

26 **Abstract**

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

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

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51 **1. Introduction**

52 Arsenic (As) is the 20th most abundant element in the earth's crust (Woolson, 1975) and
53 22nd in seawater (Brown et al., 1991); however, its relative abundance in freshwater is not
54 known. The sources, occurrence and distribution of As in the environment have been studied
55 by a number of researchers. Although natural events such as weathering, biological and
56 volcanic activities are mainly responsible for the occurrence and distribution of As in the
57 environment, anthropogenic inputs also account for its emission into the atmosphere, from
58 where it is redistributed on the earth's surface by rain and dry fallout (Cullen and Reimer,
59 1989). It is well recognized that the greatest anthropogenic atmospheric input of As is due to
60 smelting operations and fossil-fuel combustion (Cullen and Reimer, 1989), but it is still
61 difficult to conclude exactly which of the human activities contribute to the overall As cycle
62 in the environment. However, a number of reports have shown that human activities, such as
63 mining, waste disposal, and indiscriminate use of certain pesticides and herbicides, have
64 greatly increased As contamination of the environment (Morin and Calas, 2006). It has been
65 estimated that the ratio of natural to anthropogenic atmospheric input of As is 60 : 40
66 (Hutton, 1987).

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

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

77 Phytoplankton, bacteria, and other microorganisms play important roles in As speciation,
78 distribution, and cycling in freshwaters (Hasegawa et al., 1999; Hasegawa et al., 2001;
79 Hellweger and Lall, 2004; Howard et al., 1995; Sharma and Sohn, 2009). As^V is the
80 thermodynamically stable state in oxic waters, while As^{III} is predominant under reducing
81 conditions (Andreae, 1986; Cullen and Reimer, 1989). In freshwaters, the dominant inorganic
82 As is incorporated in microorganisms such as phytoplankton, and is converted to
83 methylarsenic compounds and/or higher order organoarsenic compounds such as
84 arsenosugars (Francesconi et al., 1996; Maher, 1984). In addition, the organoarsenic
85 compounds are mineralized to inorganic As and methylarsenic by bacteria (Hanaoka et al.,
86 1995). The forms of As found in freshwater systems (rivers and lakes) are summarized in
87 Table 1. Since biological activities such as growth, density, reproduction, and metabolism of
88 phytoplankton and other organisms in aquatic systems are influenced by temperature and
89 geographical distribution, seasonal variations in the occurrence and distribution of As species
90 results (Hasegawa, 1996; Kim et al., 2009; Kuhn and Sigg, 1993; Michel et al., 1999).
91 Recently, a number of field and laboratory studies have shown that eutrophic states
92 significantly correlate with the distribution and occurrence of As species in freshwaters
93 (Hasegawa et al., 2010; Hasegawa et al., 2009; Sohrin et al., 1997), and thus,
94 bioaccumulation and uptake of As species in various trophic levels of the freshwater food
95 chains may also be affected by eutrophication. Although the results of some extensive studies
96 on seawater As have been reviewed by a number of researchers, especially by Cullen and
97 Reimer (1989), recent findings on freshwater As have not been reviewed. This review will
98 provide some definitive information about how As in the freshwater environment is utilized

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

101

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

103 Arsenic concentrations in freshwaters may vary by several orders of magnitude
104 depending on the source, availability and chemistry of the environment (Smedley and
105 Kinniburgh, 2002). Typically As concentrations in freshwaters are less than $10 \mu\text{g L}^{-1}$ but
106 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
107 (Table 2). Data presented in Table 2 are of various contaminated and non-contaminated sites,
108 and thus will give an idea of the known ranges and their variations in the freshwater
109 environment.

110

111 **2.1. Rivers**

112 The baseline concentrations of As in various river waters range between 0.1 and $2.1 \mu\text{g}$
113 L^{-1} with an average of $0.8 \mu\text{g L}^{-1}$ (Table 2). These variations might be related to the
114 contamination source, surface recharge, baseflow, and the bedrock lithology. Low average As
115 concentrations of about $0.25 \mu\text{g L}^{-1}$ (range < 0.02 - $1.1 \mu\text{g L}^{-1}$) in rivers draining basement
116 rocks in Norway (Lenvik et al., 1978), and 0.15 - $0.45 \mu\text{g L}^{-1}$ in river waters of the south-
117 eastern USA have been reported (Waslenchuk, 1978). On the other hand, high concentrations
118 of naturally-occurring As have been reported in New Zealand (Waikato river, $32 \mu\text{g L}^{-1}$)
119 (McLaren and Kim, 1995; Robinson et al., 1995), USA (Madison and Missouri rivers, 10 - 370
120 $\mu\text{g L}^{-1}$) (Nimick et al., 1998), Sierra Nevada, USA ($264 \mu\text{g L}^{-1}$) (Benson and Spencer, 1983),
121 and California, USA (Owens river, 85 - $153 \mu\text{g L}^{-1}$) (Wilkie and Hering, 1998). High
122 concentration of As in these rivers occurred as a result of inputs from geothermal sources
123 (Smedley and Kinniburgh, 2002). Extremely high concentrations of naturally-occurring As

