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Effect of Eutrophication on the Distribution of Arsenic Species in Eutrophic and Mesotrophic Lakes

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Abstract:

Effects of eutrophication on arsenic speciation were studied in eutrophic Lake Kiba and mesotrophic Lake Biwa, Japan. By combining hydride generation atomic absorption spectrometry with ultraviolet irradiation, inorganic, methyl and ultraviolet-labile fractions of arsenic were determined. In both Lakes, inorganic species (As(V+III)) dominated over other forms of arsenic all the year round. Most of methylarsenic fraction was dimethylarsinic acid (DMAA), and the concentration of monomethylarsonic acid (MMAA) was bellow the detection limit. Measurements of size-fractioned arsenic concentrations in water column indicate that most of the DMAA was distributed in truly dissolved fraction (<10 kDa), while ultraviolet-labile fractions were distributed in particulate (>0.45 μm) and colloidal (10 kDa – 0.45 μm) fractions. Arsenic speciation in eutrophic Lake Kiba fluctuated greatly by seasonal changes. The ultraviolet-labile fractions were observed with the increase of DMAA from May to October, and they disappeared with the decrease of DMAA in January. In mesotrophic Lake Biwa, the ultraviolet-labile fractions of arsenic were not influenced as much as those in eutrophic Lake Kiba. On the other hand DMAA concentration was higher in Lake Biwa compared to that in Lake Kiba. The results suggest that the biosynthesis of complex organoarsenicals was enhanced by eutrophication, and the arsenic speciation would be influenced by the balance of biological processes in natural waters.

Introduction

Arsenic exists in a variety of chemical forms in natural waters and sediments. Arsenate, ($AsO(OH)_3$; As(V)) is the thermodynamically stable state in oxic waters, while arsenite ($As(OH)_3$; As(III)) is predominant in reduced redox potential conditions (Andreae 1986; Cullen and Reimer 1989). Biological processes also reduce the oxidation state of arsenic in surface waters (Andreae 1986; Cullen and Reimer 1989).

The metabolism of arsenic by aquatic organisms results in the occurrence of thermodynamically unstable arsenite and methylarsenic compounds in natural waters. The inorganic forms (As(V) and As(III)) and the methylated forms (methylarsonic acid $CH_3AsO(OH)_2$; MMAA(V) and dimethylarsinic acid $(CH_3)_2AsO(OH)$; DMAA(V)) are the main species of arsenic in natural waters (Cullen and Reimer 1989). The bulk of the total dissolved arsenic is inorganic species in seawater (Peterson and Carpenter 1983) and in freshwater (Seyler and Martin 1989; Kuhn and Sigg 1993). Although the predominant form of methylarsenicals is consistently DMAA(V) followed by MMAA(V), the existence of methylarsenic(III) species in the environment has also been reported in literatures (Sohrin et al. 1997; Hasegawa et al. 1994, 1996).

Previously, the speciation of arsenic in natural waters was determined by hydride generation followed by atomic absorption spectrophotometry (Braman et al. 1977; Andreae 1977). Arsenosugars and arsenobetaine can not be detected by the conventional hydride generation technique. Howard and Comber (1989) discovered and defined hidden arsenic in coastal water, which had not been detected previously by hydride generation atomic absorption spectrometry. Hasegawa et al. (1999) also reported the presence of organoarsenicals other than methylarsenicals in natural waters. Hasegawa et al. (1999) classified hidden arsenic into different fractions based on their photochemical degradation

ability. This hidden arsenic in natural waters is predicted to be related to the arsenic speciation and biological production in organisms.

In natural waters, the cycling of arsenic species would depend on the bioactivity of organisms (Cullen and Reimer 1989; Sanders 1980). Microorganisms produce methylarsenicals (MMAA and DMAA) in natural waters (Sanders and Riedel 1993), which exhibit seasonal cycle with maximum concentrations of methylarsenicals in summer (Sohrin et al. 1997; Hasegawa et al. 1999; Howard et al. 1995). Methylarsenicals was supposed to be produced by phytoplankton and organisms of higher trophic levels as a detoxification mechanism (Edmonds and Francesconi 1987). Recent studies propose accidental occurrences of methylarsenicals in nature (Please inset reverences here). Sanders and Riedel (1993) observed correlation between As(III)/ methylarsenicals and Chlorophyll-*a* concentrations and/or phytoplankton density. Howard et al. (1995) reported that the seasonal change in DMAA concentration is correlated with temperature but not with Chlorophyll-*a* concentrations and/or phytoplankton density. The bulk of other organoarsenicals are also found in organisms (Maeda 1994). The arsenosugars are usually found in algae and arsenobetaine is the predominant form in marine animals (Edmonds and Francesconi 1987; Francesconi and Kuehnelt 2002). The degradation and mineralization of organoarsenic compounds are supposed to be mostly depended on bacterial activities, which influence the arsenic cycling in aquatic environment (Kaise et al. 1985; Maki et al. 2005).

