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# **Arsenic in Freshwater Systems: Influence of Eutrophication on its Occurrence, Distribution, Speciation, and Bioaccumulation**

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## **Abstract**

Arsenic (As) exists in a variety of chemical forms, and microbial metabolism results in the occurrence of thermodynamically unstable arsenite ( $\text{As}^{\text{III}}$ ) and methylarsenic compounds in freshwaters (rivers and lakes). The inorganic forms ( $\text{As}^{\text{V}}$  and  $\text{As}^{\text{III}}$ ) and the methylated forms (methylarsonic acid;  $\text{MMAA}^{\text{V}}$  and dimethylarsinic acid;  $\text{DMAA}^{\text{V}}$ ) are the main species of As in freshwaters while the bulk of the total dissolved As is inorganic species. Although the predominant forms of methylarsenic compounds are consistently  $\text{DMAA}^{\text{V}}$  followed by  $\text{MMAA}^{\text{V}}$ , the  $\text{DMAA}^{\text{III}}$  and  $\text{MMAA}^{\text{III}}$  species have also been found in freshwaters. Several observations have revealed that phytoplankton activities are responsible for seasonal variations of methylarsenic compounds in freshwaters. Although it was unclear if the occurrences of methylarsenic compounds were from the breakdown of larger molecules or the end-products of phytoplankton biosynthesis, recent studies have revealed that less toxic As-glutathione complexes are intermediates in the biosynthesis of organoarsenic compounds by phytoplankton. Recent studies have also revealed that eutrophication plays an important role in the production, distribution, and cycling of methylarsenic compounds in freshwaters. In this review, recent reports on the influence of eutrophication on distribution, speciation, and bioaccumulation in freshwaters are discussed.

**Keywords:** Arsenic, Freshwaters, Eutrophication, Bioaccumulation, Biotransformation.

## 1. Introduction

Arsenic (As) is the 20<sup>th</sup> most abundant element in the earth's crust (Woolson, 1975) and 22<sup>nd</sup> in seawater (Brown et al., 1991); however, its relative abundance in freshwater is not known. The sources, occurrence and distribution of As in the environment have been studied by a number of researchers. Although natural events such as weathering, biological and volcanic activities are mainly responsible for the occurrence and distribution of As in the environment, anthropogenic inputs also account for its emission into the atmosphere, from where it is redistributed on the earth's surface by rain and dry fallout (Cullen and Reimer, 1989). It is well recognized that the greatest anthropogenic atmospheric input of As is due to smelting operations and fossil-fuel combustion (Cullen and Reimer, 1989), but it is still difficult to conclude exactly which of the human activities contribute to the overall As cycle in the environment. However, a number of reports have shown that human activities, such as mining, waste disposal, and indiscriminate use of certain pesticides and herbicides, have greatly increased As contamination of the environment (Morin and Calas, 2006). It has been estimated that the ratio of natural to anthropogenic atmospheric input of As is 60 : 40 (Hutton, 1987).

Arsenic contamination of natural waters (groundwater, seawater and freshwaters) has been one of the important environmental concerns because of its harmful effects on organisms directly by ingestion and inhalation or indirectly through the food chain. Arsenic toxicity to organisms depends on its concentration, speciation, bioavailability, and uptake. Arsenic shows toxicity to living organisms at different concentrations depending on the resistance ability and detoxification mechanisms of the organisms. Inorganic As is more toxic than organoarsenic (Meharg and Hartley-Whitaker, 2002; Ng, 2005), and is a proven carcinogen to humans (Ng, 2005). Arsenite ( $\text{As}^{\text{III}}$ ) is usually more toxic than arsenate ( $\text{As}^{\text{V}}$ )

while dimethylarsinous acid ( $\text{DMAA}^{\text{III}}$ ) and monomethylarsonous acid ( $\text{MMAA}^{\text{III}}$ ) are more toxic than their parent compounds (Mass et al., 2001; Petrick et al., 2000).

Phytoplankton, bacteria, and other microorganisms play important roles in As speciation, distribution, and cycling in freshwaters (Hasegawa et al., 1999; Hasegawa et al., 2001; Hellweger and Lall, 2004; Howard et al., 1995; Sharma and Sohn, 2009).  $\text{As}^{\text{V}}$  is the thermodynamically stable state in oxic waters, while  $\text{As}^{\text{III}}$  is predominant under reducing conditions (Andreae, 1986; Cullen and Reimer, 1989). In freshwaters, the dominant inorganic As is incorporated in microorganisms such as phytoplankton, and is converted to methylarsenic compounds and/or higher order organoarsenic compounds such as arsenosugars (Francesconi et al., 1996; Maher, 1984). In addition, the organoarsenic compounds are mineralized to inorganic As and methylarsenic by bacteria (Hanaoka et al., 1995). The forms of As found in freshwater systems (rivers and lakes) are summarized in Table 1. Since biological activities such as growth, density, reproduction, and metabolism of phytoplankton and other organisms in aquatic systems are influenced by temperature and geographical distribution, seasonal variations in the occurrence and distribution of As species results (Hasegawa, 1996; Kim et al., 2009; Kuhn and Sigg, 1993; Michel et al., 1999). Recently, a number of field and laboratory studies have shown that eutrophic states significantly correlate with the distribution and occurrence of As species in freshwaters (Hasegawa et al., 2010; Hasegawa et al., 2009; Sohrin et al., 1997), and thus, bioaccumulation and uptake of As species in various trophic levels of the freshwater food chains may also be affected by eutrophication. Although the results of some extensive studies on seawater As have been reviewed by a number of researchers, especially by Cullen and Reimer (1989), recent findings on freshwater As have not been reviewed. This review will provide some definitive information about how As in the freshwater environment is utilized

and metabolized preliminarily by phytoplankton and thus how As speciation, distribution, and bioaccumulation in the freshwater environment are influenced by eutrophication.

## **2. Sources and distributions of As species in freshwater systems**

Arsenic concentrations in freshwaters may vary by several orders of magnitude depending on the source, availability and chemistry of the environment (Smedley and Kinniburgh, 2002). Typically As concentrations in freshwaters are less than  $10 \mu\text{g L}^{-1}$  but range between  $0.02$  and  $7900 \mu\text{g L}^{-1}$  in rivers and between  $< 0.2$  and  $21,000 \mu\text{g L}^{-1}$  in lakes (Table 2). Data presented in Table 2 are of various contaminated and non-contaminated sites, and thus will give an idea of the known ranges and their variations in the freshwater environment.

