EUTROPHICATION AND ARSENIC SPECIATION IN LAKE WATERS

Hiroshi Hasegawa[1]*, M. Azizur Rahman[1], Ismail M. M. Rahman[1,2]

[1]Graduate School of Natural Science and Technology, Kanazawa University
Kakuma, Kanazawa 920-1192, Japan
[2]Department of Chemistry, Faculty of Science, University of Chittagong
Chittagong 4331, Bangladesh

ABSTRACT

Arsenic (As) is widely distributed in aquatic environments in various forms. 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. In addition, the organoarsenicals are mineralized to iAs and methylarsenicals by bacteria. The cycling of As species would depend on the bioactivity of organisms. Microorganisms, such as phytoplankton and organisms of higher trophic levels, produce methylarsenicals in natural waters with maximum concentrations in summer. The degradation and mineralization of organoarsenic compounds are thought to depend mostly on bacterial activities, which influence the As cycling in aquatic environment. 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 arsenic species present in natural waters. 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.

Researchers reported the correlation between As(III)/methylarsenicals and chlorophyll-*a* concentrations and/or phytoplankton density, while others found that the seasonal changes of DMAA concentration is related to the temperature rather than the biological activity of phytoplankton. Eutrophication increases the concentration of nutrient salts and multiplies the primary producers, such as phytoplankton, in lake 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. Very recently, reports showed that the eutrophication influences As speciation in lake water too. In this chapter, the influence of eutrophication on arsenic speciation will be discussed.

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* E-mail: hhiroshi@t.kanazawa-u.ac.jp; Tel/Fax +81-76-234-4792

INTRODUCTION

Arsenic is taken up by aquatic organisms which produce a variety of dissolved forms through reduction and methylation [1]. Aquatic organisms metabolize arsenic, forming organoarsenic compounds such as non-toxic arsenic-containing ribofuranosides and arsenobetaine [2–5]. The metabolism also 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 $(AsO(OH)_3; As(V))$ is the thermodynamically stable state in oxic waters, while arsenite $(As(OH)_3; As(III))$ is predominant in reduced redox conditions [2, 3]. As(V) is a chemical analogue of phosphate and may interfere with oxidative phosphorylation and As(III) inhibits the activity of enzymes by binding to thiol groups [2]. Monomethylarsonic acid $[CH_3AsO(OH)_2; MMAA(V)]$ and dimethylarsinic acid $[(CH_3)_2AsO(OH); DMAA(V)]$ also form anions in natural water but are much less toxic than As(V) [6]. In eutrophic regions, the proportion of arsenite and methylarsenicals is significantly large, while arsenate is the thermodynamically stable form in oxic environment [2, 3, 7].

In natural waters, the cycling of As species would depend on the bioactivity of organisms [3, 8]. Microorganisms produce methylarsenicals in natural waters [9], which exhibit seasonal cycle with maximum concentrations of methylarsenicals in summer [6, 10, 11]. Methylarsenicals are considered to be produced by phytoplankton and organisms of higher trophic levels [7]. Sanders and Riedel [9] observed the correlation between As(III)/methylarsenicals and chlorophyll-*a* concentrations and/or phytoplankton density, while Howard et al. [11] 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 [5]. The arsenosugars are usually found in algae and arsenobetaine is the predominant form in marine animals [4, 7]. The degradation and mineralization of organoarsenic compounds are thought to depend mostly on bacterial activities, which influence the As cycling in aquatic environment [12, 13].

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. Recent studies showed that the eutrophication affects the arsenic circulation and speciation in lakes [6, 14, 15]. In this chapter, we would like to discuss about the effect of eutrophication on distribution and speciation of arsenic in lake waters.

ARSENIC CYCLE IN THE ENVIRONMENT

Microorganisms, plants and many other organisms are involved in the global distribution and cycling of arsenic. The arsenic cycling includes reduction, oxidation, and methylation of the element by those organisms. Human activity also contributes to the cycling of arsenic in the environment.

Arsenic compounds are reduced and methylated by anaerobes to give dimethylarsine and trimethylarsine as volatile products [16]. Fortunately, these arsines are readily oxidized to less toxic variants, such as cacodylic acid. However, cacodylic acid has been shown to be an intermediate in the synthesis of dimethylarsine from arsenic salts. Arsenic emission into the atmosphere occurs mainly from coal burning in power generation plants, vegetation burning, and volcanism. Inputs of arsenic into the atmosphere also include industrial and fossil fuel emissions, mining, and continental and volcanic dust fluxes [17]. Biomethylation of arsenic also release arsenic into the atmosphere. Microorganisms including bacteria, fungi, and yeast produce volatile methylated derivatives of arsenic under both aerobic and anaerobic conditions [18]. It is estimated that about 210×10^5 kg of arsenic is emitted from land surface into the atmosphere in the vapor state annually [17].

