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Metals in sediment/pore water in Chaohu Lake: Distribution, trends and flux

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Abstract

Nine metals, Cd, Cu, Ni, Pb, As, Cr, Zn, Fe, and Mn in sediment and pore water from 57 sampling sites in Chaohu Lake (Anhui Province, China) were analyzed for spatial distribution, temporal trends and diffuse flux in 2010. Metals in the surface sediment were generally the highest in the western lake center and Nanfei-Dianbu River estuary, with another higher area of As, Fe, and Mn occurring in the Qiyang River estuary. Metal contamination assessment using the New York sediment screening criteria showed that the sediment was severely contaminated in 44% of the area with Mn, 20% with Zn, 16% with Fe, 14% with As, and 6% with Cr and Ni. An increasing trend of toxic metals (Cd, Cu, Ni, Pb, As, Cr, Zn) and Mn with depth was shown in the western lake. Compared with metal content data from the sediment survey conducted in 1980s, the metal content of surface sediment in 2010 was 2.0 times that in the 1980s for Cr, Cu, Zn, and As in the western lake, and less than 1.5 times higher for most of the metals in the eastern lake. Among the metals, only Mn and As had a widespread positive diffuse flux from the pore water to overlying water across the whole lake. The estimated flux in the whole lake was on average 3.36 mg/(m^2·day) for Mn and 0.08 mg/(m^2·day) for As, which indicated a daily increase of 0.93 μg/L for Mn and 0.02 μg/L for As in surface water. The increasing concentration of metals in the sediment and the flux of metals from pore water to overlying water by diffusion and other physical processes should not be ignored for drinking-water sources.

Key words: toxic metal; spatial distribution; contamination assessment; temporal trends; pore water; diffuse flux

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Introduction

Chaohu Lake (Anhui Province, China), a drinking-water source for Hefei City and Chaohu City, is currently suffering an outbreak of frequent cyanobacterial blooms (Shang and Shang, 2005). Many researchers have studied the eutrophication problem, and showed that the rapid development of industry, expansion of cities and intensified agriculture produced increasing industrial wastewater and domestic sewage as well as runoff, and caused eutrophic spatial heterogeneity in Chaohu Lake (Gao and Zhang, 2010; Zhou and Gao, 2011; Yu et al., 2011; Zhang and Shan, 2008a). The presence of toxic metals, which may be brought in by rivers along with nutrient input, can act as important indices for drinking water sources. Since metals can be removed from the water column efficiently by sedimentation processes, lake sediment cores are frequently used as archives to provide insight into metal pollution (Foster and Charlesworth, 1996; Von et al., 1997). The sediment contaminated with metals not only has potential impact on benthic organisms or humans by bioaccumulation along the food chain (Bryan and Langston, 1992), but also serves as a diffuse source of metals to the overlying water in some cases (Eggleton and Thomas, 2004).

Some studies in Chaohu Lake referenced metal enrich-

ment factors and geo-accumulation indexes to highlight the human contamination (Zan et al., 2011; Liu et al., 2012). However contamination is not simply enrichment of foreign substances, but harmful impacts to some organisms, species and community (US EPA, 1998). The New York sediment screening criteria were a technical guidance established to identify areas of sediment contamination and to make a preliminary assessment of the risk to human health or aquatic life (Gorge and John, 1999). With the screening level approach, the total metal concentrations are correlated directly to a measurable ecological impact based on observed effects from field studies. Background concentrations were not considered, because the fact that metal concentrations naturally occur in sediment does not mean they do not cause adverse ecological effect.

The diffuse fluxes across the sediment-water interface are of concern for many researchers. The *in situ* passive pore water sampling methods of diffusive equilibrium in thin-films (DET), diffusive gradient in thin-films (DGT), dialysis peepers and rhizon suction cup are most commonly used to obtain pore water concentrations. DGT, DET, and peepers utilize diffuse and equilibration theory to determine metals in pore water, and hours to days are needed for one pore water profile (Gao et al., 2006; Thomas and Arthur, 2010; Davison and Zhang, 2012). The rhizon suction cup utilizes tensiometry and lysimetry theory to sample pore water, so several minutes is

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sufficient to sample pore water from a certain sediment layer (Göttlein et al., 1996; Seeberg-Elverfeldt et al., 2005; Shotbolt, 2010). Its inexpensive and simple application make rhizon a powerful tool for pore water sampling (Seeberg-Elverfeldt et al., 2005).

Metals in the surface sediment of Chaohu Lake were at a relatively low level in the 1980s when eutrophication began to occur (Tu et al., 1990). Subsequently, many toxic metals in the sediment showed continuous increases within the multi-pond system in the Chaohu Lake catchment due to the extensive use of fertilizers on farmlands in the past three decades (Zhang and Shan, 2008b; Tang et al., 2010). A few studies were conducted to analyze the toxic metal content of sediment in Chaohu Lake (Yin et al., 2011; Zan et al., 2011; Liu et al., 2012; Yu et al., 2012), however the results did not give us an exhaustive distribution and contamination level of sediment metals on an entire lake-scale, and the potential risks arising from the diffuse flux of metals from pore water to the overlying water were never evaluated due to the lack of a convenient pore water sampling method.

The objectives of this study were: (1) to demonstrate the spatial variability of metals (Cr, Ni Cu, Zn, As, Cd, Pb, Fe, and Mn) in sediment by dense grid sampling and evaluate the areal extent of contamination in Chaohu Lake sediments using the New York sediment screening criteria; (2) to investigate the temporal trend of metal contamination using the vertical profile of sediments and relate this to historical data from the lake survey conducted in the 1980s; (3) to evaluate the potential health risk of metals in sediment by estimation of the diffuse flux of metals from pore water to the overlying water with a rhizon-corer pore water sampling system.

