total iron/arsenate ratio $\approx 8:1$ at pH 5.0 at an initial

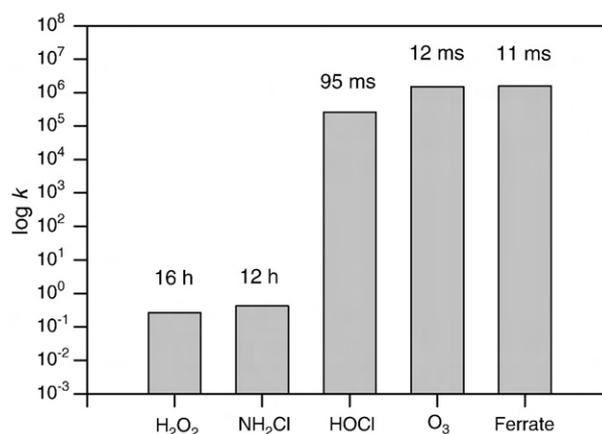


Fig. 9. Rate constants ($M^{-1} s^{-1}$) and half-lives ($t_{1/2}$) for oxidation of $As(III)$ at pH 7.0. Data were taken from Sharma et al., 2007 and half-lives were calculated using $2 mg L^{-1}$ dose of oxidant.

arsenic concentration of $50 \mu\text{g L}^{-1}$ in deionized water. In river water, the concentration of arsenic was lowered from 517 to below $50 \mu\text{g L}^{-1}$ with the addition of $2 \text{ mg L}^{-1} \text{ Fe}^{\text{VI}}$ (Lee et al., 2003). Laboratory results also showed removal of arsenic by ferrate(VI) (Sharma et al., 2007). Vogel and Johnson (1998) found that a small dose of Fe^{VI} (0.5 mg L^{-1}) in combination with the major coagulant Fe^{III} at doses of 2.0 and 4.0 mg L^{-1} was required to remove arsenic from riverwater. Removal of MMA^{V} and DMA^{V} by ferrate has also been sought (Vogel and Johnson, 1998). The removal efficiency follows the trend: $\text{iAs}^{\text{V}} > \text{MMA}^{\text{V}} > \text{DMA}^{\text{V}}$.

Finally, a combination of Fe^{II} and H_2O_2 (i.e. Fenton reaction) has been shown to oxidize As^{III} (Hug and Leupin, 2003). At low pH (≤ 5.0), a hydroxyl radical ($\cdot\text{OH}$) ($\text{Fe}^{\text{II}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{\text{III}} + \cdot\text{OH} + \text{OH}^-$) has been suggested as an oxidizing species. However, at neutral pH, Fe^{IV} , instead of hydroxyl radical, can possibly oxidize As^{III} ($\text{As}^{\text{III}} + \text{Fe}^{\text{IV}} \rightarrow \text{As}^{\text{IV}} + \text{Fe}^{\text{III}}$) (Hug and Leupin, 2003). The use of the Fenton reagent, followed by passage through a column of zero valent Fe has been found to be effective in remediating arsenic (Krishna et al., 2001).