ARSENIC IN AQUATIC SYSTEMS

Although open-ocean systems are relatively constant, the possibility of anthropogenic additions of arsenic can result in higher arsenic concentrations in coastal areas and fresh water [8]. The concentration of arsenic is between 1.4 and 1.8 $\mu g\ L^{-1}$ in deep Pacific and Atlantic oceans [19]. In contrast, arsenic concentrations in freshwaters (rivers and lakes) vary widely with the geological composition of the drainage area and the extent of anthropogenic input. The geometric mean of arsenic concentration is about 1.4 $\mu g\ L^{-1}$ in European and some North and South American rivers with a range of 0.5–75 $\mu g\ L^{-1}$ [3]. It is extremely difficult to suggest typical arsenic levels in freshwater systems due to very high variations, but most values are in the $\mu g\ L^{-1}$ range [3].

Arsenate is the major form of arsenic in most seawater samples, and arsenite can occur at significant levels as a consequence of reduction by marine phytoplankton and bacteria [20]. Methylarsonate and dimethylarsinate are not particularly stable in seawater though they can exist as significant species in surface waters where primary productivity is high [21]. Seasonal changes and factors associated with biological activity might also influence the amounts of methylarsonate and dimethylarsinate in seawaters [22–24]. There have been reports of unknown arsenic compounds, often referred to as 'hidden arsenic', in seawater [10, 25] and freshwater [10, 26]. In aquatic systems, arsenic also exists as complex organoarsenic compounds (arsenobetaine, arsenocholine, etc.) [18]. Microorganisms (mostly by bacteria) involve in the degradation of DMAA into inorganic arsenic species [27]. 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 [13, 28].

In marine algae, arsenosugars are the major arsenic species. The concentrations of arsenosugars in brown algae are much higher than those in red and green algae [4]. Arsenate occurs generally as a minor compound, and arsenite and methylarsonate appear to be trace constituents only. Marine algae also contained a considerable amount of lipid soluble arsenic [29]. On the other hand, freshwater algae have been little studied, but their pattern of arsenic compounds appears to be similar [30].

EFFECT OF EUTROPHICATION ON ARSENIC SPECIATION

Eutrophication is the natural aging 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 whereby 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. The chlorophyll-*a* and total phosphate are two important parameters of trophic state of aquatic systems [31, 32]. Although there are several trophic state indices (TSI) for the assessment of lake water quality [31, 33–35], the trophic classification of the lakes was performed on the basis of chlorophyll-*a* (Chl-a) and total phosphate (T-P) concentrations according to the OECD's criteria [36–38] 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 [31, 39–42].

Both in eutrophic and mesotrophic lakes, the total As concentrations in the summer is higher than in the winter [14]. These trends of As occurrence and distribution in lake waters have also been reported by a number of researchers [15, 43, 44]. This is because inorganic As is 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. The ultraviolet-labile fraction comprises about 30–40% of the total organoarsenicals in the mesotrophic lakes, with a few exceptions. In contrast, it comprised about 50–90% of the total organoarsenicals in eutrophic lakes [14]. Therefore it can be elucidate 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 [1, 3, 5].

Without some exceptions, the concentrations of UV-As is higher usually in high-eutrophic lakes than those in low-eutrophic lakes during summer. On the other hand, the concentrations of DMAA are higher in low-eutrophic lakes during winter than those in summer [14]. Thus 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 [15, 45], and in laboratory experiments [1]. DMAA occurs frequently than that of As(III) at higher water temperatures [11], and the concentration of DMAA correlates with water temperature in fresh water lake [46] in estuarine waters [24]. The microbial activities, which influence the methylarsenicals' production [13], 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 [15]. Higher concentrations of DMAA might also be resulted from the long-term accumulation of DMAA excreted by phytoplankton.

ARSENIC DISTRIBUTION IN RELATION TO THE EUTROPHICATION

In freshwater systems, the proportions of arsenic species vary with the scope of anthropogenic input and biological activity. A number of freshwater organisms contain organoarsenic compounds. Several strains of phytoplankton produce methylarsenicals [1]. As(V) is bio-transformed to organoarsenic compounds in freshwater food chains [5]. The decrease of total arsenic concentration and relative increase of methylarsenicals with the trophic level augmentation is observed in most of the food chains [47]. The 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 [48].