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

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

143

144 2.2. Lakes

145 Data presented in Table 2 reveal that As concentrations in lake waters are similar to or
146 lower than those in river waters. Arsenic concentrations in a number of lakes in British
147 Columbia (B.C.), Canada have been investigated (Azcue and Nriagu, 1995; Azcue et al.,
148 1994; Azcue et al., 1995). Results showed that the lowest concentration of As was in Bowron

149 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
150 these lakes was thought to be the abandoned Cariboo Gold mine tailings (Azcue et al., 1995),
151 from where As was transported to the lakes. Most of the As (up to $1104 \mu\text{g g}^{-1}$) was
152 accumulated in bottom sediments of these lakes and its concentration in the lake waters was
153 observed to be low (between < 0.2 and $2.08 \mu\text{g L}^{-1}$). Elevated concentrations of As (between
154 22.0 and $47.0 \mu\text{g L}^{-1}$) in the output of Moira Lake, Ontario, Canada has also been reported
155 (Table 2). The persistent input of soluble As into Moira Lake indicates the existence of a
156 continuous source of As (Azcue and Nriagu, 1995).

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

173 Variations in As concentrations with thermal stratification in lake waters have also been
174 reported by several researchers (Azcue and Nriagu, 1995; Hasegawa, 1996; Hasegawa et al.,
175 2010; Sohrin et al., 1997). The dissolved As concentrations in surface water of Moira Lake,
176 Ontario, Canada have been reported to be highest during summer, with an average
177 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,
178 1995). Hasegawa et al. (2010) investigated the seasonal changes of As speciation in 18 lakes
179 around Ishikawa, Nagano, Fukui and Shiga prefectures in Japan and found that the total As
180 concentrations in surface waters of these lakes were higher in summer than in winter. Similar
181 results in the occurrence and distribution of As in lake waters have also been reported by
182 other researchers (Crecelius, 1975; Hasegawa et al., 2009; Takamatsu and Kawashima,
183 1985). Seasonal variations in the occurrence of As in lake waters were due to the release of
184 inorganic As from the sediments into the water of the bottom layer under anaerobic
185 conditions in summer, adsorption of As^{V} onto Fe/Mn oxides, and accumulation into the
186 sediments in winter (Hasegawa et al., 2010). Depletion of O_2 levels in the bottom layer due to
187 increased biological activities during summer have also been considered to cause higher As
188 concentrations in lake waters (Smedley and Kinniburgh, 2002).

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

198 As co-precipitates in water and settles into sediment with Fe/Mn oxyhydroxides (Harrington
199 et al., 1998; Mok and Wai, 1994).

200

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

202 **3.1. Arsenic speciation**

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

217

218 **3.2. Extraction and determination of As species**

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

223 elemental speciation of As in environmental and biological samples. Arsenic in biota samples
224 is mainly found in the form of organic species (Cullen and Reimer, 1989). Arsenobetaine, the
225 main species of As in a number of marine organisms such as fish, molluscs and crustaceans,
226 was first isolated and identified in the Western rock lobster by Edmonds et al. (1977) using
227 vapour generation atomic absorption spectrometry following digestion of the sample with a
228 mixture of H_3ClO_4 and HNO_3 .