### **2.1. Rivers**

The baseline concentrations of As in various river waters range between  $0.1$  and  $2.1 \mu\text{g L}^{-1}$  with an average of  $0.8 \mu\text{g L}^{-1}$  (Table 2). These variations might be related to the contamination source, surface recharge, baseflow, and the bedrock lithology. Low average As concentrations of about  $0.25 \mu\text{g L}^{-1}$  (range  $< 0.02$ - $1.1 \mu\text{g L}^{-1}$ ) in rivers draining basement rocks in Norway (Lenvik et al., 1978), and  $0.15$ - $0.45 \mu\text{g L}^{-1}$  in river waters of the southeastern USA have been reported (Waslenchuk, 1978). On the other hand, high concentrations of naturally-occurring As have been reported in New Zealand (Waikato river,  $32 \mu\text{g L}^{-1}$ ) (McLaren and Kim, 1995; Robinson et al., 1995), USA (Madison and Missouri rivers,  $10$ - $370 \mu\text{g L}^{-1}$ ) (Nimick et al., 1998), Sierra Nevada, USA ( $264 \mu\text{g L}^{-1}$ ) (Benson and Spencer, 1983), and California, USA (Owens river,  $85$ - $153 \mu\text{g L}^{-1}$ ) (Wilkie and Hering, 1998). High concentration of As in these rivers occurred as a result of inputs from geothermal sources (Smedley and Kinniburgh, 2002). Extremely high concentrations of naturally-occurring As

have been reported in waters from the Lao river of northern Chile (up to 21,000  $\mu\text{g L}^{-1}$ ) (Cáceres et al., 1992), which might be due to geothermal input, evaporation, and groundwater input. The River Zenne, Belgium also contains high concentrations of As (up to 30  $\mu\text{g L}^{-1}$ ) which have been affected by inputs from urban and industrial sources, especially sewage (Andreae and Andreae, 1989). Mining activity may also result in the occurrence of high As in river waters. Stream waters adjacent to tailing deposits in the Clubs Lake, British Columbia contained up to 556  $\mu\text{g L}^{-1}$  As (Azcue et al., 1994). Waters of river Ron Phibum (Thailand) (Williams et al., 1996) and the Ashanti (Ghana) (Smedley et al., 1996) have been reported to have 200-300  $\mu\text{g L}^{-1}$  As, due to the effects of Sn and Au mining activities, respectively. In Australia, mining and processing of arsenopyrite ore at the Mole River mine of New South Wales during the 1920–1930s has resulted in As contamination of the Mole River (Ashley and Lottermoser, 1999).

Arsenic concentrations in river waters show distinct seasonal variations. In the Madison river, USA, As concentrations have been reported to be highest during the low-flow season which might be due to the greater contribution of As input from geothermal water and spring runoff (Nimick et al., 1998). On the other hand, maximum As concentration in Waikato river, New Zealand, during summer was supposed to be due to the influence of temperature-controlled microbial activity (reduction of  $\text{As}^{\text{V}}$  to  $\text{As}^{\text{III}}$  and the consequent mobility of  $\text{As}^{\text{III}}$  in the water column) (McLaren and Kim, 1995).

## 2.2. Lakes

Data presented in Table 2 reveal that As concentrations in lake waters are similar to or lower than those in river waters. Arsenic concentrations in a number of lakes in British Columbia (B.C.), Canada have been investigated (Azcue and Nriagu, 1995; Azcue et al., 1994; Azcue et al., 1995). Results showed that the lowest concentration of As was in Bowron

Lake ( $< 0.2 \mu\text{g L}^{-1}$ ) and the highest was in Lowhee Creek ( $2.08 \mu\text{g L}^{-1}$ ). The source of As in these lakes was thought to be the abandoned Cariboo Gold mine tailings (Azcue et al., 1995), from where As was transported to the lakes. Most of the As (up to  $1104 \mu\text{g g}^{-1}$ ) was accumulated in bottom sediments of these lakes and its concentration in the lake waters was observed to be low (between  $< 0.2$  and  $2.08 \mu\text{g L}^{-1}$ ). Elevated concentrations of As (between  $22.0$  and  $47.0 \mu\text{g L}^{-1}$ ) in the output of Moira Lake, Ontario, Canada has also been reported (Table 2). The persistent input of soluble As into Moira Lake indicates the existence of a continuous source of As (Azcue and Nriagu, 1995).

In common with river waters, As concentrations in lake waters are also influenced by geothermal inputs and mining activities (Smedley and Kinniburgh, 2002). Although mining effluents have increased As concentrations in river waters (Ashley and Lottermoser, 1999; Azcue et al., 1994; Smedley et al., 1996; Williams et al., 1996), some lake waters affected by such effluents have been found to have decreased As concentrations (Azcue et al., 1995). The lower concentration of As in mining-affected lake waters might be due to its adsorption on Fe-oxides under neutral or acidic conditions (Smedley and Kinniburgh, 2002) and accumulation in the bottom sediments (Azcue et al., 1995). Similar As concentrations in the surface and bottom waters in mining-affected Canadian lakes (in B.C.) reveal its adsorption and accumulation in the bottom sediments and its limited movement from the sediment into the overlying water (Azcue et al., 1995). In contrast to the low As concentrations in some lake waters, the occurrence of high As concentrations, due to extreme evaporation and/or geothermal inputs, has been reported in alkaline lakes (pH 9.5-10). Maest et al. (1992) reported extremely high dissolved As concentrations (between  $10000$  and  $20000 \mu\text{g L}^{-1}$ ) in Mono Lake, California, USA (Table 2) resulting from geothermal water input and evaporation.



Variations in As concentrations with thermal stratification in lake waters have also been reported by several researchers (Azcue and Nriagu, 1995; Hasegawa, 1996; Hasegawa et al., 2010; Sohrin et al., 1997). The dissolved As concentrations in surface water of Moira Lake, Ontario, Canada have been reported to be highest during summer, with an average concentration of  $47.0 \mu\text{g L}^{-1}$ , compared to that of  $22.0 \mu\text{g L}^{-1}$  in winter (Azcue and Nriagu, 1995). Hasegawa et al. (2010) investigated the seasonal changes of As speciation in 18 lakes around Ishikawa, Nagano, Fukui and Shiga prefectures in Japan and found that the total As concentrations in surface waters of these lakes were higher in summer than in winter. Similar results in the occurrence and distribution of As in lake waters have also been reported by other researchers (Crececius, 1975; Hasegawa et al., 2009; Takamatsu and Kawashima, 1985). Seasonal variations in the occurrence of As in lake waters were due to the release of inorganic As from the sediments into the water of the bottom layer under anaerobic conditions in summer, adsorption of  $\text{As}^{\text{V}}$  onto Fe/Mn oxides, and accumulation into the sediments in winter (Hasegawa et al., 2010). Depletion of  $\text{O}_2$  levels in the bottom layer due to increased biological activities during summer have also been considered to cause higher As concentrations in lake waters (Smedley and Kinniburgh, 2002).

In addition to the biological activities of aquatic organisms, organic matter also plays an important role in the distribution of As species in freshwaters. Sohrin et al. (1997) showed that the speciation of As in lake waters was affected by biological processes such as decomposition of organic matter by bacteria, and by the primary production of phytoplankton. In aquatic systems As concentrations are usually much higher in sediment (mg/kg level) than in the overlying water ( $\mu\text{g/L}$  level) since As is easily bound or adsorbed to suspended and settling particles such as Mn/Fe oxides, organic matter, sulfides, and carbonates (Ruokolainen et al., 2000). The concentration of As in lake sediment often correlates well with the amount of Fe and Mn hydrous oxides, which supports the idea that As co-precipitates in water and

settles into sediment with Fe/Mn oxyhydroxides (Harrington et al., 1998; Mok and Wai, 1994).

### **3. Distribution of As species in freshwater systems**

#### **3.1. Arsenic speciation**

Although As can be found in the environment in several oxidation states, the trivalent  $\text{As}^{\text{III}}$  and pentavalent  $\text{As}^{\text{V}}$  oxyanions are most common in freshwaters (Smedley and Kinniburgh, 2002).  $\text{As}^{\text{V}}$  is the major and thermodynamically stable form in oxic conditions, and is observed in most seawaters (Francesconi and Edmonds, 1996) and freshwaters (Hasegawa et al., 2010; Hasegawa et al., 1994; Sohrin et al., 1997), and  $\text{As}^{\text{III}}$  is produced by phytoplankton and bacteria (Francesconi and Edmonds, 1996). The relatively stable monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) are found in seawaters, and are also significant species in highly productive freshwaters (Andreae, 1979). The formation of methylarsenic (DMAA and MMAA) by phytoplankton and bacteria has been reported in highly productive (having high biological activity) freshwaters (Hasegawa, 1997; Howard et al., 1982; Maki et al., 2005), and their concentrations become comparable with those of inorganic As. The occurrences of unknown As compounds (hidden As) in seawaters and freshwaters have also been reported in the literature (Bright et al., 1996; De Bettencourt and Andreae, 1991; Hasegawa et al., 1999; Howard and Comber, 1989).