In freshwater organisms, methylarsenic species, especially DMAA is the major organoarsenic compounds [4]. DMAA increase in water column of eutrophic Lake [9, 15]. 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 [45] 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 [10].

The concentrations of UV-As and UV-DMAA correlate with that of DMAA in mesotrophic Lake. The UV-As, UV-DMAA and DMAA appear during summer though they disappeared in winter [15]. 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 does not increase in the acidified unfiltered samples. The UV-As and UV-DMAA fractions of arsenic species is distributed in the colloidal and particulate fractions, which comprise organic and inorganic matter [15]. According to Bright et al. [26] the hidden arsenic species or complex organoarsenic compounds such as arsenosugars might be absorbed tightly to organic matter. The degradation behavior of UV-As and UV-DMAA during the ultraviolet irradiation implies that the structures of UV-DMAA have DMAA fragments [15]. Although DMAA and As(V+III) could be released from the particles of organic matter by ultraviolet irradiation, the

UV-As and UV-DMAA fractions would mainly consist of complex organoarsenic compounds that were synthesized in phytoplankton and other freshwater organisms [47]. Arsenoriboses have also found in microbial mats and green algae [49]. Oxo– and thio–arsenosugars have been identified in several freshwater mussels and fishes as an important arsenic constituent, and arsenobetaine as a minor concentration [48].

The concentrations of UV-As and UV-DMAA in eutrophic Lake is higher than those in mesotrophic Lake, and is correlated with DMAA concentration. It can be elucidated by the eutrophication condition of the lakes. The eutrophication increased the microbial biomass and biosynthesis of complex organoarsenic compounds in the entire reservoir, which results in the degradation of DMAA and other organoarsenic compounds. Moreover, the degradation rate of DMAA is higher in eutrophic Lake than that in mesotrophic Lake. This is the result of direct transformation of As(V) into methylarsenicals or other organoarsenic compounds by biota, which in turn, is degraded to DMAA and arsenate [14, 15]. The composition of arsenic species in Lake Waters would attribute to the balance of biological processes; the metabolism of phytoplankton, grazing pressure due to zooplankton, and the decomposition of organic matter by microbial communities.

Total concentration of arsenic in eutrophic Lake is higher in summer compared to winter. This might be due to the release of As(V+III) from the anoxic sediments. Reductive dissolution of iron and manganese oxides decrease the adsorptive surfaces of sediment particles and release As(V+III) [44]. The dissolved arsenite (thermodynamically stable species in anoxic waters) is not as strongly adsorbed as arsenate [50]. The increase of arsenic concentration strongly correlates with the reductive dissolution of iron and manganese oxides [44]. Arsenate is adsorbed on manganese oxides in manganese-rich lakes [43]. Dissolved fractions of arsenate are transformed into particulate fractions by adsorption or coprecipitation on iron and manganese oxides [15]. The DMAA is converted almost completely to arsenate after winter mixing, and removed from the water column to the sediments [45]. This was because arsenate is particle reactive.

REFERENCE

[1]   Hasegawa, H.; Sohrin, Y.; Seki, K.; Sato, M.; Norisuye, K.; Naito, K.; Matsui, M., Biosynthesis and release of methylarsenic compounds during the growth of freshwater algae. *Chemosphere* 2001, *43*, 265–272.

[2]   Andreae, M. O., *Organic Compounds in the Environment*. Longman, New York, 1986.

[3]   Cullen, W. R.; Reimer, K. J., Arsenic speciation in the environment. *Chem. Rev.* 1989, *89*, 713–764.

[4]   Francesconi, K. A.; Kuehnelt, D., *Arsenic Compounds in the Environment*. New York, 2002; p 51–94.

[5]   Maeda, S., *Biotransformation of Arsenic in Freshwater Environment*. John Wiley: New York, 1994.

[6]   Sohrin, Y.; Matsui, M.; Kawashima, M.; Hojo, M.; Hasegawa, H., Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. *Environ. Sci. Technol.* 1997, *31*, 2712–2720.

[7]   Edmonds, J.; Francesconi, K., Transformations of arsenic in the marine environment. *Cell. Mol. Life Sci.* 1987, *43*, 553–557.

[8]   Sanders, J. G., Arsenic cycling in marine systems. *Mar. Environ. Res.* 1980, *3*, 257–266.