Eutrophication is a process whereby water bodies receive excess nutrients that stimulate excessive growth of phytoplankton, periphyton attached algae, nuisance plants and weeds. Eutrophication enhances not only the growth of phytoplankton but also the bacterial activities in the water column. On the other hand, mesotrophic lakes are lakes with an intermediate level of productivity, greater than oligotrophic lakes, but less than eutrophic lakes. These lakes are commonly clear water lakes with beds of submerged

aquatic plants and medium levels of nutrients. In the present experiment, we studied the distribution and speciation of arsenic in eutrophic and mesotrophic lakes. Determination of arsenic species, including the hidden arsenic, was performed by hydride generation atomic adsorption spectrometry using ultraviolet irradiation. The changes of hidden arsenic fractions in the water column were also studied to determine the influence of biological activity in arsenic speciation. Finally, the effects of eutrophication on arsenic speciation and distribution in natural waters have been discussed.

Experimental

Sample collection and pretreatment

Field investigations were carried out from May, 2006 to January, 2007 in Lake Kiba and Lake Biwa, Japan. Lake Biwa is the largest Lake in Japan with a surface area of 616 km^2, and an average depth of 44 m (Sohrin et al. 1997). The northern basin of the lake is located near rural area, and is thought to be mesotrophic because of higher density of phytoplankton (2500 cells/ml in 1993) at the center of the basin (DCPLB 1995). On the other hand, the surface area of Lake Kiba is about 1.26 km^2 with an average depth of 2.2 m, and located in Hokuriku area, Japan. The concentrations of Chl-*a* in Lake Kiba is higher than that in Lake Biwa, and the dissolve oxygen (DO) concentration in the Lake is comparatively less than that in Lake Biwa. Based on phytoplankton density, Chl-*a* and nutrient concentrations in the water column, Lake Kiba and Lake Biwa is classified as eutrophic and mesotrophic, respectively.

The samples were collected within 0.5 m of the water surface. For analysis of arsenic and nutrients, the samples were filtered with 0.45 μm (HA type, Millipore) and 10 kDa (Minitan-S, Millipore) filters immediately after collection. Both filtered and unfiltered

123 samples were acidified to pH 2.0 by the addition of 1.0 M hydrochloric acid (HCl), and
124 stored in refrigerator until analysis.
125
126 **Reagents**
127 Stock solutions (10^{-2} M) for the determination of arsenic compounds were prepared
128 by dissolving the corresponding sodium salts ($(CH)_3AsO_3Na_2$ was prepared by Quick's
129 method (Hasegawa et al. 1994), and $NaAsO_2$, Na_2HAsO_4 and $(CH_3)_2AsO_2Na$ were obtained
130 from Nacalai Tesque, Japan) in 0.1 M sodium hydroxide. These stock solutions were
131 standardized by using inductively coupled plasma atomic emission spectrometry (ICP-AES,
132 Optima 3300XL, Perkin Elmer) after decomposition to As(V). They were diluted to the
133 desired concentrations just before use. Sodium borohydride (Kanto Chemical, Japan) was
134 used for hydride generation. A 3% (w/v) sodium borohydride solution, stabilized in 10^{-2} M
135 sodium hydroxide solution, was prepared daily. Other reagents were of analytical grade or
136 better.
137
138 **Arsenic analysis**
139 **Inorganic and methylarsenicals**
140 Analysis of inorganic and methylarsenicals was performed by a modified technique of
141 hydride generation method (CT-HG-AAS), using an apparatus and materials similar to those
142 described in previous paper (Hasegawa et al. 1994). In this technique, arsenic species were
143 reduced to their corresponding arsines with sodium borohydride, trapped in U-tube with
144 liquid nitrogen, and sequentially evolved into a heated quartz T-tube mounted in the atomic
145 absorption spectrometer. To measure As(V+III), MMAA and DMAA, 3 mL of 0.1 M EDTA
146 and 3 mL of 5.0 M HCl were added to 30 mL of the sample in the reaction vessel. In arsenite
147 determination, 5 mL of 0.5 M potassium hydrogen phthalate buffer solution was added to 30

mL of the sample with an initial pH of 4. The detection limits were 0.11 nM and 0.14 nM for As(V+III) and MMAA, respectively (3 times the standard deviation of the blank), and the precision of five replicate determinations were 2.1% for inorganic arsenic and 5.1% for DMAA (a relative standard deviation) at 1.0 nM with a 30 ml sample size.

Ultraviolet irradiation

Ultraviolet photolytic decomposition was accomplished by 400 W high-pressure mercury lamp (Sigemi, AHH-400S) in a 3-chamber reaction vessel constructed from quartz **(**Hasegawa et al. 1999**)**. Samples were acidified to pH 2.0 using 1.0 M HCl, and introduced into the outer-chamber of the reaction vessel that was capped with natural rubber septum. They were then irradiated with a 400 W high-pressure mercury lamp mounted in the center-chamber. During irradiation, cooling water was circulated into the mid-chamber from a constant temperature bath. Aliquots were taken at selected time intervals. Arsenic analysis of the digests was performed with CT-HG-AAS as described above.

