

Occurrence, source identification and ecological risk evaluation of metal elements in surface sediment: toward a comprehensive understanding of heavy metal pollution in Chaohu Lake, Eastern China

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Abstract In the present study, surface sediment samples from 48 sites covering the whole water area and three main estuaries of Chaohu Lake were collected to determine the concentrations of 25 metal elements using microwave-assisted digestion combined with ICP-MS. Spatial variation, source appointments, and contamination evaluation were examined using multivariate statistical techniques and pollution indices. The results show that for the elements Cd, Pb, Zr, Hf, U, Sr, Zn, Th, Rb, Sn, Cs, Tl, Bi, and Ba, which had higher coefficients of variation (CV), the concentrations were significantly higher in the eastern lake than in the western lake, but other elements with low CV values did not show spatial differences. The accumulation of Cu, Zn, Rb, Sr, Zr, Cd, Sn, Cs, Ba, Hf, Ta, Tl, Pb, Bi, U, and Th in the surface sediments was inferred as long-term agricultural cultivation impact, but that of Ti, V, Cr, Mn, Co, and Ni may have been a natural occurrence. The contribution from industrial and municipal impact was

negligible, despite the rapid urbanization around the studied area. Principal component analysis-multiple linear regression (PCA-MLR) predicted the contribution from agricultural activities to range from 0.45 ± 1.31 % for Co to 92.7 ± 17.7 % for Cd. The results of the pollution indices indicate that Chaohu Lake was weakly to moderately affected by Ti, V, Cr, Mn, Co, and Ni but was severely contaminated by Hf and Cd. The overall pollution level in the eastern lake was higher than that in the western lake with respect to the pollution level index (PLI). Therefore, our results can help comprehensively understand the sediment contamination by metals in Chaohu Lake.

Keywords Metal elements · Spatial variation · Sources appointment · Contamination assessments

Introduction

Sediment quality is a pivotal indicator of water deterioration in an aquatic ecosystem because it is commonly considered as the key sink of various extraneous chemicals. Contaminated sediment, on the one hand, poses a major risk to benthic habitats (Pedro et al. 2015); on the other hand, accumulated contaminants in sediment can be released back to the water column by molecular diffusion, particle resuspension, and bioturbation. As a result, contaminated sediment plays a significant role in deteriorating water quality as a secondary source (Aleksander-Kwarczak and Helios-Rybicka 2009). Heavy metal pollution of sediments is an important environmental problem that people have been facing worldwide in recent decades. Although heavy metals and their compounds naturally occur in the Earth's crust, the accumulation of metal elements in environmental matrices is associated with human activities, such as metalliferous mining, industrial, agricultural and horticultural material usage, sewage sludge, fossil fuel

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combustion, and waste disposal. Among these sources, industrial, municipal, and domestic wastewater effluents are point sources, whereas surface runoff, soil erosion, and atmospheric deposition are generally considered diffuse sources. With the increasing attention on the heavy metal pollution, point sources might be significantly controlled by various environmental law practices and technical solutions. However, non-point inputs are becoming the major source of water and sediment pollution. For a complex aquatic system that is influenced by both point and nonpoint sources, comprehensive understanding of the source signatures of heavy metals is a major challenge.

Chaohu Lake Basin, Eastern China, is experiencing rapid urbanization and industrialization from a traditional agricultural cultivation area. Development-induced environmental pollution around the lake has received growing attention over the last two decades. Most studies have set out to investigate eutrophication and nutrients (Chen et al. 2013; Shang and Shang 2005; Shang and Shang 2007) and organic pollutants (Wang et al. 2014; Wang et al. 2012a, b, c; Wang et al. 2011). Little information on heavy metal pollution in Chaohu Lake has been obtained based on the limited number of samples and metal species. For example, sediment pollution by heavy metals was thought to be ignorable in a previous study (Chen and Li 2007), in which ten heavy metals (As, Hg, Pb, Cd, Cr, Cu, Zn, Mn, Ni, and Mo) were determined in five sediment samples. The residual heavy metals in the sediment of the lake were inferred from municipal, domestic, and industrial wastewater discharge (Li et al. 2010) using the concentrations of six metal elements (Al, Cu, Zn, Pb, Cd, and Cr) found in 30 surface sediment samples that were collected at one river estuary. However, comprehensive information on the metal pollution in Chaohu Lake is scarce.

Therefore, the objectives of the present study were (1) to investigate the elemental occurrences in the sediment of Chaohu Lake, Eastern China, on a large scale; (2) to determine the potential sources and contribution; and (3) to evaluate the pollution levels of the selected metal elements.

Materials and methods

Study area and sample collection

The study area was introduced in previous studies (Ren et al. 2015; Wang et al. 2012a). In brief, Chaohu Lake, the fifth largest shallow lake in China, is located between the Yangtze River and Huaihe River in Eastern China. The total area of the lake is approximately 780 km², with 33 tributaries. The local economic development of Chaohu Lake basin has largely depended on agricultural cultivation. However, the region is experiencing fast economic growth due to the

ongoing urbanization and industrialization. Increasing domestic, municipal, and industrial wastewater discharge coupled with agricultural intensification have caused a significant imbalance of matter and energy in the lacustrine system and have further resulted in water quality deterioration (Chen et al. 2013; Xu 1997).