#### **3.2. Extraction and determination of As species**

The determination of total As is not sufficient to assess the risks associated with consumption of As-containing foodstuffs since the toxicity of As is highly dependent on its chemical form with inorganic As being more toxic than organoarsenic species. Arsenobetaine and arsenocholine are relatively non-toxic. As a result, much attention has been given to the

elemental speciation of As in environmental and biological samples. Arsenic in biota samples is mainly found in the form of organic species (Cullen and Reimer, 1989). Arsenobetaine, the main species of As 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 vapour generation atomic absorption spectrometry following digestion of the sample with a mixture of  $\text{H}_3\text{ClO}_4$  and  $\text{HNO}_3$ .

The analytical approaches for the determining the speciation of As in biota samples generally involve the use of separation techniques coupled with a sensitive detector. High performance liquid chromatography (HPLC) has been successfully directly coupled with 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 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 to convert the As compounds into volatile arsine prior to detection. However, organoarsenic compounds such as arsenobetaine and arsenocholine do not form volatile hydrides, and, therefore, 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., 1994) and photooxidation with UV radiation (Gomez-Ariza et al., 1998; Tsalev et al., 1998). Other approaches based on hydride generation (HG) of arsine and its preconcentration using cold trapping (CT) provide very good sensitivity for inorganic As, DMAA and MMAA (Featherstone et al., 1998; Hasegawa et al., 1994). The CT-HG-AAS does not allow the determination of arsenobetaine and arsenocholine and, therefore, is not usually considered for As speciation analysis in biota.

The extraction and clean-up procedures comprise a crucial step when biota samples are considered due to possible losses of analyte, changes of the species or incomplete extraction

of the As compounds, which may lead to poor or erroneous results (Gomez-Ariza et al., 2000). Enzymatic digestion (Branch et al., 1994; Lamble and Hill, 1996) or methanol, methanol–water, methanol–water–chloroform mixtures, either with manual agitation, vortex agitation, or sonication for extraction have been reported in the literature (Ochsenkühn-Petropulu et al., 1997; Shibata and Morita, 1992; Thomas and Sniatecki, 1995). But methanol-water (1:1) mixture in an ultrasonic bath has been the most used extraction method for As speciation (Gomez-Ariza et al., 2000).

### 3.3. *Inorganic arsenic*

Arsenic in surface waters has an unusually complex and interesting chemistry with oxidation-reduction, ligand exchange, precipitation, and adsorption reactions all taking place (Ferguson and Gavis, 1972). The bulk of the total dissolved As in freshwaters is inorganic (Kuhn and Sigg, 1993; Seyler and Martin, 1989). From thermodynamic considerations, As should exist almost entirely as As<sup>V</sup> in oxygenated waters (Andreae, 1979), though it is still present even under anoxic (reducing) conditions (Cullen and Reimer, 1989). Microbial (phytoplankton, (Johnson, 1972; Johnson and Burke, 1978) and bacterial, (Howard et al., 1995)) reduction of As<sup>V</sup> results in the occurrence of thermodynamically unstable As<sup>III</sup> which is readily oxidized to more stable As<sup>V</sup> form in oxic waters (Francesconi and Edmonds, 1996). The microbial ‘ArsC’ As<sup>V</sup> reductase protein (a small protein of 13-16 kilodaltons) mediates the reduction of As<sup>V</sup> to As<sup>III</sup> (Lloyd and Oremland, 2006).

Positive correlation between As<sup>III</sup> concentration and primary productivity reveals that phytoplankton and algae are important agents in the transformation of As<sup>V</sup> in the aquatic systems (Andreae, 1978, 1979). Phytoplankton uptake As<sup>V</sup> and release As<sup>III</sup> in the water (Andreae, 1979), but the increase of As<sup>V</sup> concentration in the photic zone indicates rapid oxidation of As<sup>III</sup> and demethylation by phytoplankton (Francesconi and Edmonds, 1996).

Sohrin et al. (1997) studied the distribution of As speciation in Lake Biwa, the largest lake in Japan, and observed that  $\text{As}^{\text{V}}$  was the predominant species in the hypolimnion ( $> 40$  m). In the photic zone of epilimnion ( $< 10$  m),  $\text{As}^{\text{V}}$  is increased over the water mixing period, and decreased over the summer stagnant period, while  $\text{As}^{\text{III}}$  increased over spring and fall, and reached up to 94% of the total As (Sohrin et al., 1997). The same vertical distributions of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  have also been observed in the Northeast Pacific (Andreae, 1978, 1979), in estuaries in southern England (Howard et al., 1982; Howard et al., 1995), and Davis Creek Reservoir, CA (Anderson and Bruland, 1991) which suggest that the distribution pattern of inorganic As in freshwaters as well as in seawaters is identical.

In addition to the microbial reduction of  $\text{As}^{\text{V}}$ , high concentration of  $\text{As}^{\text{III}}$  in lakes receiving  $\text{As}^{\text{III}}$  rich riverine input reveals that  $\text{As}^{\text{III}}$  can also occur in lake waters from anthropogenic and atmospheric inputs. Arsenic in the Carnon River (Great Britain) consisted predominantly (95% of the total As) of  $\text{As}^{\text{III}}$  which was influenced by long-term mining activity in the region (Klumpp and Peterson, 1979). On the other hand, high concentrations of  $\text{As}^{\text{III}}$  (between 2.9 and 20% of the total inorganic As) in the Tejo River (Portugal) was probably due to atmospheric emissions counting a large amount of As from a nearby pyrite roasting plant (Andreae et al., 1983). Although the As composition in the emissions was not determined, the high percentage of  $\text{As}^{\text{III}}$  from the nearest atmospheric emission source suggests that  $\text{As}^{\text{III}}$  was not oxidized in the surface waters over a short period (Andreae et al., 1983).

Nitrate also strongly influences the occurrence of inorganic As under anoxic conditions by oxidizing ferrous iron ( $\text{Fe}^{+2}$ ) to As-sorbing particulate hydrous ferric oxides ( $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ,  $\text{FeOOH}$ ; HFO) and resulting a more oxidized  $\text{As}^{\text{V}}$  which is more particle-reactive than that of  $\text{As}^{\text{III}}$  under these conditions (Senn and Hemond, 2002). In spring and summer, biotic oxidation of both  $\text{As}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  leads to the precipitation of insoluble mixed

Fe<sup>III</sup>-As<sup>V</sup> hydrous oxides (Morin and Calas, 2006), which suggests that both biotic and abiotic oxidations of Fe<sup>II</sup> play important roles in the distribution of inorganic As in surface waters.

