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Arsenic Speciation in Organisms from two Large Shallow Freshwater Lakes in China

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Abstract This study measured the elemental and species concentrations of arsenic (As) in the water, sediments and food webs of two shallow Chinese freshwater lakes. Organic As species were widely detected in various organisms from the two lakes (60%–100% of the total). Among these organisms, dimethylarsinic acid (DMA) was predominant in most of the samples. The average concentrations and corresponding proportions were 0.59 mg/kg, 81% in fish; 3.24 mg/kg, 70.63% in zoobenthos; and 1.34 mg/kg, 79% in plants. The average concentrations and corresponding proportions of monomethylarsonic acid (MMA) and inorganic As were much lower, ranging from n.d. (not detected) to 1.94 mg/kg and from n.d. to 1.54 mg/kg, with an average proportion of 14 and 7.4%, respectively. In Lake Taihu, the mean As concentrations in different fish tissues were generally low and in the following order: eggs (0.47) < skin (0.62) < muscles (0.91) < gills (1.65) < livers (5.47) mg/kg. DMA occupied 75%–100% of the total As species, while MMA and inorganic As were much less prevalent.

Keywords Arsenic · Fishes · Macrophytes · Zoobenthos

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The element arsenic (As) ranks 20th in abundance in the earth's crust and is a toxic and carcinogenic element to humans and other organisms (Mandal and Suzuki 2002). There are numerous species of As that can exist in the environment, including inorganic arsenite (iAs^{III}) and arsenate (iAs^{V}) as well as organic compounds such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO). In biological samples, additional As species including arsenobetaine (AsB) and arsenocholine (AsC) are also frequently detected (Rahman and Hasegawa 2011). Arsenic and its compounds can cause damage to human organs, including the skin, bladder, lungs, brain, liver, kidneys and stomach, and can even cause cancer (Ng et al. 2003). Inorganic As species are frequently more toxic to humans, relative to organic arsenic compounds (Ng 2005). The presence of AsB and AsC in aquatic consumers is commonly associated with the ingestion of contaminated prey, and no general toxicity effects have been associated with exposure to these As species (Rahman et al. 2012).

Previous research has demonstrated that the primary As species in freshwater ecosystems include iAs^{III}, iAs^{V}, DMA and MMA (Rahman and Hasegawa 2011). Kaise et al. (1997) found that the major As species in fishes from the Hayakawa River was inorganic As (93%); Jankong et al. (2007) also reported that iAs^{V} was dominant in *Channa striata* collected from the Stuphan River. Shiomi et al. (1995) found that AsB prevailed in cultivated *Oncorhynchus mykiss*. Fish can ingest inorganic As (iAs) and transform it into MMA, DMA and TMAO via methylation of As. DMA can be sustained at relatively high proportions among the As species (Ciardullo et al. 2010). Šlejkovec et al. (2004) found that DMA accounted for 75% of the total As in *Lota lota* obtained from the Drava River in Slovenia. Previous work has demonstrated that As compounds tend to bioaccumulate to a greater extent in liver tissues, relative to muscle tissues (Jankong et al. 2007). Compared to marine organisms, the As speciation in freshwater organisms is more diverse and complicated (Rahman et al. 2012).

The aim of the present study was to evaluate As speciation in aquatic organisms, including phytoplankton, macrophytes, zoobenthos and fishes (including different tissues and organs) collected from Lake Taihu and Lake Dianchi, two large freshwater lakes in China. By comparing As speciation, we expected to expand our understanding of As speciation in freshwater organisms, especially in the cultivated fishes, which are the main source of protein harvested for human consumption from large lakes in China.

Materials and Methods

Lake Taihu and Lake Dianchi are two large shallow freshwater lakes in China. Taihu is located in the southern Jiangsu Province and northern Zhejiang Province and covers an area of 2338 km^2, while Dianchi, with an area of 292 km^2, is located in southwest of Kunming City in Yunnan Province. Both lakes are shallow freshwater lakes, with a mean depth of 1.9 and 5.12 m, respectively. In Lake Taihu, the concentrations of As have been measured as 1.39–5.65 µg/L and 4.66–10.85 mg/kg in water and sediments, respectively, while in Lake Dianchi, the corresponding values were 3.08–10.48 µg/L and 12.49–169.25 mg/kg, respectively (Zhang et al. 2013).