7.4. Photochemical oxidation

Photochemical oxidation of iAs^{III} using UV light irradiation has been investigated in several studies. In an early study the oxidation of iAs^{III} by the photolysis of hydrogen peroxide under acidic conditions was evaluated and evidence for the existence of an intermediate species, As^{IV} , was given (Daniels, 1962). This intermediate species was also suggested in the photochemical oxidation of ferrous sulfate in the presence of arsenic acid (Wood, 1958). Dissolved As^{IV} was later characterized in pulse radiolysis of aqueous arsenous acid, iAs^{III} and iAs^{IV} (Klaning et al., 1989). Addition of Fe^{III} to As-contaminated water in perchlorate/perchloric solution at pH 0.5–2.5, followed by exposure to UV or solar light enhanced the removal of arsenic (Emett and Khoe, 2001). According to the proposed reactions in this study, Fe^{III} -hydroxide and -chloride species absorb photons to give highly oxidizing hydroxyl and dichloro radicals which convert iAs^{III} to iAs^{V} . This photochemical method is suitable for acidic mining effluents (Emett and Khoe, 2001). However, this system was also found to be useful under natural water conditions (Hug et al., 2001). An oxidation of iAs^{III} solution containing $0.06\text{--}5 \text{ mg/L Fe}^{\text{III}}$ using 90 W/m^2 UV-A light removed more than 90% of the $500 \mu\text{g L}^{-1}$ total arsenic in 2–3 h. Addition of citrate to this solution strongly accelerated the oxidation of iAs^{III} (Hug et al., 2001). Solar-light instead of UV-light can also remove arsenic from natural water upon addition of iron and citrate (Lara et al., 2006). Hug et al. (2001) suggested that the addition of a few drops of lime or lemon juice into water may be helpful in enhancing the photochemical oxidation of iAs^{III} to the less harmful iAs^{V} . The influence of dissolved organic matter on the UV-A and visible light oxidation of iAs^{III} has also been examined (Buschmann et al., 2007). The oxidation rate increased linearly with DOC using SRHA. Excited triplet and/or phenoxyl radicals were suggested as possible participants in the oxidation of iAs^{III} . The rates are also influenced by pH and the increase was of a factor of 10 from pH 4–8. Hence both DOC and pH control the half-lives of oxidation of iAs^{III} in natural waters (Buschmann et al., 2007). For example, a half-life of 0.7 h for $8 \mu\text{M iAs}^{\text{III}}$ at pH 5 and 25°C was determined under natural sun light for a solution containing 10 mg L^{-1} DOC and $18 \mu\text{M Fe}^{\text{III}}$ (Kocar and Inskip, 2003). However, the half-life is shorter by a factor of 80 for a solution containing 5 mg L^{-1} DOC and $45 \mu\text{M Fe}^{\text{III}}$ at pH 7.2 (Buschmann et al., 2007). It should be pointed out that solar-light oxidation of iAs^{III} may not be practical in high productivity waters where the reduction of iAs^{V} by algae is probably faster than the photochemical oxidation of iAs^{III} (Kuhn and Sigg, 1993; Aurillo et al., 1994; Hellweger and Laa, 2004). However, as noted above (Section 4.3.1) Redman et al. (2002) found that NOM significantly increased the oxidation of iAs^{III} even in darkness. The photochemical decomposition of other arsenic species such as MMA^{V} , DMA^{V} , and AB has also been reported (Brockbank et al., 1988).

Recently, oxidation of iAs^{III} was accomplished by using vacuum-UV lamp irradiation at 185 and 254 nm wavelengths (Yoon et al., 2008). The effects of Fe^{III} , H_2O_2 , and humic acids were examined in this study. Humic acid did not show any influence on the oxidation, but both Fe^{III} and H_2O_2 increased oxidation efficiency. Under the experimental conditions, exposure to a vacuum-UV lamp resulted in a higher efficiency of oxidation of iAs^{III} than that obtained with UV-C/ H_2O_2 and UV-A/ Fe^{III} / H_2O_2 oxidation methods (Yoon et al., 2008). The oxidation of iAs^{III} to iAs^{V} using a vacuum UV light was also equally effective in natural water samples. The total arsenic ($[\text{iAs}^{\text{III}}] + [\text{iAs}^{\text{V}}]$) could be achieved easily by adding activated alumina or FeCl_3 , which coagulates/precipitates iAs^{V} (Yoon et al., 2008).

Photochemical oxidation of iAs^{III} in the presence of potassium peroxydisulfate (KPS) has been evaluated (Woods et al., 1963a,b; Nishida and Kimura, 1989). Photochemical exposure of the KPS aqueous solution produces a sulfate anion radical ($\text{SO}_4^{\cdot-}$), which is a powerful oxidant for iAs^{III} . Earlier workers used coupled Fe-KPS and a tungsten lamp to oxidize iAs^{III} (Woods et al., 1963a,b). Photoexposure via a tungsten lamp yielded a slow rate of iAs^{III} oxidation, but the addition of Fe substantially increased the rate. A later study, carried out in 0.5 M KPS solution (Nishida and Kimura, 1989) concluded that this oxidation method was not applicable under environmental conditions. The study was also done by using KPS under visible light in the presence of the tris (2,2'-bipyridine) ruthenium(II) ions as a sensitizer (Yamazaki-Nishida and Kimura, 1990) with the application of light produced by a weak tungsten source, resulting in inefficient oxidation of iAs^{III} . A very recent study suggests the use of an intense UV light source with the KPS system in order to achieve effective oxidation of iAs^{III} (Nepolian et al., 2008). In this study, no pH effect in the range from 3–9 was observed. The presence of humic acid was initially detrimental to the oxidation, but after 30 min, the rate was similar to that without humic acid. Evidence was provided for the involvement of the $\text{SO}_4^{\cdot-}$ radical as the primary oxidant for oxidation of iAs^{III} in the KPS system.

