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Seasonal Changes of Arsenic Speciation in Lake Waters in Relation to Eutrophication

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Abstract:

In this study, the influence of eutrophication on arsenic speciation in lake waters was investigated. Surface water samples \((n = 1-10)\) were collected from 18 lakes in Japan during July 2007 and February 2008. The lakes were classified into mesotrophic (7 lakes) and eutrophic (11 lakes) based on the total phosphate (T-P) and chlorophyll-a (Chl-a) concentrations in water column. Inorganic, methylated and ultraviolet-labile fractions of arsenic species were determined by combining hydride generation atomic absorption spectrometry with ultraviolet irradiation. Organoarsenicals (mainly methylated and ultraviolet-labile fractions) comprised 30-60% of the total arsenic in most lakes during summer. On the other hand, inorganic arsenic species (As(III+V)) dominates (about 60-85%) during winter. The occurrence of ultraviolet-labile fractions of arsenic was higher in eutrophic lakes than those in mesotrophic lakes in both seasons. The concentration of dimethyl arsenic (DMAA) was high in eutrophic lakes during winter; and in mesotrophic lakes during summer. The results suggest that the conversion of As(III+V) to more complicated organoarsenicals occurred frequently in eutrophic lakes compared to that in mesotrophic lakes, which is thought to be the influence of biological activity in the water column. The distribution of arsenic species were well correlated with phosphate concentrations than those of Chl-a. This might be due to the competitive uptake of As(V) and phosphate by phytoplankton. The organoarsenicals (OrgAs)/As(V) ratio was higher at low phosphate concentration indicating that conversion of As(V) to OrgAs species was more active in phosphate-exhausted lakes with high phytoplankton density.

Keywords: Arsenic, Eutrophication, Organoarsenicals, Ultraviolet photolytic decomposition, Lake water, Chlorophyll-a
1. Introduction:

Arsenic (As) is widely distributed in aquatic environments in various forms (Cullen and Reimer, 1989). 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 conditions (Andreae, 1986; Cullen and Reimer, 1989). In natural waters, the dominant inorganoarsenicals (iAs) are incorporated into microorganisms such as phytoplankton, and are converted to methylarsenicals and/or more high order organoarsenicals such as arsenosugar (Francesconi et al., 1996; Maher, 1984). In addition, the organoarsenicals are mineralized to iAs and methylarsenicals by bacteria (Hanaoka et al., 1995).

In natural waters, the cycling of As species would depend on the bioactivity of organisms (Cullen and Reimer, 1989; Sanders, 1980). Microorganisms produce methylarsenicals in natural waters (Sanders and Riedel, 1993), which exhibit seasonal cycle with maximum concentrations of methylarsenicals in summer (Hasegawa et al., 1999; Howard et al., 1995; Sohrin et al., 1997a). Methylarsenicals are considered to be produced by phytoplankton and organisms of higher trophic levels as a detoxification mechanism (Edmonds and Francesconi, 1987). Sanders and Riedel (1993) reported the correlation between As(III)/methylarsenicals and chlorophyll-a concentrations and/or phytoplankton density, while Howard et al. (1995) found that the seasonal changes of DMAA concentration is related to the temperature rather then the biological activity of phytoplankton. 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 thought to depend mostly on bacterial activities, which influence the As cycling in aquatic environment (Kaise et al., 1987; Maki et al., 2005).
Arsenic metabolism in 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$_3$AsO(OH)$_2$); MMAA(V) and dimethylarsinic acid ((CH$_3$)$_2$AsO(OH)); DMAA(V)) are the main species of As in natural waters (Cullen and Reimer, 1989). The bulk of the total dissolved As is iAs in seawater (Peterson and Carpenter, 1983) and in freshwater (Kuhn and Sigg, 1993; Seyler and Martin, 1989). Although the predominant form of methylarsenicals is consistently DMAA(V) followed by MMAA(V), the existence of trivalent methylarsenic species in the environment has also been reported (Hasegawa, 1996; Hasegawa et al., 1994; Sohrin et al., 1997a).