Samples were randomly collected at several locations along the shores of Lakes Taihu and Dianchi in September 2009 and December 2010, respectively (Fig. 1). Each sample was collected using 2–5 replicates. At each sampling location, macrophyte samples were hand-collected from a boat; an additional phytoplankton Cyanobacteria sample was collected using a phytoplankton net (nylon material, 64 µm pore size) in Dianchi because of the very high densities of Cyanobacteria on the sampling day. Zoobenthos and fish were collected using trawls. The fish were then dissected and separated into muscles, gills, livers, skin and

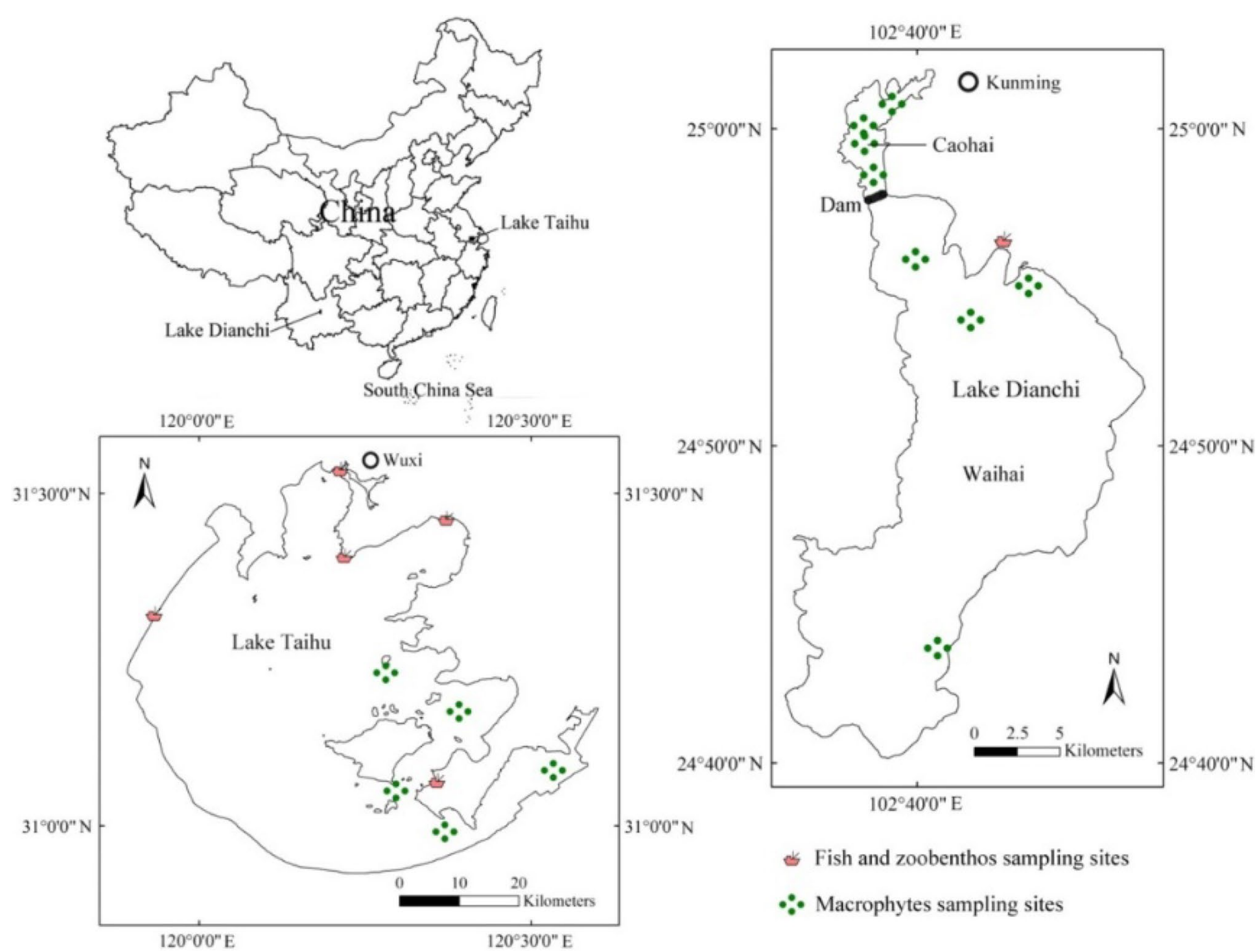

Fig. 1 Sketch map showing the location of the study area and sampling sites

eggs on site. All samples were washed several times with deionized water, stored in plastic bags and kept at 5°C in a refrigerator before being transported back to the laboratory. The samples were quickly transported in boxes covered with dry ice. In the laboratory, the samples were further freeze-dried, minced in an agate mortar and manually ground to homogeneity. The powdered samples were preserved in closed polyethylene tubes at −10°C in a refrigerator before performing the analyses.