### 3.4. Methylarsenicals

The important methylated As compounds in freshwaters are MMAA<sup>III</sup>, DMAA<sup>III</sup>, MMAA<sup>V</sup>, and DMAA<sup>V</sup> (Table 1). At natural pHs, MMAA and DMAA occur as anionic monomethylarsenate (CH<sub>3</sub>AsO<sub>2</sub>OH<sup>-</sup>) and dimethylarsinate ((CH<sub>3</sub>)<sub>2</sub>AsOO<sup>-</sup>), respectively (Anderson and Bruland, 1991). Braman and Foreback (1973) first detected DMAA and MMAA in a number of freshwater and seawater samples. They found that in inorganic As dominated water samples, the methylarsenicals comprised up to 68% of the total As (McKay Bay, Florida, USA) though it was typically between the ranges of 10-20%. Similar results were also reported by Andreae (1978) in some freshwater samples, but the percent concentration ranges were much lower (< 10% of the total As) than those of the previous findings of Braman and Foreback (1973). Hasegawa et al. (2009) found the concentrations of DMAA between 0.075 and 0.337 µg l<sup>-1</sup> in Lake Biwa (Japan) and about 0.187 µg l<sup>-1</sup> in Lake Kiba (Japan). In most samples of Lake Biwa and Lake Kiba, the concentrations of MMAA were lower than the instrumental limit of detection.

A number of studies has reported the seasonal variations in vertical distribution of methylarsenicals in seawaters and freshwaters. Compared to the freshwater systems, many more studies have been conducted on the distribution of methylarsenicals in the marine environment. Andreae (1978, 1979) reported the vertical distribution of DMAA and MMAA in deep northeast Pacific and California coastal waters. The methylarsenicals increased in photic zone with the depletion of As<sup>V</sup> and increase of As<sup>III</sup>; their concentrations decreased with increasing depth. The methylarsenic concentrations decreased to that of the detection limit near the bottom of the photic zone, and neither of DMAA nor MMAA was occasionally

detected in trace concentrations in deeper waters (Andreae, 1978, 1979). Vertical distributions of As species in lake waters have also been studied by other researchers (Hasegawa, 1997; Hasegawa et al., 2001; Howard et al., 1982; Sohrin et al., 1997). Sohrin et al. (1997) reported that DMAA<sup>V</sup> is the dominant species and its concentration increased up to 64% of total As in the epilimnion (< 10-20 m) zone of Lake Biwa, Japan, over summer. Hasegawa (1997) also reported the distribution of As species in Lake Biwa during 1993-1994. They observed that the dominant methylarsenic species in the lake was DMAA<sup>V</sup>, which comprised 64 – 99% of the total methylarsenicals. Concentrations of MMAA<sup>V</sup> and DMAA<sup>V</sup> were less than 0.05 µg l<sup>-1</sup> and 0.75 µg l<sup>-1</sup>, respectively, and the concentrations of trivalent methylarsenic species (MMAA<sup>III</sup> and DMAA<sup>III</sup>) were one or two orders of magnitude lower than those of tetravalent methylarsenic species (MMAA<sup>V</sup> and DMAA<sup>V</sup>). Howard et al. (1982) determined the concentrations of methylarsenicals at different sites of the River Beaulieu in central southern England. They found that the concentrations of DMAA and MMAA in the water were 0.07-0.38 and 0.16-0.42 µg l<sup>-1</sup>, respectively.

The occurrence of methylarsenicals in freshwaters is mediated by some aquatic organisms. Some species of algae involved in As methylation, and the ability of methylation differs among species (Sanders, 1983). Diatoms such as *Skeletonema* and *Rhizosolenia delicatula* are also reported to produce As<sup>III</sup> and DMAA (Andreae and Klumpp, 1979; Hasegawa et al., 2001; Howard et al., 1995; Sanders and Windom, 1980). The cryptophyte, *Chroomonas* spp., has been reported to be associated with the production of MMAA (Sanders and Osman, 1985). Thus, the occurrence of methylated As compounds has been attributed to methylation by phytoplankton (Cullen and Reimer, 1989; Hasegawa et al., 2009; Howard et al., 1995) or by closely associated heterotrophs (Cullen and Reimer, 1989). As<sup>V</sup> is taken up by phytoplankton in the euphotic waters and subsequently converted to As<sup>III</sup>, DMAA, and MMAA and released back to the water (Andreae, 1978, 1979; Andreae, 1986; Cullen and

Reimer, 1989; Hasegawa et al., 1999; Hasegawa et al., 2009; Howard et al., 1982; Howard et al., 1995; Sohrin et al., 1997). This conversion of As<sup>V</sup> to As<sup>III</sup> and to methylarsenicals are thought to be a detoxification mechanism of the organisms. Anderson and Bruland (1991), however, argued against the direct production of DMAA by phytoplankton because of the poor correlation between chlorophyll-*a* (chl-*a*) and DMAA in field samples.

The distribution of methylarsenicals, in the context of eutrophication and seasonal variations, in lake waters have been studied mainly by our group in recent years (Hasegawa, 1996, 1997; Hasegawa et al., 1999; Hasegawa et al., 2010; Hasegawa et al., 2009; Hasegawa et al., 1994; Hasegawa et al., 2001; Sohrin et al., 1997). From these studies, we found the highest DMAA concentration in early summer which was initially supposed to be produced from hidden As through the photodegradation under strong sunlight condition (Hasegawa et al., 1999). However, laboratory experiments revealed that the photochemical degradation by sunlight does not contribute significantly to the production of DMAA in lake waters. Therefore, we assumed that biological processes such as bacterial decomposition of the ultraviolet (UV) labile fraction of As would be the possible reason for DMAA production in lake water (Hasegawa et al., 1999). In recently published articles, we reported that the production and distribution of methylarsenicals were significantly influenced by biological activities and eutrophication (Hasegawa et al., 2010; Hasegawa et al., 2009). We found that the DMAA concentration was higher in the mesotrophic Lake Biwa compared to that in the eutrophic Lake Kiba, and the concentrations of DMAA were higher during May to October (summer) compared to those in January (winter) in both lakes. The results suggest that the biosynthesis of complex organoarsenicals and the speciation of As in freshwaters would be influenced by the biological activities and biochemical processes of organisms.

#### **4. Eutrophication and As speciation freshwater systems**



#### **4.1. Eutrophication**

Weber (1907) was the first to use the terms 'eutrophic' to describe the general nutrient conditions of soils in German bogs (Rast and Thornton, 1996). Subsequently this term was introduced in the aquatic sciences by Naumann (1919) in the 20<sup>th</sup> century. Eutrophication is the natural ageing process of lakes which transforms aquatic environments into terrestrial habitats, begins with the addition of nutrients into the system. These nutrients in turn stimulate the growth of microscopic free-floating aquatic plants known as phytoplankton and microalgae (Rast and Thornton, 1996). A more accurate term for this process is cultural eutrophication which includes the accelerated nutrient enrichment of surface waters by human activities. Like natural eutrophication, cultural eutrophication also results in the excessive growth of phytoplankton and microalgae in surface waters by nutrient enrichment (OECD, 1982). Nutrients enter rivers and streams directly from point and non-point sources (Smith et al., 1999).

#### **4.2. Trophic classification of aquatic systems**

The classification scheme developed originally by Weber (1907) for bogs has been used to categorize surface water systems according to the relative magnitude of their nutrient inputs (Hutchinson, 1969; Hutchinson, 1973). Two of the most important nutrients responsible for eutrophication are nitrogen and phosphorus. Nitrogen is commonly found in aquatic environments as nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), or ammonia ( $\text{NH}_3$ ), while phosphorus is found as phosphate ( $\text{PO}_4^{3-}$ ).