In general, eutrophication is a phenomenon involving an increased concentration of nutrient salts, which promotes the multiplication of primary producers such as phytoplankton, in inland water. Lakes progress through the oligotrophic, mesotrophic and eutrophic process in the natural environment, and these transitions are very slow. Recently, the transition speed became faster because of discharged pollutants and nutrients from human activities, and the eutrophication affects the As circulation in lakes (Sohrin et al., 1997a).

In this study, As speciation in surface water was determined by hydride generation atomic absorption spectrometry equipped with cold trap (CT-HG-AAS). The CT-HG-AAS is widely used in the analysis of As compound, such as As(V), As(III), MMAA(V) and DMAA(V) (Braman et al., 1977; Hasegawa et al., 1994). In this technique, As is reduced to hydride forms such as arsine, and is then transported to the atomization part at boiling point. There are others infinitesimal As species compared to inorgano- and methyl-arsenicals in natural waters, however, they are not hydride reactive forms. Therefore, it is necessary for the organoarsenicals to be converted to hydride reactive forms using UV irradiation (Hasegawa et al., 1999). Although the distribution and speciation of As in
eutrophic and mesotrophic lakes were discussed in our previous article (Hasegawa et al., 2009), it was difficult to interpret the influence of eutrophication on As speciation because of limited data from a less number of lakes. In the present study, the correlation between As speciation and eutrophication are inferred based on samples collected from 18 lakes in Japan during July 2007 and February 2008. Although the lakes were classified into oligotrophic, mesotrophic and eutrophic, the oligotrophic and the mesotrophic lakes were combined together, and discussed collectively for enhancing understanding.

2. Experimental

2.1. Sample Collection and Pretreatment

We collected surface water samples \( n = 1-10 \) from 18 lakes during July, 2007 to February, 2008 (Fig. 1). Chlorophyll-a (Chl-a), water temperature and pH were measured with a multiple water quality analyzer (model 6600, YSI) on site. Various basic water parameters and sampling information of the lakes are presented in Table 1.

The samples were collected within 0.2 m of the water surface near the shore of the lakes, and were well saturated with oxygen. For analysis of As and nutrients, the samples were filtered with 0.45 μm (HA type, Millipore) filters immediately after collection. Both filtered and unfiltered samples were acidified to pH 2.0 by the addition of 1.0 M hydrochloric acid (HCl), and stored in refrigerator until analysis.

2.2. Reagents

Stock solutions \( (10^{-2} \text{ M}) \) for the determination of As compounds were prepared by dissolving the corresponding sodium salts \(((CH)_3AsO_3Na_2\) was prepared by Quick’s method (Hasegawa et al.,
and NaAsO$_2$, Na$_2$HAsO$_4$ and (CH$_3$)$_2$AsO$_2$Na were obtained from Nacalai Tesque, Japan in 0.1 M sodium hydroxide. They were diluted to the desired concentrations just before use. Sodium borohydride (Kanto Chemical, Japan) was used for hydride generation. A 3% (w/v) sodium borohydride solution, stabilized in 10$^{-2}$ M sodium hydroxide solution, was prepared daily. Other reagents were of analytical grade or better.

2.3. Arsenic analysis

Analysis of inorganic and methylarsonicals was performed by a modified technique of hydride generation method (CT-HG-AAS) using an apparatus and materials identical to those described in our previous paper (Hasegawa et al., 1994). 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 As and 5.1% for DMAA (a relative standard deviation) at 1.0 nM with a 30 ml sample size.

Organoarsenic species, except for methylarsonicals, can be classified into different fractions according to their lability to the photochemical degradation; UV-As and UV-DMAA (Hasegawa et al., 1999). UV-As and UV-DMAA contain arsenosugar, arsenolipid, arsenocoline, arsenobetaine etc. Samples (30 ml) were acidified to pH 2.0 using 1.0 M HCl, and introduced into 50-ml quartz test tubes that were capped with natural rubber septums. They were then irradiated with a 400 W high-pressure mercury lamp (Sigemi, AHH-400S). Aliquots were taken at selected time intervals. Arsenic analysis of the digests was performed with CT-HG-AAS as described above.

