Bioaccumulation, Biotransformation and Trophic Transfer of Arsenic in the Aquatic Food Chain

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Abstract

The occurrence, distribution, speciation, and biotransformation of arsenic in aquatic environment (marine- and freshwater) have been studied extensively by several research groups during last couple of decades. However, most of those studies have been conducted in marine waters, and the results are available in a number of reviews. Speciation, bioaccumulation, and biotransformation of arsenic in freshwaters have been studied in recent years. Although inorganic arsenic (iAs) species dominates in both marine- and freshwaters, it is biotransformed to methyl- and organoarsenic species by aquatic organisms. Phytoplankton is considered as a major food source for the organisms of higher trophic levels in the aquatic food chain, and this autotrophic organism plays important role in biotransformation and distribution of arsenic species in the aquatic environment. Bioaccumulation and biotransformation of arsenic by phytoplankton, and trophic transfer of arsenic in marine- and freshwater food chains have been important concerns because of possible human health effects of the toxic metalloid from dietary intake. To-date, most of the studies on arsenic biotransformation, speciation, and trophic transfer have focused on marine environments; little is known about these processes in freshwater systems. This article has been reviewed the bioaccumulation, biotransformation, and trophic transfer of arsenic in marine- and freshwater food chain.

Keywords: Arsenic speciation, Bioaccumulation, Biotransformation, Food chain, Marine and Freshwaters

1. Introduction

Arsenic is one of the significant environmental contaminants which exists mainly in four oxidation states- arsenate (As^V), arsenite (As^{III}), arsenic (As^0), and arsine (As^{-III}) (Sharma and Sohn, 2009). The toxicity of arsenic to organisms depends on its concentration and speciation, and inorganic arsenic (iAs) species are generally more toxic than organoarsenic (orgAs) species (Meharg and Hartley-Whitaker, 2002; Ng, 2005). As^{III} is usually more toxic than As^V, and dimethylarsinous acid ($DMAA^{III}$) and monomethylarsonous acid ($MMAA^{III}$) are more toxic than their parent compounds (Petrick et al., 2000; Mass et al., 2001). As^V is the thermodynamically stable state in oxic waters, while As^{III} is predominant in reduced redox environment. In aquatic systems, the dominant iAs are incorporated into microorganisms such as phytoplankton, and are converted to methylarsenicals and/or high order orgAs such as arsenosugars (AsS) (Francesconi and Edmonds, 1996). The orgAs are mineralized to iAs and methylarsenicals by bacteria (Hanaoka et al., 1995). Thus, aquatic microorganisms such as phytoplankton and bacteria play important roles in arsenic speciation, distribution, and cycling in aquatic systems (Howard et al., 1995; Hasegawa et al., 2001; Hellweger and Lall, 2004; Sharma and Sohn, 2009).

Aquatic organisms accumulate, retain, and transform arsenic species inside their bodies when exposed to it through their diet and other routes/sources such as water, soil, particles etc. (Edmonds et al., 1997; Hasegawa et al., 2001; Suhendrayatna and Maeda, 2001). Although arsenic biomagnification, a process whereby chemical concentrations increase in aquatic organisms of each successive trophic level due to increasing dietary exposures (e.g. increasing concentrations from algae, to zooplankton, to forage fish, to predator fish), is not consistent (Maher et al., 2011), previous studies reveal the possibility of this process in aquatic food webs (Goessler et al., 1997). Therefore, not only contaminated water but also fishes and other aquatic foods containing arsenic may be potential sources of human health risks. This paper reviews the distribution, speciation, bioaccumulation and metabolism, and trophic transfer of arsenic in aquatic food chains in both freshwater and marine environments.

2. Source and distribution of arsenic in aquatic systems

The occurrence, distribution, and speciation of arsenic in aquatic systems are particularly important in determining its bioaccumulation and trophic transfer through the food chain. Although iAs species (As^V and As^{III}) are the major species, methylated (DMAA, MMAA and TMAA) and complex orgAs species have also been found in marine and freshwaters. Arsenic species found in natural waters and organisms of aquatic food chain are shown in Table 1. In addition to arsenic speciation, it is difficult to estimate typical arsenic levels in aquatic systems under natural conditions because of its large variations, but most values are within the µg L^{-1} range (Cullen and Reimer, 1989). Arsenic concentrations in some major contaminated freshwater (rivers and lakes) and marine (open oceans and estuaries) systems are summarized in Table 2. The data gives a broad indication of the occurrence of arsenic in the surface waters and its provable bioaccumulation in the aquatic food chain.

2.1. Freshwaters

Concentration of arsenic in surface freshwater systems (rivers and lakes) vary by more than four orders of magnitude depending on the source, availability, and geochemistry of the catchments (Smedley and Kinniburgh, 2002). Baseline concentrations of arsenic in waters of various contaminated rivers range between 0.1 and 2.1 µg L^{-1} with an average of 0.8 µg L^{-1} (Table 2), which might be due to the source of contamination, surface recharge, base flow, and the bedrock lithology. High concentrations of naturally occurring arsenic have been reported in the Waikato River, New Zealand

(32 µg L^{-1}) (McLaren and Kim, 1995; Robinson et al., 1995a), Madison and Missouri Rivers in USA (10-370 µg L^{-1}) (Nimick et al., 1998), Owens River, CA, USA (85-153 µg L^{-1}) (Wilkie and Hering, 1998), and others (Table 2). The high concentrations of arsenic in rivers are the result of geothermal inputs, evaporation, and groundwater contamination. For example, extremely high concentrations of arsenic (up to 21,000 µg L^{-1}) in Lao River of northern Chile is due to the above-mentioned processes (Cáceres et al., 1992). Mining activity can also result in the occurrence of high arsenic in river waters. Streams adjacent to the tailing deposits in the Clubs Lake, British Columbia, contained up to 556 µg L^{-1} arsenic (Azcue and Nriagu, 1995). Water of Mole River, New South Wales, Australia also contained high levels of arsenic (110-600 µg L^{-1}, up to 13900 µg L^{-1}) from mining and processing of arsenopyrite ores (Ashley and Lottermoser, 1999).

Arsenic concentrations in lake waters are close to or lower than that reported for river waters. Studies showed that the concentrations of arsenic in lakes around British Columbia, Canada ranged between 0.2 to 2.08 µg L^{-1} (Azcue et al., 1994; Azcue and Nriagu, 1995), which has been transported from the abandoned Cariboo Gold Quartz mine tailings of that area, and has accumulated in bottom sediments of the lakes in high concentration (up to 1104 µg g^{-1}) (Azcue and Nriagu, 1995). Increased concentrations of arsenic have also occurred in lake waters from geothermal sources and due to mining activities (Smedley and Kinniburgh, 2002). Arsenic concentrations in mine-affected lake waters are relatively low due to its adsorption onto Fe-oxides under neutral pH (Smedley and Kinniburgh, 2002), and also due to its accumulation in bottom sediments (Azcue and Nriagu, 1995).

Thermal stratification of arsenic concentrations in lake waters has been reported in literature (Azcue and Nriagu, 1995; Hasegawa, 1996; Sohrin et al., 1997; Hasegawa et al., 2010). The dissolved arsenic concentration in the Moira Lake, Ontario, Canada was highest during summer with an average concentration of 47.0 µg L^{-1} in surface water, compared to 22.0 µg L^{-1} in winter (Azcue and Nriagu, 1995). Similar trends in the occurrence of arsenic concentrations in lake waters have also been reported by other researchers (Hasegawa et al., 2009). Thermal stratification in lake water also cause the release of iAs into the water column from bottom sediments due to depletion of O_2 levels in the hypolimnion (due to increased biological activities) and its subsequent redistribution throughout the lake (Smedley and Kinniburgh, 2002; Hasegawa et al., 2010). This may influence thermal stratification of arsenic concentrations in lake waters.

2.2. Marine waters

Arsenic is the 22nd most abundant chemical element in marine waters, and its average concentrations tend to be less variable in marine waters than those of freshwaters (Neff, 1997; Smedley and Kinniburgh, 2002). Average arsenic concentration in open marine waters is around 1.5 µg L^{-1}, and its concentrations in deep Pacific and Atlantic waters is between 1.0 - 1.8 µg L^{-1} (Cullen and Reimer, 1989), 1.5 µg L^{-1} in southeast coast of Spain (Navarro et al., 1993), and 1.1 - 1.6 µg L^{-1} in coastal waters of southern Australia (Maher, 1985a) (Table 2). Ishikawa et al. (1987) reported mean concentration of 3.1 µg L^{-1} in marine waters of the Pacific coast near Nakaminato (Ibaraki, Japan), and 0.6 µg L^{-1} near Onagawa (Miyagi, Japan).

The concentrations of arsenic in estuarine waters are more uniform than those of open marine waters (Table 2). Arsenic concentrations in the estuarine waters may be affected by industrial and mining effluents and geothermal water (Smedley and Kinniburgh, 2002). The simple physical mixing of the fresh- and sea water masses and salinity may influence the concentration of dissolved arsenic in estuaries and continental shelves. For example, a linear increase in total arsenic concentrations, ranging from 0.13 µg L^{-1} in freshwaters to 1.8 µg L^{-1} in offshore waters, with the increase in salinity has been reported in Krka Estuary, Yugoslavia (Seyler and Martin, 1991). Bioactivities of aquatic organisms (e.g., phytoplankton and bacteria) also influence arsenic speciation and concentration in estuarine waters. Depletion of phosphate concentrations in biologically productive surface waters is related to the decrease in As^V concentrations in oxic estuarine waters, and the As^V profile showed a slight increase with depth, while As^{III} and $DMAA^{(III+V)}$ maxima were observed in biologically productive surface waters (Hasegawa, 1996). Thermal stratification influences arsenic distributions in estuarine water. For example, Abdullah et al. (1995) found that arsenic distributions in Vestfjord estuary in Norway were fairly uniform in the water column ranging between 0.75 and 1.05 µg L^{-1}, while total arsenic concentrations in Bunnefjord estuary were lower in surface water (0.52-0.75 µg L^{-1}), which increased to 1.04-1.20 µg L^{-1} in midwater, and 1.5-1.9 µg L^{-1} at 100 m depth.

3. Determination of arsenic species in biota

3.1. Arsenic speciation and toxicity

Although iAs is generally more toxic than organoarsenic species, toxicity of iAs species for aquatic organisms remains contentious. With many exceptions, marine phytoplankton are more sensitive to As^{III}, while freshwater phytoplankton are highly sensitive to As^V (Knauer et al., 1999; Yamaoka et al., 1999; Levy et al., 2005). For example, the marine phytoplankton *Dunaliella* sp. and *Polyphysa peniculus* are more sensitive to As^V than As^{III} (Cullen et al., 1994; Takimura et al., 1996). Pawlik-Skowronska et al. (2004) reported that As^V and As^{III} exerts equal toxicity to freshwater phytoplankton *Stichococcus bacillaris* at pH 8.2 with phosphate levels between 0.03 and 0.3 mg L^{-1}. They also reported that the toxicity of As^V to the phytoplankton is higher than As^{III} at lower pH. Equal toxicity of As^{III} and As^V was reported for freshwater phytoplankton *Chlorella* sp. at pH 7.6, while other reported As^V to be more toxic than As^{III} for another freshwater phytoplankton *Monoraphidium arcuatum* at the same pH (Levy et al., 2005). Thus, it is evident that the toxicity of arsenic is highly dependent on its chemical speciation, and the determination of total arsenic in environmental and biological samples is not adequate to assess the risks associated with consumption of arsenic-containing foodstuffs. Therefore, much attention has been given to the elemental speciation of arsenic in environmental and biological samples. More than twenty arsenic species have been identified from environmental and biological samples (Gong et al., 2002), and a wider diversity of arsenic species were observed in organisms comprising the food chain of aquatic systems. The identification of these arsenic species in environmental and biological samples was possible with significant development of analytical techniques over the last couple of decades.

