Arsenic Variation in Two Basins of Lake Dianchi

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Received: 11 December 2011/Accepted: 25 January 2012/Published online: 15 February 2012 © Springer Science+Business Media, LLC 2012

Abstract The spatial variation of arsenic, including arsenic speciation changes under the influence of water quality parameters in lake Dianchi, China was investigated. The water quality parameters were found to differ between the two basins of the lake (Caohai vs. Waihai), consistent with the eutrophic status. Arsenic in Caohai was greater than that in Waihai, with average values as 9.45 and 6.68 μ g L⁻¹, respectively. Expect redox potential, correlation between various water quality parameters and arsenic forms were found, supporting the hypothesis that arsenic partition in suspended particulates in Lake Dianchi was driven mainly by biota factor.

Keywords Arsenic · Forms · Arsenite · Water quality parameters

Arsenic (As) is a ubiquitous but toxic element. The range of background As levels in water is $0.1\text{--}80~\mu g~L^{-1}$. However, the elevation of As in groundwater due to the reduction and dissolution of As-containing minerals in alluvial strata occurs in some areas of the world, causing serious detriment to human health, mainly in India, Bangladesh and China (Mandal et al. 2007). Arsenic in drinking water has been legally restricted to within

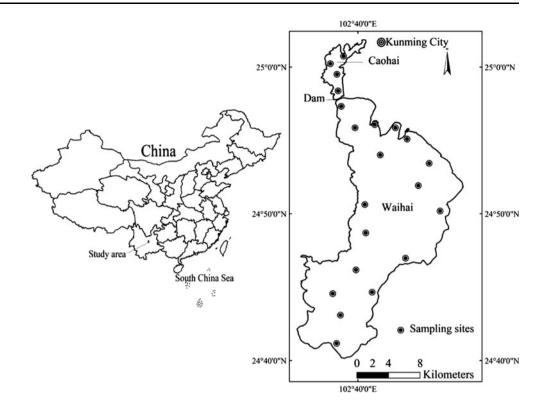
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N. Zhang Graduate University of the Chinese Academy of Sciences, Beijing 100049, China 10 µg L⁻¹ by the WHO and China to protect human health (WHO 2003). Lakes act as watershed sinks, receiving both natural and anthropogenic sources of As (Nikolaidis et al. 2004). Arsenic in the water column is equilibrated between suspended particulates and water, with sorption and desorption reactions. These reactions are influenced by various factors, such as changes of temperature, pH and redox potential, organic degradation and other reduction reactions (Couture et al. 2010). The sorption and desorption of As in lake waters have been found to be concomitant with As oxidation/reduction in the outer sphere of particulates, causing the sorption/desorption of As between the particulate and water phases (Gao et al. 2006).

Dianchi, the sixth largest fresh water lake in China, is located near Kunming city, Yunnan province. The lake covers an area of 308.6 km², with an average depth of 4.4 m and an elevation of 1,887.4 m, and is separated by a dam in the north, forming two basins as Caohai and Waihai (Fig. 1). The lake is in a hypereutrophic status, with severe algae blooms occurring annually over the past two decades. The nitrogen and phosphorus contents were found to decrease gradually from the north to south, which is consistent with the eutrophic status of the lake (Hu et al. 2006). Arsenic is a chemical analogue to phosphorus, and the relationship between phosphorus with eutrophication and the interaction of As and phosphorus has been documented in many lakes (Martin and Pedersen 2004; Rahman et al. 2008). Nevertheless, the As behavior in Lake Dianchi, especially its relationship with eutrophication, has rarely been documented to date. An investigation of As in Lake Dianchi may be helpful in understanding As behavior in hypereutrophic lakes. The objective of this study was to elucidate the spatial variation of As in relation to the eutrophic status of Lake Dianchi.