229 The analytical approaches for the determining the speciation of As in biota samples
230 generally involve the use of separation techniques coupled with a sensitive detector. High
231 performance liquid chromatography (HPLC) has been successfully directly coupled with
232 inductively coupled plasma-optical emission spectrometry (ICP-OES) (Amran et al., 1997)
233 and inductively coupled plasma-mass spectrometry (ICP-MS) (Goessler et al., 1998). Other
234 detectors such as atomic absorption spectrometry (AAS) (Velez et al., 1996) and atomic
235 fluorescence spectrometry (AFS) (Le et al., 1996) include hydride generation (HG) as an
236 intermediate step to convert the As compounds into volatile arsine prior to detection.
237 However, organoarsenic compounds such as arsenobetaine and arsenocholine do not form
238 volatile hydrides, and, therefore, the destruction of the organic part of the molecules before
239 hydride generation is required. This has been achieved by the use of both on-line microwave
240 digestion (Le et al., 1994) and photooxidation with UV radiation (Gomez-Ariza et al., 1998;
241 Tsalev et al., 1998). Other approaches based on hydride generation (HG) of arsine and its
242 preconcentration using cold trapping (CT) provide very good sensitivity for inorganic As,
243 DMAA and MMAA (Featherstone et al., 1998; Hasegawa et al., 1994). The CT-HG-AAS
244 does not allow the determination of arsenobetaine and arsenocholine and, therefore, is not
245 usually considered for As speciation analysis in biota.

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

248 of the As compounds, which may lead to poor or erroneous results (Gomez-Ariza et al.,
249 2000). Enzymatic digestion (Branch et al., 1994; Lambie and Hill, 1996) or methanol,
250 methanol–water, methanol–water–chloroform mixtures, either with manual agitation, vortex
251 agitation, or sonication for extraction have been reported in the literature (Ochsenkühn-
252 Petropulu et al., 1997; Shibata and Morita, 1992; Thomas and Sniatecki, 1995). But
253 methanol-water (1:1) mixture in an ultrasonic bath has been the most used extraction method
254 for As speciation (Gomez-Ariza et al., 2000).

255

256 **3.3. Inorganic arsenic**

257 Arsenic in surface waters has an unusually complex and interesting chemistry with
258 oxidation-reduction, ligand exchange, precipitation, and adsorption reactions all taking place
259 (Ferguson and Gavis, 1972). The bulk of the total dissolved As in freshwaters is inorganic
260 (Kuhn and Sigg, 1993; Seyler and Martin, 1989). From thermodynamic considerations, As
261 should exist almost entirely as As^V in oxygenated waters (Andreae, 1979), though it is still
262 present even under anoxic (reducing) conditions (Cullen and Reimer, 1989). Microbial
263 (phytoplankton, (Johnson, 1972; Johnson and Burke, 1978) and bacterial, (Howard et al.,
264 1995)) reduction of As^V results in the occurrence of thermodynamically unstable As^{III} which
265 is readily oxidized to more stable As^V form in oxic waters (Francesconi and Edmonds, 1996).
266 The microbial ‘ArsC’ As^V reductase protein (a small protein of 13-16 kilodaltons) mediates
267 the reduction of As^V to As^{III} (Lloyd and Oremland, 2006).

268 Positive correlation between As^{III} concentration and primary productivity reveals that
269 phytoplankton and algae are important agents in the transformation of As^V in the aquatic
270 systems (Andreae, 1978, 1979). Phytoplankton uptake As^V and release As^{III} in the water
271 (Andreae, 1979), but the increase of As^V concentration in the photic zone indicates rapid
272 oxidation of As^{III} and demethylation by phytoplankton (Francesconi and Edmonds, 1996).

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

282 In addition to the microbial reduction of As^{V} , high concentration of As^{III} in lakes
283 receiving As^{III} rich riverine input reveals that As^{III} can also occur in lake waters from
284 anthropogenic and atmospheric inputs. Arsenic in the Carnon River (Great Britain) consisted
285 predominantly (95% of the total As) of As^{III} which was influenced by long-term mining
286 activity in the region (Klumpp and Peterson, 1979). On the other hand, high concentrations of
287 As^{III} (between 2.9 and 20% of the total inorganic As) in the Tejo River (Portugal) was
288 probably due to atmospheric emissions counting a large amount of As from a nearby pyrite
289 roasting plant (Andreae et al., 1983). Although the As composition in the emissions was not
290 determined, the high percentage of As^{III} from the nearest atmospheric emission source
291 suggests that As^{III} was not oxidized in the surface waters over a short period (Andreae et al.,
292 1983).

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

298 $\text{Fe}^{\text{III}}\text{-As}^{\text{V}}$ hydrous oxides (Morin and Calas, 2006), which suggests that both biotic and abiotic
299 oxidations of Fe^{II} play important roles in the distribution of inorganic As in surface waters.