3.2. Methods for extracting arsenic species from biological samples

The extraction and clean-up procedures comprise critical steps for analyzing biological samples due to possible losses of analytes, changes of the species, or incomplete extraction of the arsenic compounds that may lead to poor or erroneous results (Gomez-Ariza et al., 2000). A number extraction procedure has been employed for the extraction of arsenic species from biological samples such as: enzymatic digestion (Branch et al., 1994; Lamble and Hill, 1996), methanol, methanol–water, methanol–water–chloroform mixtures (either with manual agitation, vortex agitation, or sonication) (Shibata and Morita, 1992; Thomas and Sniatecki, 1995; Ochsenkühn-Petropulu et al., 1997), HCl solubilization and microwave-assisted distillation (Munoz et al., 1999a; Munoz et al., 1999b), semi-automated accelerated solvent extraction (Gallagher et al., 2001). The methanol-water method is commonly used to extract arsenic species from food (Gomez-Ariza et al., 2000; McSheehy et al., 2001; Suner et al., 2001), while the sequential extraction procedure has been employed to extract arsenic species in fish tissue (McKiernan et al., 1999). McKiernan et al. (1999) found that about 5% of arsenic is extracted by acetone in the fish tissue and the extraction efficiencies of arsenic in the polar fraction were 84.9–87% by using sonication. Chloroform is another solvent that has been used to remove the lipid and fat soluble fractions of arsenic in fish and biological marine samples (Branch et al., 1994; Albertí et al., 1995).

Solubilization with HCl and microwave-assisted distillation methods have been used for the extraction of total iAs from seafood products (Munoz et al., 1999a; Munoz et al., 1999b). These methods, however, are not suitable for the determination of As^{III} and As^{V} species individually because As^{V} is converted to As^{III} during the hydrolysis and extraction processes. A semi-automated accelerated solvent extraction method was also tested for the extraction of arsenic species in seaweed products (Gallagher et al., 2001). Results showed that the extraction efficiencies for ribbon kelp was approximately 72.6%, which were fairly independent of pressure, static time and particle size, and no significant changes of the arsenosugars were observed with this method except under high-temperature (Gallagher et al., 2001).

3.3. Analytical methods for the determination of arsenic species in biological samples

Arsenic in biological samples is mainly found in the form of organic species (Cullen and Reimer, 1989), Arsenobetaine (AsB), the main species of arsenic in a number of marine organisms such as fish, molluscs and crustaceans, was first isolated and identified in the Western rock lobster by Edmonds et al. (1977) using vapor generation atomic absorption spectrometry following digestion of the sample with a mixture of perchloric and nitric acids. After that, a number of analytical methods were developed and successfully applied to determine arsenic species in biological samples.

The analytical approaches for the speciation of arsenic in biota samples generally involve the use of separation techniques coupled with a sensitive atomic detector. High performance liquid chromatography (HPLC) has been successfully coupled directly to inductively coupled plasma-optical emission spectrometry (ICP-OES) (Amran et al., 1997) and inductively coupled plasma-mass spectrometry (ICP-MS) (Goessler et al., 1998). Other atomic detectors such as atomic absorption spectrometry (AAS) (Velez et al., 1996) and atomic fluorescence spectrometry (AFS) (Le et al., 1996) include hydride generation (HG) as an intermediate step, which converts the arsenic compounds into volatile arsines prior to their detection. However, organoarsenic compounds such as AsB and AsS do not form volatile hydrides, and the destruction of the organic part of the molecules before hydride generation is required. This has been achieved by the use of both on-line microwave digestion (Le et al., 1994a) and photooxidation with UV radiation (Gomez-Ariza et al., 1998; Tsalev et al., 1998). Other approaches based on hydride generation of the arsines and their preconcentration using cold trapping (CT) provide very good sensitivity for measuring iAs, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) (Hasegawa et al., 1994; Featherstone et al., 1998). However, HG-AAS-CT does not allow for the determination of AsB and AsS, and therefore is not usually considered for arsenic speciation analysis in biota.

Capillary electrophoresis (CE) technique has also been used to determine arsenic species in water and biological samples (Gosio, 1897; Murray et al., 2003; Meyer et al., 2007; Michalke et al., 2007; Meyer et al., 2008). Van Holderbeke et a. (2007) and Michalke, and Schramel (2008) were successfully separated four anionic (As^{III}, As^{V}, MMAA and DMAA) and two cationic forms (AsB and AsC) of arsenic in a single run by coupling CE on-line with inductively coupled plasma mass spectrometry (ICP-MS). Others used coupling CE to hydride generation atomic fluorescence spectrometry (Gosio, 1897) and CE-ICP-MS with a movable reduction bed hydride generation system (Michalke et al., 2007). Yeh et al. (2003) measured six arsenic compounds (As^{III}, As^{V}, MMAA, DMAA, AsB, and AsC) in fish and oyster tissues by CE-inductively coupled plasma-mass spectrometry.

Anion-exchange chromatography-inductively coupled plasma mass spectrometry (AEC-ICP-MS) was used for the quantification of (oxy)thioarsenate (As-S) species in sulfidic waters, and electrospraytandem mass spectrometry (ES-MS-MS) for the characterization of those As-S species (Raml et al., 2007; Wallschläger and Stadey, 2007). X-ray absorption spectroscopic (XAS) methods such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) are being increasingly used for the analysis of arsenic species often in geological samples (Mass et al., 2001; Dopp et al., 2010), and also in arsenic-rich biological samples (Fricke et al., 2005; Pinyayev et al., 2011). Detail analytical methods for arsenic speciation in environmental samples have been adequately reviewed by Francesconi and Kuehnelt (2007).

4. Arsenic concentrations and speciation in aquatic food chains

As^{V} is the major and thermodynamically stable form in oxic conditions, and is observed mostly in marine waters while the unstable As^{III} is transformed by marine phytoplankton and bacteria (Francesconi and Edmonds, 1996). The MMAA and DMAA are also found in marine waters, but these are significant species in highly productive freshwaters (Hasegawa et al., 2009; Hasegawa et al., 2010). Some key plant species of aquatic food chains also contain mostly iAs (Reuther, 1992; Milton and Johnson, 1999; Koch et al., 2000; Foster et al., 2005; Peng et al., 2008; Lafabrie et al., 2011) and little methylated species (Koch et al., 2000). The occurrence of unknown arsenic compounds (hidden As) in marine waters and freshwaters has also been reported by some researchers (De Bettencourt and Andreae, 1991; Bright et al., 1996; Hasegawa et al., 1999).

In general about 85 to > 90% of arsenic found in edible portions of marine fish and shellfish are AsB, arsenocholine (AsC), and DMAA and approximately 10% are iAs species. For example, AsB concentrations in marine fish, elasmobranchs and teleosts, were about 3.1-44.3 and 0.1-166 mg kg^{-1}

wet wt., respectively, which comprised about 94% of the total arsenic in those fishes. DMAA and TMAO concentrations in marine lobsters and prawns were 4.7-26 and 5.5-20.8 mg kg^{-1} wet wt., respectively, which represented up to 95% of the total arsenic in them (Table 4). However, less is known about the forms of arsenic in freshwater fish, but the available evidence suggests that AsB and DMAA are the main species in freshwater fishes (Slejkovec et al., 2004; Soeroes et al., 2005a). For example, Slejkovec et al. (2004) found that the major fraction of extractable arsenic [47.1±3.6 - 815±22 mg kg^{-1} fresh weight (f. wt.); about 92–100%] is AsB in some species of *salmonidae*, while DMAA predominates (56.5±4.7 mg kg^{-1} f. wt.; about 75% of extractable arsenic) over AsB (7.4±2.6 mg kg^{-1} f. wt.; about 25% of extractable arsenic) in burbot (*Lota lota*). AsB is commonly known as "fish arsenic" since this species is mostly found in marine fishes. AsC (Lawrence et al., 1986; Benjamin et al., 1987) and arsenoribosides (AsR) (Kirby et al., 2002) have also been found in marine animals (fish, shellfish, lobsters, shrimp etc.). Arsenic speciation pattern in marine and freshwater fishes is almost identical, however, few studies reported iAs as the predominate species over orgAs (AsB, AsC) in freshwater fishes (Henry, 2003).

Lipid soluble arsenicals are the major species in marine macroalgae (Morita and Shibata, 1990), and about 16 AsS (four are most common) have been identified from marine macroalgae. Thomson et al. (2007) reported that total arsenic concentrations varied between classes of algae, and significant differences between algal classes and habitats were found for the proportion of arsenic species. Green algae have a higher proportion of lipid soluble arsenic (19–44%) than red inter-tidal (5–34%) or estuarine algae (10–24%) (Thomson et al., 2007). However, Vivian et al. (1997) reported that the concentrations of arsenic compounds in freshwater macroalgae appear to have similar patterns to those in marine macroalgae.

4.1. Marine food chain

Since the first determination of arsenic in fish and other marine organisms by Thiergardt and by Gautier and Clausman (Lunde, 1977), there has been a series of investigations in which researchers have analyzed arsenic species in biological and non-biological samples in the marine environment. Arsenic concentrations in marine biological samples (flora and fauna) comprising the food chain are listed in Table 3.

As^{V} and As^{III} are the major inorganic forms of arsenic, and the bulk of the total dissolved arsenic is iAs in marine waters (Peterson and Carpenter, 1983). Although arsenic should exist almost entirely as As^{V} in oxygenated marine waters, it is found even under anoxic (reduced) waters (Cullen and Reimer, 1989). iAs being the major species in waters, they are also found in the biota of marine food chains. Phytoplankton is the most common primary producer in marine food chains, which uptake As^{V} from surrounding water and reduce it to thermodynamically unstable As^{III} (Sanders et al., 1989); but this As^{III} is readily oxidized to the more stable As^{V} form in oxic marine waters upon excretion (Francesconi and Edmonds, 1996). The reduction of As^{V} to As^{III} by marine phytoplankton explains the observed As^{III}/As^{V} ratios in marine waters.

Arsenic concentration and speciation vary greatly in macroalgae and phytoplankton, the important primary producer in marine food chains. In general, brown algae contain much higher levels of total arsenic (up to 230 µg g^{-1} d. wt.) than green (up to 23.3 µg g^{-1} d. wt.) and red (up to 39 µg g^{-1} d. wt.) algae (Francesconi and Edmonds, 1993). Higher concentrations of total arsenic have also been reported for red macroalgae (4.3-24.7 µg g^{-1}) than green macroalgae (8.0–11.0 µg g^{-1}) and bluegreen algae (10.4–18.4 µg g^{-1}) (Thomson et al., 2007). Andreae (1978) in investigating arsenic speciation in water and in some marine macroalgae from Southern California, USA, and observed large variations in the concentrations of iAs and methylated arsenic species in marine macroalgae. For example, significantly higher concentrations of methylated arsenic species were found in *Pelagophycus porra* compared with iAs species, while the opposite trend was found in other macroalgae (*Eisenia arborea*, *Agarum fimbriatum*, *Cystoseira osmundacea*). High concentrations of iAs species in marine macroalgae and phytoplankton have also been reported by other researchers (Francesconi and Edmonds, 1993; Francesconi and Edmonds, 1996). Edmonds et al. (1987) measured substantial amounts of As^V (≥ 20% of total water soluble arsenic) in Japanese edible seaweed *Hizikia fusiforme*. Senders (1979a) observed significant variations in total arsenic concentrations in marine macroalgae, ranging from an average of 10.3 $\mu g\ g^{-1}$ in the Phaeophyceae to 1.54 $\mu g\ g^{-1}$ in the Chlorophyceae and 1.43 $\mu g\ g^{-1}$ in the Rhodophyceae. The chemical speciation in these marine macroalgae revealed that an average of 22% of the total arsenic in the Phaeophyceae was iAs species while that in the Chlorophyceae and Rhodophyceae it was about 45%.

The large variations in the concentrations of iAs and methylarsenic species in marine phytoplankton were due to the biotransformation of iAs species to methylated species within the phytoplankton cell. The variations in the occurrence of inorganic and methylated species may also be dependent to the phytoplankton species because of their different biotransformation efficiencies. After being taken up by marine phytoplankton from the surrounding water, As^V is incorporated into an array of carbohydrate compounds and is biosynthesized to organoarsenicals (Francesconi and Edmonds, 1993). According to Kaise et al. (1997), most of the orgAs in marine phytoplankton are AsS, and these species are the precursors in the metabolic pathway to AsB and AsC (Hansen et al., 2003). Marine algae can hold 1000 times higher arsenic concentration than that in the surrounding water (Sanders and Windom, 1980), which may contribute to the trophic transfer of arsenic to higher levels of the marine food chain thus posing a real threat to human health.

