

Arsenic Biogeochemistry Affected by Eutrophication in Lake Biwa, Japan

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The seasonal variations of arsenic species were studied in the mesotrophic northern and eutrophic southern basins of Lake Biwa in Japan. The variations of arsenic species in lake water largely depend on biological processes, such as the metabolism of phytoplankton, decomposition of organic matter by bacteria, and microbial reduction of iron and manganese oxides in sediments. These results show that eutrophication affects the concentration and speciation of arsenic in the lake water.

Keywords : Arsenic/Methylarsenic/Organoarsenic/Lake water/Eutrophication/Biogeochemistry

Aquatic organisms metabolize arsenic, forming organoarsenic compounds such as non-toxic arsenic-containing ribofuranosides and arsenobetaine. The metabolism results in the occurrence of thermodynamically unstable arsenite and methylarsenic compounds in natural waters. So far, mainly four arsenic species have been determined in natural waters. Arsenate [$\text{AsO}(\text{OH})_3$; As(V)] is the thermodynamically stable form under oxic conditions, of which one or two protons are dissociated at natural pHs. As(V) is a chemical analogue of phosphate and may interfere with oxidative phosphorylation. Monomethylarsonic acid [$\text{CH}_3\text{AsO}(\text{OH})_2$; MMAA(V)] and dimethylarsinic acid [$(\text{CH}_3)_2\text{AsO}(\text{OH})$; DMAA(V)] also form anions in natural water but are much less toxic than As(V). Arsenite [$\text{As}(\text{OH})_3$; As(III)] is a neutral species at natural pHs and inhibits the activity of enzymes by binding to thiol groups. Since there are large differences

in chemical behavior and toxicity among the arsenic species, the determination of speciation is very important in the study of the biogeochemistry of arsenic.

We have studied the seasonal variations of arsenic speciation in Lake Biwa in order to elucidate the effect of eutrophication on the biogeochemistry of arsenic [1, 2]. Lake Biwa is geographically divided into two parts, the mesotrophic northern and the eutrophic southern basins (Figure 1). In addition, the new analytical technique used in this study allowed us to determine trivalent methyl arsenicals, that is, monomethylarsonous acid, [$\text{CH}_3\text{As}(\text{OH})_2$; MMAA(III)] and dimethylarsinous acid [$(\text{CH}_3)_2\text{AsOH}$; DMAA(III)] [3]. MMAA(III) and DMAA(III) have high toxicity, since they are lipophilic and inhibit the activity of enzymatic SH-groups. They are assumed to be intermediates in the biosynthesis of organoarsenicals. This is the first report of the distribu-

INTERFACE SCIENCE — Separation Chemistry —

Scope of research

Our research activities are concerned in the behavior of chemical substances in geochemistry and the biochemical reactions. Major subjects of the research are followings: (1) Biogeochemistry of trace elements in the hydrosphere. Analytical methods for trace elements are developed using the selective complex formation systems. The behavior of trace elements in hydrosphere is explored to realize the significance of them for ecosystem. (2) Design and synthesis of the selective complex formation systems. Ligands (host molecules) that have novel functions in separation of metal ions and guest molecules are designed and synthesized.



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tion of trivalent methyl arsenicals in lake water.

Figure 2 shows the seasonal variations of arsenic species in Lake Biwa. Within the surface water of the northern basin, arsenic speciation changed seasonally. As(III) increased in spring and fall, and DMAA(V) increased and became the dominant species in summer. The concentration of As(III) and DMAA(V) reached 94% and 64% of total arsenic, respectively. Though MMAA(V) also increased in the euphotic zone during summer and fall, it was usually an order of magnitude less than DMAA(V). In the hypolimnion of the southern basin, the concentration of total arsenic greatly increased in summer with the depletion of DO. Although the species of arsenic most contributing to the increase were As(V) and As(III), high concentration of DMAA(V) was also observed in the hypolimnion.