Speciation of organoarsenic species

Organoarsenic species can be classified into different fractions according to their lability to the photochemical degradation; UV-As and UV-DMAA (Hasegawa et al. 1999). The decomposition of UV-As and UV-DMAA to As(V) followed the steps as described bellow-

$$\text{UV-As} \longrightarrow \text{As(V)}$$

$$\text{UV-DMAA} \longrightarrow \text{DMAA(V)} \longrightarrow \text{As(V)}$$

, where UV-DMAA was stepwise decomposed to As(V) through DMAA(V) by ultraviolet irradiation with a time. The UV-As was transformed to As(V) directly. A flow chart of the calculation is shown in Fig. 1. The UV-As and UV-DMAA were estimated from the

concentration changes of As(V+III) and DMAA during the ultraviolet irradiation by a non-linear least-squares computation, respectively (Figs. 2, 3).

Results and Discussions:

Photolysis of hidden arsenic species in natural waters

In the present experiment, irradiation test was performed for a time period of 0-12 hrs (Figs. 2, 3). Water samples were collected from surface level (0 m depth) of Lake Kiba on May 25, 2006. The unfiltered and filtered samples of Lake Kiba initially contained both As(V+III) and DMAA. The concentrations of As(V+III) in unfiltered and filtered samples were 5.7±0.5 and 4.2±0.2 nM, respectively, whereas DMAA concentrations were 1.9±0.1 and 2.0±0.8 nM, respectively. Immediately after irradiation, both As(V+III) and DMAA concentrations in the unfiltered samples rapidly increased and attained equilibrium in 3-4 h. On the other hand, there was no increase of As(V+III) in filtered samples after irradiation, though DMAA increased a little (Fig. 3). The concentration of MMAA in both unfiltered and filtered samples was bellowing the instrumental limit of detection (< 0.14 nM).

Water samples were collected from Lake Biwa on July 31, 2006, and irradiated for a time period of 0-12 hrs. The initial concentrations of As(V+III) and DMAA in Lake Biwa were 10.1 and 3.5 nM in unfiltered samples, and 9.5 and 3.3 nM in filtered samples, respectively. The DMAA concentrations in both unfiltered and filtered samples increased immediately after irradiation and then decreased gradually. On the other hand, the concentrations of As(V+III) in both unfiltered and filtered samples remained almost unchanged with the increase of irradiation time.

Other samples collected from natural waters also showed similar changes in arsenic speciation during irradiation though they varied in their concentrations. Hasegawa et al. (1999) observed similar changes of arsenic speciation in estuarine waters. Determination of

198 hidden arsenic fraction in seawater after photolytic decomposition has been described by
199 Castro et al. (2007). Howard and Comber (1989) showed that irradiation of coastal seawater
200 from a short-arc mercury lamp gave a large increases in As(V), MMAA and DMAA
201 concentrations at natural pH. Both unfiltered and filtered samples were acidified to pH 2.0
202 during the irradiation by the addition of 1.0 M HCl solution. Howard and Comber (1989)
203 reported no increase of DMAA in acidified samples (about 0.011 M HCl) during ultraviolet
204 irradiation, though Hasegawa et al. (1999) observed an increase of DMAA concentrations
205 during ultraviolet irradiation. From their observations, Hasegawa et al. (1999) proposed that
206 the inhibition effect of ultraviolet irradiation on DMAA concentration in acidified sample (as
207 reported by Howard and Comber (1989)) may depend on the wavelength of ultraviolet light,
208 rather then the acidity. The possibility of adsorption of arsenic on the particles, and of
209 complexation of arsenic by organic substances is very low. Because the samples were
210 acidified using 1.0 M HCl, and therefore, no changes of arsenic concentrations were observed
211 in the samples at this very low pH.

212 Brockbank et al. (1988) reported that methylarsenic was demethylated during
213 irradiation by 254 nm ultraviolet light without a digestion reagent. Hasegawa et al. (1999)
214 also observed that DMAA gradually decreased after 4 h of irradiation by the high pressure
215 mercury light. In the present study, it was observed that the DMAA concentration in
216 unfiltered samples was increased rapidly within 3-4 h of irradiation though the concentration
217 decreased gradually with the increase of irradiation time. It would be due to the
218 decomposition of DMAA into As(V).

219

220 **Fractional distribution of arsenic speciation in Lake Kiba**

221 Dissolved and particulate fractions of arsenic were estimated by filtration through
222 0.45 μm membrane filters. Tangential flow filtration system with 10 kDa pore size was used

to divide the dissolved fractions of arsenic species (<0.45 µm) into colloidal (10 kDa - 0.45 µm) and truly dissolved (<10 kDa) fractions. Hidden arsenic was determined in filtered and unfiltered samples after irradiation with a 400 W high-pressure mercury lamp. Data of arsenic species distribution in Lake Kiba during May 25, 2006 to January 17, 2007 are summarized in Fig. 4 and Table 1.

In July, 4.74±0.13 nM of As(III) was recorded in filtered samples (0.45 µm membrane filter) whereas the As(V) concentration was 1.95±0.17 nM. In May, the concentration of As(III) was also higher than that of As(V). During October 26, 2006 and January 17, 2007 the concentrations of As(III) were lower than those of As(V) (Table 1).