300

301 **3.4. Methylarsenicals**

302 The important methylated As compounds in freshwaters are MMAA^{III} , DMAA^{III} ,
303 MMAA^{V} , and DMAA^{V} (Table 1). At natural pHs, MMAA and DMAA occur as anionic
304 monomethylarsenate ($\text{CH}_3\text{AsO}_2\text{OH}^-$) and dimethylarsinate ($(\text{CH}_3)_2\text{AsOO}^-$), respectively
305 (Anderson and Bruland, 1991). Braman and Foreback (1973) first detected DMAA and
306 MMAA in a number of freshwater and seawater samples. They found that in inorganic As
307 dominated water samples, the methylarsenicals comprised up to 68% of the total As (McKay
308 Bay, Florida, USA) though it was typically between the ranges of 10-20%. Similar results
309 were also reported by Andreae (1978) in some freshwater samples, but the percent
310 concentration ranges were much lower (< 10% of the total As) than those of the previous
311 findings of Braman and Foreback (1973). Hasegawa et al. (2009) found the concentrations of
312 DMAA between 0.075 and 0.337 $\mu\text{g l}^{-1}$ in Lake Biwa (Japan) and about 0.187 $\mu\text{g l}^{-1}$ in Lake
313 Kiba (Japan). In most samples of Lake Biwa and Lake Kiba, the concentrations of MMAA
314 were lower than the instrumental limit of detection.

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

323 detected in trace concentrations in deeper waters (Andreae, 1978, 1979). Vertical
324 distributions of As species in lake waters have also been studied by other researchers
325 (Hasegawa, 1997; Hasegawa et al., 2001; Howard et al., 1982; Sohrin et al., 1997). Sohrin et
326 al. (1997) reported that DMAA^V is the dominant species and its concentration increased up to
327 64% of total As in the epilimnion (< 10-20 m) zone of Lake Biwa, Japan, over summer.
328 Hasegawa (1997) also reported the distribution of As species in Lake Biwa during 1993-
329 1994. They observed that the dominant methylarsenic species in the lake was DMAA^V,
330 which comprised 64 – 99% of the total methylarsenicals. Concentrations of MMAA^V and
331 DMAA^V were less than 0.05 µg l⁻¹ and 0.75 µg l⁻¹, respectively, and the concentrations of
332 trivalent methylarsenic species (MMAA^{III} and DMAA^{III}) were one or two orders of
333 magnitude lower than those of tetravalent methylarsenic species (MMAA^V and DMAA^V).
334 Howard et al. (1982) determined the concentrations of methylarsenicals at different sites of
335 the River Beaulieu in central southern England. They found that the concentrations of DMAA
336 and MMAA in the water were 0.07-0.38 and 0.16-0.42 µg l⁻¹, respectively.

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

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

353 The distribution of methylarsenicals, in the context of eutrophication and seasonal
354 variations, in lake waters have been studied mainly by our group in recent years (Hasegawa,
355 1996, 1997; Hasegawa et al., 1999; Hasegawa et al., 2010; Hasegawa et al., 2009; Hasegawa
356 et al., 1994; Hasegawa et al., 2001; Sohrin et al., 1997). From these studies, we found the
357 highest DMAA concentration in early summer which was initially supposed to be produced
358 from hidden As through the photodegradation under strong sunlight condition (Hasegawa et
359 al., 1999). However, laboratory experiments revealed that the photochemical degradation by
360 sunlight does not contribute significantly to the production of DMAA in lake waters.
361 Therefore, we assumed that biological processes such as bacterial decomposition of the
362 ultraviolet (UV) labile fraction of As would be the possible reason for DMAA production in
363 lake water (Hasegawa et al., 1999). In recently published articles, we reported that the
364 production and distribution of methylarsenicals were significantly influenced by biological
365 activities and eutrophication (Hasegawa et al., 2010; Hasegawa et al., 2009). We found that
366 the DMAA concentration was higher in the mesotrophic Lake Biwa compared to that in the
367 eutrophic Lake Kiba, and the concentrations of DMAA were higher during May to October
368 (summer) compared to those in January (winter) in both lakes. The results suggest that the
369 biosynthesis of complex organoarsenicals and the speciation of As in freshwaters would be
370 influenced by the biological activities and biochemical processes of organisms.

371

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

373 **4.1. Eutrophication**

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

386

387 **4.2. Trophic classification of aquatic systems**

388 The classification scheme developed originally by Weber (1907) for bogs has been
389 used to categorize surface water systems according to the relative magnitude of their nutrient
390 inputs (Hutchinson, 1969; Hutchinson, 1973). Two of the most important nutrients
391 responsible for eutrophication are nitrogen and phosphorus. Nitrogen is commonly found in
392 aquatic environments as nitrate (NO_3^-), nitrite (NO_2^-), or ammonia (NH_3), while phosphorus
393 is found as phosphate (PO_4^{3-}).