Fish are the most important consumers in marine food chain. Arsenic is mainly accumulated into marine animals from water and lower trophic level organisms, which the animals feed on. Since As^V is taken up from water by marine phytoplankton, the most important food for animals of higher trophic level, and is converted largely to As^{III}, there is a possibility of the existence of iAs species in marine animals. Peshut et al. (2008) reported that some marine species of fish and shellfish from the islands of American Samoa in the South Pacific contained iAs of about 0.5% (in some samples the concentrations ranged between 1 and 5%) of total arsenic. Some studies also found low levels of iAs in marine fish and animals (Maher et al., 1999; Kirby et al., 2002). Wrench (1979) investigated the bioaccumulation and speciation of arsenic in a three-step marine food chain consisting of an autotroph, a grazer, and a carnivore. Results suggested that iAs in marine food chains are derived from *in vitro* synthesis of the primary producer and are transferred through the food chain. Marine animals themselves could not form/biosynthesize iAs. Although AsB is the major species in marine animals such as fish, lobster, shrimp, and other crustaceans, it occurs in all trophic levels of the marine food chain. AsB concentration also increased (or constituted a greater percentage of the total arsenic) with the increase in trophic levels (Francesconi and Edmonds, 1996) suggesting it does biomagnify through the marine food chain.

4.2. Freshwater food chain

The bulk of the total dissolved arsenic species in freshwaters are also iAs as it is in marine waters (Seyler and Martin, 1989; Kuhn and Sigg, 1993). Arsenic concentrations in organisms of freshwater food chains are summarized in Table 4. Bioaccumulation of dissolved arsenic in aquatic organisms occurs through absorption through the gills or integument and/or consumption of prey. Arsenic concentrations in freshwaters are usually higher than that in marine waters because of atmospheric deposition (Nriagu, 1983) and direct input from geothermal and anthropogenic sources as well as mine effluent (Bright et al., 1994; Bright et al., 1996; Romero et al., 2003). Therefore, freshwater organisms will potentially be exposed to higher arsenic concentrations compared with their marine counterparts, which may result in greater bioaccumulation of arsenic in freshwater food chains.

As in marine waters, phytoplankton and macroalgae are also important primary producers in freshwater food chains. Arsenic content in freshwater algae is lower than that in marine algae, and most of the arsenic compounds in them are water-soluble (Kaise et al., 1988; Phillips, 1990). Lai et al. (1997) report that 93% of total arsenic in *Nostoc* sp. was oxo-arsenosugar-glycerol, while Koch et al. (1999) found As^V to be the dominant species. In accordance with the previous reports, AsS in the freshwater green alga *Cladophora* sp. is oxo-arsenosugar-glycerol (Schaeffer et al., 2006). Schaeffer et al. (2006) investigated arsenic species in biological samples from the Danube River in Hungary and found AsS as the dominant arsenic species in freshwater algae, whereas As^V was present only as a minor constituent. Kaise et al. (1997) studied the arsenic species in freshwater algae and observed that the content of water-soluble dimethylarsenic was significantly higher than other arsenic species. The concentrations of dimethylarsenic compounds in freshwater green algae (*Clodophora glomerata*) and diatoms were 0.39 and 0.10 µg g^{-1} f. wt. (85 to 81% of the total arsenic, respectively), while iAs content was 0.044 and 0.01 µg g^{-1} f. wt., respectively. The results indicates that the accumulated iAs in the green algae and diatoms were converted mainly to dimethylarsinic compounds in their tissue (Kaise et al., 1997).

Arsenic enters the aquatic food chain through direct consumption of water or biota, and through non-dietary routes such as uptake through absorbing epithelia. Gills, skin, and digestive tract are potential sites of absorption of water soluble arsenic species for fishes. Skin may serve as a particularly important arsenic absorbing site for small fishes because of their high surface area to volume ratio of their bodies. Although AsB is the main species of arsenic in marine fish, there have been contentious reports about arsenic speciation in freshwater food chains. Chemical speciation of arsenic in whole body tissue of consumers of the freshwater food chain varies greatly between species. Caddisfly larvae and pupae have been reported to contain mostly DMAA comprising about 86 and 56% of the total arsenic, respectively, while its content in the marsh snail was about 27% (Henry, 2003). The remainder of the total arsenic in the marsh snail was orgAs compounds (mainly AsB and AsC), and a little amount of iAs (Henry, 2003).

Kaise et al. (1997) found that the major arsenic species in fishes from the Hayakawa River was iAs (93%) followed by trimethylarsenicals (7%). Other researchers reported AsB as the major arsenic species in freshwater fish (Shiomi et al., 1995; Slejkovec et al., 2004), while Zheng and Hintelmann (2004) found trace amounts of AsB, and Lawrence et al. (1986) did not detect AsB at all in freshwater fish. Koch et al. (2001) and Soeroes et al. (2005b) reported AsS as the predominant species in some freshwater fishes, while AsB was found in a small amount. Kaise et al. (1997) found that the content of trimethylarsenicals was higher than dimethylarsenicals in freshwater fishes and the marsh snail except for *Tribolodon hakoensis*.

Burger et al. (2002) investigated arsenic bioaccumulation in 11 species of freshwater fishes from the Savannah River near the Savannah River Site, USA representing different trophic levels of the food chain. Arsenic concentrations in fish of lower trophic level was higher (0.32 µg g^{-1} f. wt. in the bowfin (*Amina calva*); a primary consumer) than that in fish of higher trophic level (0.03 µg g^{-1} f. wt. in the spotted sucker (*Minytrema melanops*); a top level consumer) (Table 4). On the basis of the above discussion, it can be concluded that arsenic speciation and distribution in freshwater organisms are more diverse and complicated than that in marine organisms. This might be due to greater spatial and seasonal variability in arsenic mobilization in various studied catchments, contamination, and sources of contamination.

5. Biosynthesis and biotransformation of arsenic species in aquatic food chain

Arsenic is ubiquitous in living tissues and is oxidized, reduced, or otherwise metabolized. Background arsenic concentrations in living organisms are usually < 1 µg g^{-1} f. wt. in terrestrial flora and fauna, birds, and freshwater biota. Plants and animals collected from naturally arseniferous areas or near anthropogenic sources, however, may contain significantly elevated tissue residues of arsenic. Marine organisms, especially crustaceans, may contain more than 100 µg g^{-1} d. wt., usually as water soluble AsB that poses less risk to the organism or its consumer.

It has been assumed that the occurence of AsB in this organism was the consequence of biological cycling of As in the marine environment. As^{V}, the stable and predominant species of arsenic in aquatic environment, is transformed to As^{III} by phytoplankton, methylated to MMAA and DMAA by phytoplankton (Aurilio et al., 1994; Sohrin et al., 1997; Hasegawa et al., 2001; Hellweger and Lall, 2004). Kuroiwa et al. (1994) studied the biotransformation of arsenic compounds (As^{V}, MMAA, DMAA, and AsB) in the freshwater shrimp (*Neocaridina denticulata*) and the killifish (*Oryzias latipes*). The shrimps and fishes were cultured in 1.5, 10, 40, and 150 µg mL^{-1} of As^{V}, MMAA, DMMA, and AsB, respectively. Results showed that *N. denticulata* accumulated arsenic from the aqueous phase containing 1.5 µg mL^{-1} of As^{V}, 10 µg mL^{-1} of MMAA, 30 µg mL^{-1} of DMAA or 150 µg mL^{-1} of AsB, and biotransformed, and excreted a part of these species. Both methylation and demethylation of the arsenicals were observed *in vivo*. The accumulation of methylated arsenic species relative to the total arsenic increased successively with the elevation in the trophic level. Only trace amounts of MMAA were detected in the shrimp and fish tested.

In the biotransformation pathway, phytoplankton actively absorb As^{V} because they mistake it for PO_4^{3-}, and the similarities between As^{V} and PO_4^{3-} break down inside the their cells and As^{V} produce toxicity to the organism (Hellweger and Lall, 2004). The biotransformation of arsenic species by phytoplankton is summarized in Figure 1. In the biotransformation pathway, phytoplankton reduce As^{V} to As^{III}, and methylate to MMAA and DMAA. Some researchers speculated this process of arsenic biotransformation as a detoxification mechanism of phytoplankton (Knauer et al., 1999; Murray et al., 2003), while others opposed this assumption, since As^{III} and trivalent methylated species ($DMAA^{III}$ and $MMAA^{III}$) are highly toxic (Petrick et al., 2000; Mass et al., 2001; Dopp et al., 2010). However, a study by Hasegawa et al. (Hasegawa et al., 2001) showed that freshwater phytoplankton (*Closterium acicolare*) convert As^{V} predominantly (~80%) into pentavalent methylated intermediate ($DMAA^{V}$), which is less toxic, and the order of arsenic toxicity to organisms (most to least) is $MMAA^{III} > As^{III} > As^{V} > MMAA^{V} = DMAA^{V}$ (Mass et al., 2001). Therefore, biotransformation of iAs to methyl- and organoarsenicals followed by excretion is the main detoxification/defense mechanisms in phytoplankton.

The phytoplankton biotransformation of As^{V} to As^{III}, and subsequent methylation to DMAA, MMAA are correlated to the growth rate of the organisms and to the phosphorus nutrient status in the environment (Hellweger et al., 2003). At slow growth rates and under P-limited conditions, the phytoplankton take up more As^{V}, reduce it to As^{III}, methylate it to MMAA and DMAA, and then excrete it as DMAA (Fig. 1). In contrast, at fast growth rates under P-sufficient conditions, As^{V} is biotransformed to both As^{III} and DMAA, but the reduction to As^{III} is faster than the methylation to DMAA (Hellweger and Lall, 2004). Besides the methylation of As^{V} to DMAA and MMAA by phytoplankton, demethylation of methylarsenicals by bacteria has also been reported. Maki et al. (2006a) isolated MMAA-mineralizing bacteria. The demethylation and oxidation of methylarsenicals by bacteria have been studied in marine waters by Senders (1979b) and in freshwaters by Maki et al. (2005; 2006b).

5.1. Inorganic arsenicals

The main source of iAs in organisms in the aquatic food chains is water they live in. Both in marine and freshwater food chains, phytoplankton take up iAs and therefore, these compounds constitute a significant fraction in them (Cullen et al., 1994). As^V uptake by aquatic phytoplankton is supposed to occur unintentionally through the phosphate uptake mechanisms due to the chemical and structural similarities between arsenate and phosphate (Hellweger and Lall, 2004). The biotransformation and cycling of arsenic species within the aquatic components/organisms is shown in Figure 2.

Biotransformation of iAs by trophic level 2 organisms such as fish, shellfish, crustaceans have not been evident. In general, for trophic level 2 organisms exposed to either As^V or As^{III} under laboratory conditions, approximately 80% of their tissue burden remained in the iAs forms, while less than 20% was biomethylated (Henry, 2003). Suhendrayatna and Maeda (2001) studied bioaccumulation and biotransformation of As^{III} by the waterflea (*Daphnia magna*) and red cherry shrimp (*Neocaridina denticulate*). Results showed that upon exposure to As^{III} for 7 days under static conditions, *D. magna* contained about 63-75% As^{III} and 24-36% As^V, with geometric means of approximately 70% and 28%, respectively. The relative fraction of DMAA measured in their whole body tissues was less than 2%. In contrast *N. denticulate* contained from 37-48% As^{III} and 22-56% As^V, with geometric means of approximately 43% and 35%, respectively. The relative fraction of DMAA in *N. denticulate* was markedly higher (about 7-32%) than that in *D. magna*.

Suhendrayatna and Maeda (2001) also studied the biotransformation of iAs within the freshwater food chain by feeding a diet of As^{III}-dosed phytoplankton (*Chlorella vulgaris*) to herbivorous grazers (*D. magna* and *N. denticulata*) and then the herbivores were fed to the carnivorous fish (*Tilapia mossambica* and *Zacco platypus*). Results showed that feeding a diet of As^{III}-dosed *C. vulgaris* containing 83% As^{V}, 9% As^{III} and 6% DMAA, tissue As^{V} and As^{III} concentrations were 44% and 56% for *D. magna*, respectively, while these were 9% and 91% for *N. denticulate*, respectively. In both cases, regardless of exposure type (water or dietary phytoplankton), iAs accumulated and remained as the predominant species in these organisms, with relatively little indication of biomethylation. In other studies, Suhendrayatna et al. (2002a; 2002b) investigated bioaccumulation and biotransformation of As^{V} and As^{III} by Japanese Medaka (*Oryzuas latipes*) and *T. mossambica*, and observed a similar trend to that of Suhendrayatna and Maeda (2001) for *T. mossambica* and *Z. platypus*. Similar observations were also reported for the red cherry shrimp exposed to As^{V} (Maeda et al., 1990b; Maeda et al., 1992a; Maeda et al., 1993). It is evident from these studies that As^{III} and As^{V} were accumulated as the predominant species in freshwater organisms, and the concentrations of total arsenic in the organisms decreased by an order of magnitude for each trophic step up the food chain. Little methylation of arsenic in organisms occurred at each step in the food chain (Suhendrayatna and Maeda, 2001).