In all seasons, total concentrations of arsenic were higher in the unfiltered samples compared to those in filtered samples, and the inorganic species of arsenic (As(V+III)) dominate over DMAA and other arsenic fractions (Fig. 4). The concentrations of inorganic species (As(V+III)) were higher in the unfiltered samples compared to those in the filtered samples, except in July. The results imply that As(V) and As(III) were distributed in both the dissolved and particulate fractions. On the other hand, DMAA concentrations were comparable between the filtered and the unfiltered samples all the year round, which indicate that most of the DMAA consists of the truly dissolved fraction. The other methylarsenicals were totally absent or bellow the instrumental limit of detection. The UV-As and UV-DMAA in the filtered samples were lower than those in the unfiltered samples (Fig. 4). The results indicate that the UV-As and UV-DMAA were distributed mainly in the particulate fraction, and partially in the truly dissolved fraction.

Seasonal variations of arsenic species in Lake Kiba

Arsenic species in water column of Lake Kiba fluctuated greatly during May 2006 to January 2007 by the seasonal variation. From May to October, 0.9-2.1 nM of DMAA was

248 detected though MMAA was less than 0.14 nM (Fig. 4). The high concentrations of DMAA
249 might be due to the conversion of inorganic arsenic into organoarsenic compounds by aquatic
250 organisms. Some organisms such as fungi and plankton uptake inorganic arsenic, and excrete
251 DMAA in freshwater (Cullen and Reimer 1989; Maeda 1994; Hasegawa et al. 2001). A
252 substantial amount of hidden arsenic, UV-As and UV-DMAA were also detected in the water
253 column during May to October (Fig. 4). On the other hand, about 90% of the total arsenic
254 was As(V+III) in January. The amount of UV-As was about 2-10%. The UV-As(V+III), UV-
255 DMAA and other organoarsenicals were totally absent or bellow the instrumental limit of
256 detection (Fig. 4).

257 In the present study, it was observed that the concentrations of DMAA and UV-
258 degradable fractions of arsenic in water column of Lake Kiba were higher during summer
259 (May to October) compared to those in winter (January), when the rations of
260 phosphate/As(V+III) were low. During summer, phosphate concentrations ranged between
261 0.05-0.10 µM, which were much lower than those in winter (0.31 µM) (Table 2). The
262 behavior of DMAA has been reported to be consistent in other geographical areas (Anderson
263 and Bruland 1991), and in laboratory experiments (Hasegawa et al. 2001). Howard et al.
264 (1995) reported that DMAA is more frequently observed at higher water temperatures than
265 As(III). Sohrin et al. (1997) reported that the DMAA concentrations were well correlated
266 with water temperature in Lake Biwa, Japan whereas As(III) was not. Hasegawa (1996) also
267 reported that the concentrations of DMAA follow the rise of water temperature in estuarine
268 waters. Bright et al. (1994) demonstrated that microbes from anaerobic lake sediments
269 methylate arsenic, and DMAA is produced by bacterial methylation in the suspended solids,
270 which is subsequently released into the water column. Thus, bacterial methylation is
271 responsible for the increase of DMAA concentration in surface water. Higher concentrations
272 of DMAA might also be resulted from the long-term accumulation of DMAA excreted by

phytoplankton. However, Hasegawa (1996) reported that the concentrations of DMAA and chlorophyll-*a* in estuarine waters were not correlated significantly (r = 0.181, *n* = 205).

Our results also indicate that UV-As and UV-DMAA concentrations increased when the phosphate conditions were low (Fig. 4 and Table 2). The result suggests that the production of UV-As and UV-DMAA might increase with the increase of biological activities in proportion to the water temperature.

Comparison of Lake Kiba and Lake Biwa:

Concentration ranges of arsenic species, nitrate, phosphate, ammonium and chlorophyll-*a* in surface waters of Lake Kiba and Lake Biwa are presented in Table 3. The concentrations of chlorophyll-*a* have been considered as crude indicator of the net primary productivity, which is influenced by both phytoplankton productivity and grazing pressure in lake waters. The concentrations of nitrate, phosphate and ammonium in Lake Kiba were higher than those in Lake Biwa (Table 3). On the basis of chlorophyll-*a* and nutrient concentrations in water column, Lake Kiba is classified as eutrophic, and Lake Biwa as mesotrophic.

The concentrations of DMAA and MMAA in Lake Biwa were much higher than those in Lake Kiba. The DMAA concentrations ranged between <0.11-2.5 nM and 1.0-4.5 nM in Lake Kiba and Lake Biwa, respectively. On the other hand, MMAA concentration in Lake Kiba was bellow the instrumental limit of detection though it's concentrations ranged between 0.14-0.50 nM in Lake Biwa. The concentrations of UV-As and UV-DMAA were higher in Lake Kiba than those in Lake Biwa (Fig. 5). In Lake Kiba, most of the UV-As and the UV-DMAA were in particulate (>0.45 µm) and colloidal (10 KDa – 0.45 µm) fractions, while As(V+III) and DMAA were distributed mainly in truly dissolved fraction (<10 kDa).