Fig. 1 Map showing location of lake Dianchi and sampling sites



Materials and Methods

Water samples were collected at 21 sites covering the whole area of Lake Dianchi in November 2010. At each site, a portable multiparameter instrument was used in situ to monitor the water quality factors at approximately 10 cm of the depth near the surface, including temperature (T), dissolved oxygen (DO), total dissolved solids (TDS), redox potential (Eh) and electrical conductivity (EC). Water samples from the surface (20–30 cm) and bottom (near the bottom at each site) of the lake were collected at each site using a water sampler. The water was filtered through a 0.45-µm film to obtain the dissolved water samples. These unfiltered and filtered water samples were brought back to the lab for analysis of the total and dissolved As, respectively. In addition, a cartridge for the separation of arsenic in the III and V valences was used in situ. Arsenic measured in such filtered waters through this cartridge was regarded as As in the III valence (arsenite, As(III)) (Meng and Wang 1998).

Arsenic determination as well as the QA/QC procedure were performed using the protocols described in our previous study in Lake Taihu (Wei et al. 2011). The average recovery for As determination in this study was $102.3\% \pm 13.6\%$.

Student's t tests were used to compare As in various forms, the water quality factors and As partition coefficients between Caohai and Waihai and between surface and bottom layers. Correlation analysis was performed to

Table 1 Arsenic concentrations, partition coefficients and some selected water quality factor values in lake Dianchi

	Caohai (n = 4)	Waihai (n = 17)	Dianchi (n = 21)							
pН	$7.59 \pm 0.55^{\mathrm{b}}$	9.17 ± 0.76^{a}	8.87 ± 0.95							
Eh	70.8 ± 15.2^{a}	25.1 ± 42.7^{b}	33.8 ± 42.8							
DO	3.69 ± 3.16^{a}	7.02 ± 1.88^a	6.39 ± 2.47							
TDS (mg/L)	293.0 ± 15.2^{a}	215.8 ± 14.6^{b}	231.2 ± 34.8							
EC (µs/cm)	523 ± 33^a	$378 \pm 77^{\rm b}$	407 ± 92							
Total As (µg/	(L)									
Surface	9.45 ± 1.69^{a}	6.68 ± 1.72^{b}	7.21 ± 2.01							
Bottom	9.84 ± 2.37^{a}	6.72 ± 1.64^{a}	7.31 ± 2.14							
Dissolved As	$(\mu g/L)$									
Surface	8.23 ± 1.75^{a}	4.00 ± 0.69^{b}	4.81 ± 1.93							
Bottom	8.76 ± 1.59^{a}	4.37 ± 0.79^{b}	5.21 ± 2.00							
As(III) (μ g/L)										
Surface	1.29 ± 0.77^{a}	0.36 ± 0.27^{b}	0.54 ± 0.54							
Bottom	3.12 ± 2.50^{a}	1.67 ± 0.90^{a}	1.95 ± 1.39							
Dissolved/tota	al As (%) [§]									
Surface	87.7 ± 14.3	62.3 ± 14.2	67.1 ± 17.2							
Bottom	91.4 ± 17.5	68.3 ± 20.3	72.7 ± 21.5							
As(III)/total A	As (%) ^{§§}									
Surface	45.9 ± 29.6	23.7 ± 9.4	27.9 ± 16.8							
Bottom	31.9 ± 22.4	26.6 ± 16.8	27.2 ± 17.2							

 $^{\$, \$\$}$ The percentages of dissolved or As(III) to total As, respectively. Different lower case letters indicate significant difference of the parameters between Caohai and Waihai (p < 0.05)



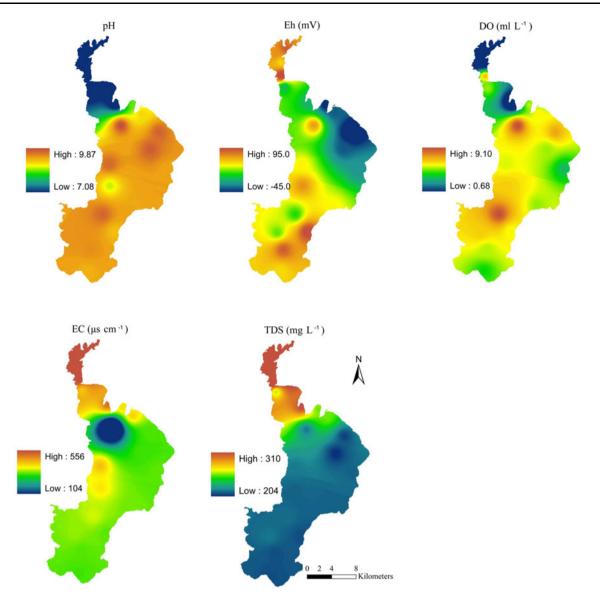


Fig. 2 Spatial variation of selected water quality factors, each map was generated based on data from 21 sites covering the whole area of Dianchi using inverse distance weighted (IDW) interpolation method in ArcGIS software

reveal the relationship between As in various forms and the various water quality parameters monitored in this study. The statistics were computed using SPSS software.