5.2. Methylarsenicals

Methylarsenicals in aquatic systems are produced by phytoplankton, bacteria, and microbial degradation of biological materials from iAs. Biomethylation of iAs to di- and trimethylated species has been observed in both marine and freshwater systems. Diatoms such as *Skeletonema* sp. and *Rhizosolenia delicatula* are also produce DMAA (Howard et al., 1995; Hasegawa et al., 2001). The cryptophyte, *Chroomonas* spp., has been reported to be associated with the production of MMAA in Chesapeake Bay (Sanders and Osman, 1985). The occurrence of methylated arsenic compounds in marine waters has long been attributed to methylation by phytoplankton (Howard et al., 1995; Hasegawa et al., 2009) (Fig. 1). Anderson and Bruland (1991) dispute the direct production of DMAA by phytoplankton in field samples. Since photochemical degradation by sunlight contributes a little to the production of DMAA in lake waters, microbial degradation of complex orgAs compounds is assumed to be the possible reason for DMAA production too (Hasegawa et al., 1999). Thus, it is evident that As^{V} is taken up by phytoplankton in the euphotic surface waters and subsequently converted to As^{III}, DMAA, and MMAA and released back to the water column (Howard et al., 1995; Sohrin et al., 1997; Hasegawa et al., 1999; Hasegawa et al., 2009). For freshwater phytoplankton, generally $MMAA^{V}$, $DMAA^{V}$ and some trimethylated species were found (Murray et al., 2003). Other studies also revealed that freshwater phytoplankton (e.g., *Closterium acicolare*) biotransform iAs predominantly to pentavalent methylarsenicals ($MMAA^{V}$ and $DMAA^{V}$) (Hasegawa et al., 2001), prior to release into the water.

Methylarsenicals are the intermediate compounds in the biosynthesis of complex arsenosugars in marine phytoplankton. In this biosynthetic pathway, marine phytoplankton reduce iAs to methylarsenicals through stepwise oxidative methylation from S-adenosylmethionine to $DMAA^{V}$, which is then reduced to $DMAA^{III}$ (Murray et al., 2003). The production of methylarsenic species is related to the growth phage or phytoplankton and nutrient status. Hasegawa (2001) observed that the production of $DMAA^{V}$ was increased gradually, while trimethylarsenicals ($DMAA^{III}$ and $MMAA^{III}$) remain relatively steady during the stationary phage of phytoplankton (*Closterium acicolare*) growth. The production of $DMAA^{V}$ is high when the ratio of phosphate and arsenate decreases in the culture medium indicating that $DMAA^{V}$ production is increased at P-replete conditions (Hasegawa et al., 2001; Hellweger and Lall, 2004).

In addition to the methylation by phytoplankton, anaerobic members of archaea and bacteria have also been reported to biotransform iAs species into both volatile (e.g., methylarsines) and nonvolatile (e.g., MMAA and DMAA) compounds (Bentle and Chasteen, 2002; Meyer et al., 2008). The biosynthesis of volatile arsenic compounds, which was subsequently identified as trimethylarsenic, by several ascomycetes was reported by Gosio (1897) for the first time. Recent studies have also reveal that several methanoarchaea e.g., *Methanosphaera stadtmanaea* DSM 3091^T, *Methanococcus vannielii* DSM 1224^T, *Methanoplanus limicola* DSM 2279^T, *Methanobacterium formicicum* DSM 1535^T (Michalke et al., 2007), *Methanobrevibacter smithiia* DSM 2374 (Meyer et al., 2008) and bacteria e.g., strain ASI-1 of the species *Clostridium glycolicum* (Meyer et al., 2007) produce volatile methylarsenic species. Maeda et al. (1992b) identified two arsenic-resistant bacteria (*Klebsiella oxytoca* and *Xanthomonas* sp.) that can bioaccumulate and biomethylate As^V. It has been revealed that microorganisms such as phytoplankton, archaea and bacteria have the ability to biotransform iAs species to methylarsenicals (MMAA and DMAA) and/or high order organoarsenic species such as arsenosugars.

5.3. Thioarsenicals

Thioarsenicals, structural analogues of oxyarsenicals in which sulfur replaces oxygen, are formed by exposure of oxyarsenicals to hydrogen sulfide (H_2S) (Fricke et al., 2005). The existence of thioarsenicals in the environment has not been reported until the recent development of analytical techniques. Based on geochemical considerations, it was predicted that reduced (oxy)thioarsenic species should be produced from the reaction between arsenite and sulfide, and Wallschläger and Stadey (2007) have shown the evidence that four homologue (oxy)thioarsenates (AsO_3S^{3-}, $AsO_2S_2^{3-}$, $AsOS_3^{3-}$ and AsS_4^{3-}) can be formed in geochemical model reactions between As^{III} and sulfide under anoxic conditions. They hypothesized that these compounds appear to be major arsenic species in natural sulfidic waters. In a recent study, Wallschläger and London (2008) have confirmed the existence of four methylated thioarsenicals [monomethylmonothioarsenate, $(CH_3)AsO_2S^{2-}$; monomethyldithioarsenate, $(CH_3)AsOS_2^{2-}$; dimethylmonothioarsenate, $(CH_3)_2AsOS^-$; and dimethyldithioarsenate, $(CH_3)_2AsS_2^-$] in groundwater collected from an aquifer impacted by methylated arsenic pesticides.

Biosynthesis of thioarsenicals, either from the inorganic forms or from the methylated forms, by aquatic microorganisms (e.g., phytoplankton, bacteria) has not been reported to date; however, it has been shown that some thioarsenicals are formed during the metabolism of arsenic oxyanions in animal tissues (Hansen et al., 2004; Suzuki et al., 2004). Thiolated arsenicals have also been detected in human's gastrointestinal tissue and urine after exposure to iAs and $DMAA^V$ (Naranmandura et al., 2006; Raml et al., 2007). Studies have also shown that anaerobic microbiota from mouse cecum or human feces can convert $DMAA^V$ into thiolated metabolites (e.g., dimethylthioarsenate; DMMTA) and trimethylated metabolites (trimethylarsine oxide; TMAO, and trimethylarsine sulfide; TMAS) (Kubachka et al., 2009). The prevalence of H_2S-producing organisms in the microbiota and the relatively high pH of the distal gastrointestinal tract favour the production of thioarsenicals (Pinyayev et al., 2011).

The toxicological relevance of thioarsenical compounds to organisms are still unclear, but there is some evidence that methylated thioarsenic compounds are significantly more toxic than their oxyanion counterparts (Styblo et al., 1997). Most studies have been dealing with the production of thioarsenicals in underground drinking water and animals (e.g., in gastrointestinal tissues of human) because of toxicological relevance of these compounds to human. Since anaerobic condition favour the production of the thioarsenic compounds (Kubachka et al., 2009), microorganisms in sulfide-rich anaerobic aquatic sediments may play a crucial role in the production of thioarsenicals in the aquatic environment that may affect the health of aquatic organisms. But there is no report on biosynthesis and biotransformation of thioarsenicals by aquatic organisms. Since this review mainly focuses on the biotransformation of arsenic in aquatic systems, in-depth discussion on thioarsenic compounds in animals is not continued.

5.4. Organoarsenicals

5.4.1. Arsenosugars

The presence of AsS in marine organisms was not confirmed until the isolation and identification of these species from the brown kelp (algae) *Ecklonia radiata* (Edmonds and Francesconi, 1981). After that a total of 15 AsS has been identified from brown algae and other algal families (Francesconi and Edmonds, 1993). McSheehy et al. (2002) identified 15 orgAs species in *Tridacna derasa* kidney, eight of which were ribofuranosides. Dimethylarsinoylribosides mostly being the AsS in marine sources, trimethylarsonioribosides have also been identified and isolated from a marine brown algae (Francesconi and Edmonds, 1996). Two triaklylarsonioriboside diastereoisomers have also been isolated as a mixture from marine brown algae (Francesconi et al., 1991). Details of the synthesis and characterization of AsS are described elsewhere (Francesconi and Edmonds, 1996).

Although the reason is unclear, it has been suggested that marine algae absorb As^V from marine waters and convert it to AsS (Edmonds and Francesconi, 2003). It is supposed that, like other plant species, marine algae readily absorb dissolved As^V through the phosphate uptake mechanism. Sanders and Windom (1980) demonstrated an antagonistic relationship between As^V and phosphate during uptake by phytoplankton while other workers reported independent uptake of As^V and phosphate in phytoplankton (Andreae and Klumpp, 1979) and macroalgae (Klumpp, 1980). Since As^V uptake into the macroalgae *Fucus spiralis* and *Ascophyllum nodosum* was not inhibited by phosphate levels in the water (Klumpp and Peterson, 1979), a common mechanism for As^V and phosphate uptake into algae is suggested (Francesconi and Edmonds, 1993). So, arsenic uptake mechanisms are not identical for all organisms in marine food chains, and the mechanism differs between phytoplankton species.

Whatever the uptake mechanisms of arsenic, marine phytoplankton convert As^V to As^{III} and transform it, through several chemical reactions, into less toxic orgAs that dissolves in fats and membranes of the plants. Klumpp and Peterson (1981) reported that the macroalgae *Fucus spiralis* transforms As^V into one major lipid-type arsenical and 12 water-soluble orgAs compounds. A number of other studies have shown that marine algae produce AsS (Cooney and Benson, 1980; Edmonds and Francesconi, 1981; Edmonds et al., 1982; Edmonds and Francesconi, 1983; Francesconi et al., 1998) as by-products of their detoxification process (Edmonds and Francesconi, 1987; Francesconi and Edmonds, 1993), and is provably biosynthesized by various arsenic methylation pathways (methylation and adenosylation) by microorganisms (Edmonds and Francesconi, 2003). The possible pathway for the methylation and adenosylation of arsenic to produce dimethylarsinoylribosides has been discussed in detail elsewhere (Francesconi and Edmonds, 1993; Edmonds and Francesconi, 2003), and the pathway was supported by the discovery of the intermediate dimethylarsinoyladenosine in the giant clam (*Tridacna maxima*) kidney (Francesconi et al., 1992). It is noted that AsS has not been identified outside the marine environment apart from their presence in the urine of humans who had eaten seafood (Le et al., 1994b).

5.4.2. Arsenobetaine

AsB has been reported mainly in marine animals. The biosynthesis of a number of AsB compounds in the marine and freshwater food chains has been reported in a number studies (Hanaoka et al., 1995; Ochsenkühn-Petropulu et al., 1997; Goessler et al., 1998; Francesconi et al., 2000). Dimethylarsinylribosides and trimethylarsonioribosides have been assumed to be the precursors of AsB within the marine food chain (Francesconi and Edmonds, 1993; Edmonds and Francesconi, 2003). Several studies have shown that direct conversion of dimethylarsinylribosides to AsB is not possible in marine animals (Cooney and Benson, 1980; Edmonds and Francesconi, 1981) and in the marine food chain (Klumpp and Peterson, 1981). The conversion of dimethylarsinylribosides to AsB requires cleavage of the C3-C4 bond of the ribose ring which might occur in marine sediments with subsequent oxidation at C4 and reduction and further methylation of arsenic (Francesconi and Edmonds, 1993). There are a number of reports of AsB coexisting with dimethylarsinoylribosides in marine animals, but it is unclear whether they were biosynthetically connected or accumulated independently (Edmonds and Francesconi, 1998). However, the metabolism of dimethylarsinoylribosides in *Tridacna derasa* kidney suggests that it might be at least one pathway of the biosynthesis of the ubiquitous AsB (McSheehy et al., 2002). AsS contained therein were degraded by successive oxidation and decarboxilation to yield dimethylarsinoylacetic acid which only requires methylation to be converted to AsB (Edmonds and Francesconi, 2003).

6. Bioavailability and bioaccumulation of arsenic in aquatic food chains

6.1. Bioavailability

It has been argued that, because the bioavailability of arsenic varies with environmental matrices, a single default value is not recommended for risk assessment in all environmental settings. Many studies on the toxicity of heavy metals have shown that health risks to humans or animals do not always correlate with the external exposure dose of the metals. This is because virtually all risk estimates ignore the bioavailability component in the assessment process.