[9]   Sanders, J. G.; Riedel, G. F., Trace element transformation during the development of an estuarine algal bloom. *Estuaries* 1993, *16*, 521–532.

[10] Hasegawa, H.; Matsui, M.; Okamura, S.; Hojo, M.; Iwasaki, N.; Sohrin, Y., Arsenic speciation including 'hidden' arsenic in natural waters. *Appl. Organomet. Chem.* 1999, *13*, 113–119.

[11] Howard, A. G.; Comber, S. D. W.; Kifle, D.; Antai, E. E.; Purdie, D. A., Arsenic speciation and seasonal changes in nutrient availability and micro-plankton abundance in Southampton water, U.K. *Estuar. Coast. Shelf Sci.* 1995, *40*, 435–450.

[12] Kaise, T.; Hanaoka, K.; Tagawa, S., The formation of trimethylarsine oxide from arsenobetaine by biodegradation with marine microorganisms. *Chemosphere* 1987, *16*, 2551–2558.

[13] Maki, T.; Hasegawa, H.; Ueda, K., Seasonal dynamics of dimethylarsinic-acid-decomposing bacteria dominating in Lake Kahokugata. *Appl. Organomet. Chem.* 2005, *19*, 231–238.

[14] Hasegawa, H.; Rahman, M. A.; Kitahara, K.; Itaya, Y.; Maki, T.; Ueda, K., Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. *Sci. Total Environ.* 2010, *408*, 1684–1690.

[15] Hasegawa, H.; Rahman, M. A.; Matsuda, T.; Kitahara, T.; Maki, T.; Ueda, K., Effect of eutrophication on the distribution of arsenic species in eutrophic and mesotrophic lakes. *Sci. Total Environ.* 2009, *407*, 1418–1425.

[16] McBridet, B. C.; Wolfez, R. S., Biosynthesis of dimethylarsine by methanobacterium. *Biochemistry (Moscow)* 1971, *10*, 4312–4317.

[17] Mackenzie, F.; Lantzy, R.; Paterson, V., Global trace metal cycles and predictions. *Math. Geol.* 1979, *11*, 99–142.

[18] Tamaki, S.; Frankenberger, W. T. J., Environmental chemistry of arsenic. In *Rev. Environ. Contam. Toxicol.*, Springer-Verlag: New York, 1992; Vol. 124, pp 79–110.

[19] Andreae, M. O., Arsenic speciation in seawater and interstitial waters: the influence of biological-chemical interactions on the chemistry of a trace element. *Limnol. Oceanogr.* 1979, *24*, 440–452.

[20] Francesconi, K. A.; S., E. J., Arsenic and marine organisms. *Adv. Inorg. Chem.* 1997, *44*, 147–189.

[21] Andreae, M. O., Distribution and speciation of arsenic in natural waters and some marine algae. *Deep Sea Res.* 1978, *25*, 391–402.

[22] Santosa, S. J.; Wada, S.; Tanaka, S., Distribution and cycle of arsenic compounds in the ocean. *Applied Organometallic Chemistry* 1994, *8*, 273–283.

[23] Millward, G. E.; Ebdon, L.; Walton, A. P., Seasonality in estuarine sources of methylated arsenic. *Appl. Organomet. Chem.* 1993, *7*, 499–511.

[24] Hasegawa, H., Seasonal changes in methylarsenic distribution in Tosa Bay and Uranouchi Inlet. *Appl. Organomet. Chem.* 1996, *10*, 733–740.

[25] Howard, A. G.; Comber, S. D. W., The discovery of hidden arsenic species in coastal waters. *Appl. Organomet. Chem.* 1989, *3*, 509–514.

[26] Bright, D. A.; Dodd, M.; Reimer, K. J., Arsenic in subArctic lakes influenced by gold mine effluent: the occurrence of organoarsenicals and 'hidden' arsenic. *Sci. Total Environ.* 1996, *180*, 165–182.

[27] Maki, T.; Takeda, N.; Hasegawa, H.; Ueda, K., Isolation of monomethylarsonic acid-mineralizing bacteria from arsenic contaminated soils of Ohkunoshima Island. *Appl. Organomet. Chem.* 2006, *20*, 538–544.

[28] Kaise, T.; Hanaoka, K.; Tagawa, S., The formation of trimethylarsenic oxide from arsenobetaine by biodegradation with marine microorganisms. *Chemosphere* 1985, *16*, 2551–2558.

[29] Morita, M.; Shibata, Y., Chemical form of arsenic in marine macroalgae. *Appl. Organomet. Chem.* 1990, *4*, 181–190.