Degradation of DMAA by microorganisms:

Water samples were collected from Lake Kiba and Lake Biwa on July 31 and 29, 2006, respectively, and spiked with 1000 nM DMAA. The samples were then incubated for 80 days under dark conditions and observed the changes of arsenic species. In the spiked samples of Lake Kiba, the DMAA was quantitatively degraded to As(V+III) within 45 days of incubation. The production of MMAA was below 0.14 nM during the experiment. On the other hand, it took about 80 days for the complete degradation of DMAA in water samples of Lake Biwa. The rates of DMAA degradation were 12.6 and 22.3 nM/day in Lake Biwa and Lake Kiba, respectively. Thus, degradation of DMAA would be related to the trophic condition of the lakes and the DMAA degradation would be higher in eutrophic lakes compared to that in mesotrophic lakes. Microbial degradation (mostly by bacterial activity) of DMAA into inorganic arsenic species was reported by Maki et al. 2006. Methylarsenic species in the lake water was assumed to be converted into inorganic arsenic species by some anaerobic microbial reactions. The degradation of organoarsenic compounds is also predicted to be mostly depended on bacterial activities, which influence the arsenic cycles in the aquatic system (Kaise et al. 1985; Maki et al. 2005). Thus, eutrophication would play an important role in the degradation of DMAA in lake waters.

Effects of eutrophication on arsenic speciation:

In freshwater systems, the proportions of arsenic species vary with the scope of anthropogenic input and biological activity. In this study, we investigated the distribution of arsenic species in mesotrophic and eutrophic lakes in relation to the biological activity. A number of freshwater organisms have been reported to contain organoarsenic compounds. Hasegawa et al. (2001) reported the direct production of methylarsenicals in several strains of phytoplankton. As(V) is biotransformed to organoarsenic compounds in freshwater food

chains (Maeda 1994). The decrease of total arsenic concentration and relative increase of methylarsenicals with the trophic level augmentation is observed in most of the food chains (Kuehnelt and Goessler 2003). The recent development of HPLC-ICP-MS for the determination of arsenic species has revealed the constituents and the behavior of arsenic, including complex organoarsenic compounds such as arsenosugars and arsenobetaine in freshwater organisms (Schaeffer et al. 2006).

In freshwater organisms, methylarsenic species, especially DMAA is the major organoarsenic compounds (Francesconi and Kuehnelt 2002). The increase of DMAA in water column of eutrophic Lake Kiba was observed from May to October in the present study (Fig. 4). Similar trend of DMAA distribution in relation to the seasonal variations was reported in other lakes (Sandars and Riedel 1993). The source of DMAA could be the direct production of phytoplankton, or the decomposition of organic matter containing complex organoarsenic compounds by microorganisms or sunlight. Anderson and Bruland (1991) denied the direct phytoplankton excretion of DMAA because of the lack of correlation between chlorophyll-*a* and DMAA in the field studies. The photochemical degradation by sunlight does not contribute to the production of DMAA in lake waters, which suggests the degradation of complex organoarsenic compounds by microbial activity would be the possible reason for DMAA production (Hasegawa et al., 1999).

The concentrations of UV-As and UV-DMAA was correlated with that of DMAA in Lake Kiba. The UV-As, UV-DMAA and DMAA appeared from May to October though they disappeared in January (Fig. 4). The production of UV-As and UV-DMAA would be related to the biological activity as the similar manner of DMAA. Most of the UV-As and UV-DMAA is supposed to be derived from organic matter as the concentrations of As(V+III) and DMAA did not increase in the acidified unfiltered samples. The decrease of UV-As and UV-DMAA concentrations in filtered and ultra-filtered samples suggests that these fractions of

348 arsenic species were distributed in the colloidal and particulate fractions, which comprise
349 organic and inorganic matter. Bright et al. (1996) also suggested that the hidden arsenic
350 species or complex organoarsenic compounds such as arsenosugars might be absorbed tightly
351 to organic matter. The degradation behavior of UV-As and UV-DMAA during the ultraviolet
352 irradiation implies that the structures of UV-DMAA have DMAA fragments. Although
353 DMAA and As(V+III) could be released from the particles of organic matter by ultraviolet
354 irradiation, the UV-As and UV-DMAA fractions would mainly consist of complex
355 organoarsenic compounds that were synthesized in phytoplankton and other freshwater
356 organisms (Kuehnelt and Goessler 2003). Koch et al. (1999) reported the presence of
357 arsenoriboses in microbial mats and green algae. Oxo- and thio-arsenosugars have been
358 identified in several freshwater mussels and fishes as an important arsenic constituent, and
359 arsenobetaine as a minor concentration (Schaeffer et al. 2006; Schmeisser et al. 2004).

360 The concentrations of UV-As and UV-DMAA in eutrophic Lake Kiba were higher
361 than those in mesotrophic Lake Biwa, and were correlated with DMAA concentration (Fig. 4).
362 It can be elucidated by the eutrophication condition of the lakes. The eutrophication increased
363 the microbial biomass and biosynthesis of complex organoarsenic compounds in the entire
364 reservoir, which results in the degradation of DMAA and other organoarsenic compounds.
365 Moreover, the degradation rate of DMAA was higher in eutrophic Lake Kiba than that in
366 mesotrophic Lake Biwa. The result suggests direct transformation of As(V) into
367 methylarsenicals or other organoarsenic compounds by biota, which in turn is degraded to
368 DMAA and arsenate. The composition of arsenic species in Lake Kiba and Lake Biwa,
369 shown in Fig. 5, would attribute to the balance of biological processes; the metabolism of
370 phytoplankton, grazing pressure due to zooplankton, and the decomposition of organic matter
371 by microbial communities.