The chl-*a* content in surface waters has been considered for the determination of phytoplankton density which is influenced by phosphorus input in aquatic systems (Carpenter et al., 1996). Therefore, chl-*a* content in surface water is considered as an important factor in trophic classification of aquatic systems. Based on the amount of phytoplankton density (chl-

*a* content) and the concentration of nutrients (particularly nitrogen and phosphorus), the degree of eutrophication in aquatic systems can be classified as oligotrophic, mesotrophic, eutrophic, or hypereutrophic (Rast and Thornton, 1996; Smith et al., 1999). Oligotrophic environments are characterized by clear waters, little suspended organic matter or sediment, and low primary production (phytoplankton growth). Mesotrophic environments have higher nutrient inputs and rates of primary production. Eutrophic environments have extremely high nutrient concentrations and biological productivity. Hypereutrophic environments are characterized by murky, highly productive waters in which many clear water organisms cannot survive (Allen and James, 1972; Genkai-Kato and Carpenter, 2005; Moncreiff, 2002; Smith et al., 2006; Smith et al., 1999).

The trophic state classification system (TSCS), developed by Forsberg and Ryding (1980), has widely been used for grouping water bodies. Some other researchers also have classified aquatic systems based on total nitrogen (TN), total phosphorus (TP), chl-*a* content, and Secchi disk (SD) (Dodds et al., 1998; Hakanson, 1994; Nürnberg, 1996), which are summarized in Table 3. We used these TSCSs in our studies to classify freshwater lakes into oligotrophic, mesotrophic, and eutrophic states to investigate the relationship between eutrophication and As speciation.

#### **4.3. Influence of PO<sub>4</sub><sup>3-</sup>, chl-*a* and dissolved oxygen on As distribution in lake water**

In a recent study, we observed that the distribution of As species in lake waters was influenced by phosphate (PO<sub>4</sub><sup>3-</sup>) concentration and phytoplankton density (chl-*a* content) (Hasegawa et al., 2010). Results showed that the distribution of As species was better correlated with PO<sub>4</sub><sup>3-</sup> concentration compared to that of chl-*a*. Moreover, As<sup>V</sup> uptake by phytoplankton was less in phosphate-rich lakes compared to that in phosphate-poor lakes (Hasegawa et al., 2010). The conversion of As<sup>V</sup> to As<sup>III</sup> and to organoarsenicals by organisms

is more dynamic in phosphate-exhausted lakes (Hasegawa et al., 2010), and the exhaustion of phosphate has been considered to be important for the conversion of As<sup>V</sup> (Froelich et al., 1985b; Sohrin et al., 1997).

We also observed that dissolved oxygen influenced the occurrence of As<sup>III</sup> in lake waters (Hasegawa et al., 2010). Biological activities, which use a substantial amount of dissolved oxygen, are higher in eutrophic lakes while the activities are limited in mesotrophic lakes (Ærtebjerg et al., 2003; Genkai-Kato and Carpenter, 2005; Kennish and Townsend, 2007; Moncreiff, 2002; OECD, 1982; Smith et al., 2006; Smith et al., 1999). Therefore, the amount of dissolved oxygen tend to decrease in eutrophic lakes compared to that in mesotrophic lakes (Meyer-Reil and Köster, 2000). Comparatively highly oxic conditions in mesotrophic lakes favour the oxidation of As<sup>III</sup> to As<sup>V</sup> which results in high concentration of As<sup>V</sup> in such lakes (Hasegawa et al., 2010).

#### **4.4. Distribution of As species in lake waters in relation to eutrophication**

In freshwater systems, the proportions of As species vary with anthropogenic input of As and biological activity. We investigated the concentrations and distribution of As species in mesotrophic and eutrophic lakes to determine the effect of eutrophication on As speciation in relation to biological activity (Hasegawa et al., 2010; Hasegawa et al., 2009; Hasegawa et al., 2001). The increase of DMAA in the water column of eutrophic lakes (Hasegawa et al., 2009) and the similar trend of DMAA distribution in relation to the seasonal variations in other lakes (Sanders and Riedel, 1993) revealed that the source of DMAA was due to the direct production of phytoplankton, or decomposition of organic matter containing complex organoarsenic compounds by microorganisms or sunlight (Hasegawa et al., 2009).

The insignificant correlation between chl-*a* and DMAA in field studies does not concur with the direct excretion of DMAA by phytoplankton (Anderson and Bruland, 1991).

But recent As speciation studies using UV photolytic decomposition and the modified technique of hydride generation method (CT-HG-AAS) (Hasegawa et al., 1994) showed that the concentrations of UV-labile fractions of As (UV-As) and UV-DMAA (hidden As) correlate with that of DMAA in eutrophic lakes (Hasegawa et al., 2009). The UV-As, UV-DMAA and DMAA appeared in the summer although they disappeared in the winter, and the production of these UV-labile fractions of As species was related to the biological activity. The UV-As and UV-DMAA fractions of As species derived from colloidal and particulate fractions (Hasegawa et al., 2009), and the hidden As species or complex organoarsenic compounds such as arsenosugar might be derived from organic matter to which they were tightly adsorbed (Bright et al., 1996). Although there is a possibility of release DMAA and inorganic As from particulate of organic matter by UV irradiation (Hasegawa et al., 2009), the UV-As and UV-DMAA fractions would mainly consist of complex organoarsenic compounds that were synthesized in phytoplankton and other freshwater organisms (Kuehnelt and Goessler, 2003). Maeda (1994) reported the biotransformation of As<sup>V</sup> to organoarsenic compounds in freshwater food chains. Hasegawa et al. (2001) also identified several strains of phytoplankton which produce methylarsenicals in lake water. Kuehnelt and Goessler (2003) observed the decrease of total As concentration and relative increase of methylarsenicals as it move through higher trophic level in most aquatic food chains. The presence of arsenoriboses in microbial mats and green algae (Koch et al., 1999) and the identification of oxo- and thio-AsS in several freshwater mussels and fishes as an important As constituent, and Arsenobetaine as a minor concentration (Schaeffer et al., 2006; Schmeisser et al., 2004) support the observations of Kuehnelt and Gossler (2003).

The higher concentrations of UV-As and UV-DMAA in eutrophic lakes compared to those in mesotrophic lakes, and their correlation with DMAA concentration, reported by Hasegawa et al. (2009), can be explained by the trophic states of the lakes. Eutrophication

increased the microbial biomass and biosynthesis of complex organoarsenic compounds in reservoir, which resulted in the degradation of DMAA and other organoarsenic compounds (Hasegawa et al., 2009). Moreover, the higher degradation rate of DMAA in eutrophic lakes than that in mesotrophic lakes was due to the direct transformation of  $As^V$  into methylarsenicals or other organoarsenic compounds by the biota, which in turn is degraded to DMAA. The composition of As species in mesotrophic and eutrophic lakes is attributed to the balance of biological processes of the lakes such as metabolism of phytoplankton, grazing pressure by zooplankton, and the decomposition of organic matter by microbial communities.

#### **4.5. Seasonal variation of As distribution in levels of different trophic states**

A number of studies has shown distinct variation of As distribution in lakes of different trophic states. Recently, we studied the distribution of As species in 18 lakes in Japan and observed that the total As concentrations in summer were higher than that in winter in both eutrophic and mesotrophic lakes (Fig. 1) (Hasegawa et al., 2010). These trends of As distribution in lake waters were also reported in our previous study (Hasegawa et al., 2009) and also by other researchers (Creelius, 1975; Takamatsu and Kawashima, 1985). The distribution of As species in eutrophic and mesotrophic lakes was hypothesized to be due to the release of inorganic As into the water from the sediments in the bottom layer under anaerobic conditions in summer, while  $As^V$  was adsorbed onto Fe/Mn oxides which then settled on the sediments in winter. A large difference in the composition of organoarsenicals was observed between mesotrophic and eutrophic lakes in summer. Organoarsenicals comprised major fractions of the total As in mesotrophic and eutrophic lakes in summer (Hasegawa et al., 2010). Most of the UV-labile fractions and total organoarsenicals were distributed in eutrophic lakes compared to those in mesotrophic lakes. This was due to the greater conversion of inorganic and methylarsenicals to more complex organoarsenicals by

aquatic organisms in eutrophic lakes in summer (Hasegawa et al., 2010). Aquatic organisms have also been reported to uptake inorganic As and excrete DMAA in freshwaters (Cullen and Reimer, 1989; Hasegawa et al., 2001; Maeda, 1994).