7.5. Photocatalytic oxidation

The efficient oxidation of iAs^{III} to iAs^{V} by photocatalytic oxidation (PCO) can be achieved (Yang et al., 1999; Bissen et al., 2001). Oxidation using titanium dioxide (TiO_2), PCO of iAs^{III} to iAs^{V} followed by adsorption of iAs^{V} by TiO_2 has been proposed by Dutta et al. (2004, 2005). The adsorption of iAs^{V} onto TiO_2 is influenced by pH, type of TiO_2 , initial arsenic concentration, and the presence of anions (e.g. CO_3^{2-} and PO_4^{3-}) and NOM (Dutta et al., 2004; Bang et al., 2005; Ferguson and Hering, 2006; Pena et al., 2005, 2006; Liu et al., 2008, in press). Adsorption of iAs^{V} onto TiO_2 is more extensive at low pH than at high pH (Lee and Choi, 2002; Dutta et al., 2004; Pena et al., 2005). The presence of $2\text{--}15 \text{ mg L}^{-1}$ NOM present in TiO_2 suspensions decreased the adsorption of iAs^{V} on the surfaces, probably due to the competition of NOM with iAs^{V} for available binding sites on the TiO_2 surface (Liu et al., 2008, in press). Another possibility is that NOM adsorption modifies the surface charge of TiO_2 . The PCO of iAs^{III} in suspensions with low TiO_2 loadings followed by subsequent adsorption of iAs^{V} onto TiO_2 surfaces in slightly acidic media reduced arsenic to concentrations below the WHO drinking water limit of $10 \mu\text{g L}^{-1}$ in water (initial $[\text{As}] = 66.7 \mu\text{M}$) (Dutta et al., 2005). A slag-iron oxide- TiO_2 adsorbent has also been used for removal of arsenic after PCO oxidation of iAs^{III} (Zhang and Itoh, 2006). Adsorption was efficient and the necessary amount of adsorbent was 2 and 5 g L^{-1} for removal of 20 and $50 \text{ mg L}^{-1} \text{ iAs}^{\text{III}}$, respectively, in water.

The mechanism of PCO of As^{III} in TiO_2 suspensions has been investigated in detail. Some initial studies suggested the superoxide ion as the major oxidant species Lee and Choi, 2002; Ryu and Choi, 2004; Ferguson et al., 2005). Several studies thereafter proposed the hydroxyl radical as an important oxidant in the PCO of iAs^{III} (Dutta et al., 2005; Xu et al., 2005; Yoon and Lee, 2005). Subsequently,

photoelectrochemical measurements during the PCO of iAs^{III} were conducted which lent support to the proposed mechanism of superoxide as the main species responsible for oxidation (Ryu and Choi, 2006). However, recently, an argument was made which invalidates the electrochemical measurements in this study and rules out the proposed role of the superoxide species (Leng et al., 2007). Finally, it has been suggested that the superoxide ion is involved when PCO occurs under normal conditions of only dissolved oxygen and water (Rye and Choi, 2007).

Recently, photocatalytic degradation of MMA^V and DMA^V using Degussa P25 and nanocrystalline TiO_2 have been investigated (Xu et al., 2007, 2008). The adsorption of MMA^V and DMA^V onto TiO_2 shifted the isoelectric point of the TiO_2 surface from 5.8 to 4.1 for MMA^V and from 5.8 to 4.8 for DMA^V (Jing et al., 2004). The bidentate and monodentate inner sphere complexes of MMA^V and DMA^V with TiO_2 surfaces are formed, respectively (Jing et al., 2004). In the use of Degussa P25 TiO_2 , both MMA^V and DMA^V were readily mineralized to iAs^V (Xu et al., 2007). The photocatalytic oxidation of DMA^V formed MMA^V as the intermediate, which was subsequently oxidized to iAs^V . The pH had little effect on the degradation of MMA^V and DMA^V in the pH range between 3 and 7. Evidence for the hydroxyl radical as the primary oxidant was discussed (Xu et al., 2007). A later study using nanocrystalline TiO_2 also suggested the hydroxyl radical as a primary oxidant (Xu et al., 2008). In addition, this study determined

concentrations of total organic carbon (TOC), total carbon (TC), and formic acid during the photocatalytic oxidation of MMA^V and DMA^V (Fig. 10). The mass balance of carbon in the oxidation of MMA^V suggested that the methyl group in MMA^V may be oxidized to methanol and formaldehyde. Formaldehyde can be oxidized to formic acid under the conditions and was observed as a product of the reaction (Fig. 10). The oxidation of methanol is slow, hence it can be another product of the oxidation of MMA^V . Similar results were obtained with DMA^V , which indicated that all methyl groups of the molecule were transformed to organic compounds such as formic acid (Fig. 10).