Results and Discussion

A remarkable difference in pH was observed between Caohai and Waihai; the waters in Caohai were approximately neutral, whereas they were quite alkaline in Waihai (Table 1; Fig. 2). In addition, the EC values in Caohai were greater than in Waihai (Table 1), while the DO values, although not significant, were generally lower in Caohai than in most parts of Waihai (Table 1; Fig. 2). The lower pH but higher EC in Caohai may indicate a stronger effect of anthropogenic

activities than in Waihai. Several studies have confirmed that the pollution status in Caohai is generally worse than that in Waihai (Hu et al. 2006; Yang et al. 2010). Yang et al. (2010) conducted a spatial analysis of the eutrophication pattern in Lake Dianchi using 4 continuous years (2003–2007) of water quality data. They found that eutrophication in Lake Dianchi gradually increased from south to north, with Caohai evidently worse than Waihai, demonstrating the evident influence of anthropogenic activities. Shi et al. (2010) also found that the total suspended particulates were composed mainly of organic suspended matter (OSM), with 80% of the OSM to TSM. These findings indicate that the particulates in Lake Dianchi are mainly composed of biota-containing grains. In this study, a positive relationship between pH and DO was found (Table 2), suggesting the water properties in Lake



Table 2 Correlation coefficients of arsenic contents in various forms and water quality factors in lake Dianchi (n = 21)

	pН	Eh	DO	TDS	EC	STAs	BTAs	SSAs	BSAs	SAsIII	BAsIII
рН											
Eh	NS										
DO	0.779**	NS									
TDS	-0.608**	NS	-0.510*								
EC	-0.557**	NS	NS	0.715**							
STAs	NS	NS	NS	NS	NS						
BTAs	NS	NS	NS	NS	NS	0.501*					
SSAs	-0.527*	0.527*	NS	0.685**	0.521*	0.652**	0.616**				
BSAs	-0.507^{*}	NS	-0.458*	0.739**	0.555**	0.697**	0.643**	0.892**			
SAsIII	-0.501*	NS	NS	0.591**	0.457*	0.443*	0.701**	0.659**	0.650**		
BAsIII	NS	NS	NS	NS	NS	NS	NS	NS	NS	0.508*	

Correlation are based Pearson test. **,* Correlation is significant at the 0.01 and 0.05 level (2-tailed), respectively. NS not significant STAs total arsenic in surface water, BTAs total arsenic in bottom water, SSAs dissolved arsenic in surface water, BSAs dissolved arsenic in bottom water, SAsIII As(III) in surface water, BAsIII As(III) in bottom water

Dianchi are strongly driven by biotic factors. Because Dianchi is a hypereutrophic lake, the degradation of biota can release large quantities of organic matter to the waters, resulting in a substantial depletion of oxygen and a decrease of the pH.

Arsenic in Lake Dianchi was generally lower than the regulatory limit for drinking water in China. Anthropogenic activities around the lake, especially Caohai, are intensive, so industrial, agricultural and domestic wastewater contribute to the elevation of As in the lake to some extent, as seen with the higher mean total As content of nearly $10 \ \mu g \ L^{-1}$ in Caohai compared with $7 \ \mu g \ L^{-1}$ in Waihai (Table 1). The results are generally consistent with the pollution status of Lake Dianchi (Hu et al. 2006).

Arsenic levels in total and dissolved forms differed little between the surface and bottom layers, whereas large differences in As (III) were observed, both between water layers and between the two basins, with As at the bottom greater than at the surface, and with the content in Caohai generally greater than in Waihai (Table 1; Fig. 3). The results are consistent with the correspondingly greater proportions of dissolved and As (III) to total As contents in Caohai (Table 1). Because As (III) is more labile than As (V), it can easily be desorbed from the particulates and enter into water as the dissolved form (Couture et al. 2010). As (III) accounted for nearly half of the total As at the surface of Caohai. At the bottom of Caohai, and in both layers of Waihai, the proportions were much lower, within the range of 24%-32%, suggesting the As reduction in lake Dianchi was strong, with Caohai generally stronger than Waihai.