Bioavailability represents the percentage of the external dose that reaches the systemic circulation of the organism, that is the fraction of the external dose absorbed (Caussy, 2003). Bioavailability of arsenic is generally expressed in absolute or relative terms. Absolute bioavailability is the function or percentage of the absorbed dose to the administered dose (Candy et al., 1997) while the relative bioavailability is a measure of the extent of absorption between two arsenic compounds (Caussy, 2003). Relative bioavailability is important for environmental studies. Bioavailability is usually determined by dosing an experimental organism with various concentrations of arsenic and measuring the response. The key determinants of bioavailability are the ability of arsenic to be released from its environmental matrices, the chemical species and molecular structure, and complex interaction of the host and chemical factors. These factors include reactivity, solubility, and ability to form organic metal complexes, oxidation state and physical forms (Caussy, 2003).

6.2. Bioaccumulation

The term “bioaccumulation” refers to the net accumulation of a chemical by an aquatic organism as a result of uptake from environmental sources. Aquatic organisms accumulate and retain certain chemicals when exposed to these chemicals through water, their diet, and other sources. The magnitude of bioaccumulation can vary widely depending on the chemicals and their properties. The biomagnification of chemicals, a process whereby chemical concentrations increase in aquatic organisms of each successive trophic level due to increasing dietary exposures (e.g. increasing concentrations from algae, to zooplankton, to forage fish, to predator fish), may also occur in aquatic food chains (Henry, 2003).

Bioaccumulation of arsenic and/or its metabolites in some aquatic organisms such as algae and lower invertebrates that are consumed by predator fishes has been reported by a number of researchers

(Maeda et al., 1990a; Chen and Folt, 2000; Mason et al., 2000). Rooted aquatic macrophytes are presumed to have a function in arsenic toxicity because these plants are directly associated with sediments. Studies on aquatic macrophytes of lakes contaminated from gold mine effluent in the Northwest of Canada (Dushenko et al., 1995; Koch et al., 2000); Taupo Volcanic Zone, New Zealand (Robinson et al., 2006) and Waikato River system, North Island, New Zealand (Robinson et al., 1995b) showed that macrophytes tended to bioaccumulate more arsenic compared to other aquatic biota. This suggests that most of the arsenic occurs in a highly bioavailable form in the aquatic system and is a function of many conditions such as the environmental compartment it is in (water column, sediment pore water), sediment particle type and size, pH, and presence of other metals (Caussy, 2003).

6.3. Bioaccumulation of arsenic in freshwater food chain

Although arsenic bioaccumulation is obvious, its biomagnification in the aquatic food chain is not frequent (Henry, 2003). Arsenic biomagnification has been reported in fishes (Maher and Butler, 1988) and gastropods (Goessler et al., 1997), but mainly as AsB, a rapidly eliminated and less toxic form of arsenic, which may pose less of a health risk to humans (Maher et al., 1999; Caussy, 2003). Despite the recent attention on arsenic uptake and accumulation in aquatic biota, much uncertainty still exists on the mechanisms and bioaccumulation potential of the various forms of arsenic in the environment. It has been reported that about 85 to > 90% of the total arsenic found in edible portions of marine fish and shellfish are orgAs (AsB and AsC) and DMA and approximately 10% is iAs (Goessler et al., 1997; Ochsenkühn-Petropulu et al., 1997; De Gieter et al., 2002). Less is known about the forms of arsenic in freshwater fish, but it is evident from field (Kaise et al., 1987) and laboratory (Maeda et al., 1990a; Maeda et al., 1990b; Maeda et al., 1992a; Maeda et al., 1993) studies that orgAs would be dominant.

6.4. Bioaccumulation factor (BAF) for arsenic in freshwater food chain

The United States Environmental Protection Agency (USEPA) presented a methodology and guidelines for the estimation of Bioaccumulation factors (BAFs) for various contaminants to reflect the uptake of contaminants by aquatic organisms such as fishes, shellfish, etc. from all sources (e.g. foods, sediment, etc.) rather than just from the water column (USEPA, 2000). The BAF is the ratio of the concentration of a chemical in water to its concentration in commonly consumed aquatic organisms in a specified trophic level where both the organism and its food are exposed (USEPA, 2000; Henry, 2003). The BAF for arsenic can be calculated as:

$$BAF = \frac{C_{tAs}}{C_{wAs}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Equ. 1)}$$

, where; C_{tAs} is the concentration of arsenic in wet tissue (whole organism or specific tissue) and C_{wAs} is the concentration of arsenic in water.

Several attributes of the bioaccumulation process are important to understand and use BAF. The concept of bioaccumulation is broader than that of bioconcentration. Bioaccumulation refers to the uptake and retention of a chemical by an aquatic organism from all surrounding sources (e.g. water, food, sediment, etc.) while bioconcentration refers to uptake from water only (USEPA, 2000). There are two procedures for the measurement of BAF for inorganic and organometallic chemicals, and procedure 5 (one of the two procedures) is recommended for deriving BAFs for arsenic (Henry, 2003).

The BAF for arsenic in organisms of aquatic trophic levels can be derived from available field data or can be predicted from acceptable laboratory-measured BCFs using the Equation 1. Henry (2003) derived BAFs for arsenic in trophic levels 2, 3, and 4 of freshwater and marine food chains from available field- and laboratory-measured data. Spehar et al. (1980) estimated BCFs for four freshwater invertebrate species and for rainbow trout exposed for 28-days to As^{III}, As^{V}, DMA, or MMA. Results showed that stoneflies, snails, and daphnids accumulated greater amounts of arsenic than fish. Tissue arsenic concentrations in treated rainbow trout were generally the same as those in control fish while in stoneflies and snails they were generally higher. Total arsenic accumulation in stoneflies and snails exposed to 1,000 μg L^{-1} of arsenic did not appear to be greatly affected by the form of arsenic in water, although some animals exposed to inorganic arsenicals did exhibit higher tissue concentrations than that in the environment. Chen et al. (2000) studied the accumulation and fate of arsenic in large and small zooplankton from numerous lakes in the northeastern USA, and found that arsenic BAFs of small zooplankton and large phytoplankton were significantly higher (between 369 and 19,487) than those of larger zooplankton (between 154 and 2,748). Chen and Folt (2000) also studied the trophic transfer of arsenic in a metal-contaminated Upper Mystic Lake in NY, USA on a seasonal basis and observed that arsenic concentrations in small zooplankton reflected the fluctuation of arsenic concentrations in water while arsenic in larger zooplankton progressively increased, indicating the potentially greater influence of dietary arsenic on the larger size class organisms.

Henry (2003) calculated arsenic BAFs for freshwater lotic organisms from field data of Mason et al (2000) and (1997). From the study of Mason et al. (2000), it was calculated that BAFs for herbivorous aquatic insects (trophic level-2 organisms) from Blacklick Run (2401–5619) were consistently higher than those from Harrington Creek Tributary (393–2543), western Maryland. Kaise et al (1997) investigated arsenic in water and biota samples from the Hayakawa River, Japan. BAFs were calculated on the basis of estimated concentration of dissolved arsenic in this river water and caddisfly larvae, caddisfly pupa, and marsh snails. Results showed that BAFs were 81, 9, and 7 for caddisfly larvae, caddisfly pupa, and marsh snails, respectively (Henry, 2003).

Chen et al. (2000) studied arsenic bioaccumulation in large phytoplankton, macro- and microzooplankton from a numbers of lakes around the northeastern United States. Results showed that arsenic BAFs for microzooplankton and large phytoplankton (369–19487) were significantly higher than those for macrozooplankton (154–2748) (Henry, 2003). In another study, Chen and Folt (2000) measured arsenic bioaccumulation in five different forage fish species: alewife, black crappie, bluegill sunfish, killifish, and yellow perch to investigate bioaccumulation and biodiminution (trend of decreased chemical concentration in tissues of organisms as trophic level increases) of arsenic in food chain of Upper Mystic Lake, NY. Results showed that arsenic burdens for all fishes in the lake were 30 to 100 times lower than its burdens in zooplankton. Alewife and killifish (predominantly planktivor fish species) had higher burdens than those of other fish species. Two other studies (Baker and King, 1994; Chen and Folt, 2000) also reported that the average arsenic burden for largemouth bass (trophic level 4 organism) was approximately 60 to 95 times lower than its burdens in zooplankton.

Baker and King (1994) measured the total arsenic concentrations in water and fish from San Carlos Reservoir and Talkalai Lake, Arizona. From the estimated concentration of dissolved arsenic in the water of San Carlos Reservoir and in fish (whole body), the BAFs were calculated to be 30 for channel catfish and 15 for carp. The BAF for carp from Talkalai Lake was 30 (Henry, 2003). Skinner (1985) determined trace element concentrations in wastewater treatment basin-reared fishes to determine if fish consumption from those treatment basin posed any risk to human health. Henry (2003) calculated arsenic BAFs for fishes from reported arsenic concentrations in water and fish tissue. Since arsenic concentrations in most fish tissue were below the detection limit, BAF for carp from various basins were calculated to be between 2 and 71.

In addition to forage fishes, Chen and Folt (2000) also measured arsenic concentrations in the whole body of largemouth bass from Upper Mystic Lake. The average arsenic burden in the bass was approximately 0.36 µg g^{-1}, and had arsenic BAF of 46. Baker and King (1994) also found a similar BAF value (45) for largemouth bass from Upper Gila River, Arizona (Henry, 2003). In a recent study, Culioli et al. (2009) investigated bioaccumulation and trophic transfer of arsenic in food chain of Presa and Bravona Rivers in Corsica, France. They determined arsenic in a wide range of bryophytes, benthic macroinvertebrates, and fishes of the rivers and calculated BAFs for the organisms. Arsenic concentrations in waters of Presa and Bravona Rivers were about 18.2–2330.8 µg L^{-1} and 7.4–313.7 8 µg L^{-1}, respectively. Results showed that BAFs for benthic macroinvertebrates ranged between 10 and 827 from Presa River. Culioli et al. (2009) also reported arsenic diminish at the higher trophic level of the food chain in Presa and Bravona Rivers. A number of other studies also showed that the fish species of lower trophic level (alewife, killifish) had higher BAFs than those species of higher trophic level (perch, crappie, catfish, carp, sunfishes) (Skinner, 1985; Chen and Folt, 2000).

6.5. Bioaccumulation of arsenic in marine food chain

Marine organisms have been reported to bioaccumulate high concentrations of arsenic (Francesconi and Edmonds, 1996). Kirby et al. (2002) measured arsenic concentrations and species in marine animals and epiphytic algae/fungi from a temperate mangrove ecosystem, NSW, Australia. They found that epiphytic algae/fungi associated with mangrove fine roots had higher arsenic concentrations than that on the main roots of mangrove plants. They reported that arsenic accumulation in various feeding groups of the mangrove ecosystem differed sugnificantly. The concentrations of arsenic in detritivores (8.5–55 µg g^{-1}) were significantly higher than that of the major primary producers (0.3–1.5 µg g^{-1}), herbivores (8.0–14.0 µg g^{-1}) and omnivores (2–16.6 µg g^{-1}). In addition, there was a significant difference in arsenic concentrations within the feeding group of omnivore species. Zooplankton (16 µg g^{-1}) had the highest arsenic concentration followed by oyster *S. commercialis* (now *S. glomerata*) (8.6 µg g^{-1}) and palemonid shrimps (7.7 µg g^{-1}).

Foster et al. (2006) also studied arsenic accumulation in marine animals of saltmarsh ecosystems in Australia and found that the range of arsenic concentrations in gastropods, crabs, and amphipods were similar to those reported in marine/terrestrial herbivorous gastropods and crabs (Kirby et al., 2002), but lower than those normally found in carnivorous gastropods (Francesconi et al., 1998). The large variability in arsenic concentrations in gastropods and amphipods could be partially explained by the relationship between arsenic concentrations in *S. quinqueflora*, which is the primary source of detritus (food) for the gastropods and amphipods in the saltmarsh ecosystems (Foster et al., 2006). Thus, arsenic accumulation in marine animals cannot be attributed to their position in the food web or feeding mode, but is likely to be related to their dietary intake and ability to assimilate, metabolize, and retain arsenic species inside their body (Kirby et al., 2002).

Goessler et al. (1997) investigated arsenic bioaccumulation in a tree-organism food chain (seaweed (*Hormosira banksii*), gastropod (*Austrocochlea constricta*), and gastropod (*Morula marginalba*)) within a rock pool at Rosedale, NSW, Australia. They found that total arsenic concentration in the seaweed (*H. banksii*) (primary producer in the trophic level) was 27.2 µg g^{-1} d. wt. (mainly dimethylarsine oxide). Arsenic concentration in herbivorous gastropod *A. constricta* (trophic level 2 organism), which consumed the seaweed, was 74.2 µg g^{-1} d. wt., most of which was transformed to AsB by the gastropod. Finally, arsenic concentration in carnivorous gastropod *M. marginalba* (trophic level 3 organism), which ate *A. constricta*, was 233 µg g^{-1} d. wt. The results reveal arsenic biomagnification in the aquatic food chain although some researchers disagree with this finding.