1 Experimental

1.1 Description of the study area and sampling sites

The Chaohu Lake watershed (30°58′–32°06′N, 116°24′–118°00′E) sits along the left bank of the Yangtze River and covers an area of 13,486 km^2 (Ji, 2009). The watershed is subject to a transitional subtropical-warm temperate monsoon climate with 1000–1158 mm annual average precipitation (Ji, 2009). Chaohu Lake is a typical shallow lake with a depth of 3 m and surface area of 760 km^2. There are eight important estuaries in the lake separately connected to the Nanfei-Dianbu, Pai, Fengle-Hangbu, Baishishan, Tongshang, Qiyang, Zhegao and Yuxi Rivers (Fig. 1). The lake is divided into the eastern lake and western lake by the connecting line of Zhongmiao Temple and Qizui Cape. The western part suffers more serious eutrophication than the eastern part (Shang and Shang, 2005).

In order to obtain the lake-scale spatial distribution of sediment metals, 57 sampling grids with a width of 3.8 km were set up in Chaohu Lake, according to the lake survey guidelines (Håkanson and Jansson, 1983) in July 2010. Each sampling grid had one sampling point (Fig. 1), and two sediment cores were taken at the same time in each sampling point for sediment and pore water analysis. In addition, taking the lake morphology and flow distribution into account, six sediment cores W1, W2, M1, M2, E1 and E2 (Fig. 1) from the western, middle and eastern part of lake were chosen to analyze the vertical metal concentration profile of the sediment.

1.2 Sample collection and analytical methods

Sediment cores were collected by a gravity corer (Austria UWITEC) with PVC sampling tubes (diameter 6.3 cm and length 60 cm). A rhizon-corer method was established to sample pore water with rhizon suction cups and adapted corer tubes. The corer tubes were modified with four column (perpendicular direction along the cross-section circle) holes at a distance of 1 cm in the vertical direction. The first holes in the four columns (clockwise) had a distance of 0.25 cm in the vertical direction. The vertical distance of adjacent holes along the clockwise spiral was 0.25 cm (Fig. 2a). The corer tubes were first affixed with waterproof tape, which would be punctured when sampling pore water, to get sediment cores with the gravity corer. A pore water extracting system consisting of macro rhizon suction cups (Netherlands Rhizon CSS) with porous ceramic tubes (pore size of 0.1 μm) and vacuum bottles was used to get stratified pore water from sediment cores to avoid sediment oxidation in the extraction process
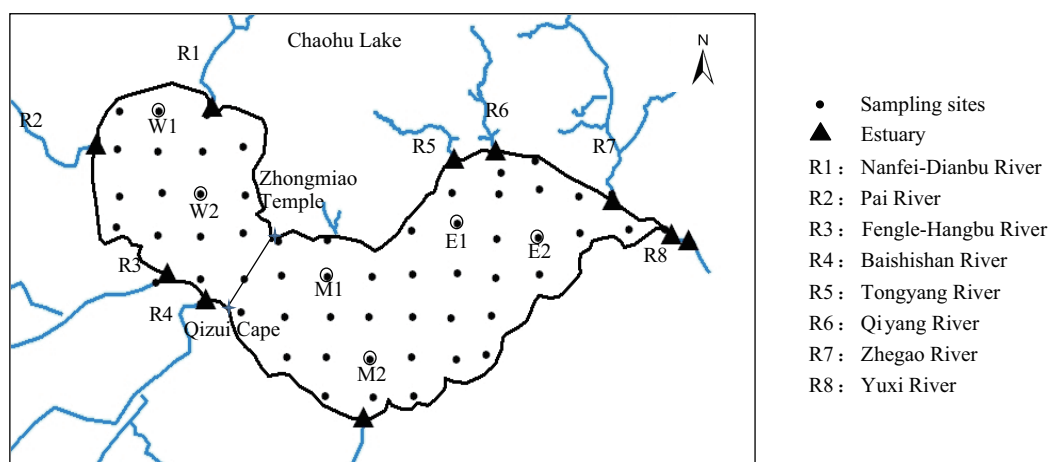

Fig. 1 Locations of the sampling sites within Chaohu Lake. The sediment cores were chosen to represent the western (W1, W2), middle (M1, M2) and eastern (E1, E2) lake sediment vertical trends.

(Seeberg-Elverfeldt et al., 2005; Shotbolt, 2010). The measurement interval for stratified pore water was 0.25 cm for 0–3 cm depth, 0.5 cm for 3–7 cm depth, 1 cm for 7–15 cm depth, and 2 cm for 15 cm to end depth, where depth is the distance between the interface of the overlying water and sediment (Fig. 2b). The sediment cores used for sediment analysis were cut into sections of 0.9 cm length by a cutting device attached to the gravity corer. Sediments from 0–0.9 cm depth were used as surface sediment to analyze the horizontal distribution of metals in lake. The measurement interval of sediment sections for vertical distribution of metals was 0.9 cm for 0–12.6 cm depth, 1.8 cm for 12.6–27.0 cm depth, and 3.6 cm for 27.0 cm to end depth, where depth is the distance between the interface of the overlying water and sediment. Sediment cores collected by the gravity corer had a length of 25, 36, 40, 9, 26, and 39 cm in W1, W2, M1, M2, E1 and E2, respectively.

Surface water, overlying water (near the sediment-water interface) and pore water samples from the 57 sampling points were acidified using nitric acid and analyzed by ICP-MS (Agilent 7500a, USA) for the nine metals (Cd, Cu, Ni, Pb, As, Cr, Zn, Fe, and Mn). Sediment samples were freeze-dried and digested with aqua regia and hydrogen fluoride (V/V = 3:1) using microwave high-pressure digestion (CEM MARS Xpress, USA) and analyzed with ICP-OES (OPTIMA 2000DV, USA) for the nine metals.