For the determination of total As, 100 mg of each powdered sample was accurately weighed (±0.5 mg) into a 25 mL graduated test tube and 4 mL HNO_3 was added. Each tube was left overnight, then digested in a multi-block electric hot plate at 80°C for 1–2 h without the glass stopper. Approximately 1 mL H_2O_2 was added to the tube during the digestion, and then the solutions in the tube were evaporated at 140°C until 1–2 mL remained. After cooling, the solutions were transferred to a 20 mL tube and brought to volume with deionized water (18.2 MΩ cm). An aliquot of this solution was added to a composite reductive solution containing 2.0% ascorbic acid, 2.0% thiourea, and 5% HCl. The total As was measured by a hydride generation atomic fluorescence spectrometer (HG-AFS, AFS8230, Beijing Titan Co., China). All reagents (Sinopharm Chemical Reagent Beijing Co., Ltd) used were analytical grade or better.

For As speciation analysis, 400 mg of each powder sample was weighed into a 50 mL centrifuge tube. Then, 15 mL of a methanol/water mixture (1:1) was added to the tube, which was ultrasonically extracted for 20 min, and the extracts were centrifuged at 8000 *g* for 15 min. The supernatant was subsequently removed. This procedure was repeated three times, and the supernatants were then combined. Methanol was removed from the extractions using a pressured N_2 gas-blowing concentrator. The extractions were concentrated to less than 20 mL and brought to 25 mL using Milli-Q water. The extracts were then stored in a refrigerator at 4°C and filtered using 0.22 µm filter membranes prior to analysis. Arsenic speciation was determined using high performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICP-MS). An anion column (Hamilton PRP-X100 150×4.6 mm, 3 µm) with a mobile phase of 20 mmol L^{-1} $NH_4H_2PO_4$ (pH 5.78) was used for the As species chromatograph, while As was monitored as ^{91}AsO isotopes with an Elan ICP-MS instrument in DRC mode (PerkinElmer, USA).

For QA/QC procedures, two reference materials from scallops (GBW10024) and shrub branches (GBW07603) (China Reference Materials Center) were used, and the average recoveries were 100.18 ± 2.14 and 112.71 ± 9.98%. Representative samples of phytoplankton, macrophytes, zoobenthos and fishes were also tested for additional iAs^{III}, iAs^{V}, MMA, DMA, AsB and AsC; however, no AsB and AsC were detected (data not shown). Therefore, only the former four As species were tested for all remaining samples. Standard solutions of As species, including iAs^{III} (GBW08667), iAs^{V} (GBW08666), MMA (GBW08668), and DMA (GBW08669) (China Reference Materials Center), were used to check the spiked recoveries, which were 61% for iAs^{III}, 78% for iAs^{V}, 117% for DMA, and 93% for MMA. The detection limits for iAs^{III}, iAs^{V}, MMA and DMA were 0.41, 0.30, 0.66 and 0.56 µg/L, respectively.

The concentrations of total As and the speciation of As in various aquatic organisms were presented as the mean values with standard deviations, while the corresponding values in a specific organism or its tissues/organs were presented as the mean values. The statistical analyses were conducted using SPSS software. The Student *t* test was performed for comparison of As concentrations between two datasets, e.g., macrophytes from Lakes Taihu and Dianchi, while an ANOVA test was used to analyse the difference among more than two datasets, e.g., As concentrations among various organs/tissues from fishes in Lake Taihu.

Results and Discussion

The concentrations and speciation of As in the samples from various aquatic organisms are presented in Table 2. The highest As concentration was recorded in the phytoplankton sample (11.71 mg/kg). Four As species were detected in the phytoplankton Cyanobacteria from Lake Dianchi, with concentrations in the decreasing order of MMA (5.54 mg/kg), DMA (1.89 mg/kg), iAs^{III} (0.52 mg/kg), and iAs^{V} (0.08 mg/kg) (Fig. 2). This is not in agreement with previous works. In three As-contaminated Canadian freshwater lakes, As in phytoplankton primarily consisted of iAs^{V}, which accounted for 92%–98% of the total As, while no organoarsenic species were detected (Caumette et al. 2011). The difference between our results and previous works may lie in the As levels in ambient waters. Higher levels in waters may trigger greater accumulation of iAs^{V} and its rapid transformation to iAs^{III}, which is then released into waters, leaving no opportunity for iAs^{III} to be transformed into organoarsenic within cells and tissues (Knauer and Hemond 2000).

