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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.

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 higher 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 than 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 ($CH_3AsO(OH)_2$); MMAA(V) and dimethylarsinic acid ($(CH_3)_2AsO(OH)$); 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

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primary producers such as phytoplankton, in inland water. Lakes progress through the oligotrophic, mesotrophic and eutrophic processes 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 effects 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 few 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} 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., 1994), and $NaAsO_2$, Na_2HAsO_4 and $(CH_3)_2AsO_2Na$ 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 methylarsenicals 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 methylarsenicals, 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

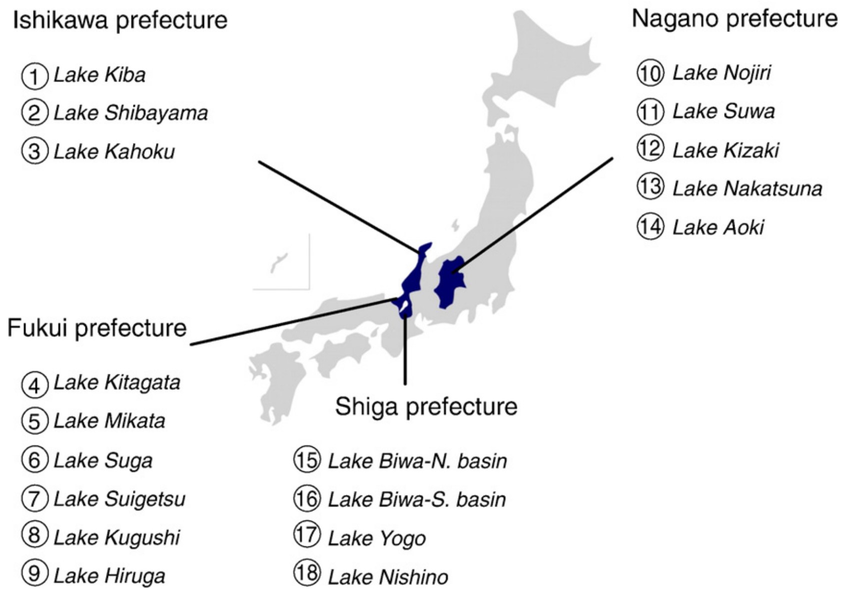

Fig. 1. Water samples were collected from 18 lakes around Ishikawa, Nagano, Fukui, and Shiga prefectures in Japan.