Total concentration of arsenic in Lake Kiba was higher in summer compared to winter (Fig. 4). This might be due to the release of As(V+III) from the anoxic sediments. The increase of As(V+III) concentration was also correlated with the water temperature. Because, reductive dissolution of iron and manganese oxides decrease the adsorptive surfaces of sediment particles and release As(V+III) (Crecelius 1975). The dissolved arsenite (thermodynamically stable species in anoxic waters) is not as strongly adsorbed as arsenate (Leckie et al. 1984). The increase of arsenic concentration strongly correlates with the reductive dissolution of iron and manganese oxides (Crecelius 1975).

Compared to filtered samples, higher concentrations of As(V+III) in unfiltered samples of Lake Kiba suggests that the dissolved fractions of arsenate were transformed into particulate fractions by adsorption or coprecipitation on iron and manganese oxides. Takamatsu et al. (1985) also reported the adsorption of arsenate on manganese oxides in manganese-rich lakes. The DMAA is converted almost completely to arsenate after winter mixing, and removed from the water column to the sediments (Anderson and Bruland 1991). This was because arsenate is particle reactive.

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Table 1: Distribution of arsenic species in filtered water of Lake Kiba. Water samples were collected from the surface level during May 2006 to January 2007, and filtered through 0.45 μm membrane filters.

Sampling time	Concentrations (nM)					
	Arsenate	Arsenite	MMAA	DMAA	UV-As	UV-DMAA
May 25, 2006	1.41±0.12	1.99±0.20	[§] N.D.	1.72±0.14	0.96±0.12	0.94±0.10
Jul. 31, 2006	1.95±0.17	4.74±0.13	[§] N.D.	0.95±0.23	0.40±0.11	1.20±0.08
Oct. 26, 2006	2.83±0.32	2.42±0.17	[§] N.D.	2.08±0.15	0.60±0.09	2.10±0.13
Jan. 17, 2007	2.14±0.04	1.51±0.08	[§] N.D.	[§] N.D.	0.20±0.04	[§] N.D.

[§] N.D. “Not detected” because the concentrations were bellow the instrumental limit of detection.

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516 Table 2: Water temperature, nitrate and phosphate concentrations in Lake Kiba from May

517 2006 to Jan. 2007

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Elements	May 25, 2006	Jul. 31, 2006	Oct. 26, 2006	Jan. 17, 2007
Water temperature (ºC)	19.20	27.5	18.20	6.90
Chl. a (μgL^{-1})	47.70	33.00	50.00	7.50
NO_3-N (µM)	1.08	1.34	3.03	14.27
NO_2-N (µM)	0.02	0.02	0.13	0.50
NH_4-N (µM)	0.40	1.17	2.91	8.04
PO_4-P (µM)	[§] N.D.	0.05	0.10	0.31
DOC (μgL^{-1})	3.02	3.22	3.21	1.65

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520 [§] N.D. "Not detected" because the concentrations were bellow the instrumental limit

521 of detection.

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Table 3: Comparison in elemental concentration ranges between eutrophic Lake Kiba and mesotrophic Lake Biwa.

Elements	Lake Kiba*	Lake Biwa**
As(V) (nM)	2.3-7.6	2.0-6.0
As(III) (nM)	§N.D. -4.1	1.0-3.0
MMAA (nM)	§N.D.	§N.D.-0.5
DMAA (nM)	§N.D. -2.5	1.0-4.5
NO_3-N (µM)	0.4-57	<0.7-14
NH_4-N (µM)	0.3-19	<0.7-1.4
PO_4-P (µM)	0.1-0.3	<0.032
Chl-*a* (µg/L)	3.0-89	0.8-10

§N.D. "Not detected" because the concentrations were bellow the instrumental limit of detection.

* Concentration range during the period of Apr. 2004 to Mar. 2006.

** Concentration range during the period of Feb. 1993 to Dec. 1994.

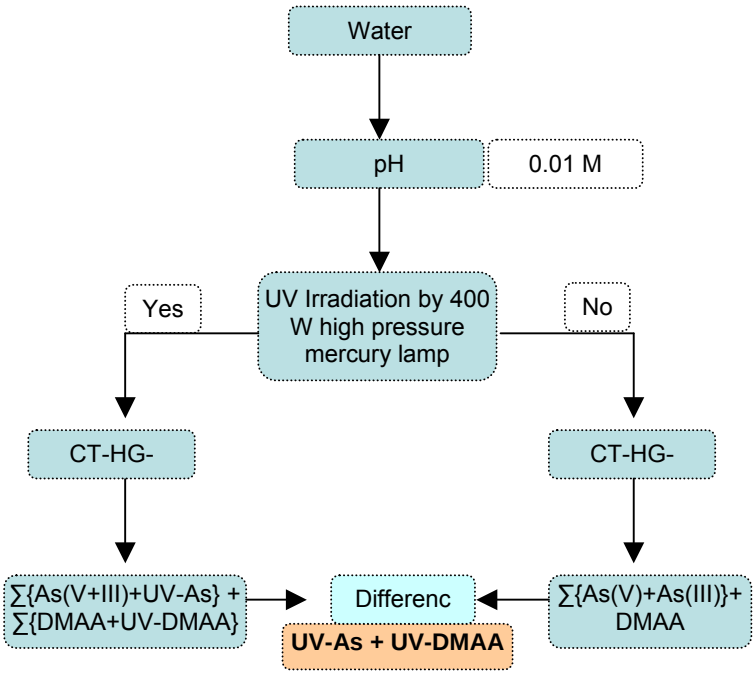

Fig. 1: Schematic diagram showing the protocol for the determination of ultraviolet-labile fractions (UV-As and UV-DMAA) of arsenic in Lake water following UV-Irradiation.