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

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

408 The trophic state classification system (TSCS), developed by Forsberg and Ryding
409 (1980), has widely been used for grouping water bodies. Some other researchers also have
410 classified aquatic systems based on total nitrogen (TN), total phosphorus (TP), chl-*a* content,
411 and Secchi disk (SD) (Dodds et al., 1998; Hakanson, 1994; Nürnberg, 1996), which are
412 summarized in Table 3. We used these TSCSs in our studies to classify freshwater lakes into
413 oligotrophic, mesotrophic, and eutrophic states to investigate the relationship between
414 eutrophication and As speciation.

415

416 **4.3. Influence of PO₄³⁻, chl-*a* and dissolved oxygen on As distribution in lake water**

417 In a recent study, we observed that the distribution of As species in lake waters was
418 influenced by phosphate (PO₄³⁻) concentration and phytoplankton density (chl-*a* content)
419 (Hasegawa et al., 2010). Results showed that the distribution of As species was better
420 correlated with PO₄³⁻ concentration compared to that of chl-*a*. Moreover, As^V uptake by
421 phytoplankton was less in phosphate-rich lakes compared to that in phosphate-poor lakes
422 (Hasegawa et al., 2010). The conversion of As^V to As^{III} and to organoarsenicals by organisms

423 is more dynamic in phosphate-exhausted lakes (Hasegawa et al., 2010), and the exhaustion of
424 phosphate has been considered to be important for the conversion of As^V (Froelich et al.,
425 1985b; Sohrin et al., 1997).

426 We also observed that dissolved oxygen influenced the occurrence of As^{III} in lake
427 waters (Hasegawa et al., 2010). Biological activities, which use a substantial amount of
428 dissolved oxygen, are higher in eutrophic lakes while the activities are limited in mesotrophic
429 lakes (Ærtebjerg et al., 2003; Genkai-Kato and Carpenter, 2005; Kennish and Townsend,
430 2007; Moncreiff, 2002; OECD, 1982; Smith et al., 2006; Smith et al., 1999). Therefore, the
431 amount of dissolved oxygen tend to decrease in eutrophic lakes compared to that in
432 mesotrophic lakes (Meyer-Reil and Köster, 2000). Comparatively highly oxidic conditions in
433 mesotrophic lakes favour the oxidation of As^{III} to As^V which results in high concentration of
434 As^V in such lakes (Hasegawa et al., 2010).

435

436 **4.4. Distribution of As species in lake waters in relation to eutrophication**

437 In freshwater systems, the proportions of As species vary with anthropogenic input of
438 As and biological activity. We investigated the concentrations and distribution of As species
439 in mesotrophic and eutrophic lakes to determine the effect of eutrophication on As speciation
440 in relation to biological activity (Hasegawa et al., 2010; Hasegawa et al., 2009; Hasegawa et
441 al., 2001). The increase of DMAA in the water column of eutrophic lakes (Hasegawa et al.,
442 2009) and the similar trend of DMAA distribution in relation to the seasonal variations in
443 other lakes (Sanders and Riedel, 1993) revealed that the source of DMAA was due to the
444 direct production of phytoplankton, or decomposition of organic matter containing complex
445 organoarsenic compounds by microorganisms or sunlight (Hasegawa et al., 2009).

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

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

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

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

481

482 **4.5. Seasonal variation of As distribution in levels of different trophic states**

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

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

501 With few exceptions, the concentration of UV-As was higher in highly eutrophic lakes
502 than in low-eutrophic lakes during summer (Fig. 1A), while DMAA concentration was higher
503 in low-eutrophic lakes during winter than in summer (Fig. 1B). The occurrence of DMAA has
504 also been reported in other aquatic systems (Anderson and Bruland, 1991; Hasegawa et al.,
505 2009), and in laboratory experiments (Hasegawa et al., 2001). Frequent occurrence at high
506 water temperature of DMAA relative to As^{III} has been reported by Howard et al. (1995).
507 Sohrin et al. (1997) also reported a correlation between the concentration of DMAA and
508 water temperature in Lake Biwa, Japan. Hasegawa (1996) reported that the concentration of
509 DMAA follows the rise of water temperature in estuarine waters.

510

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

512 **5.1. Bioavailability**

513 It has been argued that, because the bioavailability of As varies with environmental
514 matrices, a single default value is not recommended for risk assessment in all environmental
515 settings. Many studies on the toxicity of heavy metals have shown that health risks to humans
516 or animals do not always correlate with the external exposure dose of the metals. This is
517 because virtually all risk estimates ignore the bioavailability component in the assessment
518 process. Bioavailability represents the percentage of the external dose that reaches the
519 systemic circulation, that is, the fraction of the external dose that is absorbed by the
520 organisms (Caussy, 2003).