Bioaccumulation of arsenic from water and sediments in different species of molluscs from a coastal area in Taiwan was investigated by Hung et al. (2001). Different size specimens of molluscs were collected along the western coast of Taiwan over 1994–1998. Results showed that the bioaccumulation of arsenic in *Perna viridis* (29.1 µg g^{-1}) was higher than that in *Littoraria scabra* (22.3 µg g^{-1}). The bioaccumulation of arsenic in 13 finfish species and three crustacean species from the Arabian Gulf have been reported by Attar et al. (1992). The range was 0.16–32.3 µg g^{-1} wet wt. for finfish, and averages of 15.8, 6.28, and 12.7 µg g^{-1} wet wt. for the prawn, crab, and lobster, respectively. Maher (1985b) investigated the distribution of arsenic in marine animals in relation to their diet. Results revealed that the ranges of arsenic concentrations were 20–60, 8–22, and 7–84 µg g^{-1} d. wt. in plankton, herbivores, and carnivores, respectively. Arsenic in marine animals was mainly of methanol-water soluble and lipid soluble orgAs (70–98% of the total arsenic), and the relative proportion of each form depends not only on the animal species but also on their diet (Maher, 1985b). In another study, Maher and Clarke (1984) measured total arsenic concentrations in some selected macroalgae specimens from Stenhouse Bay, Yorke Peninsula, and offshore from Aldinga Beach, St. Vincent's Gulf, South Australia. They found that Phaeophyta contained elevated concentrations of arsenic (42.2–179 and 26.3–65.3 µg g^{-1}) compared to those of Rhodophyta (17.6–31.3 and 12.5–16.2 µg g^{-1}) and those of Chlorophyta (6.3–16.3 and 9.9–10.8 µg g^{-1}) from both areas.

Marine organisms usually do not contain iAs or simple methylated arsenicals, but contain a variety of orgAs species. The main arsenic compounds in these organisms are AsB (animals) and arsenoribosides (macroalgae) (Morita and Shibata, 1990). Small amounts of tetramethylarsonium ion, phosphatidylarsenocholine, AsC, and trimethylarsoniopropionate are also found in them (Francesconi et al., 2000; Kirby et al., 2002). Kirby et al. (2002) reported that most marine animal tissues, collected from a mangrove ecosystem, NSW, Australia, contained large percentages of AsB (28 – 81%) followed by glycerol arsenoribose (1–23%) arsenoriboside in the digestive tissues of two crab species (13–23%), trimethylarsoniopropionate (1–8%), tetramethylarsonium ion (1–7%), sulfate arsenoribose (2–13%) and trace amounts of AsC (<1%), trimethylarsine oxide (TMAO) (<1%), DMAA (<2%), phosphate arsenoribose (<2%), arsenate (<1%), and sulfonate arsenoribose (<3%). They did not find methylarsonic acid in any tissues of these animals although unknown cationic arsenic compounds (1–2%) and three anionic arsenic compounds (1–17%) were measured in some of the animals' tissues.

6.6. Bioaccumulation factor (BAF) for arsenic in marine food chain

Bioaccumulation of arsenic in marine organisms can occur from the water, from suspended particles, from sediments, and through food chains. The accumulation rate depends not only on the availability of this metalloid, but also on biological, chemical and environmental factors. Arsenic speciation, biological activities, phytoplankton density, water temperature, pH, concentrations of other nutrients, especially iron, aluminum and phosphorus, dissolved oxygen, and seasonal variation influence the bioavailability and bioaccumulation of arsenic in the marine food chain (Sohrin et al., 1997; Jain and Ali, 2000; Hellweger and Lall, 2004; Price and Pichler, 2005; Hasegawa et al., 2009; Casado-Martinez et al., 2010; Hasegawa et al., 2010). The BAF for arsenic in marine food chain may also be influenced by these factors since BAF is calculated from its concentration in organisms and water. Both field and laboratory studies have been performed to determine bioaccumulation of arsenic in marine food chain, however, results of field investigations may produce more reliable BAF for the metalloid because the biological, chemical and environmental factors, which influence arsenic bioavailability and bioaccumulation, were not modified in the field. The BAF for arsenic in marine food chains, presented in this review, have been calculated from available data on arsenic bioaccumulation in organisms and its concentrations in water.

Giusti and Zhang (2002) investigated trace element distribution in sediments, marine water and mussel *Mytilus galloprovincialis* from four sites of the Venetian Lagoon around the Island of Murano, Italy. Arsenic concentrations were measured between 12–18 µg g^{-1} d. wt. with a mean of 14.6 µg g^{-1} d. wt. in soft tissue of *M. galloprovincialis,* and between 0.4–2.7 µg g^{-1} d. wt. in the shells of the animals. Dissolved arsenic in water from the corresponding sites ranged between 1–4.7 µg L^{-1} with a mean of 2.4 µg L^{-1}. The calculated BAF for arsenic in *M. galloprovincialis* was between 383 and 12000. In a recent study, Valette-Silver et al. (1999) investigated the arsenic concentrations in bivalve (oysters and mussels) samples collected from the southeastern coasts of the USA, from North Carolina to the Florida panhandle. Results showed that the BAFs for arsenic in oysters and mussels collected from the mouth of the Miami River, Biscayne Bay were 8382 and 5303, respectively (Henry, 2003).

Conclusion

Bioaccumulation is obvious in aquatic food chains. Aquatic organisms accumulate arsenic mainly as inorganic forms, and some of the organisms such as phytoplankton, bacteria, etc. transform them into methylated and organic forms. The biotransformation of toxic iAs species into less toxic $MMAA^V$, $DMAA^V$, and orgAs species was supposed to be the detoxification mechanism of these organisms. Thus, aquatic organisms play important roles in arsenic speciation and cycling in marine- and freshwater environments. Although bioaccumulation of arsenic in aquatic organisms is apparent, it may pose less effect to health of the organisms because of their ability to metabolize this metalloid.

Besides bioaccumulation, biomagnification is unusual in aquatic food chains. With some exceptions, most of the studies reveal that arsenic concentrations decrease with the increase of trophic level in both marine- and freshwater food chains. Dietary exposure to arsenic from aquatic foods would not be a serious problem for humans due to its biodiminution and biotransformation to less toxic orgAs species. But aquatic foods would contribute to the total dietary intake of arsenic by humans in addition to other sources such as drinking water, rice, vegetables etc. in which iAs species are dominant.

Previous studies mainly focused on arsenic speciation, bioaccumulation, and biotransformation in the marine environment. Since large populations in South and South-East Asia consume considerable amounts of freshwater fishes and other foods in their daily diet, knowledge on arsenic speciation and bioaccumulation in freshwaters is important. In addition, more intensive studies on trophic transfer of arsenic in both marine- and freshwater food chains are necessary to understand and predict the real health hazard of this element for humans, especially in some Asian countries were arsenic contamination is extensive. Unfortunately, little or no studies have been done on arsenic speciation, bioaccumulation and trophic transfer in freshwaters in this region.

Acknowledgements

The authors wish to thank the Japan Society for the Promotion of Science (JSPS) for financial support by Grants-in-Aid for Scientific Research (20·08343) in preparing this review paper. The authors wish to thank the University of Technology, Sydney (UTS) for financial support. The authors are also thankful to the anonymous reviewers for their thoughtful comments and constructive suggestions that has improve the quality of the paper.

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Table 1: Chemical forms of arsenic found in aquatic systems

Name	Abbreviation	Formula/Structure	organisms	Reference
Inorganic arsenicals				
Arsenious acid or arsenite	As^{III}	$As^{3+}(OH)_3$	Fish, Gastropods, Crustacean, Carnivores, Herbivores, Saltmarsh plants, Marine algae, Diatom, seaweed	(Edmonds et al., 1997; Goessler et al., 1997; Gallagher et al., 2001; Kirby et al., 2002; Rattanachongkiat et al., 2004; Foster et al., 2006)
Arsenic acid or arsenate	As^{V}	$H_3As^{5+}O_4$	Fish, Gastropods, Crustacean, Carnivores, Herbivores, Saltmarsh plants, Marine algae, Diatom, seaweed	(Goessler et al., 1997; Gallagher et al., 2001; Kirby et al., 2002; Rattanachongkiat et al., 2004; Foster et al., 2006)
Methylated arsenicals				
Monomethylarsonous acid	$MMAA^{III}$	$CH_3As(OH)_2$	Aquatic animals, Fish, Crustacean, Marine and freshwater algae	(Ackley et al., 1999; Hasegawa et al., 2001; Rattanachongkiat et al., 2004)
Dimethylarsinous acid	$DMAA^{III}$	$(CH_3)_2AsOH$	Aquatic animals, Fish, Crustacean, Marine and freshwater algae	(Andreae, 1978; Goessler et al., 1997; Kaise et al., 1997; Ackley et al., 1999; Gallagher et al., 2001; Hasegawa et al., 2001; Rattanachongkiat et al., 2004)
Monomethylarsonic acid	$MMAA^{V}$	$AsO(OH)_2CH_3$	Aquatic animals, Fish, Crustacean, Marine and freshwater algae, Seaweed	(Goessler et al., 1997; Ackley et al., 1999; Gallagher et al., 2001; Hasegawa et al., 2001; Rattanachongkiat et al., 2004)
Dimethylarsinic acid	$DMAA^{V}$	$AsO(OH)(CH_3)_2$	Aquatic animals, Fish, Crustacean, Marine and freshwater algae, Seaweed	(Goessler et al., 1997; Kaise et al., 1997; Ackley et al., 1999; Hasegawa et al., 2001; Kirby et al., 2002; Rattanachongkiat et al., 2004)
Trimethylarsine acid	TMAA	$(CH_3)_3As$	Marine animals	(Anderson and Bruland, 1991; Francesconi and Edmonds, 1996; Francesconi et al., 2000)
Thioarsenicals				
Monomethylmonothioarsenate	$MMMTAs^{V}$	$(CH_3)AsO_2S^{2-}$	Groundwater	(Wallschläger and London, 2008)
Monomethyldithioarsenate	$MMDTAs^{V}$	$(CH_3)AsOS_2^{2-}$	Groundwater	(Wallschläger and London, 2008)
Dimethylmonothioarsenate	$DMMTA^{V}$	$(CH_3)_2AsOS^{-}$	Groundwater	(Wallschläger and London, 2008)

Dimethyldithioarsenate	$DMDTA^V$	$(CH_3)_2AsS_2^-$	Groundwater	(Wallschläger and London, 2008)
Organoarsenic compounds				
Arsenocholine	AsC	$(CH_3)_3As^+CH_2CH_2O$	Fish, Shellfish, Shrimp, Seafood, Lobster	(Mürer et al., 1992)
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2COO^-$	Marine animals, Fish, Lobster, Shrimp, Crustacean, Gastropod, Seaweeds	(Goessler et al., 1997; Goessler et al., 1998; Kirby et al., 2002; Edmonds and Francesconi, 2003; Rattanachongkiat et al., 2004)
Arsenosugars	AsS			
Arsenoribosides			Marine animals	(Kirby et al., 2002)
Sulfate arsenoribose			Marine animals	(Kirby et al., 2002)
Sulfonate arsenoribose			Marine animals	(Kirby et al., 2002)
Phosphate arsenoribose			Marine animals	(Kirby et al., 2002)
Glycerol arsenoribose			Marine animals	(Kirby et al., 2002)
Dimethylarsinoylribosides			Marine algae, Shellfish	(Larsen, 1995; Francesconi et al., 2000; Madsen et al., 2000; Edmonds and Francesconi, 2003)
Trimethylarsonioribosides			Marine brown algae	(Francesconi and Edmonds, 1996)
Triaklylarsonioribosides			Marine brown algae	(Madsen et al., 2000; Edmonds and Francesconi, 2003)
Trimethylarsoniopropionate			Marine animals	(Kirby et al., 2002)
Tetramethylarsonium ion			Marine animals	(Kirby et al., 2002)

Table 2: Arsenic concentrations in some major aquatic systems (rivers, lakes, estuaries and marine)