No difference was found in the average concentrations of As between macrophytes from the two lakes (5.55 ± 4.39 and 5.34 ± 4.53 mg/kg in Taihu and Dianchi, respectively) (Table 2). Inorganic As was found in less than half of the tested plant samples, the concentrations of the iAs were also much lower than those of DMA and MMA (Fig. 2). DMA was the main As species in all macrophytes, with a mean percentage of 75 and 63% in each lake (Table 2). This observation is in contrast with that observed in the As contaminated Lake Moria, Canada. There, the As in the macrophytes was mainly iAs^{V} (up to 92% in proportion)

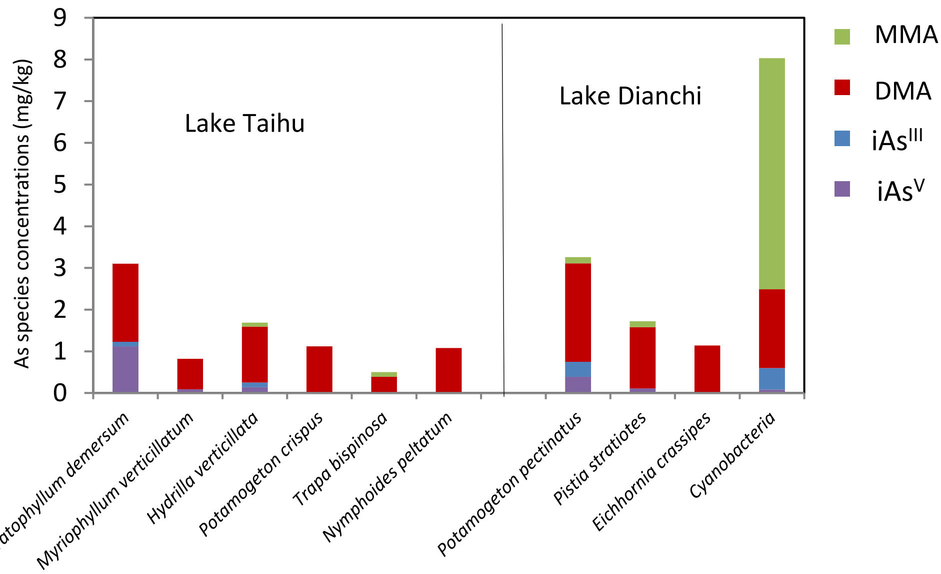

Fig. 2 Arsenic species concentrations in macrophytes and one phytoplankton Cyanobacteria of Lake Taihu and Lake Dianchi; each sample has two to three replicates except Cynobacteria, which is a composite

(Zheng et al. 2003). In general, macrophytes have the capability to take up iAs^V, quickly reduce it to iAs^{III}, methylate it to DMA and MMA, and excrete it to ambient waters as DMA (Rahman and Hasegawa 2011). Macrophytes that possess this capacity should be expected to accumulate more organoarsenic than inorganic As species, which agrees well with the results of the current study. The contradictions between previous results and this study could stem from the fact that the macrophytes were growing in an area with higher ambient As levels in the previous studies (75–140 μg/L) compared to those in our study (3.04–9.65 μg/L). The macrophytes could take in iAs via surface physical adsorption, resulting in higher proportions of iAs detected in plant bodies in previous studies as compared with the conditions in the present study (Zheng et al. 2003; Robinson et al. 2006; Zhang et al. 2013). These differences suggest that macrophytes growing in low As level environments tend to transform the inorganic As into organoarsenic in their bodies.