1.3 Sediment contamination assessment methods

Sediment contamination levels were assessed by the New York sediment screening criteria. The New York sediment screening criteria established two levels of risk (the lowest effect level, LEL, and the severe effect level, SEL) for metal contamination in sediments. The criteria integrated procedures and data developed by the Ministry of Ontario (Persaud et al., 1992) and the National Oceanic and Atmospheric Agency (NOAA) (Long and Morgan, 1990), both of which were based on field data of the co-occurrence of benthic animals and contaminants (Table 1). Persaud et al. (1992) derived the LEL and SEL from Great Lakes data, while Long and Morgan (1990) got effect range-low (ERL) and effect range-moderate (ERM) from both fresh

Table 1   Sediment contamination assessment criteria (unit: μg/g)

Metal	New York sediment screening criteria		Ministry of Ontario		National Oceanic and Atmospheric Agency	
	LEL	SEL	LEL	SEL	ERL	ERM
As	6	33	6	33	33	85
Cd	0.6	9	0.6	10	5	9
Cr	26	110	26	110	80	145
Cu	16	110	16	110	70	390
Fe	20000	40000	20000	40000	–	–
Pb	31	110	31	250	35	110
Mn	460	1100	460	1100	–	–
Ni	16	50	16	75	30	50
Zn	120	270	120	820	120	270

LEL: the lowest effect level, SEL: the severe effect level, ERL: effect range-low, ERM: effect range-moderate.

and salt water data. The LEL for each metal in the New York sediment screening criteria is the lowest of either the LEL from Persaud et al. (1992) or the ERL from Long and Morgan (1990), and the SEL for each metal is the lowest of either the SEL from Persaud et al. (1992) or the ERM from Long and Morgan (1990).

If either criterion is exceeded, sediment is considered to be contaminated and potentially cause harmful impacts to aquatic ecosystems (Gorge and John, 1999). The LEL indicates a level of sediment contamination that can be tolerated by the majority of benthic organisms, but still causes toxicity to a few species. Metal concentration between the LEL and SEL means the sediment is moderately impacted. If metal concentration exceeds the SEL, the sediment is considered severely impacted and will cause significant harm to benthic aquatic life. A site-specific sediment test is required to determine what actual risks to the environment are present and if remediation is necessary to eliminate or minimize adverse effects.

1.4 Flux estimation methods

Diffuse flux rates of dissolved metal from pore water to overlying water were estimated from the gradients of metal concentration present at the interface of water and sediment according to Fick's first law (Eqs. (1) and (2)) (Berner, 1971).

$$F = \varphi \times D_s \times \frac{dc}{dx} \tag{1}$$

$$D_s = \varphi^n \times D_0 \tag{2}$$

where, φ is the porosity of the sediment; dc/dx is the content gradient of dissolved metal species between the surface pore water and the overlying water column; D_s is the sediment diffusion coefficient of the species derived from the diffusion coefficient (D_0) of the species at infinite dilution; and n is a constant that varies according to the sediment grain size regime ($n = 2$ for $\varphi > 0.7$). A coefficient of molecular diffusion of 4.4×10^{-6} cm^{-2}sec^{-1} for Mn and 3.6×10^{-6} cm^{-2}sec^{-1} for As, and a porosity of 0.79 for the surface sediment in Chaohu Lake were used (Berner, 1980; Tu et al., 1990).
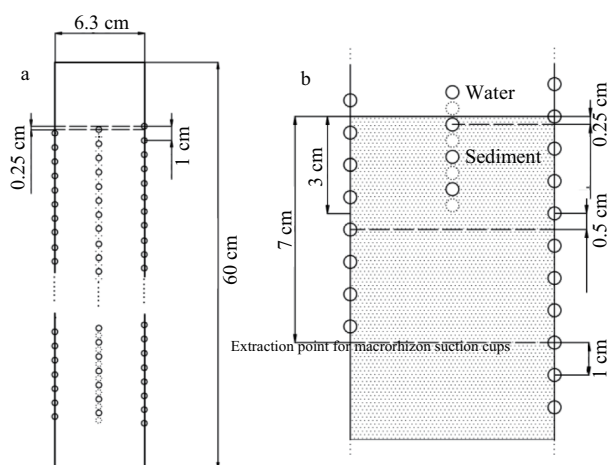

Fig. 2   Sketch map of sampling tube (a) and stratified pore water sampling sites (b).

1.5 Statistical analysis

The experimental data were analyzed using SPSS 13.0 for Windows. ANOVA was used to assess whether there were significant differences in the heavy metal contents between different parts of the lake. Contour maps of metals were plotted by Surfer 8.0 and other maps were made by Origin 8.0.

2 Results

2.1 Metal levels and spatial distribution in surface sediments

As evaluated by the New York screening sediment criteria, Mn, Cr, Fe, Ni, As, and Cu in the surface sediment widely exceeded the LEL for 62%–100% of the area of sediment, and Mn, Fe, Zn, As, Cr, and Ni exceeded the SEL for 14%–44% of the area. Mn was the metal with the highest level of contamination in sediment with 56% of sediment area moderately impacted and 44% of sediment area severely impacted. Fe, As and Zn had the second highest contamination levels with 76%, 52% and 20% of sediment area moderately impacted, and 16%, 14% and 20% of sediment area severely impacted, respectively. Cr and Ni had lower contamination levels, with 84%–94% of sediment area exceeding the LEL, and only 6% of sediment area beyond the SEL. Cu, Cd and Pb levels in sediment were all less than the SEL, and the effects were acceptable (Fig. 3).

Within the lake, the metal contents in the surface sediment were generally higher in the western lake than in the eastern lake, with the highest content found in the western lake center and the Nanfei-Dianbu River estuary (Fig. 3). The metals showed a different distribution in the eastern lake, with Cr, Ni, Cu, Zn, and Pb higher in the Zhegao River estuary, and As, Fe, and Mn higher in the Tongshang River and Qiyang River estuary. The Fengle-Hangbu River estuaries, Baishishan River estuaries and the south bank of the eastern lake had lower metal content.