With few exceptions, the concentration of UV-As was higher in highly eutrophic lakes than in low-eutrophic lakes during summer (Fig. 1A), while DMAA concentration was higher in low-eutrophic lakes during winter than in summer (Fig. 1B). The occurrence of DMAA has also been reported in other aquatic systems (Anderson and Bruland, 1991; Hasegawa et al., 2009), and in laboratory experiments (Hasegawa et al., 2001). Frequent occurrence at high water temperature of DMAA relative to As<sup>III</sup> has been reported by Howard et al. (1995). Sohrin et al. (1997) also reported a correlation between the concentration of DMAA and water temperature in Lake Biwa, Japan. Hasegawa (1996) reported that the concentration of DMAA follows the rise of water temperature in estuarine waters.

## **5. Bioavailability and bioaccumulation of As**

### **5.1. Bioavailability**

It has been argued that, because the bioavailability of As 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, that is, the fraction of the external dose that is absorbed by the organisms (Caussy, 2003).

Bioavailability of As 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 As compounds (Caussy, 2003). Relative bioavailability is important for environmental studies. Bioavailability is usually determined by dosing an experimental organism with various concentrations of As and measuring the response. The key determinant of bioavailability is the ability of As to be released from its environmental matrices, and also with the chemical species and molecular structure and complex interaction of host and chemical factors. These factors include reactivity, solubility, and ability to form organic metal complexes, oxidation state and physical forms (Caussy, 2003).

## **5.2. 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 such as soil, suspended particles etc. The magnitude of accumulation can vary widely depending on the chemical and its properties. These chemicals may also biomagnify in aquatic food webs, 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) (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 (Chen and Folt, 2000; Maeda et al., 1990a; Mason et al., 2000). Rooted aquatic macrophytes are presumed to have a function in arsenic toxicity because these plants are closely associated with sediments. Studies of 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., 1995](#)) reported that macrophytes tended to bioaccumulate more As relative to other aquatic biota. It has been suggested that the amount of As occurred in a highly bioavailable form in the aquatic system is a function of multiple factors such as the environmental compartment, water column, sediment pore water, pH, presence of other metals and sediments particles ([Caussy, 2003](#)).

### **5.3. Bioaccumulation of As in freshwater organisms**

Bioaccumulation and biomagnification of As in fresh- and seawater have been studied by a number of researchers. Despite the recent attention on As uptake and accumulation in aquatic biota, much uncertainty in the mechanisms and bioaccumulation potential of the various forms of As in the environment still exists. It has been reported that about 85 to > 90% of the total As found in edible portions of marine fish and shellfish is organic As (arsenobetaine, arsenocholine, and DMAA) and approximately 10% is inorganic As ([De Gieter et al., 2002](#); [Goessler et al., 1997](#); [Ochsenkühn-Petropulu et al., 1997](#)). Less is known about the forms of As in freshwater fish, but it is evident from field ([Kaise et al., 1987](#)) and laboratory ([Maeda et al., 1990a](#); [Maeda et al., 1993](#); [Maeda et al., 1992](#); [Maeda et al., 1990b](#)) studies that organic As would comprise the major fraction in these fishes. In addition to the organoarsenicals, the presence of inorganic As in some freshwater fishes from Pak Pa-Nang Estuary and catchments located in Southern Thailand has been reported ([Rattanachongkiat et al., 2004](#)). The concentrations of inorganic As in sardines, catfish, tiger prawn and swimming crab from Pak Pa-Nang Estuary and catchments were 0.3, 0.2, 0.8, and 0.9  $\mu\text{g g}^{-1}$  dry weights, which were about 6%, 12%, 7%, and 5% of the total As contents, respectively.

Although biomagnification of As in the aquatic food chain is rare ([Henry, 2003](#)), it has been reported in fishes ([Maher and Butler, 1988](#)) and gastropods ([Goessler et al., 1997](#))



mainly as Arsenobetaine, a rapidly eliminated and thus non-toxic form of As, which poses minimal health problems for humans (Caussy, 2003; Maher et al., 1999). However, bioaccumulation factors (BAFs) of As have been estimated from its uptake by freshwater organisms, both in laboratory and field experiments, to investigate the trophic transfer and health hazards of this toxic element. Spehar et al. (1980) estimated BAFs for some freshwater invertebrate species and rainbow trout exposed to  $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$ , DMAA, or MMAA under laboratory conditions. Results showed that stoneflies, snails, and daphnids accumulated greater amounts of As than fish. Tissue As concentrations in treated rainbow trout were generally the same as those in control fish while in stoneflies and snails the concentrations were generally higher. Total As accumulation in stoneflies and snails exposed to  $1,000 \mu\text{g l}^{-1}$  of the As did not appear to be greatly affected by the form of As in water, although some animals exposed to inorganic As exhibited higher tissue burdens.

Wagemann et al. (1978) measured As concentrations in several aquatic invertebrate species from lakes in the vicinity of Yellowknife, Northwest Territories, Canada. The BAFs estimated for the various invertebrates sampled from Grace Lake (reference lake) were consistently higher (between 28.3 and  $377.8 \text{ L kg}^{-1}$ ) than those for the same species from Kam Lake (contaminated lake) (between 3.4 and  $63.6 \text{ L kg}^{-1}$ ). Chen et al. (2000) studied the accumulation and fate of As in large and small planktons from numerous lakes in the northeastern USA, and found that As BAFs of small zooplankton and large phytoplankton were significantly higher (between 369 and  $19,487 \text{ L kg}^{-1}$ ) than those of larger zooplankton (between 154 and  $2,748 \text{ L kg}^{-1}$ ). Chen and Folt (2000) also studied the trophic transfer of As in the metal-contaminated Upper Mystic Lake in NY, USA on a seasonal basis and observed that As concentrations in small zooplankton reflected the fluctuation of As concentrations in water, while As in larger zooplankton progressively increased, indicating the potentially greater influence of dietary As on the larger size class.

Wagemann et al. (1978) also investigated BAFs for several predatory insects from Kam Lake and Grace Lake. BAFs estimated for the predatory insects from Grace Lake were consistently higher than those for the same species from the Kam Lake. Chen and Folt (2000) measured As accumulation 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 As in the food chain of the Upper Mystic Lake. Results showed that As burdens for all fishes in the lake were 30 to 100 times lower than the burdens for zooplankton. Alewife and killifish (predominantly planktivorous fish species) had higher burdens than those of other fish species. Two other studies (Baker et al., 1994; Chen and Folt, 2000) also reported that the average As burden for largemouth bass (organism of higher trophic level) was approximately 60 to 95 times lower than the burdens for zooplankton. A number of other studies also showed that fish species lower on the trophic scale (alewife, killifish) had higher BAFs than species that are slightly higher on the trophic scale (perch, crappie, catfish, carp, sunfishes) (Baker et al., 1994; Chen and Folt, 2000; Skinner, 1985; Wagemann et al., 1978). However, preliminary assessment of BAFs determined from laboratory-measured bioconcentration factors indicates that the estimated values were lower than those derived using data from the field BAFs.