8. Concluding remarks

Tremendous progress has been made in understanding the mechanisms of the toxicity of iAs^{III} , but much remains to be learned about mechanisms of the toxic effects of activated As^V species. The biogeochemistry of As in the environment is very complex and much has been elucidated in the last few decades about As speciation and the important parameters and processes that affect the speciation and mobility of As under different conditions. Speciation studies on As have been greatly affected by the evolution of analytical methods, which have increased differentiating power and lowered detection limits for As species. Arsenic mobility is greatly influenced by the concentration and nature of adsorbent surfaces and the adsorption process itself is affected by many factors including but not limited to pH, E_h , the presence of organic matter (OM) and competing ions. Under environmentally relevant conditions, dissolved organic matter (DOM) tends to compete with dissolved arsenic species for active sites on adsorbents and thus increases arsenic mobility. However, OM is also capable of facilitating redox reactions of arsenic species and thus affects As speciation. More research is needed on the effects of noncommercially obtained or natural POM, such as humic acids, on As speciation and mobility. Phosphate, carbonate and bicarbonate ions are most commonly reported as competing ions of consequence in the environment and can inhibit As adsorption or increase As leaching from mineral surfaces.

Although As^V species predominate in oxygenated waters and As^{III} dominates under reducing conditions, the redox speciation of As is typically not at equilibrium conditions but is affected by the kinetics of interwoven processes. Sulfidic groundwaters may also be characterized by nonequilibrium distributions of arsenic species including thioarsenates, thioarsenites, and both inorganic and other organic arsenicals.

Arsenosugars, though of considerably lesser toxicity than their inorganic counterparts, are of special interest because they are widespread in many different aquatic organisms, many of which are food sources. Arsenobetaine (AB) is very commonly found in seafood while monomethylarsonic acid (MMA^V) and dimethylarsinic acid (DMA^V) are the most commonly reported degradation products of AB formed upon cooking aquatic organisms.

Although photo-oxidation of As species has been studied as a means of remediation and as an analytical tool, little is known about the possible importance of the effects of natural levels of sunlight over prolonged time periods on As speciation in diverse aquatic environments such as marine, brackish and freshwater systems. Effective methods based on chemical, photochemical, and photocatalytic oxidation and adsorption onto coagulants exist for removing arsenic from drinking water supplies. More information of the removal efficiency of these methods in environmental-relevant conditions is needed.

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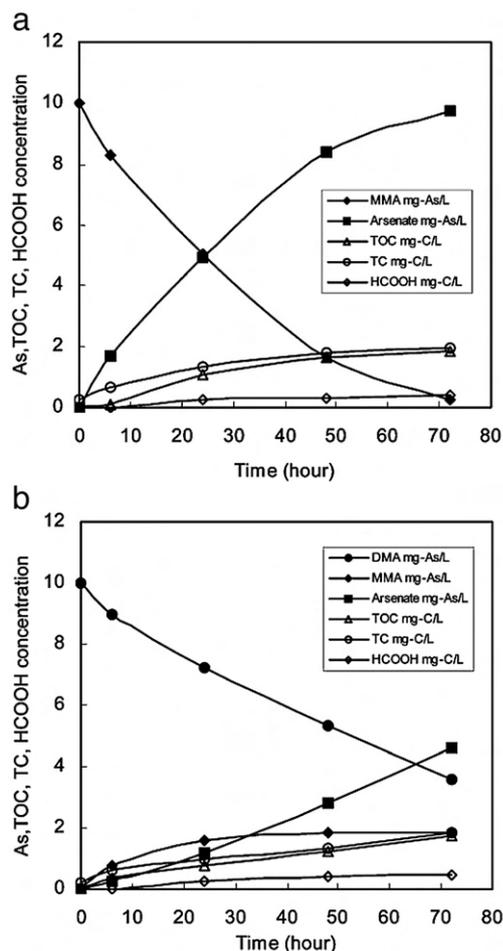


Fig. 10. Variation of TOC, TC, and HCOOH concentrations during the photodegradation process of MMA (a) and DMA (b). Initial MMA = DMA = 10 mg-As/L, TiO_2 = 0.02 g/L, ionic strength = 0.04 M NaCl (reproduced from Xu et al., 2008 with permission from the American Chemical Society).

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