In zoobenthos from Lake Taihu, DMA was the dominant As species, occupying an average proportion of 72.26% of the extracted As (Table 2). In Lake Dianchi, *Caridina dianchiensis* contained high proportions of MMA (50%) and iAs^{III} (40%). The highest concentration of DMA, 8.63 mg/kg, was recorded in *Anodonta woodiana*, while the concentration of DMA in the other five zoobenthos in Lake Taihu was approximately 2.5 mg/kg. Only DMA and MMA were detected in *Macrobrachium nipponensis* and *Exopalaemon modestus* from Lake Taihu. However, in mollusks, i.e., *Novaculina chinensis, Bellamya aeruginosa, Corbicula fluminea*, and *Anodonta woodiana*, a small amount of inorganic As, primarily iAs^{III}, was observed (Fig. 3). These results are remarkably different with previous findings regarding freshwater zoobenthos. For instance, arsenosugars and AsB were the dominant species in mussels from the Danube River in Hungary, with arsenosugars comprising up to 96% of the total extractable As (Schaeffer et al. 2006). AsB occupied 75% of total As in *Macrobrachium nipponense* from Hayakawa River in Japan (Miyashita et al. 2009). Various studies have demonstrated that AsB in organisms does not come from the transformation of As in the bodies but rather from the ingestion of AsB-contaminated prey. In this study, both Lake Taihu and Lake Dianchi had no sources of potential dietary AsB, hence the absence of AsB in the collected samples.

In this study, the As speciation of freshwater fishes revealed remarkable differences among the fish species (Fig. 4). DMA was the dominant As species in most fishes from Lakes Taihu and Dianchi, with a proportion of 75%–100% depending on the tissue (Table 2). Minor amounts of MMA were detected in *Aristichthys nobilis* and *Ophiocephalus argus* in Taihu as well as *Cyprinus carpio* and *Erythroculter ilishaeformis* in Dianchi. In the muscles of certain fish, i.e., *Cyprinidae* and *Pelteobagrus fulvidraco* from Taihu and *Cyprinidae, Hypophthalmichthys molitrix*, and *Cyprinus carpio* from Dianchi, DMA was prevalent. No iAs^V was observed in all fish species, but minor levels of iAs^{III} were present (Fig. 4). Previous studies have demonstrated that higher trophic level organisms have a greater ability to methylate As (Takayoshi et al. 1994; Watanabe et al. 2008). The present study has groups of two herbivorous, three omnivorous and eight carnivorous fishes (Table 1). In Lake Taihu, two herbivorous feeders (consumers at a lower trophic level) were sampled, including *Hypophthalmichthys molitrix*, which primarily feeds on phytoplankton, and *Ctenopharyngodon idella*, which generally consumes detritus and plants. Both organisms were found to contain DMA only. In the omnivorous group, no

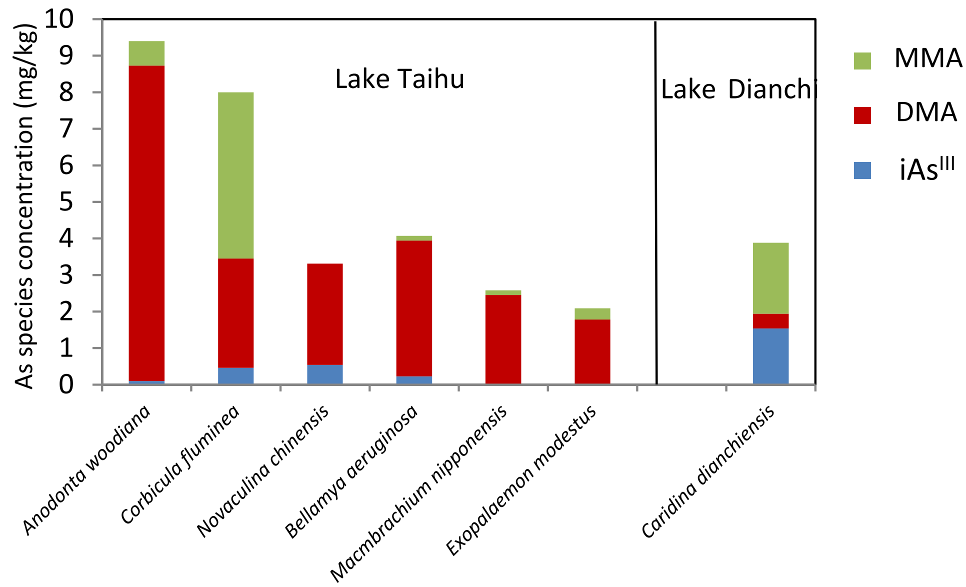

Fig. 3 Arsenic species concentrations in zoobenthos of Lake Taihu and Lake Dianchi; each sample has three to five replicates