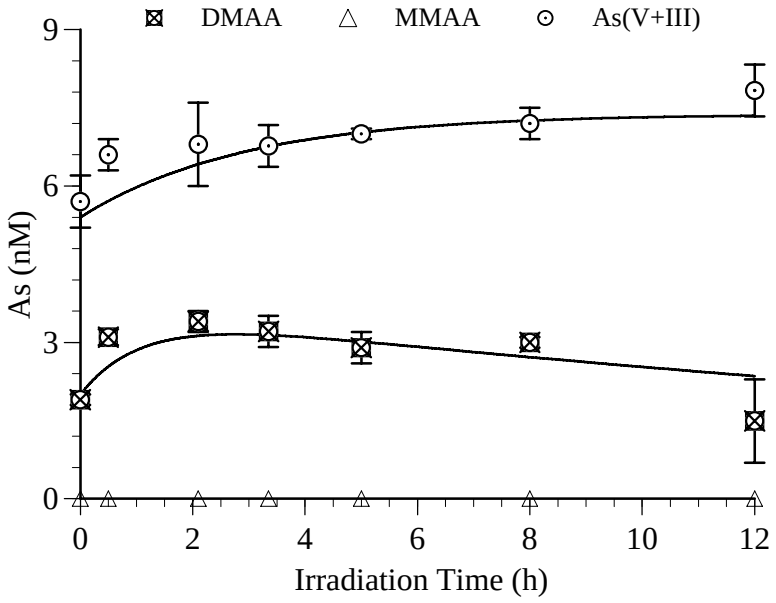

Fig. 2: Effect of irradiation time with a 400 W high-pressure mercury lamp on arsenic speciation in unfiltered water sample. Samples were collected from surface level of Lake Kiba on May 25, 2006. Error bars represent mean ± S.D.

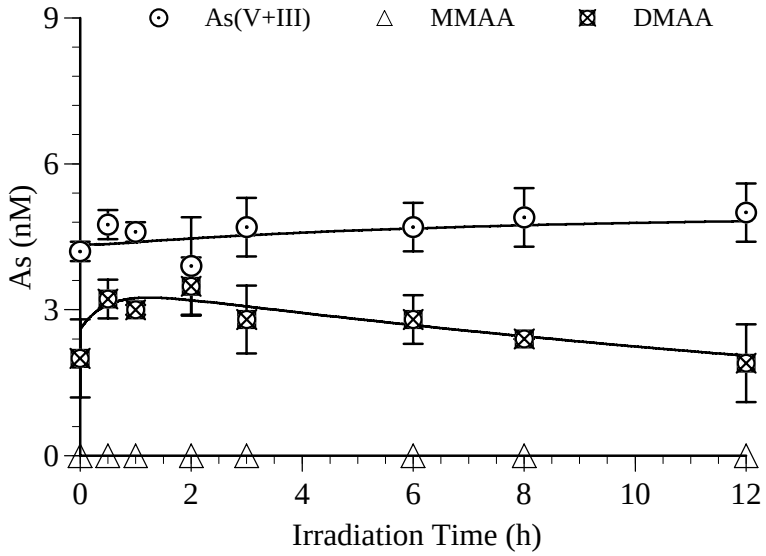

Fig. 3: Effect of irradiation time with a 400 W high-pressure mercury lamp on arsenic speciation in filtered water sample. Samples were collected from surface level of Lake Kiba on 25 May, 2006. Error bars represent mean ± S.D.