The average content of metals in the sediments in 2010 (this research) and the 1980s (Tu et al., 1990) is shown in Fig. 4. In 2010 the sediment content of the seven toxic metals (Cd, Cu, Ni, Pb, As, Cr, Zn) in the western lake was significantly higher than that in the eastern lake ($P < 0.01$), while Fe and Mn concentrations did not show significant differences between the eastern and western
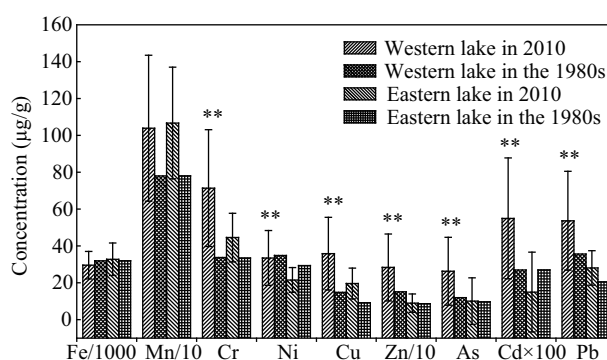
Fig. 4 Metals in surface sediment in Chaohu Lake in 2010 (this study) and the 1980s (Tu et al., 1990). ** indicates a significant difference in sediment metal content between the western lake and the eastern lake in 2010 ($P < 0.01$).

Cr   Area > SEL (110 μg/g): 6%

Ni   Area > SEL (50 μg/g): 6%

Cu   Area > SEL (110 μg/g): 0%

Zn   Area > SEL (270 μg/g): 20%

Cd   Area > SEL (9 μg/g): 0%

Pb   Area > SEL (110 μg/g): 0%

As   Area > SEL (33 μg/g): 14%

Fe   Area > SEL (40000 μg/g): 16%
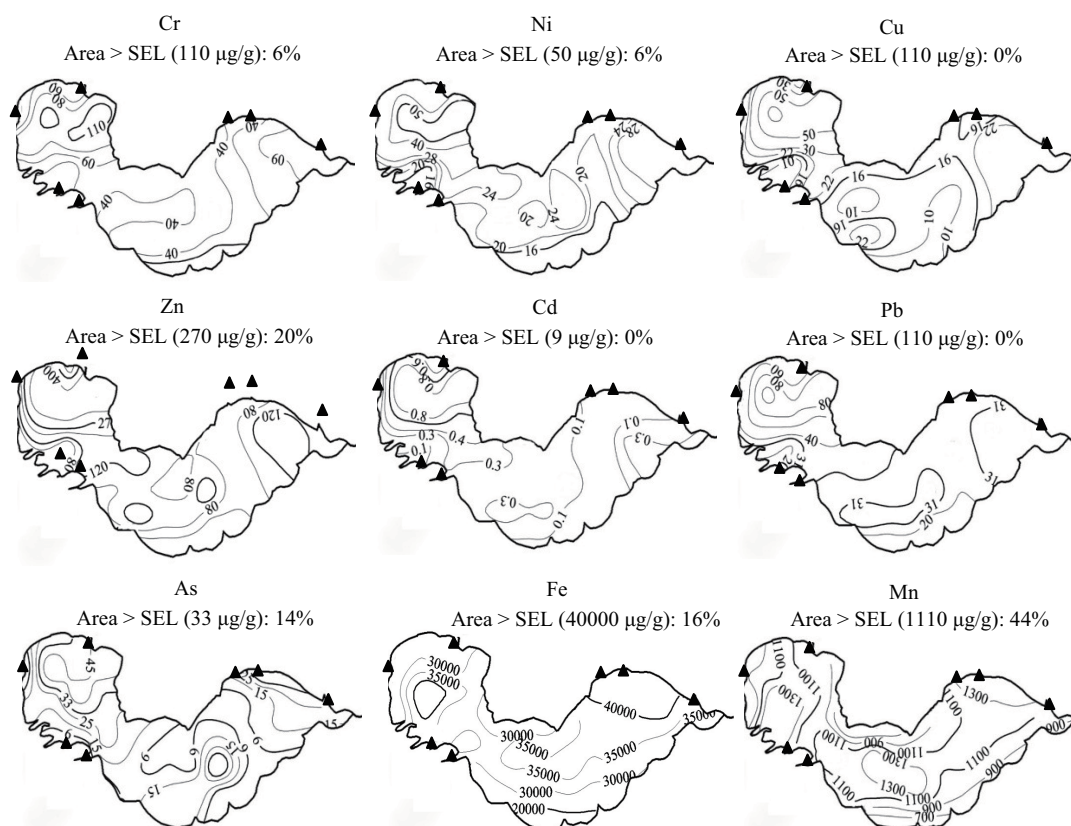
Mn   Area > SEL (1110 μg/g): 44%

Fig. 3 Contour map of metal content in surface sediments within Chaohu Lake. SEL: the severe effect level.

lake. Compared with metal content data from the sediment survey conducted in 1980s (Tu et al., 1990), the metal contents of surface sediment in 2010 increased 0–1.4 times, with metal contents in the western lake increasing more than those in the eastern lake. The contents of Cr, Cu, Zn, and As in the surface sediment of the western lake in 2010 were about 2.0–2.4 times those in the 1980s, the other metals in western lake and all metals in eastern lake were less than 1.5 times those in the 1980s. Zn and As in the eastern lake and Fe in the whole lake in 2010 were almost the same as in the 1980s.

2.2 Metal profiles in sediment cores

The vertical distribution of metals in sediment showed a trend of increasing concentration with reduced depth for all metals investigated, the extent of which was metal-specific. Compared to the lower contents in deeper layers, the surface layers showed enrichment by a factor of 1.4–

6.0 times for Cr, Ni, Cu, Pb, As, and Cd, 1.6–13.3 times for Zn (Fig. 5), and 1.0–2.1 times for Mn and Fe (Fig. 6). The metal contents in the western lake sediment cores were higher than those in the eastern lake sediment cores.