Aquatic systems and Location	**Arsenic concentrations (average/range (μg L^{-1})**	**References**
Rivers		
Dordogne, France	0.7	(Seyler and Martin, 1990)
Po River, Italy	1.3	(Pettine et al., 1992; Pettine et al., 1997)
Cordoba, Argentina	7-114	(Lerda and Prosperi, 1996)
Madison and Missouri rivers, USA	44 (19-67), 10-370	(Robinson et al., 1995b; Nimick et al., 1998)
Waikato, New Zealand	32 (28-36)	(McLaren and Kim, 1995; Robinson et al., 1995b)
Ron Phibun, Thailand	218 (4.8-583)	(Williams et al., 1996)
Ashanti, Ghana	284 (<2-7900)	(Smedley et al., 1996)
Owens River, CA, USA	85-153	(Wilkie and Hering, 1998)
Mole River, NSW, Australia	110-600 (up to 13900)	(Ashley and Lottermoser, 1999)
Lakes		
Moira Lake, Ontario, Canada	20.4 (22.0-47.0)	(Azcue and Nriagu, 1995)
Lake Biwa, Japan	2.2 (0.6-1.7)	(Hasegawa et al., 2010)
Mono Lake, California, USA	10000-20000	(Maest et al., 1992)
Marine and Estuaries		
Vestfjord, Norway	0.7-1.0	(Abdullah et al., 1995)
Bunnefjord, Norway	0.5-1.9	(Abdullah et al., 1995)
Saanich Inlet, B.C., Canada	1.2-2.5	(Peterson and Carpenter, 1983)
Uranouchi Inlet, Japan	22.0-32.0	(Hasegawa, 1996)
Rhone Estuary, France	2.2 (1.1-3.8)	(Seyler and Martin, 1990)
Krka Estuary, Yugoslavia	0.1-1.8	(Seyler and Martin, 1991)
Tamar Estuary, UK	2.7-8.8	(Howard et al., 1988)
Schelde Estuary, Belgium	1.8-4.9	(Andreae and Andreae, 1989)
Deep Pacific and Atlantic	1.0-1.8	(Cullen and Reimer, 1989)
Coastal Malaysia	1.0 (0.7-1.8)	(Yusof et al., 1994)
Southeast coast, Spain	1.5 (0.5-3.7)	(Navarro et al., 1993)
Coastal Nakaminato, Japan	3.1	(Ishikawa et al., 1987)
Southern coast, Australia	1.3 (1.1-1.6) (inorganic)	(Maher, 1985a)

Table 3: Arsenic concentrations in organisms (flora and fauna) comprising the marine food chain

Organisms	Arsenic con. (mg kg^{-1})	Trophic group (rank in the food chain, 1-5)	Diet	References
Typical Taxa				
All taxa	0-2,739 d. wt.			(Neff, 1997)
Algae	0.1-382 d. wt.	Primary producer		(Neff, 1997)
Seagrass	0.16-0.6 d. wt.	Primary producer		(Neff, 1997)
Zooplankton	0.2-24.4 d. wt.	Primary producer		(Neff, 1997)
Polychaetes	5-2739 d. wt.	Consumer (1)	Tiny aquatic animals and plants.	(Neff, 1997)
Crustaceans	0.1-270.5 d. wt.	Consumer (1)	Insects, algae, worms, molluscs and small fish.	(Neff, 1997)
Bivalves	0.6-214 d. wt.	Consumer (1)	Microorganisms suspended in the water.	(Neff, 1997)
Snails	8.0-533 d. wt.	Consumer (1)	Plant and vegetation.	(Neff, 1997)
Cephalopods	4.0-49.5 d. wt.	Consumer (2)	Carnivores	(Neff, 1997)
Fish	0.05-449.5 d. wt.	Consumer (1) Consumer (2) Consumer (3, 4, 5)	Phytoplankton, plant, algae, small fish.	(Neff, 1997)
Marine mammals	0.05-0.9 d. wt.	Consumer (3, 4, 5)	Fish, squid, seals, shellfish, other mammals.	(Neff, 1997)
Plants				
Algae				
Laminaria japonica	43.2 d. wt.	Primary producer		(Hulle et al., 2002)
Porphyra crispata	31.0 d. wt.	Primary producer		(Hulle et al., 2002)
Eucheuma denticulatum	5.6 d. wt.	Primary producer		(Hulle et al., 2002)
Fucus vesiculosus	up to 40 d. wt.	Primary producer		(Stoeppler et al., 1986)
Phacelocarpus adopus	26.2 d. wt.	Primary producer		(Maher and Clarke, 1984)
Dictymenia harveyana	17.6 d. wt.	Primary producer		(Maher and Clarke, 1984)
Gigartina sp.	20.1 d. wt.	Primary producer		(Maher and Clarke, 1984)
Coelarthrum muelleri	31.3 d. wt.	Primary producer		(Maher and Clarke, 1984)
Areschougia congesta	24.5 d. wt.	Primary producer		(Maher and Clarke, 1984)
Sargassum bracteolosum	62-125 d. wt.	Primary producer		(Maher and Clarke, 1984)
Ecklonia radiata	84.7 d. wt.	Primary producer		(Maher and Clarke, 1984)
Cystophora platylobium	179 d. wt.	Primary producer		(Maher and Clarke, 1984)

Cystophora moniliformis	65.3-123 d. wt.	Primary producer		(Maher and Clarke, 1984)
Cystophora monilifera	35.5-42.2 d. wt.	Primary producer		(Maher and Clarke, 1984)
Cystophora racemosa	83.8 d. wt.	Primary producer		(Maher and Clarke, 1984)
Cystophora subfarcinata	37.3-54.9 d. wt.	Primary producer		(Maher and Clarke, 1984)
Cyst ophora siliquosa	61.3 d. wt.	Primary producer		(Maher and Clarke, 1984)
Ulva sp.	11.6 d. wt.	Primary producer		(Maher and Clarke, 1984)
Caulerpa cactoides	16.3 d. wt.	Primary producer		(Maher and Clarke, 1984)
Caulpera flexilis	12 d. wt.	Primary producer		(Maher and Clarke, 1984)
Caulerpa scalpelliformis	13.4 d. wt.	Primary producer		(Maher and Clarke, 1984)
Seaweeds				
Sarcocornia quinqueflora	0.03-6.0 d. wt.	Primary producer		(Foster et al., 2006)
Sargassum fluitans	19.5 d. wt.	Primary producer		(Eisler, 1988)
Sargassum linearifolium	58.4 d. wt.	Primary producer		(Maher and Clarke, 1984)
Laminaria digitata	42.0-109.0 d. wt.	Primary producer		(Lunde, 1977; NAS, 1977)
Laminaria saccharina	45.0-52.5 d. wt.	Primary producer		(NAS, 1977)
Lobospira bicuspidata	29.4 d. wt.	Primary producer		(Maher and Clarke, 1984)
Dictyota dichotoma	26.3 d. wt.	Primary producer		(Maher and Clarke, 1984)
Halidrys siliquosa	26.0-30.0 d. wt.	Primary producer		(NAS, 1977)
Ecklonia radiata	49.6 d. wt.	Primary producer		(Maher and Clarke, 1984)
Fucus nodosus	45.0 d. wt.	Primary producer		(NAS, 1977)
Fucus serratus	28.0-67.5 d. wt.	Primary producer		(NAS, 1977)
Entarompha compressa	11.2 d. wt.	Primary producer		(NAS, 1977)
Piocamicum coccineum	7.5 d. wt.	Primary producer		(NAS, 1977)
Ulva latissima	6.0 d. wt.	Primary producer		(NAS, 1977)
Gigartina mammillosa	4.5-17.2 d. wt.	Primary producer		(NAS, 1977)
Laminaria hyperborea	142.0 d. wt.	Primary producer		(Eisler, 1988)
Pelvetia canaliculata	15.0-22.0 d. wt.	Primary producer		(NAS, 1977)
Ascophyllum nodosum	22.0-44.0 d. wt.	Primary producer		(Lunde, 1977)
Animals				
Talitrid amphipod	5.9-8.0 d. wt.	Detritivores	Debris.	(Foster et al., 2006; Peshut et al., 2008)
Oyster	1.8-40.0 f. wt.	Consumer (1)	Planktons.	(Lunde, 1977)
Saccostrea cuculluta	8.3-32.9 d. wt.			(Peshut et al., 2008)
Striostrea cf mytloides	9.5-38.4 d. wt.	Consumer (1)	Planktons.	(Peshut et al., 2008)

Arc clams (*Anadara* sp.)	13.0-23.0 d. wt.	Consumer (1)	Planktons.	(Morrison et al., 1997)
Mullet (*Mugilidae* spp.)	0.3-1.9 f. wt.	Consumer (1)	Detritus, diatoms, algae.	(Peshut et al., 2008)
Gafarium sp.	3.4-80 d. wt.	Consumer (1)	Planktons.	(Peshut et al., 2008)
Asaphis violascens	1.3-5.9 f. wt.	Consumer (1)	Planktons, diatoms, algae.	(Peshut et al., 2008)
Carpetshark (*Orectolobus ornatus*)	9.0-31.0 d. wt.	Consumer (1)	Invertebrates.	(Foster et al., 2006)
Striped Surgeon (*Acanthurus lineatus*)	0.3-0.6 f. wt.	Consumer (1)	Planktons, algae.	(Peshut et al., 2008)
Chamids (*Chama brassica*)	23.6-51.6 d. wt.	Consumer (1)	Planktons.	(Denton et al., 1999)
Sardine (*Sardina* sp.)	5.8 d. wt.	Consumer (1)	Phytoplankton and small zooplankton.	(Rattanachongkiat et al., 2004)
Spondylus sp.	33.0-195.0 d. wt.	Consumer (1)	Planktons.	(Peshut et al., 2008)
Chamids (*Chama lazarus*)	21.6-331 d. wt.	Consumer (1)	Phytoplankton, diatom.	(Denton et al., 1999)
Tigerprawn (*Penaeus monodon*)	11.0 d. wt.	Consumer (1)	Molluscs, crustaceans, polychaete worms.	(Rattanachongkiat et al., 2004)
Grooved tiger prawn (*Penaeus semisulcatus*)	6.05-35.2 f. wt.	Consumer (1)	Molluscs, crustaceans, polychaete worms.	(Attar et al., 1992)
Shellfishes	1.1-30.0 f. wt.	Consumer (1)	Phytoplankton, Zooplankton.	(FDA, 1993)
White-spotted spinefoot (*Siganus canaliculatus*)	0.25-0.77 f. wt.	Consumer (1)	Benthic algae and some seagrass	(Attar et al., 1992)
Golden toothless trevally (*Gnathanodon speciousus*)	4.51-7.08 f. wt.	Consumer (2)	Small fishes.	(Attar et al., 1992)
Black-banded bream (*Acanthopagrus bifasciatus*)	8.36-73.7 f. wt.	Consumer (2)	Molluscs	(Attar et al., 1992)
Blackspotted Rubberlips (*Plectorhinchus gaterinus*)	7.54-14.4 f. wt.	Consumer (2)	Benthic invertebrates	(Attar et al., 1992)
Sharp-tooth snapper (*Pristipomoides typus*)	2.38-4.44 f. wt.	Consumer (2)	Benthic invertebrates and fishes.	(Attar et al., 1992)
Spider Crab (*Neosarmatium meinerti*)	9.0-16.0 d. wt.	Consumer (2, 3)	Small fishes.	(Foster et al., 2006)
Crab (*Lupa pelagica*)	4.21-10.7 f. wt.	Consumer (2, 3)	Small fishes.	(Attar et al., 1992)
Narrow-barred Spanish mackerel (*Scomberomorus commerson*)	1.37-3.89 f. wt.	Consumer (2, 3)	Small fishes like anchovies, clupeids, carangids, squids and shrimps.	(Attar et al., 1992)
Cobia (*Rachycentron canadus*)	2.87-4.80 f. wt.	Consumer (2, 3)	Crustaceans, fish, and squids.	(Attar et al., 1992)
Brassy trevally (*Caranx papuensis*)	0.3-0.9 f. wt.	Consumer (2, 3)	Fishes.	(Peshut et al., 2008)
Orange-spotted trevally (*Carangoides bajad*)	0.84-5.21 f. wt.	Consumer (2, 3)	Fishes.	(Attar et al., 1992)