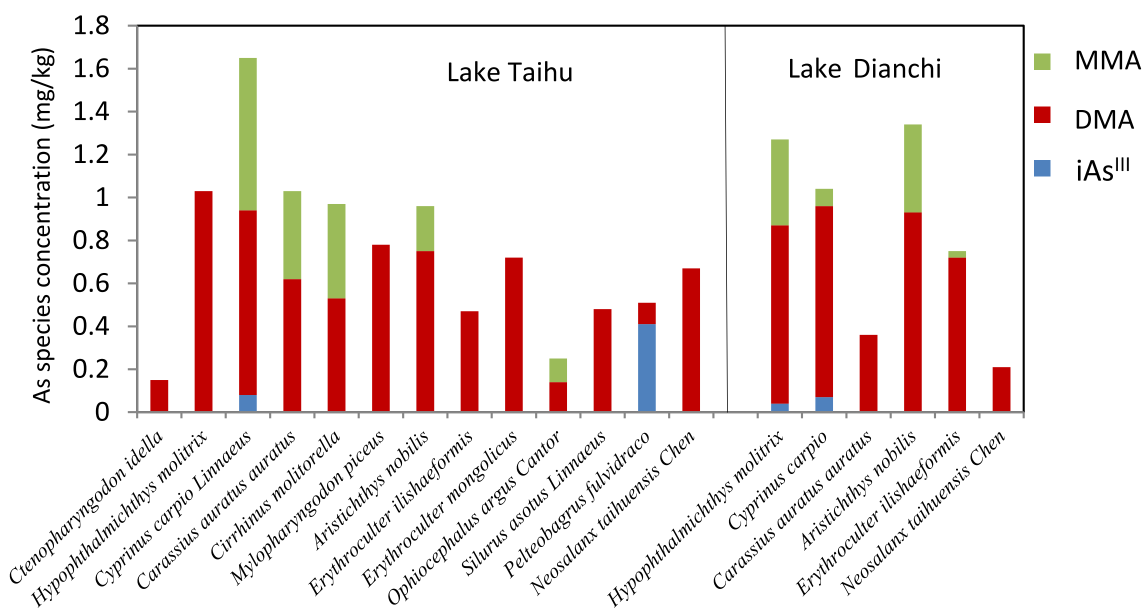

Fig. 4 Comparison of As speciation found in fish muscle samples from Lake Taihu and Lake Dianchi. Each sample has three replicates

Table 1 Feeding habits and food sources of the fishes sampled in this study

Food habits	Diet	Species
Herbivorous	Phytoplankton	*Hypophthalmichthys molitrix*
	Detritus and plants	*Ctenopharyngodon idella*
Omnivorous	Plankton, insects, plant and detritus	*Cyprinus carpio Linnaeus, Carassius auratus auratus, Cirrhinus molitorella*
Carnivorous	Zooplankton, small fishes	*Aristichthys nobilis*
	Benthic invertebrates	*Mylopharyngodon piceus, Pelteobagrus fulvidraco*
	Fishes, invertebrates	*Silurus asotus Linnaeus* and others

Table 2 Various As species detected and their proportions in the aquatic organisms collected from Lake Taihu and Lake Dianchi

Organisms	Lake	Tissues	Total As (mg/kg)	Proportions of As species(%)			
				MMA	DMA	iAs^{III}	iAs^{V}
Phytoplankton	Dianchi		11.71	69.00	0.10	6.48	23.54
Macrophytes	Taihu(n = 10)		5.55 ± 4.39^{A}	5.25 ± 8.82	74.55 ± 15.20	1.83 ± 2.76	9.92 ± 14.02
	Dianchi(n = 8)		5.34 ± 4.53^{A}	22.86 ± 32.54	62.92 ± 33.18	4.58 ± 5.39	4.97 ± 5.52
Zoobenthos	Taihu(n > 10)		12.32 ± 9.44	15.49 ± 21.34	72.26 ± 21.64	5.00 ± 6.23	n.d
	Dianchi(n = 3)		4.33	50.00	10.31	39.69	n.d
Fishes	Taihu(n > 30)	muscle	0.91 ± 0.52^{cA}	15.32 ± 20.43	74.84 ± 27.10	7.68 ± 22.23	n.d
		skin	0.62 ± 0.37^{c}	n.d	100	n.d	n.d
		gill	1.65 ± 0.71^{b}	n.d	86.75 ± 10.54	4.49 ± 10.54	n.d
		egg	0.47 ± 0.27^{c}	n.d	100	n.d	n.d
		liver	5.47 ± 3.27^{a}	12.19 ± 13.91	74.90 ± 12.96	5.62 ± 7.56	n.d
	Dianchi(n > 20)	muscle	0.97 ± 0.42^{A}	12.66 ± 14.81	75.97 ± 15.45	1.81 ± 2.79	n.d