The higher As (III) level in Caohai was also consistent with the lower DO and pH, whereas the TDS and EC values were higher than those in Waihai (Figs. 2, 3). Because

eutrophication is higher in Caohai than in Waihai (Yang et al. 2010), As (V) tends to be reduced to As (III) concomitantly with the degradation of biota-containing particulates in Caohai, which can induce anaerobic conditions only in the outer sphere of the particulates (Lievremont et al. 2009). The low DO with high As (III) in Caohai and the southern edge of Waihai was consistent, whereas inconsistency was seen in low Eh with low but not high As (III) in these two lake areas (Figs. 2, 3), further suggesting that biotic degradation, but not the redox potential of the water, determines the As reduction in the lake. Previous studies have also found that, in some conditions, the relative proportions of As(III) and As(V) were largely determined by the abundance and species of biota present in lake and estuary waters, whereas the redox potential exerted little impact on As speciation (Cullen and Reimer 1989).

The various forms of arsenic (total, dissolved and As(III)) all demonstrated a close relationship with each other (Table 2), suggesting that changes in As speciation happened mainly in the particulates in Lake Dianchi. The absence of correlation between Eh and various As forms exclude that the As partition in lake Dianchi was influenced by the redox potential in lake waters.

Great proportions of dissolved As (62%–91%) were found in lake Dianchi, suggesting the As in Lake Dianchi is quite labile. The As partition between suspended particulates and the water largely determines the bioavailability of As to fish and other organisms in lakes (Cantwell et al. 2002). The TSM contents were reported to be much lower than those in lake Taihu, and the percentage of OSM in lake Dianchi was much higher than that in lake Taihu, demonstrating again that the OSM in the particulates, being composed primarily of biota (Sun



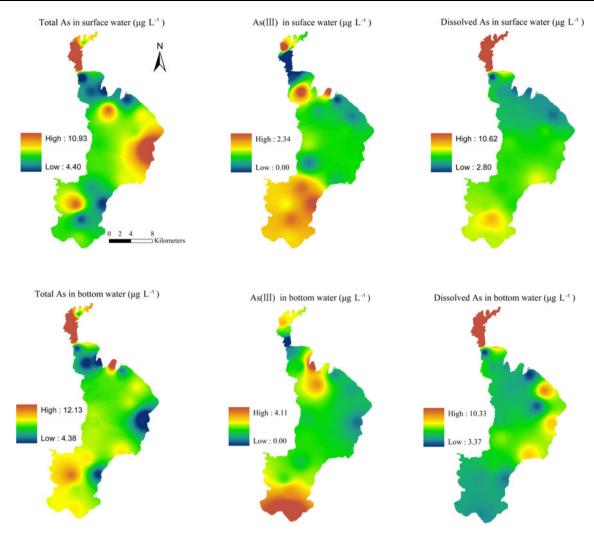


Fig. 3 Spatial variation of total, dissolved and trivalent As at surface and bottom water in lake Dianchi, each map was generated based on data from 21 sites covering the whole area of Dianchi using inverse distance weighted (IDW) interpolation method in ArcGIS software

et al. 2007; Shi et al. 2010), possessed weaker sorption capabilities compared with the inorganic mineral phases in the particulates.

In summary, remarkable differences in water quality parameters (i.e., pH, Eh, TDS and EC) were found between the two basins of Lake Dianchi, reflecting the different eutrophic status of the two basins. Except for redox potential, the As variations were consistent with the differentiation of one or more of the water quality parameters in the lake; in addition, correlations were found between the water quality factors and various As forms, corroborating that As sorption—desorption is driven mainly by biota-induced anoxia processes in Lake Dianchi.

Acknowledgments This study was financially supported by the Major State Basic Research Development Program of China (973 Program) (No. 2008CB418201). We thank Mr. Hailong Wen and Ms. Zhaofeng Ge for their assistance in the field surveys.

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