The detailed sample collection was described elsewhere (Wang et al. 2012b; Wang et al. 2011). In brief, the sampling campaign was conducted from 25 to 30 October 2009. Surface sediment (top ~5 cm) was sampled from 48 sites covering the whole lake and three main estuaries (Fig. S1) using a stainless steel grab. Among these sampling sites, 35 sites were selected at a 0.05°×0.05° latitude/longitude resolution to investigate the full-scale elemental accumulation. Six sites were at the estuary of the Nanfei River, which runs through the urban area of a metropolis (Hefei City); four samples were collected from the estuary of the Hangbu River, which is the largest inflowing tributary in runoff volume; and three surface sediments were sampled at the estuary of the Yuxi River, which is the only outflow river of the lake. To verify the result of the high concentration of Cd in the surface sediment, a second sampling campaign was conducted in July 2012 (Ren et al. 2015). Four sediment cores (~30 cm) were collected at four estuaries of the main rivers, including the Nanfei River, Hangbu River, Tongyang River, and Yuxi River, using a sediment core sampler (Fig. S1). Sediment cores were sectioned immediately into 1-cm slices. Samples were transferred to pre-cleaned polythene bags and sealed and were stored, frozen, at -20 °C prior to laboratory processing.

Analytical methods

The analytical methods of the surface sediment were described elsewhere (Liu et al. 2013). Concisely, samples were freeze-dried and sieved using a 100-mesh nylon sieve. Powdered sediment (0.2000±0.0005 g) was digested by a guaranteed grade of HNO₃ and HF supplied by Merck & Co., Inc. (Darmstadt, Germany) using a MARS microwave digestion system (supplied by CEM company, Matthews, USA) based on EPA recommended method (EPA method 3052) (Agency 1996). Before the samples were diluted to 50 mL with Milli-Q deionized water, HF was evaporated. Twenty-five elements, including Tl, Bi, Ta, Mo, Cs, Co, Sn, Th, Nb, U, Cu, Cd, Ni, Ga, Cr, V, Rb, Pb, Hf, Sr, Ba, Zn, Mn, Zr, and Ti, were determined by an Elan6000 inductively coupled plasma-mass spectrometer (PerkinElmer, MA, USA). The operating parameters were given in a previous study (Sun and Sun 2007). The concentration of each element was quantified by the internal standard method by adding 50 µg/L of Rh into each sample before instrumental analysis. The analytical method used for the determination of Cd in the core sediment was given in the Supplementary Materials.

Quality control

Chemical and instrumental analyses of the surface sediment samples were performed in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science, prior to December 2009. With respect to quality control and assurance, procedural blanks and standards and replicates of samples were run in each batch of ten sediment samples. The recovery efficiencies ranged from 76±8.3 % for Cu to 108±4.0 % for Pb. All analyses were performed in triplicate, and the relative standard deviation ranged from 2.5 to 13 %. The results were expressed as the mean.

Pollution assessment

To quantify the degree of pollution based on the observed metal elements, the contamination factor (CF), pollution level index (PLI), geoaccumulation index (I_{geo}), and enrichment factor (EF) were computed.

1. CF was calculated as the ratio between the observed concentration in the sediment sample and its baseline or background value:

$$CF_i = \frac{C_i(\text{sediment})}{C_i(\text{background})} \quad (1)$$

The soil background values of Anhui Province were adopted as the background values (Chen et al. 2012) and are summarized in Table S1. Generally, a CF value less than 1.0 indicates low contamination, and CF values from 1.0 to 3.0 and from 3.0 to 6.0 suggest moderate and considerable contamination, respectively. $CF > 6.0$ denotes high contamination (Hakanson 1980).

2. PLI was developed to assess the overall pollution level by all observed metal elements for a given sample, and it is calculated using Eq. (2):

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n} \quad (2)$$

$PLI < 1.0$ indicates no metal pollution, and PLI larger than 1.0 suggests metal contamination (Varol 2011).

3. I_{geo} was calculated using the following equation:

$$I_{geo} = \text{Log}_2 \left(\frac{C_i(\text{sediment})}{1.5C_i(\text{background})} \right) \quad (3)$$

The calculated results can be broken into seven classes (Zheng et al. 2010) as follows: class I, $I_{geo} \leq 0$, practically uncontaminated; class II, $0 < I_{geo} \leq 1.0$, uncontaminated to moderately contaminated; class III, $1.0 < I_{geo} \leq 2.0$, moderately contaminated; class IV, $2.0 < I_{geo} \leq 3.0$, moderately to heavily

contaminated; class V, $3.0 < I_{geo} \leq 4.0$, heavily contaminated; class VI, $4.0 < I_{geo} \leq 5.0$, heavily to very heavily contaminated; and class VII, $I_{geo} > 5.0$, very heavily contaminated.