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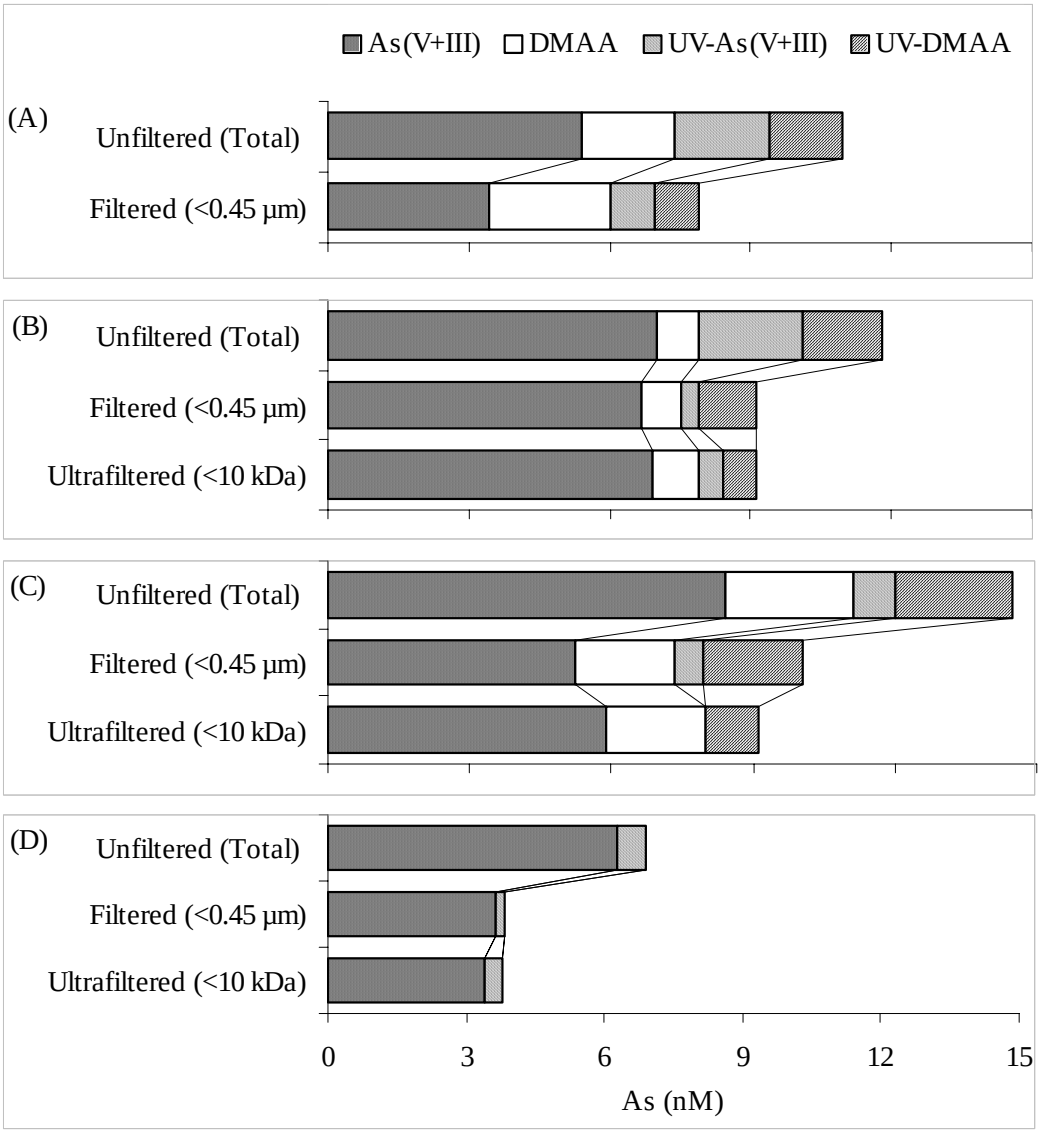

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602 Fig. 4: Concentration and distribution of arsenic species in surface water (depth 0 m) of Lake
603 Kiba collected from 25 May, 2006 (A), 31 Jul., 2006 (B), 26 Oct., 2006 (C) and 17
604 Jan., 2007 (D).

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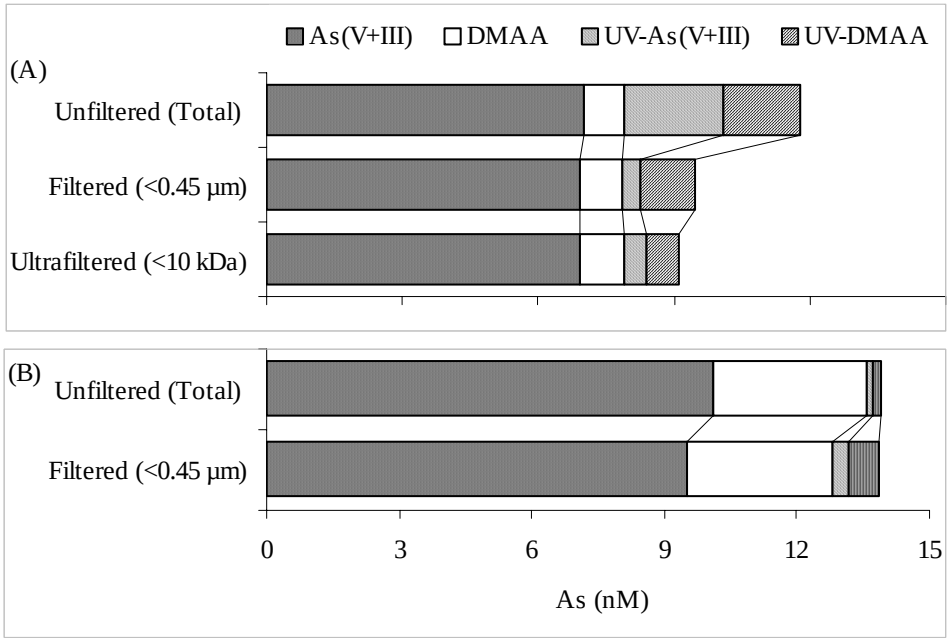

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612 Fig. 5: Mean concentration and distribution of arsenic in surface water (depth 0 m) of Lake
613 Kiba (A), and Lake Biwa (B) collected on 31 Jul., 2006 and 29 Jul., 2006,
614 respectively.