The 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. The detail of the organoarsenic speciation is shown elsewhere (Hasegawa et al., 2009). 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 (Hasegawa et al., 1999).

3. Results and Discussion

3.1. Trophic classification of lakes

Eutrophication is the natural ageing process of lakes. This is a very slow process, which ultimately transforms aquatic environments into terrestrial habitats, begins with the addition of nutrients into the system. These nutrients, in turn, stimulate the growth of microscopic free-floating aquatic plants known as phytoplankton. The term ‘eutrophication’ is also used to describe the human induced process where by human activity such as agriculture, use of fertilizers and changes in land surrounding aquatic environments, accelerates the growth of phytoplankton.

Nitrogen and phosphorus usually control the growth of phytoplankton in the aquatic environment. Based on the amount of phytoplankton growth and the concentration of nutrients, the degree of eutrophication in aquatic environments can be classified as oligotrophic, mesotrophic, eutrophic, or hypereutrophic. In the present study, water samples from a total of 18 lakes in Japan were collected for the investigation (Fig. 1). The lakes were classified into oligotrophic, mesotrophic, and eutrophic lakes to assess the influence of eutrophication on As cycling and speciation (Fig. 2). The Chl-a and phosphate are two important parameters of trophic state of aquatic systems (Carpenter et al., 1996; Smith et al., 1999). Although there are several trophic state indices (TSI) for the assessment of lake water quality (Carlson, 1977; Carlson, 1980; Smith et al., 1999; Stefanou et al., 2000), the trophic classification of the lakes was performed on the basis of chlorophyll-a and total phosphate (T-P) concentrations (Figs. 3A, 3B) according to the OECD’s criteria (Karydis and Coccossis, 1990; Moriki and Karydis, 1994; OECD, 1982) as; oligotrophic lakes (mean Chl-a; < 2.5
µg/l, mean T-P; < 0.32 µmol/l), mesotrophic lakes (mean Chl-a; 2.5-8 µg/l, mean T-P; 0.32-1.13 µmol/l), and eutrophic lakes (mean Chl-a; 8 > µg/l, mean T-P; >1.13 µmol/l).

Oligotrophic environments are characterized by clear waters, little suspended organic matter or sediment, and low primary production (phytoplankton growth). Mesotrophic environments have higher nutrient inputs and rates of primary production. Eutrophic environments have extremely high nutrient concentrations and biological productivity. Hypereutrophic environments are characterized by murky, highly productive waters in which many clear water species cannot survive (Allen and James, 1972; Genkai-Kato and Carpenter, 2005; Moncreiff, 2002; Smith et al., 2006; Smith et al., 1999). However, the results of the oligotrophic and the mesotrophic lakes did not differ significantly from each other in the present study. Thus, among the 18, 7 were classified as mesotrophic lakes and 11 as eutrophic lakes.

Figure 3 shows mean Chl-a and T-P concentrations in mesotrophic and eutrophic lakes. The Chl-a content in eutrophic lakes was clearly higher than that in mesotrophic lakes. Among eutrophic lakes the highest Chl-a content was recorded in lake Suigetsu (81.2 µg L\(^{-1}\)) whereas the lowest was in lake Nishino (9.71 µg L\(^{-1}\)). The Chl-a content in mesotrophic lakes was below 10 µg L\(^{-1}\). The trend of T-P concentration in lake waters followed the same pattern of Chl-a. However, the T-P concentration in surface water of eutrophic lakes was significantly higher than that in mesotrophic lakes. The highest T-P was found in lake Kahuku (4.14 µg L\(^{-1}\)) while the lowest was in lake Suwa (1.12 µg L\(^{-1}\)). Although the T-P concentration in Lake Hiruga was higher than that in Lake Suwa, the lake Hiruga was considered as mesotrophic and Lake Suwa as eutrophic lake on the basis of Chl-a content.