Toxic metal content in the western lake sediment cores (W1 and W2) was constant in the deeper sections of the depth profile, but a sharp increase was evident in the shallower sections, and then remained at a constantly high level for a distance of 10 cm above the transitional zone (Fig. 5). The toxic metal content in the sediment core W1 increased from 22.01 to 76.14 μg/g for Cr, 12.12 to 37.87 μg/g for Ni, 12.66 to 45.32 μg/g for Cu, 35.45 to 457.05 μg/g for Zn, 0.62 to 26.53 μg/g for As, 0.00 to 0.41 μg/g for Cd and 12.29 to 75.80 μg/g for Pb. The increasing trend was quite similar within the W2 sample for all the toxic metals analyzed. Within the middle and eastern lake sediment cores (M1, M2, E1, E2), metal content climbed slowly with reduced depth, reaching the
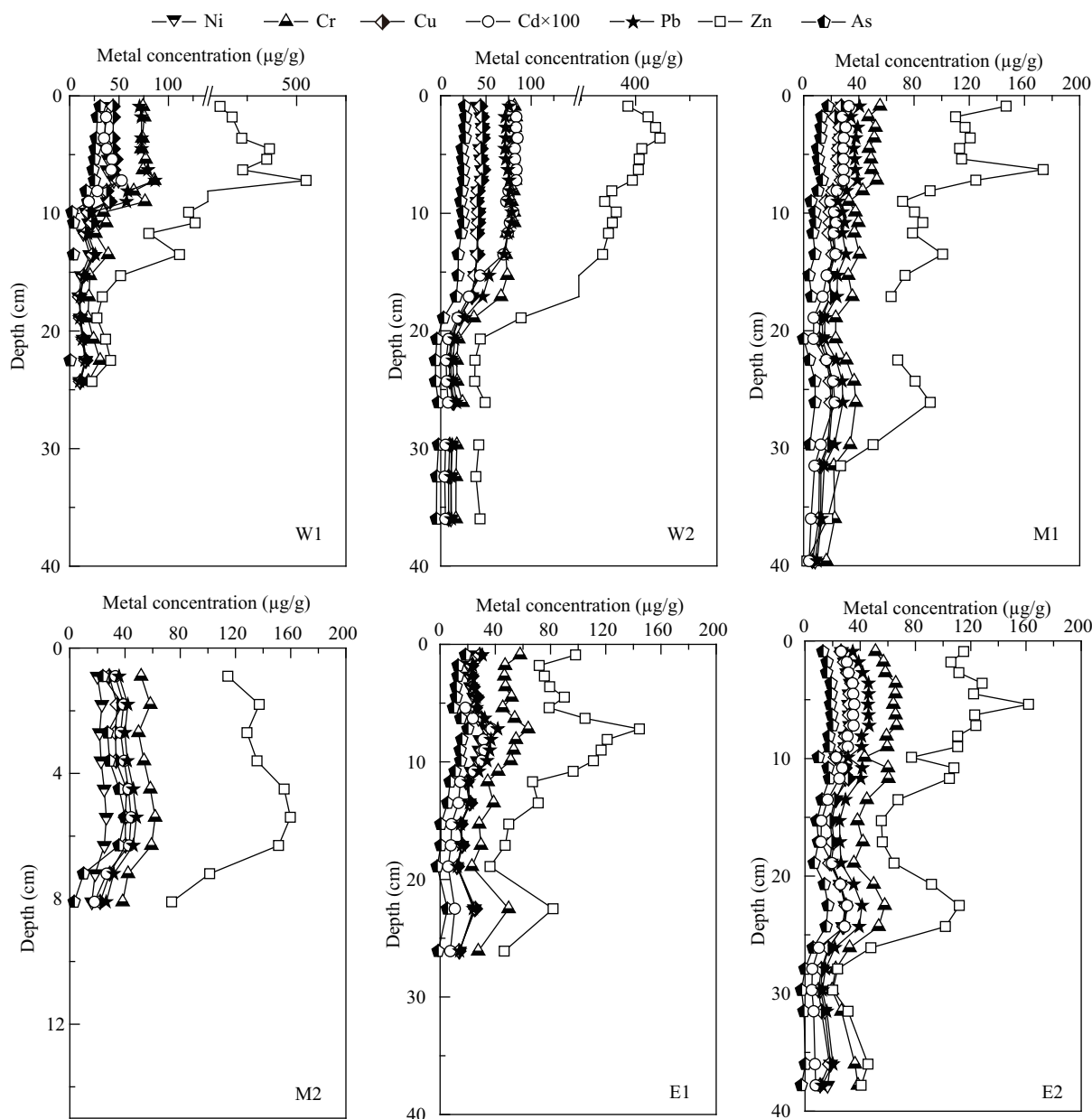

Fig. 5 Vertical profile of toxic metals in sediment cores from different parts of Chaohu Lake.
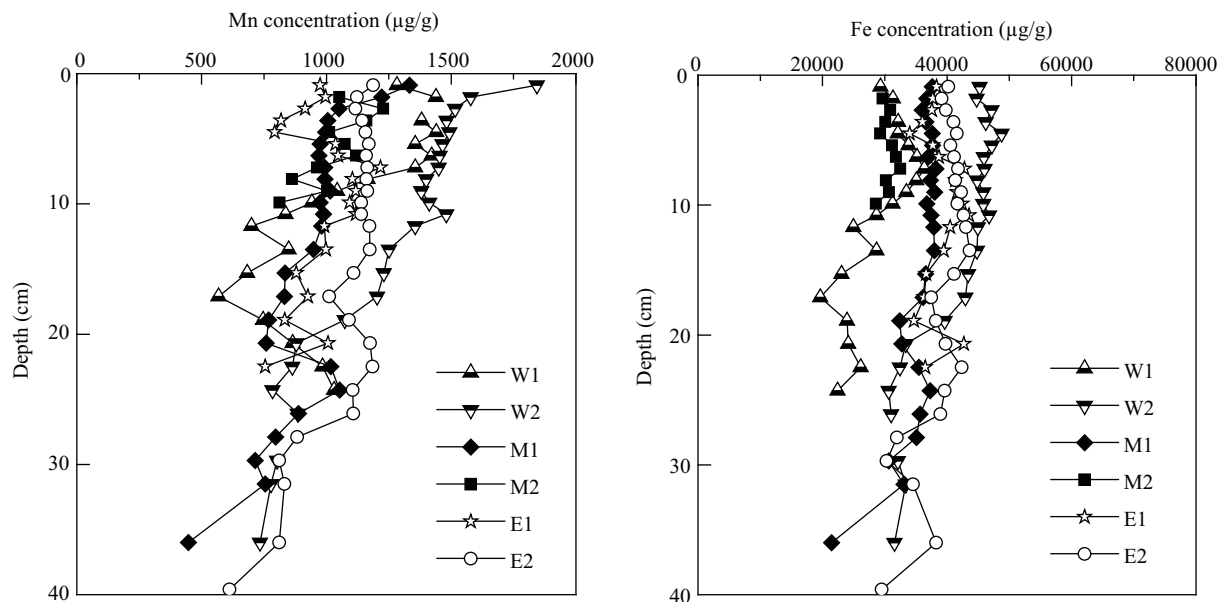
Mn concentration (μg/g)