DMAA(V) and As(III) originate from phytoplankton. Uptake of As(V) by algae and subsequent increase in the concentration of As(III) and methylarsenic(V) species in water have been observed in culture and during the development of blooms in enclosure experiments. However, the correlation of DMAA(V) and Chl. a in Figure 1 suggests that the relation between the DMAA(V) concentration and primary productivity is very dependent on the sampling time. It is not clear whether methylarsenic(V) species are produced directly by living phytoplankton or indirectly as a degradation product of organoarsenicals by bacteria. In the southern basin, high concentrations of DMAA(V) are observed in the low DO ranges. The results suggest that DMAA(V) could be produced by the anaerobic decomposition of algal matter sinking from the surface [1].

In both basins, MMAA(III) and DMAA(III) were minor components, of which concentrations usually did not exceed 0.3 nM. They were distributed not only in the epilimnion but also in the hypolimnion and did not show a clear seasonal change. MMAA(III) and DMAA(III) have been thought to be in the form of $(\text{CH}_3\text{AsO})_x$ and $(\text{CH}_3)_2\text{As-O-As}(\text{CH}_3)_2$. However, we confirmed through

liquid-liquid distribution experiments that MMAA(III) and DMAA(III) are monomeric below the concentrations of 10^{-3} and 10^{-8} M, respectively. Data for $^1\text{H-NMR}$ chemical shift suggested that MMAA(III) and DMAA(III) are undissociated at pH values around neutral. Thus, we presume their chemical forms to be $\text{CH}_3\text{As}(\text{OH})_2$ and $(\text{CH}_3)_2\text{AsOH}$ [2, 3].

Eutrophication affects the concentration and speciation of arsenic in the lake water. The total arsenic concentration was increased by 2-4 times in the southern basin in summer, while it was nearly constant in the northern basin. The enhancement of total arsenic was due to the increase of As(V) from the sediment, which was accompanied by the increase of iron, manganese and phosphorous [4]. Arsenicals adsorbed onto iron and manganese oxides are redissolved, when the iron and manganese oxides are reduced under anoxic condition. Phosphate, which is a chemical analogue of As(V), is concurrently released from the sediment. Another distinction between the northern and southern basins is the efficiency of methylarsenic formation. The large load of phosphorus in the southern basin may have decreased the arsenic metabolism efficiency of phytoplankton. The variations of arsenic species depend on biological processes, such as the metabolism of phytoplankton, decomposition of organic matter by bacteria, and microbial reduction of ferromanganese oxides in sediments.

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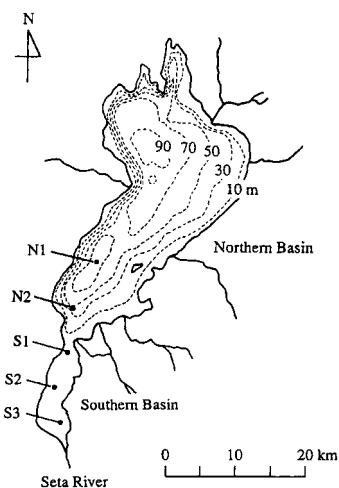


Figure 1. Sampling stations in Lake Biwa.

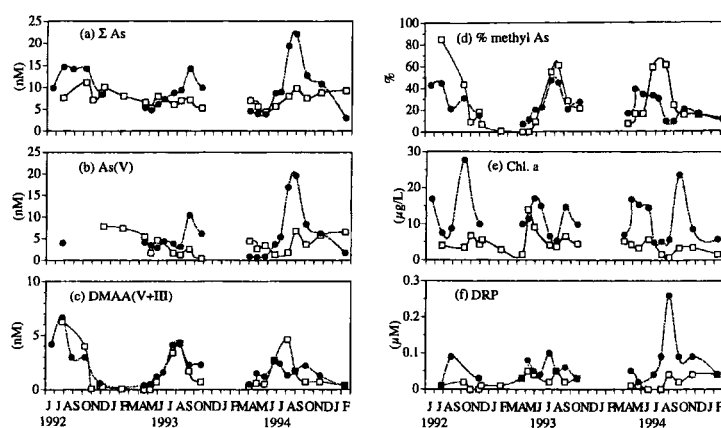


Figure 2. The seasonal variation in the average concentrations of arsenic species, Chl. a and DRP in the epilimnion (0–10 m for N1, 0–4 m for S3). Total methyl As is the sum of DMAA(V+III) and MMAA(V+III). □, station N1; ●, station S3.