521 Bioavailability of As is generally expressed in absolute or relative terms. Absolute
522 bioavailability is the function or percentage of the absorbed dose to the administered dose

523 ([Candy et al., 1997](#)) while the relative bioavailability is a measure of the extent of absorption
524 between two As compounds ([Caussy, 2003](#)). Relative bioavailability is important for
525 environmental studies. Bioavailability is usually determined by dosing an experimental
526 organism with various concentrations of As and measuring the response. The key determinant
527 of bioavailability is the ability of As to be released from its environmental matrices, and also
528 with the chemical species and molecular structure and complex interaction of host and
529 chemical factors. These factors include reactivity, solubility, and ability to form organic
530 metal complexes, oxidation state and physical forms ([Caussy, 2003](#)).

531

532 **5.2. Bioaccumulation**

533 The term “bioaccumulation” refers to the net accumulation of a chemical by an
534 aquatic organism as a result of uptake from environmental sources. Aquatic organisms
535 accumulate and retain certain chemicals when exposed to these chemicals through water,
536 their diet, and other sources such as soil, suspended particles etc. The magnitude of
537 accumulation can vary widely depending on the chemical and its properties. These chemicals
538 may also biomagnify in aquatic food webs, a process whereby chemical concentrations
539 increase in aquatic organisms of each successive trophic level due to increasing dietary
540 exposures (e.g. increasing concentrations from algae, to zooplankton, to forage fish, to
541 predator fish) ([Henry, 2003](#)).

542 Bioaccumulation of arsenic and/or its metabolites in some aquatic organisms such as
543 algae and lower invertebrates that are consumed by predator fishes has been reported by a
544 number of researchers ([Chen and Folt, 2000](#); [Maeda et al., 1990a](#); [Mason et al., 2000](#)).
545 Rooted aquatic macrophytes are presumed to have a function in arsenic toxicity because these
546 plants are closely associated with sediments. Studies of aquatic macrophytes of lakes
547 contaminated from gold mine effluent in the Northwest of Canada ([Dushenko et al., 1995](#);

548 [Koch et al., 2000](#)); Taupo Volcanic Zone, New Zealand ([Robinson et al., 2006](#)) and [Waikato](#)
549 [River system, North Island, New Zealand](#) ([Robinson et al., 1995](#)) reported that macrophytes
550 tended to bioaccumulate more As relative to other aquatic biota. It has been suggested that
551 the amount of As occurred in a highly bioavailable form in the aquatic system is a function of
552 multiple factors such as the environmental compartment, water column, sediment pore water,
553 pH, presence of other metals and sediments particles ([Caussy, 2003](#)).

554

555 **5.3. Bioaccumulation of As in freshwater organisms**

556 Bioaccumulation and biomagnification of As in fresh- and seawater have been studied
557 by a number of researchers. Despite the recent attention on As uptake and accumulation in
558 aquatic biota, much uncertainty in the mechanisms and bioaccumulation potential of the
559 various forms of As in the environment still exists. It has been reported that about 85 to >
560 90% of the total As found in edible portions of marine fish and shellfish is organic As
561 (arsenobetaine, arsenocholine, and DMAA) and approximately 10% is inorganic As ([De](#)
562 [Gieter et al., 2002](#); [Goessler et al., 1997](#); [Ochsenkühn-Petropulu et al., 1997](#)). Less is known
563 about the forms of As in freshwater fish, but it is evident from field ([Kaise et al., 1987](#)) and
564 laboratory ([Maeda et al., 1990a](#); [Maeda et al., 1993](#); [Maeda et al., 1992](#); [Maeda et al., 1990b](#))
565 studies that organic As would comprise the major fraction in these fishes. In addition to the
566 organoarsenicals, the presence of inorganic As in some freshwater fishes from Pak Pa-Nang
567 Estuary and catchments located in Southern Thailand has been reported ([Rattanachongkiat et](#)
568 [al., 2004](#)). The concentrations of inorganic As in sardines, catfish, tiger prawn and swimming
569 crab from Pak Pa-Nang Estuary and catchments were 0.3, 0.2, 0.8, and 0.9 $\mu\text{g g}^{-1}$ dry
570 weights, which were about 6%, 12%, 7%, and 5% of the total As contents, respectively.