Fe concentration (μg/g)

Fig. 6 Vertical profile of Fe and Mn in sediment cores from different parts of Chaohu Lake.

highest concentrations at a depth of 5 cm, and subsequently decreased. The toxic metal content in the shallow section was 18.88–26.82 μg/g for Cr, 6.44–13.86 μg/g for Ni, 8.19–16.10 μg/g for Cu, 29.57–86.82 μg/g for Zn, 14.49–14.90 μg/g for As, 0.01–0.23 μg/g for Cd, and 9.35–20.30 μg/g for Pb, greater than those in the deeper section for M1, E1 and E2. The increase in toxic metal content in the western lake sediment cores (W1 and W2) was 2.0–2.4 times for Cr, Ni, Cu, and As, 2.7–3.2 times for Cd and Pb, and 4.7 times for Zn compared with levels in eastern lake sediment cores (M1, E1, and E2).

Mn and Fe contents in sediment cores showed a slowly increasing trend with reduced depth, except for Mn in the western lake sediment cores (W1 and W2) (Fig. 6). Mn content in the eastern lake sediment cores and Fe in all lake

sediment cores showed enrichment of 1.0–1.4 times from deeper layers to surface layers. Mn content in sediment cores from the western lake increased from 715 to 1361 μg/g (W1), and from 812 to 1832 μg/g (W2).

2.3 Estimated metal diffuse flux from pore water to overlying water

Profiles of the nine metals in pore water were determined for the 57 sediment cores. Among the metals, only Mn and As had a widespread positive flux from the pore water to overlying water across the whole lake. The pore water profiles of Mn and As for sediment cores W1, W2, M1, M2, E1 and E2 are shown in Fig. 7. Mn and As contents increased with reduced depth, arrived at the highest level at a depth of 3–5 cm, and subsequently decreased linearly
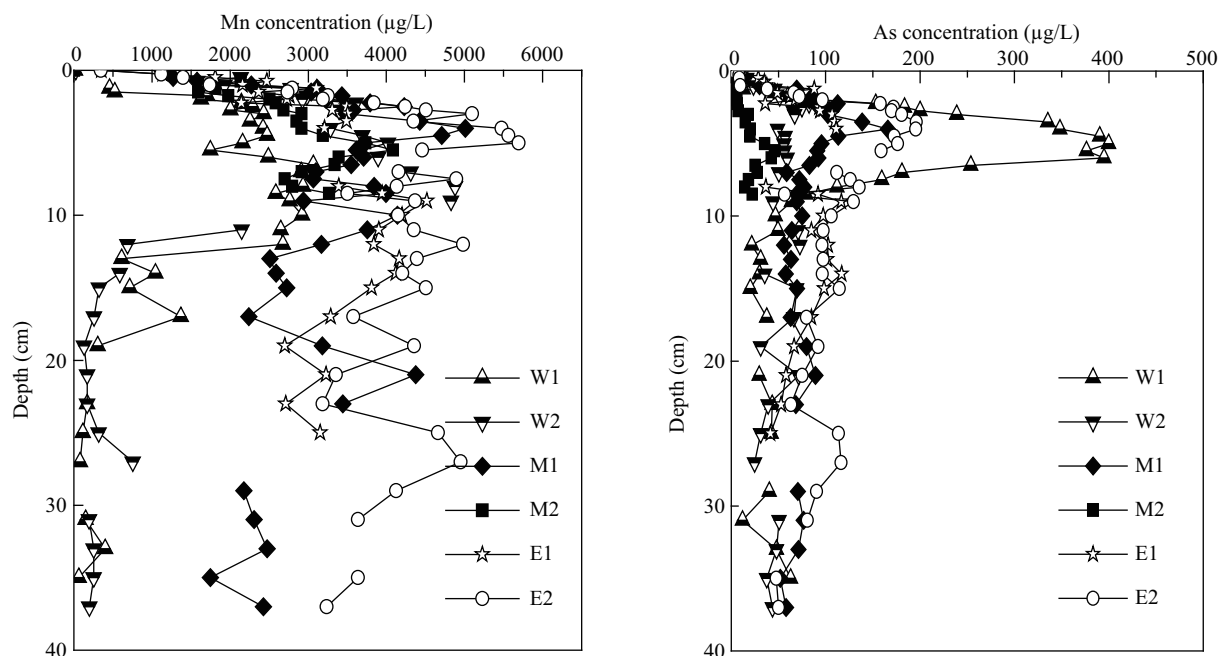
Mn concentration (μg/L)

As concentration (μg/L)

Fig. 7 Vertical profile of Mn and As in sediment pore water.

Mn (mg/(m²·day))   As (mg/(m²·day))

Fig. 8   Contour map of Mn and As diffuse flux from pore water to overlying water.

to a level similar to the overlying water.