[30] Lai, V. W.-M.; Cullen, W. R.; Harrington, C. F.; Reimer, K. J., The characterization of arsenosugars in commercially available algal products including a *Nostoc* species of terrestrial origin. *Appl. Organomet. Chem.* 1997, *11*, 797–803.

[31] Smith, V. H.; Tilman, G. D.; Nekola, J. C., Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environ. Pollut.* 1999, *100*, 179–196.

[32] Carpenter, S. R.; Kitchell, J. F.; Cottingham, K. L.; Schindler, D. E.; Christense, D. L.; Post, D. M.; Voichick, N., Chlorophyll variability, nutrient input, and grazing: Evidence from whole- lake experiments. *Ecology* 1996, *77*, 725–735.

[33] Stefanou, P.; Tsirtsis, G.; Karydis, M., Nutrient scaling for assessing eutrophication: The development of a simulated normal distribution. *Ecol. Appl.* 2000, *10*, 303–309.

[34] Carlson, R. E., A trophic state index for lakes. *Limnol. Oceanogr.* 1977, *22*, 361–369.

[35] Carlson, R. E., More complications in the chlorophyll-Secchi disk relationship. *Limnol. Oceanogr.* 1980, *25*, 379–382.

[36] OECD *Eutrophication of Waters. Monitoring, Assessment and Control*; DAS/DSI/82; Organization for Economic Co-operation and Development (OECD): Paris, 1982; p 156.

[37] Karydis, M.; Coccossis, H., Use of multiple criteria for eutrophication assessment of coastal waters. *Environ. Monit. Assess.* 1990, *14*, 89–100.

[38] Moriki, A.; Karydis, M., Application of multicriteria choice-methods in assessing eutrophication. *Environ. Monit. Assess.* 1994, *33*, 1–18.

[39] Allen, H. E.; James, R. K., *Nutrients in Natural Waters*. John Wiley and Sons, Inc.: New York, 1972; p 457.

[40] Genkai-Kato, M.; Carpenter, S. R., Eutrophication due to phosphorus recycling in relation to lake morphometry, temperature, and macrophytes. *Ecology* 2005, *86*, 210–219.

[41] Smith, V. H.; Joye, S. B.; Howarth, R. W., Eutrophication of freshwater and marine ecosystems. *Limnol. Oceanogr.* 2006, *51*, 351–355.

[42] Moncreiff, C. A., Eutrophication processes: Northwest Florida estuary responses. *Ecology* 2002, *83*, 588–589.

[43] Takamatsu, T. M.; Kawashima, M. K., The role of Mn^{2+}–rich hydrous manganese oxide in the accumulation of arsenic in lake sediments. *Water Res.* 1985, *19*, 1029–1032.

[44] Crecelius, E. A., The geochemical cycle of arsenic in lake Washington and its relation to other elements. *Limnol. Oceanogr.* 1975, *20*, 441–451.

[45] Anderson, L. C. D.; Bruland, K. W., Biogeochemistry of arsenic in natural waters: the importance of methylated species. *Environ. Sci. Technol.* 1991, *25*, 420–427.

[46] Sohrin, Y.; Matsui, M.; Kawashima, M.; Hojo, M.; Hasegawa, H. *Arsenic Biogeochemistry Affected by Eutrophication in Lake Biwa, Japan*; Institute for Chemical Research, Kyoto University: Kyoto, Japan, 1997; pp 14–15.

[47] Kuehnelt, D.; Goessler, W., *Organoarsenic Compounds in the Terrestrial Environment*. 2nd ed.; John Wiley: New York, 2003.

[48] Schaeffer, R.; Francesconi, K. A.; Kienzl, N.; Soeroes, C.; Fodor, P.; Varadi, L.; Raml, R.; Goessler, W.; Kuehnelt, D., Arsenic speciation in freshwater organisms from the river Danube in Hungary. *Talanta* 2006, *69*, 856–865.

[49] Koch, I.; Feldmann, J.; Wang, L.; Andrewes, P.; Reimer, K. J.; Cullen, W. R., Arsenic in the Meager Creek hot springs environment, British Columbia, Canada. *The Science of The Total Environment* 1999, *236*, 101–117.

[50] Leckie, J. O.; Appleton, A. R.; Ball, N. B.; Hayes, K. F.; Honeyman, B. D., *Adsorptive Removal of Trace Elements from Fly-Ash Pond Effluents Onto Iron Oxyhydroxide*. Electrical Power Institute: Palo Alto, CA., 1984.