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

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

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

598 Wagemann et al. (1978) also investigated BAFs for several predatory insects from
599 Kam Lake and Grace Lake. BAFs estimated for the predatory insects from Grace Lake were
600 consistently higher than those for the same species from the Kam Lake. Chen and Folt (2000)
601 measured As accumulation in five different forage fish species: alewife, black crappie,
602 bluegill sunfish, killifish, and yellow perch to investigate bioaccumulation and biodiminution
603 (trend of decreased chemical concentration in tissues of organisms as trophic level increases)
604 of As in the food chain of the Upper Mystic Lake. Results showed that As burdens for all
605 fishes in the lake were 30 to 100 times lower than the burdens for zooplankton. Alewife and
606 killifish (predominantly planktivorous fish species) had higher burdens than those of other
607 fish species. Two other studies (Baker et al., 1994; Chen and Folt, 2000) also reported that
608 the average As burden for largemouth bass (organism of higher trophic level) was
609 approximately 60 to 95 times lower than the burdens for zooplankton. A number of other
610 studies also showed that fish species lower on the trophic scale (alewife, killifish) had higher
611 BAFs than species that are slightly higher on the trophic scale (perch, crappie, catfish, carp,
612 sunfishes) (Baker et al., 1994; Chen and Folt, 2000; Skinner, 1985; Wagemann et al., 1978).
613 However, preliminary assessment of BAFs determined from laboratory-measured
614 bioconcentration factors indicates that the estimated values were lower than those derived
615 using data from the field BAFs.

616

617 **Conclusion:**

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

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

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

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

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

656

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662

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1048 **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 ^{III}	As(OH) ₃	Fish, Crustacean, Water, Algae	(Andreae, 1978; Hasegawa et al., 1999; Rattanachongkiat et al., 2004; Sohrin et al., 1997)
Arsenic acid or arsenate	As ^V	H ₃ AsO ₄	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 ^{III}	As(OH) ₂ CH ₃	Lake water, Freshwater organisms, Algae	(Anderson and Bruland, 1991; Hasegawa, 1997; Sohrin et al., 1997)
Dimethylarsinous acid	DMAs ^{III}	As(OH)(CH ₃) ₂	Lake water, Freshwater organisms, Algae	(Anderson and Bruland, 1991; Hasegawa, 1997; Sohrin et al., 1997)
Monomethylarsonic acid	MMAs ^V	AsO(OH) ₂ CH ₃	Fish, Crustacean, Algae, Water	(Anderson and Bruland, 1991; Hasegawa, 1997; Rattanachongkiat et al., 2004; Sohrin et al., 1997)
Dimethylarsinic acid	DMAs ^V	AsO(OH)(CH ₃) ₂	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 ₃) ₃ As ⁺ CH ₂ CH ₂ O	Fish, Shellfish, Shrimps, Lobster, Water	(Benjamin et al., 1987; Lawrence et al., 1986; Norin et al., 1983)
Arsenobetaine	-	(CH ₃) ₃ As ⁺ CH ₂ COO ⁻	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)

1050 **Table 2:** Arsenic concentrations in some freshwater systems (rivers and lakes) around the world (modified from Smedley and Kinniburgh
 1051 (2002)).

Water systems and Location	As concentrations (average/range ($\mu\text{g l}^{-1}$))	References
<i>River water</i>		
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)
<i>Lake water</i>		
Lake Echols, Tampa	3.58	(Braman and Foreback, 1973)
Lake Magdalene, Tampa	1.75	(Braman and Foreback, 1973)
Moir 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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1066 **Table 3:** Trophic classification of natural water systems (lakes, streams and coastal waters) on the basis of total nitrogen (TN), total phosphorus
 1067 (TP), Chlorophyll-*a* (chl-*a*) and Secchi disk (SD) (modified from [Smith et al. \(1999\)](#)).