The metal concentration gradients at the sediment-water interface were calculated by linear regression, and used to estimate the flux due to the diffusion from pore water to overlying water by Fick's Law. Figure 8 shows the spatial distribution of the diffuse flux of Mn and As. The vicinity of Zhongmiao Temple and the center of the middle and eastern lake released more metals than other areas. The diffuse flux of Mn and As from the sediment pore water to overlying water was on average 3.36 and 0.08 mg/(m²·day), meaning 2.10 and 0.05 ton/day in the whole lake. This flux could cause a daily increase of 0.93 μg/L for Mn and 0.02 μg/L for As in surface water under well-mixed hydrodynamic conditions, assuming the lake remains at an average depth of 3 m.

3 Discussion

3.1 Temporal trends in sediment

Compared with metal content data from the sediment survey conducted in the 1980s (Tu et al., 1990), the metal contents of surface sediment in 2010 increased 0.3–1.4 times, except for Zn and As in the eastern lake and Fe in the whole lake. Cr, Cu, Zn, and As in the western lake were the most enriched metals, with Mn, Pb following next. The result was consistent with the increasing metal profile in sediment cores from different parts of the lake (Figs. 5 and 6). Some studies in Chaohu Lake also showed that Zn, Mn (Zan et al., 2011), Cu, and Pb (Liu et al., 2012) in sediment were the most enriched elements.

Increasing pollution problems have come from the rapid development of industry, expansion of cities and intensified agriculture (Zan et al., 2011; Jiang et al., 2012, Yin et al., 2011). There are other sources of metals in the Chaohu watershed, such as exposed phosphorite at the north bank of the lake and Fe and Mn ore occurring within the southwest bank of the lake, which resulted in a high spot of As, Fe and Mn in sediment (Tu et al., 1990; Kametaka et al., 2005).

The Chaohu watershed is the grain production base of Anhui Province, with more than 60% of the Chaohu Lake watershed used for agriculture. Agricultural intensification has resulted in a dramatic increase in fertilizer, pesticide,

and herbicide usage, all of which contain toxic metals (Aoun et al., 2010). In the Yangtze–Huaihe region, chemical fertilizers including N and P fertilizer were first applied at a rate of 75 kg/ha in the early 1960s, reaching a rate of as high as 750 kg/ha in the 1980s when intensified fertilizer use began, and continuing to increase in the past two decades (Ji, 2009). As phosphate fertilizer contains toxic metals such as Cd, Pb, and Zn (Jones and Johnston, 1989), the continuous application of these fertilizers and other soil amendments potentially exacerbates the accumulation of heavy metals in agricultural soils. Although the multi-pond system could retain much of the heavy metal content through the sedimentation of particles (Zhang and Shan, 2008b), water and sediment will be flooded out in the increasing storm events (Shen and Wang, 2010) and result in metals ultimately settling in Chaohu Lake.

Hefei is the largest city within the Chaohu Lake watershed, with a dense population and industry (Liu and Li, 2003), including a chemical plant, paper mill, fertilizer factory and steel plant. The toxic metals in the western lake can be linked to the dense population and industry found in Hefei City. Hefei City had a population of 4.91 million and GDP of 166.5 billion CNY in 2010, a factor of 5 and 29 times of those in 1980 respectively (Ji, 2009). Urban sewage was discharged untreated to the Nanfei-Dianbu River before 1997, until two sewage treatment plants were put into use in 2004 (Le et al., 2010).

The Nanfei-Dianbu River, carrying abundant industrial wastewater and domestic sewage due to the population and high GDP growth rate of Hefei City, introduces abundant toxic metals. Tongshang River and Qiyang River flow through exposed phosphorite, and introduce As, Fe, and Mn through erosion processes. The Zhegao River is subject to runoff from intensified agriculture, resulting in the introduction of Cr, Ni, Cu, Zn and Pb from polluted soil to the lake. The Fengle-Hangbu and Baishishan River account for 75% of the incoming water in Chaohu Lake, and both rivers run through catchments suffering serious erosion problems. Agricultural runoff and the influence of iron and manganese ore were the main pollution sources in the lake area near the Fengle-Hangbu and Baishishan River estuaries, resulting in the introduction of Fe, Mn and SiO₂ to the lake. A circular current in the western lake was formed after a dam was established at the downstream end

of Chaohu Lake in 1960 (Tu et al., 1990). This current resulted in toxic metal pollutants being widely distributed in the sediment of the western lake. The toxic metals bound to suspended particles settled along the flow of water from the western lake to the eastern lake (Wang et al., 2007).

3.2 Metal contamination in sediment and water

Most research on metals in Chaohu Lake has referenced enrichment factors and the geo-accumulation index to highlight human contamination (Zan et al., 2011; Liu et al., 2012). Only one study assessed metals using the ERL and ERM levels set by NOAA, and showed that Ni in the upper sediment exceeded the ERM (50 μg/g) and would cause adverse biological effects (Han et al., 2011).

The New York sediment screening criteria integrate procedures and data developed by the Ministry of Ontario and the NOAA, choosing the lower criteria of LEL/SEL from the Ministry of Ontario guidelines (Persaud et al., 1992) and ERL/ERM from NOAA guidelines (Long and Morgan, 1990). Metal assessment by the New York sediment screening criteria showed that 44%, 20%, 16%, 14%, 6% and 6% of the area of Chaohu Lake sediment was severely contaminated with Mn, Zn, Fe, As, Cr and Ni, respectively. Significant harm is anticipated to benthic aquatic life in the severely contaminated area. Therefore acute and chronic toxicity tests with local sediment and benthic invertebrates should be carried out to verify the need for remediation.