n.d. not detected. As species are the extracted concentrations by methanol/water for speciation analysis, while proportions of As species are the percentage of the total As that each species constitutes. Data are presented as the mean ± SD.: this is a composite sample. The different upper case letters after data of "Total As" indicate significant differences within the same group of organism, while the lower case letters denote significant differences among various organs of fishes from Lake Taihu

difference was observed in the constitution of As species: in *Cyprinus carpio Linnaeus, Carassius auratus auratus, and Cirrhinus molitorella*, all of which primarily feed on plankton, insects, plant and detritus, the proportions of As species are similar, in the range of 52%–60% and 39%–45% for MMA and DMA, respectively (data not shown). In the carnivorous fishes (top predators in a relatively long food chain) only methylated As species are found, except in the case of *Pelteobagrus fulvidraco*. The As speciation in fishes from Lake Dianchi differed compared to those from Lake Taihu. For example, the As species found in *Hypophthalmichthys molitrix* from Diachi were DMA, MMA and iAs^{III}, while only DMA was found in those from Taihu. Differences were found in As speciation in *Carassius auratus auratus* between the two lakes (Fig. 4). In this study, As speciation differs between fishes of different trophic levels and between fishes from different lakes, suggesting dietary sources and the ambient environment determine, to a large extent, the As speciation in freshwater fishes. Similarly, Jankong et al. (2007) reported that DMA accounted for more than 90% of the total As in the muscles of *Channa striata* collected from heavy As-contaminated waters in southern Thailand, while inorganic As accounted for less than 2%. In fish muscles from the Yellowknife estuary, Canada, high percentages of inorganic As species were identified, while the organoarsenic species, i.e., MMA and DMA, occupied 11%–25%, and AsB accounted for approximately 10% of the total As (Rosemond et al. 2008).

In Lake Taihu, As species and their concentrations in various tissues and organs of fishes, such as muscles, skin, gills, eggs and livers, were analysed. The As levels followed the increasing order of livers > gills > muscles > skin > eggs (Table 2). This is consistent with a previous study by Mason (2002), who reported that As concentrations in the organs responsible for detoxification (such as liver) were relatively high. As species may bioaccumulate more in the livers and gills of fishes as opposed to the muscles (Laurence et al. 2009). In this study, As in the collected fish skin, gills and eggs was primarily composed of DMA. Concentrations ranged from 0.1 mg/kg to 0.55 mg/kg, except in the gills of *Pelteobagrus fulvidraco*, where a low concentration of iAs^{III} (0.17 mg/kg, 30%) was detected. MMA and iAs^{III} were also found in the livers and muscles but at concentrations much lower than that of DMA (Fig. 5). In livers of fishes, the dominant As species, DMA, generally ranged 0.71–0.91 mg/kg in most of the samples. These results are in agreement with previous studies. Fishes from southern Thailand were reported to contain DMA as high as 92% in livers (Jankong et al. 2007). The DMA in livers of fishes from Yellowknife in Canada comprised much higher DMA (12%–82%) than the other As species (Rosemond et al. 2008). These results suggest that in freshwater fishes, DMA is the most common As species, and the liver is the primary location where methylation occurs.

In summary, four As species, including organic DMA and MMA and inorganic iAs^{III} and iAs^{V}, were detected in organisms (phytoplankton, macrophytes, zoobenthos and fishes) collected from two large freshwater lakes, Taihu and Dianchi, in China. MMA was widespread in phytoplankton, and the occurrence of DMA and iAs^{III} was low. For macrophytes from both lakes, the most abundant As species was DMA, while iAs was less common. For zoobenthos, DMA was dominant in Lake Taihu, except in *Corbicula fluminea*, while MMA and iAs^{III} were