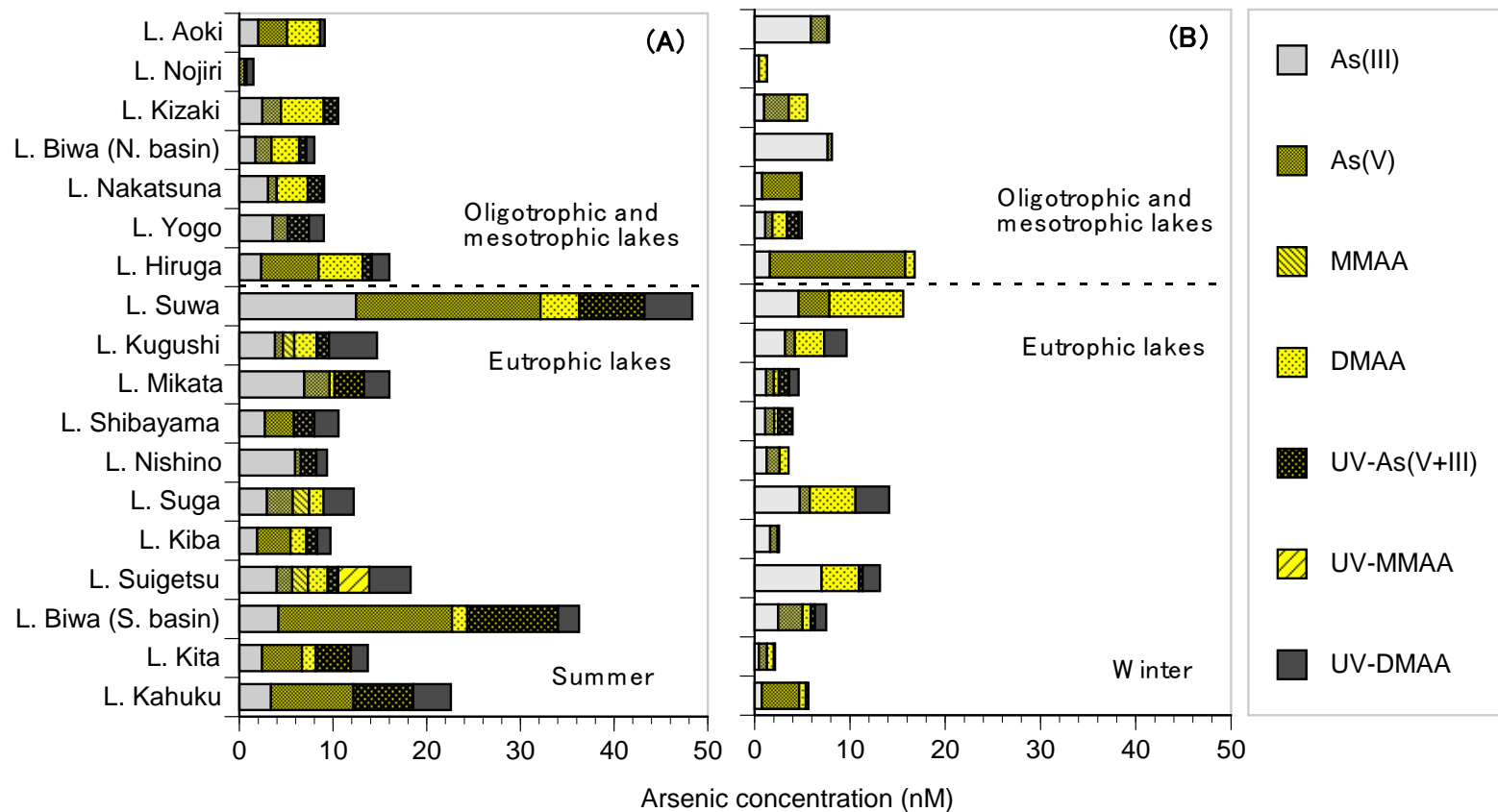
Water systems	Trophic state	TN (mg m⁻³)	TP (mg m⁻³)	Chl-<i>a</i> (mg m⁻³)	SD (m)	
Lakes	Oligotrophic	<350.0	<10.0	<3.5	>4.0	
	Mesotrophic	350.0-650.0	10.0-30.0	3.5-9.0	2.0-4.0	(Nurnberg, 1996)
	Eutrophic	650.0-1200.0	30.0-100.0	9.0-25.0	1.0-2.0	
	Hypertrophic	>1200.0	>100.0	>25.0	<1.0	
	TN (µg l⁻¹)	TP (µg l⁻¹)	Chl-<i>a</i> (µg l⁻¹)			
	Oligotrophic	<400.0	<15.0	<3.0	>4.0	(Forsberg and Ryding, 1980)
	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	
Streams	Oligotrophic	<700.0	<25.0	<10.0		(Dodds et al., 1998)
	Mesotrophic	700.0-1500.0	25.0-75.0	10.0-30.0		
	Eutrophic	>1500.0	>75.0	>30.0		
Coastal waters	Oligotrophic	<260.0	<10.0	<1.0	>6.0	(Hakanson, 1994)
	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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1073 **Fig. 1:** Distribution of As species in eutrophic, mesotrophic and oligotrophic lakes ($n = 1-10$) (Hasegawa et al., 2010).