## **Conclusion:**

Although most of the previous studies related to aquatic As focused mainly on As distribution, speciation, and bioaccumulation in seawaters and river waters, we investigated the distribution, speciation, and the seasonal variations of As species in lake waters in relation to eutrophication over the last couple of years. Eutrophication promotes biological activities in freshwaters, which affect the distribution and speciation of As in these systems. Total As

concentration was higher in eutrophic lakes than in mesotrophic lakes. Methylarsenicals are higher in oligotrophic and mesotrophic lakes while the UV-labile fraction was higher in eutrophic lakes. Our results also reveal that the conversion of inorganic and methylarsenicals to more complex organoarsenicals is higher in eutrophic lakes than in mesotrophic and oligotrophic lakes.

We also found obvious differences in the occurrence of As species in lake waters between summer and winter. With few exceptions, the concentrations of organoarsenicals were higher in summer than in winter. It was also observed that the percentage of organoarsenicals was about 30–60% of the total As in most of the lakes in summer. Although inorganic As in mesotrophic lakes decreased in summer and increased in winter, the proportions of this As species was found to be similar in both seasons. An important observation was that the concentration of the methylarsenicals in eutrophic lakes was greater in winter than that in summer. This observation indicates a significant correlation between eutrophication and As speciation in freshwaters. Other than our studies that have been conducted in lakes around Ishikawa, Nagano, Fukui, and Shiga prefectures in Japan, little or no work has been done in this field in other geographical locations. Recent reports on high As deposition in surface soils from As contaminated groundwater used for irrigation, especially in Bangladesh and West Bengal (India) ([Dittmar et al., 2010](#); [Khan et al., 2009, 2010](#)), indicate that As concentrations in surface waters of these areas would be high. Therefore, such studies would be more pertinent to As affected South and South-East Asian countries where both eutrophication rates and As concentrations are higher in freshwater systems, especially in lakes and ponds. Unfortunately, little or no studies have been done on As distribution and speciation in freshwaters of these regions.

It has been elucidated from our studies that aquatic organisms, especially the phytoplankton, play important roles in the speciation and cycling of As in freshwater systems.

In addition, organoarsenic comprises the major fraction in freshwater fishes, and the occurrence of this species in freshwaters is significantly influenced by eutrophication and phytoplankton activities. Since bioavailability of As is closely associated with its speciation, eutrophication, in combination with the microbial and biological activities, these factors may influence As bioaccumulation and trophic transfer in freshwater food chains. However, it is quite difficult to draw firm conclusions regarding the influence of eutrophication on As bioavailability, bioaccumulation, and trophic transfer in the freshwater food chains due to inadequate data. Thus, further research is still required in this field.

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1 **Table 1:** Chemical forms of As in freshwaters and freshwater organisms

Name	Abbreviation	Formula/Structure	Distribution (water/organisms)	Reference
<i>Inorganic arsenicals</i>				
Arsenious acid or arsenite	As <sup>III</sup>	As(OH) <sub>3</sub>	Fish, Crustacean, Water, Algae	(Andreae, 1978; Hasegawa et al., 1999; Rattanachongkiat et al., 2004; Sohrin et al., 1997)
Arsenic acid or arsenate	As <sup>V</sup>	H <sub>3</sub> AsO <sub>4</sub>	Fish, Crustacean, Algae, Water	(Andreae, 1978; Hasegawa et al., 1999; Rattanachongkiat et al., 2004; Sohrin et al., 1997)
<i>Methylated arsenicals</i>				
Monomethylarsonous acid	MMAs <sup>III</sup>	As(OH) <sub>2</sub> CH <sub>3</sub>	Lake water, Freshwater organisms, Algae	(Anderson and Bruland, 1991; Hasegawa, 1997; Sohrin et al., 1997)
Dimethylarsinous acid	DMAs <sup>III</sup>	As(OH)(CH <sub>3</sub> ) <sub>2</sub>	Lake water, Freshwater organisms, Algae	(Anderson and Bruland, 1991; Hasegawa, 1997; Sohrin et al., 1997)
Monomethylarsonic acid	MMAs <sup>V</sup>	AsO(OH) <sub>2</sub> CH <sub>3</sub>	Fish, Crustacean, Algae, Water	(Anderson and Bruland, 1991; Hasegawa, 1997; Rattanachongkiat et al., 2004; Sohrin et al., 1997)
Dimethylarsinic acid	DMAs <sup>V</sup>	AsO(OH)(CH <sub>3</sub> ) <sub>2</sub>	Fish, Crustacean, Algae, Water	(Anderson and Bruland, 1991; Andreae, 1978; Hasegawa, 1997; Rattanachongkiat et al., 2004; Sohrin et al., 1997)
<i>Organoarsenic Compounds</i>				
Arsenocholine	-	(CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> CH <sub>2</sub> CH <sub>2</sub> O	Fish, Shellfish, Shrimps, Lobster, Water	(Benjamin et al., 1987; Lawrence et al., 1986; Norin et al., 1983)
Arsenobetaine	-	(CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> CH <sub>2</sub> COO <sup>-</sup>	Fish, Lobster, Shrimp, Crustacean, Waters, Gastropod	(Benjamin et al., 1987; Rattanachongkiat et al., 2004)
Arsenosugars	-		Organic matters, fishes	(Bright et al., 1996; Schaeffer et al., 2006; Schmeisser et al., 2004)
Thioarsenates	-		Sulfidic waters	(Planer-Friedrich et al., 2007; Stauder et al., 2005; Wallschläger and Stadey, 2007)

3 **Table 2:** Arsenic concentrations in some freshwater systems (rivers and lakes) around the world (modified from Smedley and Kinniburgh (2002)).

<b>Water systems and Location</b>	<b>As concentrations (average/range (<math>\mu\text{g l}^{-1}</math>))</b>	<b>References</b>
<b><i>River water</i></b>		
Various	0.8 (0.13-2.1)	(Andreae et al., 1983; Froelich et al., 1985a; Seyler and Martin, 1991)
Norway	0.3 (<0.02-1.1)	(Lenvik et al., 1978; Smedley and Kinniburgh, 2002)
Dordogne, France	0.7	(Seyler and Martin, 1990)
Po River, Italy	1.3	(Pettine et al., 1992; Pettine et al., 1994; Pettine et al., 1997)
Polluted European rivers	4.5-45.0	(Seyler and Martin, 1990)
Schelde catchment, Belgium	0.75-3.8 (up to 30)	(Andreae and Andreae, 1989)
Lao river, Northern Chile	19-21000	(Cáceres et al., 1992)
Cordoba, Argentina	7-114	(Lerda and Prospero, 1996)
Walker River, Sierra Nevada, USA	0.20-264	(Benson and Spencer, 1983)
Madison and Missouri rivers, USA	44 (19-67), 10-370	(Nimick et al., 1998; Robinson et al., 1995)
Waikato, New Zealand	32 (28-36)	(McLaren and Kim, 1995; Robinson et al., 1995)
Ron Phibun, Thailand	218 (4.8-583)	(Williams et al., 1996)
Ashanti, Ghana	284 (<2-7900)	(Smedley et al., 1996)
Willow River, B.C., Canada	0.6 (0.3-0.8)	(Azcue et al., 1995)
<b><i>Lake water</i></b>		
Lake Echols, Tampa	3.58	(Braman and Foreback, 1973)
Lake Magdalene, Tampa	1.75	(Braman and Foreback, 1973)
Moira Lake, Ontario, Canada	20.4 (22.0-47.0)	(Azcue and Nriagu, 1995)
Jack of Clubs Lake, B.C., Canada	0.3 (0.2-0.4)	(Azcue et al., 1995)
Bowron Lake, B.C., Canada	<0.2	(Azcue et al., 1995)
Lowhee Creek, B.C., Canada	1.5 (0.2-2.0)	(Azcue et al., 1995)
Lake Biwa, Japan	2.2 (0.6-1.7)	(Hasegawa et al., 2010)
Lake Kahuku	1.1 (0.4-1.7)	(Hasegawa et al., 2010)
Lake Kiba, Japan	0.5 (0.2-0.7)	(Hasegawa et al., 2010)
Sweden	0.06-1.2	(Reuther, 1992)