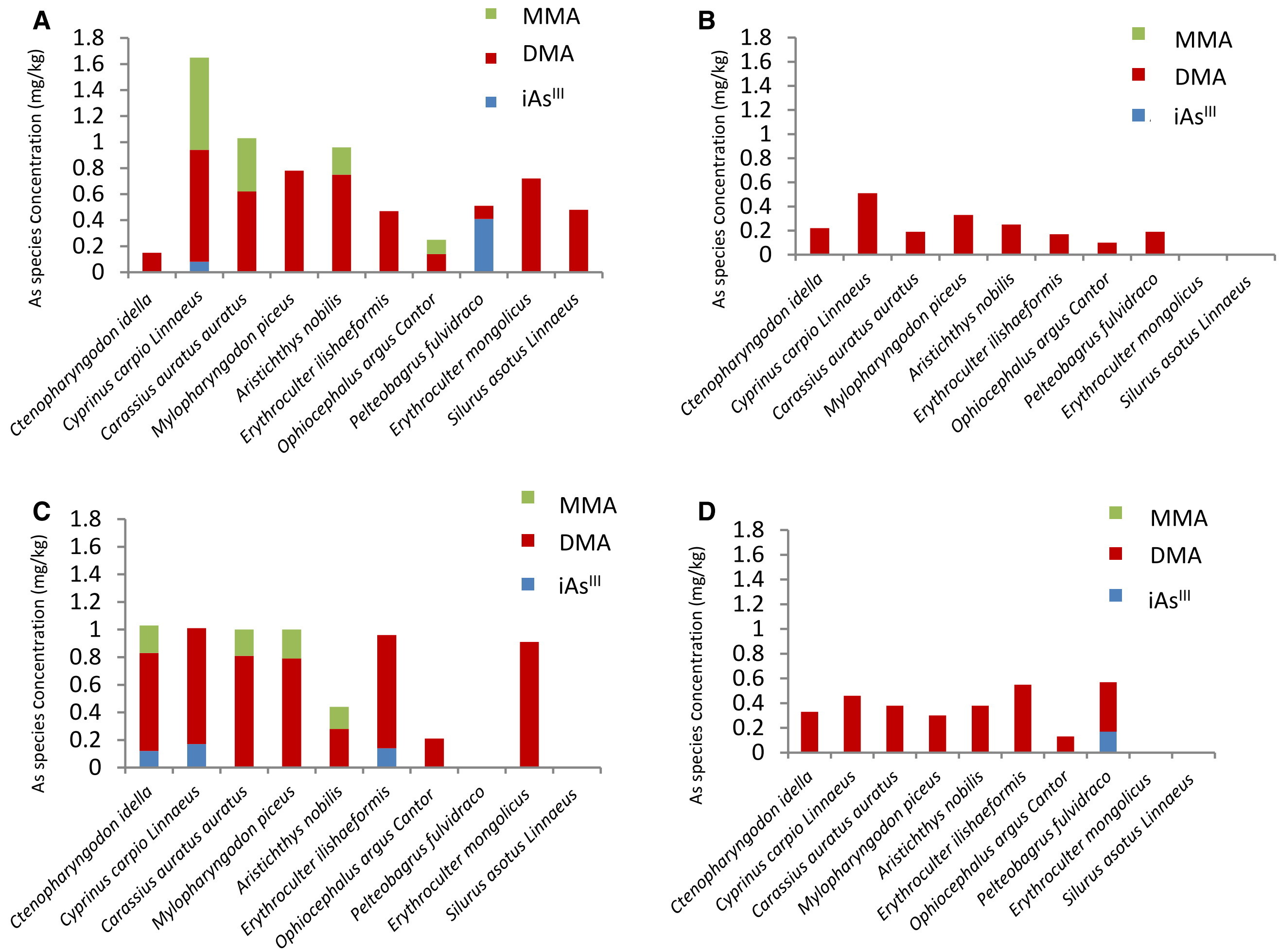

Fig. 5 Arsenic species quantified in Lake Taihu fish **a** muscles, **b** skin, **c** livers and **d** gills

equivalent as the two major As species in Lake Dianchi. In all fishes from the two lakes, DMA and MMA were dominant, while only minor levels of iAs^{III} were observed. Arsenic concentrations in the organs/tissues of the fishes followed the decreasing order of livers, gills, muscles, skin and eggs. In fish skin, gills and eggs, DMA prevailed; in fish livers, MMA and iAs^{III} were found in equivalent proportions, along with minor levels of DMA. These results indicate that the liver was an important organ for As methylation and metabolism in fishes. The occurrence of DMA and MMA along with inorganic As, mainly iAs^{III}, in Lakes Taihu and Dianchi, suggests that the aquatic organisms from large freshwater lakes can methylate As to the stage of DMA to various extents.

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