Mn was the metal with the most severe contamination in sediment, with all of the area exceeding the LEL and 44% of the area exceeding the SEL. Recently, elevated Mn in drinking water has been identified as an underlying threat to the human population worldwide (Buschmann et al., 2007; Ljung and Vahter, 2007). Prolonged consumption of drinking water containing high Mn may cause neurotoxic effects, such as diminished intellectual function in children (Wasserman et al., 2006). Mn was once only common in groundwater due to the favorable redox conditions prevailing in aquifers (Jaudon et al., 1989); however, Mn contamination has begun to occur in surface water (Buschmann et al., 2007). Although Mn concentration in the surface water (1.27–18.65μg/L in this research) was far below the criterion for drinking-water sources (100 μg/L), there was much more Mn in the overlying water near the sediment-water interface (3.05–3105 μg/L in this research), which was seriously affected by the release of dissolved Mn from contaminated sediment pore water. Mn in sediment will act as a source for surface water under the low redox potentials caused by eutrophication (Gao and Zhang, 2010). In Chaohu Lake, the Mn flux (3.36 mg/(m^2·day)) from the sediment pore water to overlying water implied an increase of 0.93 μg/L for Mn in surface water per day under well-mixed hydrodynamic conditions. Other metal flux studies in lakes and oceans showed that Mn fluxes across the water-sediment interface ranged from –57.52 to 391.23 mg/(m^2·day) (Blasco et al., 2000). The increasing Mn and organic matter in sediment of Chaohu Lake (1.4 and 1.6 times of those in 1980s) will make Mn flux from sediment to water a serious problem for the lake's drinking-water source function.

Zn in sediment exceeded the LEL for 40% of the area of the lake, but as high as 20% of the sediment area exceeded the SEL. The highest concentration (653 μg/g) was 2.4 times the SEL (270 μg/g), meaning significant harm to benthic aquatic life, situated in the western lake near the Nanfei-Dianbu River estuary. Zn in the eastern lake was almost below the LEL, meaning acceptable effect. The Zn distribution was similar to the result from Zan et al. (2011). There was positive flux from the pore water to overlying water in several sampling grids in the western lake, but significant flux did not exist in other areas. The toxicity of Zn to benthic animals was greater than to the drinking-water source function.

The As concentration in sediment was between the LEL and SEL for 52% of the area, while 14% of the area was beyond the SEL. Yu et al. (2012) evaluated the As pollution level using the geo-accumulation index and sediment quality guidelines in Chaohu Lake sediment, showing that the As pollution and potential risk were lower. Although severely contaminated sediments were not widespread, there was extensive positive diffuse flux from pore water to overlying water. As diffuse flux across the whole lake was 0.01–0.70 mg/(m^2·day), implying a daily increase of 0.02 μg/L for the As concentration in surface water under well-mixed hydrodynamic conditions. Although the As concentration in surface water (1.54 μg/L in this research) was lower than the concentration criterion for drinking-water sources (10 μg/L), the diffuse flux makes As a relatively high risk in Chaohu Lake as a drinking water source.

The metal profiles in pore water obtained by the rhizon-corer showed similar tendencies with profiles measured by other pore water methods (Gao et al., 2006). The rhizon-corer method obtained the pore water profile in several minutes per sediment core, and achieved a resolution of 0.25 cm. This made it convenient to estimate fluxes in a large quantity of sites across the lake. Although only Mn and As diffuse fluxes across the whole lake were estimated here, the other metals such as Zn, Ni and Cd also had positive diffusion flux from sediment to water in some sampling sites. The porosity used in the flux estimation was an average value for surface sediment in Chaohu Lake, but the sediment particle size analysis showed particle sizes were larger in the western lake (Wen et al., 2012), indicating that more toxic metal could potentially be released from the pore water to the overlying water. It also should be noted that no physical or biological processes have been taken into consideration. Therefore, the diffuse flux calculated here could only be regarded as the lower limits of the net benthic flux of trace metals from sediment to water. Bioturbation, irrigation, wave action and re-suspension can increase diffuse flux by a factor of several times (Almroth et al., 2009). It is anticipated that contributions from physical processes to the flux of trace metals from the sediment pore water should be significant in shallow water as extreme weather events occur more and more frequently, which may compromise the drinking-water source function of Chaohu Lake.

4 Conclusions

Metals in the surface sediment were generally the highest in the western lake center and Nanfei-Dianbu River estuary, with another higher area of As, Fe, and Mn occurring in the Qiyang River estuary. Across the lake, the seven toxic metal (Cd, Cu, Ni, Pb, As, Cr, and Zn) contents of sediment in the western lake were significantly higher than those in the eastern lake ($P < 0.01$). Metal contamination assessment using the New York sediment screening criteria showed that the sediment was severely contaminated for 44% of the area with Mn, 20% with Zn, 16% with Fe, 14% with As, 6% with Cr and 6% with Ni.

An increasing trend of metals with depth was found in sediment cores, with toxic metals and Mn in the western lake increasing more than those in the eastern lake. Compared with the lower contents in deeper layers, the surface layers showed enrichment of a factor of 1.4–6.0 times for Cr, Ni, Cu, Pb, As, and Cd, 1.6–13.3 times for Zn and 1.0–2.1 times for Mn and Fe. The metal contents of surface sediment in 2010 were 2.0 times those in the 1980s for Cr, Cu, Zn, and As in the western lake, and less than 1.5 times higher for most of the metals in the eastern lake.

The high toxic metal content of the sediments in the Nanfei-Dianbu River and the Zhegao River estuary was a result of the input from increasing industrial wastewater, domestic sewage discharge and runoff from polluted agricultural soil. Fe and Mn content in the sediments showed a different distribution, attributed to the presence of phosphorite at the north bank of the lake and iron and manganese ore within the southwest bank of the lake.

Among the metals, only Mn and As had a widespread positive diffuse flux from the pore water to overlying water across the whole lake. The estimated flux in the whole lake was on average 3.36 mg/(m^2·day) for Mn and 0.08 mg/(m^2·day) for As, which indicated a daily increase of 0.93 μg/L for Mn and 0.02 μg/L for As in surface waters. The influence of the diffuse flux of Mn and As from pore water should be seriously considered in shallow water lakes used as a drinking water source.

Acknowledgments

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