3.2. Seasonal distribution of As species in lake waters
Figures 4A and 4B show the distribution of As species in the 18 lakes. Both in eutrophic and mesotrophic lakes, the total As concentrations in the summer were higher than in the winter. These trends of As occurrence and distribution in lake waters were also reported previously (Crecelius, 1975; Hasegawa et al., 2009; Takamatsu and Kawashima, 1985). Inorganic As was released into the water from the sediments in the bottom layer under anaerobic conditions in summer, while As(V) was adsorbed onto Fe/Mn oxides and then settled down into the sediments in winter.

Organoarsenicals (mainly methylarsenicals and UV-labile fractions) comprised about 30-60% and 30-70% of the total As in mesotrophic and eutrophic lakes, respectively, in summer (Fig. 5). A large difference was observed between mesotrophic and eutrophic lakes in the composition of organoarsenicals in summer. The ultraviolet-labile fraction comprised about 30-40% of the total organoarsenicals in the mesotrophic lakes, with the exception of two lakes. In contrast, it comprised about 50-90% of the total organoarsenicals in eutrophic lakes. The results indicate that the conversion of inorganic and methylarsenicals to more complex organoarsenicals is higher in the eutrophic lakes in the summer.

The high concentrations of organoarsenicals during summer might be due to the conversion of inorganic As into organoarsenic compounds by aquatic organisms. Some aquatic organisms uptake inorganic As and excrete DMAA in freshwater (Cullen and Reimer, 1989; Hasegawa et al., 2001; Maeda, 1994). A substantial amount of UV-labile fractions of As were also detected in the water of most lakes during summer (Fig. 4A). On the other hand, about 85% of the total As was As(V+III), the amount of UV-As was minimal, and the UV-As, UV-DMAA and other organoarsenicals were totally absent or bellow the instrumental limit of detection during winter season (Fig. 4B).

Results of the present study show that without some exceptions, the concentrations of UV-As were higher usually in high-eutrophic lakes (Lake Suga, Lake Suigetsu, Lake Biwa (southern basin),
Lake Kita, and Lake Kahuku) than those in low-eutrophic lakes during summer (Fig. 4A). On the other hand, the concentrations of DMAA were higher in low-eutrophic lakes during winter than those in summer (Fig. 4B). Results suggest that the occurrence of UV-degradable fractions of As is higher in high eutrophic lakes and the production of DMAA is related to the water temperature in low eutrophic lakes. The occurrence of DMAA has been reported in other geographical areas (Anderson and Bruland, 1991; Hasegawa et al., 2009), and in laboratory experiments (Hasegawa et al., 2001). Frequent occurrence of DMAA than that of As(III) has been reported by Howard et al. (1995) at higher water temperatures. Sohrin et al. (1997b) also observed correlation between the concentration of DMAA and water temperature in Lake Biwa, Japan. Hasegawa (1996) reported that the concentration of DMAA follows the rise of water temperature in estuarine waters. The microbial activities, which influence the methylarsenicals’ production (Maki et al., 2005), are related to the water temperature. The DMAA is produced by bacterial degradation of complex organoarsenicals in the suspended solids, which is subsequently released into the water column. Thus bacterial activity is responsible for the increase of DMAA concentration in surface water (Hasegawa et al., 2009). Higher concentrations of DMAA might also be resulted from the long-term accumulation of DMAA excreted by phytoplankton.

3.3. Effect of eutrophication on As distribution in lake waters

In freshwater systems the proportions of As species vary with the scope of anthropogenic input and biological activity. A number of freshwater organisms have been reported to contain organoarsenic compounds. Production of methylarsenicals or bio-transformation of organoarsenicals from As(V) have been reported in literatures ((Hasegawa et al., 2001; Maeda, 1994). The decrease of total As concentration and the relative increase of methylarsenicals with the increasing trophic level
have been observed in most of the aquatic food chains (Kuehnelt and Goessler, 2003).