Greater amberjack (*Seriola dumerili*)	< 0.25-1.02 f. wt.	Consumer (2, 3)	Fishes.	(Attar et al., 1992)
Torpedo scad (*Megalaspis cordyla*)	1.2-1.6 f. wt.	Consumer (2, 3)	Fish, squid and cuttlefish, shrimps, prawns, crabs etc.	(Peshut et al., 2008)
Squirrelfish (*Sargocentron* spp.)	2.1-60.0 f. wt.	Consumer (2, 3)	Small fish, invertebrates.	(Peshut et al., 2008)
Flathead locust lobster (*Thenus orientalis*)	4.91-19.6 f. wt.	Consumer (2, 3)	Small fish, invertebrates.	(Attar et al., 1992)
Lobsters (*Panulirus* sp.)	19.8-98.2 f. wt.	Consumer (2, 3)	Fish, mollusks, worms, crustaceans.	(Peshut et al., 2008)
Spangled emperor (*Lethrinus nebulosus*)	1.03-3.58 f. wt.	Consumer (2, 3)	Echinoderms, mollusks, crustaceans, and some polychaetes and fish.	(Attar et al., 1992)
Halibut (*Hippoglossus sp.*)	2.5-10.0 d. wt.	Consumer (3, 4, 5)	Almost any animal they can fit into their mouths.	(Lunde, 1977)
Mackerel (*Scomberomorus sp.*)	2.0-6.6 d. wt.	Consumer (3, 4, 5)	Fishes	(Lunde, 1977)
Shark (*Carcharhinus sp.*)	1.9-5.9 d. wt.	Consumer (4, 5)	Fishes, crustaceans, squid, other aquatic animals.	(Lunde, 1977)

Table 4: Arsenic concentrations in organisms (flora and fauna) comprising the freshwater food chain

Organisms	Arsenic con. (mg kg^{-1})	Trophic group (rank in the food chain, 1-5)	Diet	References
Plants				
Green alga				
Clodophora glomerata	0.45 f. wt.	Primary producer		(Kaise et al., 1997)
Clodophora sp.	5.06-9.33 d. wt.	Primary producer		(Schaeffer et al., 2006)
Diatom	0.12 f. wt.	Primary producer		(Kaise et al., 1997)
Hot water algae	1058-8617 d. wt.	Primary producer		(Robinson et al., 2006)
Cold water algae	7.3-184.9 d. wt.	Primary producer		(Robinson et al., 2006)
Pondweed (*Potamogeton* sp.)	11-436 d. wt.	Primary producer		(Eisler, 1988)
Water-milfoil (*Myriophyllum* sp.)	5.42 d. wt.	Primary producer		
Hornwort (*Ceratophyllum demersum*)	3.4 d. wt.	Primary producer		
Animals				
Bowfin (*Amina calva*)	0.32 f. wt.	Consumer (1)	Piscivore.	(Burger et al., 2002)
Largemouth bass (*Micropterus salmoides*)	0.03 f. wt. 0.05-0.22 f. wt.	Consumer (1, 2)	Piscivore, carnivorous (small fish, crayfish, worms, frogs, insects)	(Eisler, 1988; Burger et al., 2002)
Smallmouth bass (*Micropterus dolomieui*)	0.05-0.3 f. wt.	Consumer (1, 2)	Carnivorous (small fish, crayfish, worms, frogs, insects)	(Eisler, 1988)
Striped bass (*Morone saxatillis*)	0.2-0.7 f. wt.	Consumer (1, 2)	Carnivorous (small fish, crayfish, worms, frogs, insects, crustaceans)	(Eisler, 1988)
Coho salmon (*Oncorhynchus kisutch*)	0.07-0.5 f. wt.	Consumer (1)	Plankton and insects (in fresh water).	(Eisler, 1988)
Lake trout (*Salvelinus namaycush*)	0.06-0.7 f. wt.	Consumer (1, 2)	Plankton, whitefish, grayling, sticklebacks, and sculpins.	(NAS, 1977)
Rainbow trout (*Salmo gairdneri*)	< 0.4 f. wt.	Consumer (1, 2)	Insects, flies, small mollusks, Fish eggs and baitfish.	(NAS, 1977)
Carp (*Cyprinus carpio*)	0.05-0.6 d. wt.	Consumer (1, 2, 3, 4)	Plants, insects, crayfish, dead fish, mollusks.	(NAS, 1977; Wiener et al., 1984)
Channel catfish (*Ictalurus punctatus*)	0.09 f. wt. 0.05-0.3 f. wt.	Consumer (2)	Large invertebrates, piscivore.	(Burger et al., 2002) (NAS, 1977)

Chain pickerel (*Esox niger*)	0.05 f. wt.	Consumer (2)	Large invertebrates, piscivore.	(Burger et al., 2002)
Northern pike (*Esox lucius*)	0.05-0.9 f. wt.	Consumer (2, 3)	Fish, Frogs, insects, leeches.	(NAS, 1977)
Yellow perch (*Perca flavescens*)	0.05 f. wt. < 0.16 f. wt.	Consumer (3)	Large invertebrates, small fish.	(Burger et al., 2002) (Eisler, 1988)
Black crappie (*Pomoxis nigromaculatus*)	0.04 f. wt.	Consumer (3)	Large invertebrates, small fish.	(Burger et al., 2002)
Green sunfish (*Lepomis cyanellus*)	19.7-64.2 d. wt.		Insects and small fish.	(Eisler, 1988)
American eel (*Anguilla rostrata*)	0.04 f. wt.	Consumer (4)	Detritus, invertebrates, piscivore.	(Burger et al., 2002)
Shellcracker (*Lepomis microlophus*)	0.06 f. wt.	Consumer (5)	Medium-large invertebrates.	(Burger et al., 2002)
Bluegill sunfish (*Lepomis macrochirus*)	0.05 f. wt. 0.2-1.3 f. wt.	Consumer (5)	Medium-large invertebrates.	(Burger et al., 2002) (Eisler, 1988)
Red-breasted sunfish (*Lepomis auritus*)	0.07 f. wt.	Consumer (5)	Medium-large invertebrates.	(Burger et al., 2002)
Spotted sucker (*Minytrema melanops*)	0.03 f. wt.	Consumer (6)	Plant and invertebrates.	(Burger et al., 2002)
White sucker (*Catostomus commersoni*)	0.05-0.16 f. wt.	Consumer (6)	Plants and animals.	(NAS, 1977)
Some freshwater fishes				(Kaise et al., 1997)
Plecoglossus altivelis	0.05 f. wt.			(Kaise et al., 1997)
Pncorhynchus masou	0.15 f. wt.			(Kaise et al., 1997)
Rhinogobius sp.	0.33 f. wt.			(Kaise et al., 1997)
Phoxinus steindachneri	0.27 f. wt.			(Kaise et al., 1997)
Tribolodon hakonensis	0.10-0.37 f. wt.			(Kaise et al., 1997)
Prawn (*Macrobranchiura nipponense*)	0.82 f. wt.			(Kaise et al., 1997)
Marsh snail (*Semisulcospira libertina*)	0.19 f. wt.			(Schaeffer et al., 2006)
Sponge (*Ephydatia fluviatilis*)	8.07 d. wt.			(Schaeffer et al., 2006)
Mussel (*Unio pictorum*)	9.31-11.60 d. wt.			(Schaeffer et al., 2006)
White bream (*Blicca bjoerkna*)	0.48-1.58 d. wt.			(Schaeffer et al., 2006)
Roach (*Rutilus rutilus*)	0.37-0.48 d. wt.			(Schaeffer et al., 2006)
Razorfish (*Pelecus cultratus*)	0.42 d. wt.			(Schaeffer et al., 2006)
Ide (*Leuciscus idus*)	0.25 d. wt.			(Schaeffer et al., 2006)
Pikeperch (*Stizostedion lucioperca*)	0.26 d. wt.			(Schaeffer et al., 2006)
Frog (*Rana* sp.)	2.52 d. wt.			(Schaeffer et al., 2006)

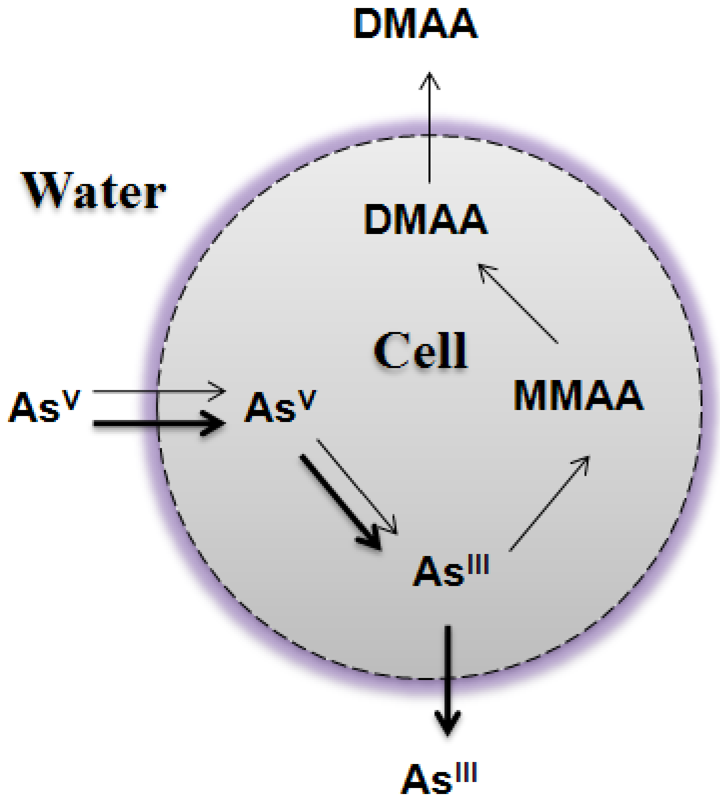

Fig. 1: Transformation of iAs species to methylated species by phytoplankton in the aquatic environment. Arrows represent the phosphate (P) condition in the medium (thick and thin arrows are for P-limited and P-replete conditions, respectively).

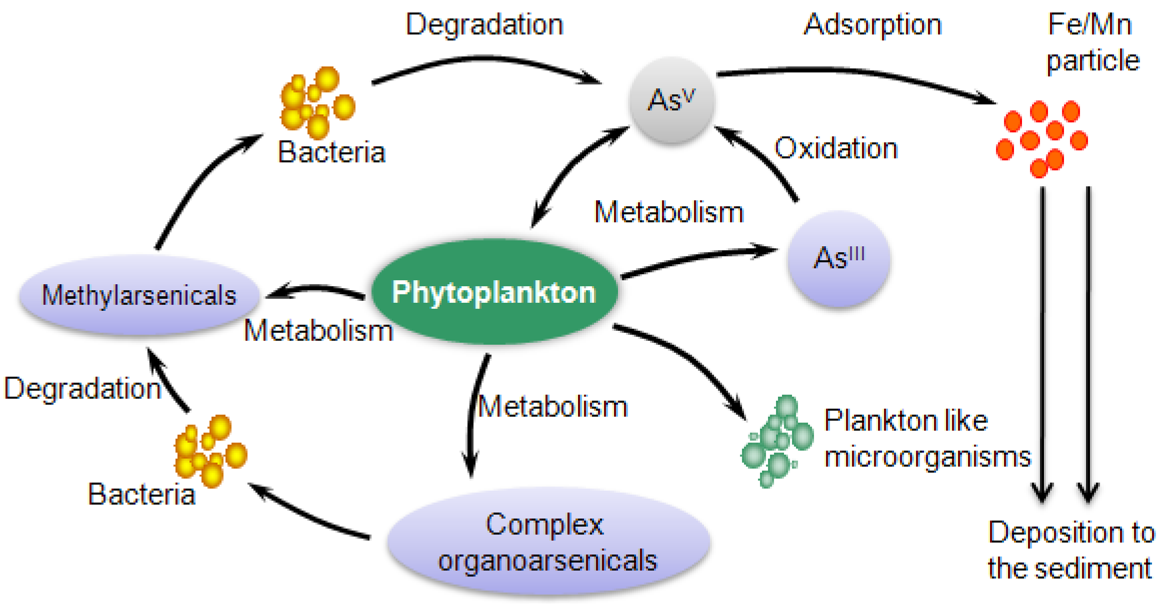

Fig. 2: The roles of microorganisms (e.g., phytoplankton and bacteria) in biotransformation and biogeochemical cycle of arsenic species in aquatic systems. Phytoplankton, the most important primary producers and food sources of higher trophic levels of the food chains in aquatic systems, bioaccumulate inorganic arsenicals (iAs), biotransform to methylarsenicals and complex organoarsenicals inside their cells, and then release back to the water. Arsenic release in water could occur from phytoplankton lysis mediated by viruses, bacteria and grazing by other planktonic microorganisms. Bacteria involve in the demineralization of methyl- and organo-arsenicals producing iAs species in the aquatic systems. As illustrated here phytoplankton and bacteria play important roles in arsenic speciation and cycling in the aquatic systems.