Western USA	0.38-1000	(Benson and Spencer, 1983)
Mono Lake, California, USA	10000-20000	(Maest et al., 1992)
Northwest territories, Canada	270 (64-530)	(Bright et al., 1996)

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18 **Table 3:** Trophic classification of natural water systems (lakes, streams and coastal waters) on the basis of total nitrogen (TN), total phosphorus  
 19 (TP), Chlorophyll-*a* (chl-*a*) and Secchi disk (SD) (modified from [Smith et al. \(1999\)](#)).

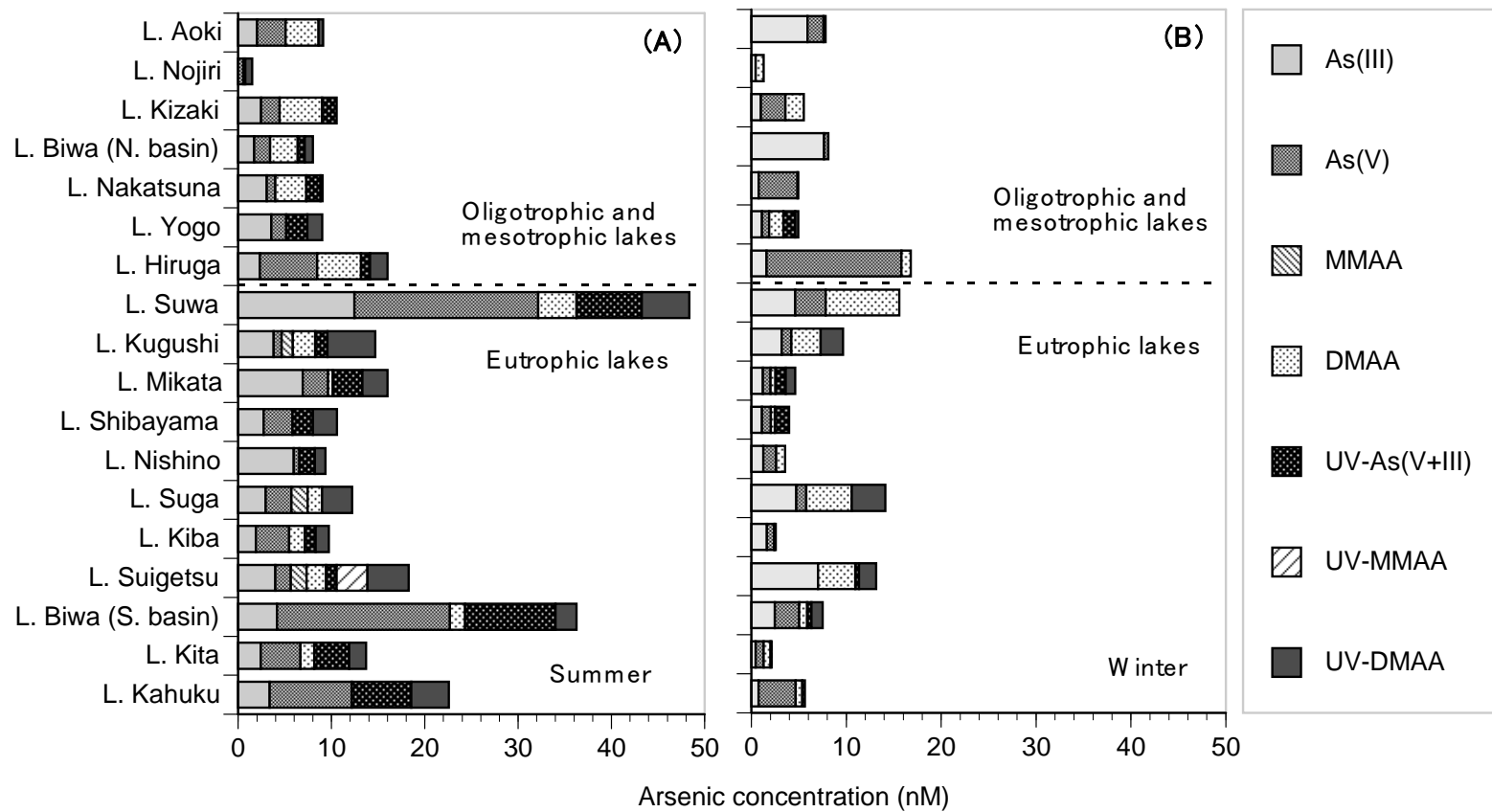
<b>Water systems</b>	<b>Trophic state</b>	<b>TN (mg m<sup>-3</sup>)</b>	<b>TP (mg m<sup>-3</sup>)</b>	<b>Chl-<i>a</i> (mg m<sup>-3</sup>)</b>	<b>SD (m)</b>	
<b>Lakes</b>	Oligotrophic	<350.0	<10.0	<3.5	>4.0	<a href="#">(Nurnberg, 1996)</a>
	Mesotrophic	350.0-650.0	10.0-30.0	3.5-9.0	2.0-4.0	
	Eutrophic	650.0-1200.0	30.0-100.0	9.0-25.0	1.0-2.0	
	Hypertrophic	>1200.0	>100.0	>25.0	<1.0	
		<b>TN (µg l<sup>-1</sup>)</b>	<b>TP (µg l<sup>-1</sup>)</b>	<b>Chl-<i>a</i> (µg l<sup>-1</sup>)</b>		
	Oligotrophic	<400.0	<15.0	<3.0	>4.0	<a href="#">(Forsberg and Ryding, 1980)</a>
	Mesotrophic	400.0-600.0	15.0-25.0	3.0-7.0	2.4-4.0	
	Eutrophic	600.0-1500.0	25.0-100.0	7.0-40.0	1.0-2.4	
	Hypertrophic	>1500.0	>100.0	>40.0	<1.0	
<b>Streams</b>	Oligotrophic	<700.0	<25.0	<10.0		<a href="#">(Dodds et al., 1998)</a>
	Mesotrophic	700.0-1500.0	25.0-75.0	10.0-30.0		
	Eutrophic	>1500.0	>75.0	>30.0		
<b>Coastal waters</b>	Oligotrophic	<260.0	<10.0	<1.0	>6.0	<a href="#">(Hakanson, 1994)</a>
	Mesotrophic	260.0-350.0	10.0-30.0	1.0-3.0	3.0-6.0	
	Eutrophic	350.0-400.0	30.0-40.0	3.0-5.0	1.5-3.0	
	Hypertrophic	>400.0	>40.0	>5.0	<1.5	

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25 **Fig. 1:** Distribution of As species in eutrophic, mesotrophic and oligotrophic lakes ( $n = 1-10$ ) (Hasegawa et al., 2010).