Total As concentrations in surface water of eutrophic lakes were higher than those in mesotrophic lakes in both seasons. Figures 4A and 4B show that the proportion of UV-labile fractions of As were higher in eutrophic lakes compared to those in mesotrophic lakes. The increase of UV-labile fractions of As well correlates with the phosphate and Chl-a concentrations (Figs. 3A, 3B). Since phosphate and Chl-a are important determinants of eutrophication, the results suggest that the occurrences of UV-As and UV-DMAA in lake waters are influenced by eutrophication. The sum of UV-labile As and DMAA concentrations in surface water of eutrophic lakes was increased in summer (Fig. 4A). The result is consistent with the previous report of Hasegawa et al. (2009). High concentration of Chl-a in most eutrophic lakes in the present study (Fig. 3A) reveal that the source of UV-labile As and methylarsenicals would be the direct production of phytoplankton, or the decomposition of organic matter containing complex organoarsenic compounds by microorganisms or sunlight. As the photochemical degradation by sunlight does not contribute to the production of DMAA in lake waters (Hasegawa et al., 1999), the possible reason for DMAA production would be the degradation of complex organoarsenic compounds by microbial activity.

The concentrations of UV-As and UV-DMAA was correlated with that of DMAA in eutrophic lakes. The UV-As and UV-DMAA appeared in summer though their occurrences decreased in winter (Fig. 4A, 4B). The production of UV-As and UV-DMAA would be related to the biological activity as the similar manner of DMAA (Hasegawa et al., 2009). Although DMAA and As(V+III) could be released from the particles of organic matter by ultraviolet irradiation, the UV-As(III+V) and UV-DMAA fractions would mainly consist of complex organoarsenic compounds which were synthesized in phytoplankton and other freshwater organisms.
The ratios of UV-fractions of As were higher in eutrophic lakes during summer, while those of As(III+V) were high in mesotrophic lakes during winter. On the other hand, the ratios of methylarsenicals (DMAA and MMAA) were almost same in eutrophic lakes during winter and in mesotrophic lakes during summer (Fig. 5). It can be elucidated by the biological/microbial activities in the lake waters. The eutrophication increased the microbial biomass and biosynthesis of complex organoarsenetic compounds in the lakes, which results in the degradation of DMAA and other organoarsenetic compounds. Moreover, the concentration of methylarsenic species was significantly lower in eutrophic lakes in summer than those in winter, though the amount of As(III+V) remain unchanged (Fig. 5). The result also suggests the degradation of methylarsenic (mainly DMAA) in eutrophic lakes during summer.

3.4. Relationship between As and phosphate or Chl-a in lake waters

Figure 6 shows the correlation of Chl-a and phosphate (PO$_4^{3-}$) concentrations with the occurrences of As(III) and organoarsenicals (sum of methylarsenicals, UV-As, and UV-DMAA) in the lake waters. The distribution of arsenic species was well correlated with phosphate (PO$_4^{3-}$) concentrations than those of Chl-a. As(III)/As(V) ratio was low in phosphate-rich lakes (> 0.2 µmol L$^{-1}$) in Fig. 6C. The result indicates that the As(V) intake by phytoplankton and other aquatic organisms was limited in phosphate-rich lakes. Since PO$_4$ and As(V) have similar chemical properties (Cullen and Reimer, 1989; Sohrin et al., 1997a), phytoplankton intakes As(V) as well as phosphate, competitively. In phosphate sufficient condition, organisms usually intake phosphate instead of As(V) for their metabolic activity (Meharg and Hartley-Whitaker, 2002; Rahman et al., 2008; Wang et al., 2002). On the other hand, high As(III)/As(V) and OrgAs/As(V) ratios were observed in phosphate-poor lakes in Fig. 6D. The correlation explains the influence of phosphate on the conversion of As(V) to As(III)
and organoarsenic species by phytoplankton. The conversion of As(V) to As(III) and organoarsenicals was more active in phosphate-exhausted lakes. Thus, the exhaustion of phosphate was considered to be essential for the conversion of As(V). These results are consistent with those of Sohrin et al (1997a) and Froelich et al (1985).

Dissolved oxygen (DO) also plays an important role in the occurrence of As(III) in lake water. Biological activities, which use a substantial amount of dissolved oxygen, are higher in eutrophic lakes while the activities are limited in mesotrophic lakes (Ærtebjerg et al., 2003; Genkai-Kato and Carpenter, 2005; Kennish and Townsend, 2007; Moncreiff, 2002; OECD, 1982; Smith et al., 2006; Smith et al., 1999). Therefore, the amount of dissolved oxygen in the bottom layers decreased in eutrophic lakes compared to that in mesotrophic lakes (Meyer-Reil and Köster, 2000). Comparatively high oxic condition in mesotrophic lakes favor the oxidation of As(III) to As(V) resulting high concentration of As(V).

4. Conclusions:

Eutrophication promotes the biological activity in lake water, which has significant effect on arsenic cycling in aquatic systems. From the correlation between arsenic speciation and eutrophication state of 18 lakes in Japan, it was observed that the percentage of organoarsenicals was about 30-60% of the total arsenic in most of the lakes in the summer, and there was not much difference in the occurrence of arsenic speciation between oligotrophic and eutrophic lakes. The ratio of methylarsenicals was higher in oligotrophic and mesotrophic lakes, while the ratio of the ultraviolet-labile fraction was higher in eutrophic lakes. Thus, it can be elucidated the conversion of inorganic and methylarsenicals to more complicated organoarsenicals is higher in eutrophic lakes compared to that in mesotrophic or oligotrophic lakes.
Acknowledgement:

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References:


Table 1: The table shows various basic water parameters and the sampling information of the lakes studied. In the table, summer and winter are of the year 2007 and 2008, respectively.

<table>
<thead>
<tr>
<th>Name of the lakes</th>
<th>Mean depth (m)</th>
<th>Tem. (°C)</th>
<th>Salinity (%)</th>
<th>pH</th>
<th>Chl-a (µg L⁻¹)</th>
<th>TOC (mg L⁻¹)</th>
<th>Sampling time (day/month)</th>
</tr>
</thead>
<tbody>
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<td>1.6</td>
<td>26.7</td>
<td>3.5</td>
<td>0.05</td>
<td>8.6</td>
<td>6.1</td>
<td>Summer: 30/7, Winter: 8/1</td>
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<td>Lake Shibayama</td>
<td>2.2</td>
<td>28.4</td>
<td>4.1</td>
<td>0.06</td>
<td>8.8</td>
<td>9.4</td>
<td>Summer: 22/9, Winter: 24/2</td>
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<td>27.0</td>
<td>4.8</td>
<td>0.09</td>
<td>7.9</td>
<td>9.0</td>
<td>Summer: 23/9, Winter: 23/2</td>
</tr>
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<td>0.6</td>
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<td>9.4</td>
<td>Summer: 20/7, Winter: 26/1</td>
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<td>8.9</td>
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<td>Summer: 21/9, Winter: 25/1</td>
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<td>3.9</td>
<td>0.12</td>
<td>6.8</td>
<td>8.5</td>
<td>Summer: 21/9, Winter: 26/1</td>
</tr>
</tbody>
</table>
Fig. 1: Water samples were collected from 18 lakes around Ishikawa, Nagano, Fukui, and Shiga prefectures in Japan.

Fig. 2: Classification of lakes using mean total phosphate (T-PO₄) and mean total chlorophyll-a (T-Chl-a) concentrations (OECD, 1982).
Fig. 3: Chlorophyll-α (Chl-α) and phosphate (PO₄) concentrations in surface water of mesotrophic and eutrophic lakes (n = 1-10). Chlorophyll-α (A) and total phosphate (T-P) (B).
Fig. 4: Mean concentration and distribution of arsenic species in lake waters ($n = 1-10$). The charts show the average data of the 7 oligotrophic and mesotrophic lakes and the 11 eutrophic lakes in Japan.
Fig. 5: Ratio of inorganic arsenic, methyl arsenic and the UV-fractions of organic and inorganic arsenic during summer and winter season. The charts show the average data of 7 mesotrophic and 11 eutrophic lakes in Japan ($n = 1-10$).
Fig. 6: Correlation between chlorophyll-a (Chl-a) and the ratio of As(III) or organoarsenicals (OrgAs) to As(V); and between phosphate (PO₄) and the ratio of As(III) or OrgAs to As(V) concentrations in lake waters during summer and winter.