4. EF is used to diagnose the degree of enrichment of a given element from anthropogenic activities and is calculated as following Eq. (5)

$$EF_i = \frac{C_i(\text{sediment})/C_{\text{reference}}(\text{sediment})}{C_i(\text{background})/C_{\text{reference}}(\text{background})} \quad (4)$$

In the present study, Ti was selected as the reference element because of the low residual concentration in the sediment samples, which was close to the background concentration. An EF_i value less than 1.0 indicates no enrichment of element i , and $1.0 < EF \leq 3.0$, $3.0 < EF \leq 5.0$, $5.0 < EF \leq 10.0$, $10.0 < EF \leq 25.0$, $25.0 < EF \leq 50.0$, and $EF > 50.0$ suggest minor, moderate, moderately severe, severe, very severe, and extremely severe enrichment, respectively (Varol 2011).

Data analysis

All elemental concentrations were reported as $\mu\text{g/g}$ dry weight. The coefficient of variation (CV) for each element was calculated as the standard deviation divided by the respective mean concentration. The Kolmogorov–Smirnov test was performed to check the normal distribution of the concentration and the log-transformed concentration of individual elements. Data of the total organic carbon (TOC), normal alkanes (n -alkanes), polycyclic aromatic hydrocarbons (PAHs), and linear alkylbenzene (LABs) in the surface sediment samples were reported in our previous studies (Wang et al. 2012b; Wang et al. 2011; Wang et al. 2012c). Bivariate analysis was applied to test the correlations of each element against the TOC, n -alkanes, PAHs, and LABs. Sites L1 to L10, L14, L15, I2, I3, I4, I5, E0, E1, E12, E17, E19, and E27 were located in the western lake, and the other sites were situated in the eastern lake. The spatial variation of individual concentrations and the pollution load index (PLI) was tested using the independent-samples t test. Hierarchical cluster analysis and principal component analysis combined multiple linear regression (PCA-MLR) were applied to apportion the sources of sediment associated metal elements. PCA-MLR was performed, as described in detail elsewhere (Kavouras et al. 2001; Wang et al. 2012c). Briefly, factor scores were obtained by performing PCA using the logarithm-transformed concentrations of all elements, and multiple linear regression models were developed with the standardized normal deviation. All statistical analyses were conducted using the SPSS 16.0 software (Chicago, IL, USA). In addition, Golden Surfer 9.0 (Golden Software, Golden, CO, USA) was employed to plot the spatial distribution of individual elements and PLI using the gridding method of kriging.

Results and discussion

Description statistics of metal pollution

Detailed description statistics of the individual metal concentrations are shown in Table S1. Overall, the algorithmic concentrations of metals are listed in ascending order: Tl ($0.92 \pm 0.37 \mu\text{g/g}$) < Bi ($1.30 \pm 0.81 \mu\text{g/g}$) < Ta ($1.66 \pm 0.89 \mu\text{g/g}$) < Mo ($2.89 \pm 1.53 \mu\text{g/g}$) < Cs ($5.16 \pm 3.14 \mu\text{g/g}$) < Co ($10.9 \pm 2.92 \mu\text{g/g}$) < Sn ($13.0 \pm 30.7 \mu\text{g/g}$) < Th ($14.3 \pm 11.0 \mu\text{g/g}$) < Nb ($20.8 \pm 4.72 \mu\text{g/g}$) < U ($21.9 \pm 17.0 \mu\text{g/g}$) < Cu ($27.1 \pm 7.07 \mu\text{g/g}$) < Cd ($34.5 \pm 33.8 \mu\text{g/g}$) < Ni ($36.2 \pm 11.7 \mu\text{g/g}$) < Ga ($36.4 \pm 10.8 \mu\text{g/g}$) < Cr ($61.2 \pm 16.6 \mu\text{g/g}$) < V ($81.7 \pm 22.3 \mu\text{g/g}$) < Rb ($87.7 \pm 79.2 \mu\text{g/g}$) < Pb ($93.1 \pm 88.2 \mu\text{g/g}$) < Hf ($251 \pm 204 \mu\text{g/g}$) < Sr ($332 \pm 271 \mu\text{g/g}$) < Ba ($337 \pm 332 \mu\text{g/g}$) < Zn ($376 \pm 422 \mu\text{g/g}$) < Mn ($487 \pm 159 \mu\text{g/g}$) < Zr ($529 \pm 430 \mu\text{g/g}$) < Ti ($5300 \pm 1280 \mu\text{g/g}$) (Fig. 1). The concentrations of Ti and Cu followed the normal distribution (all $p > 0.5$), but the logarithmic transformations of the concentrations were not normally distributed (Fig. S2). For Ta and Cs, the concentrations did not fit the normal distribution but did fit the log normal distribution (Fig. S3). Tl, Mo, Co, Ni, Cr, V, and Mn had both normal and log normal distributions in concentrations (Fig. S4). The concentrations of Bi, Sn, U, Cd, Nb, Th, Ga, Pb, Rb, Sr, Hf, Ba, Zn, and Zr fit neither the normal nor log normal distributions (Figs. S5 and S6). Generally, a metal from a single origin with random dissemination generates a normal or log normal distribution (Keith et al. 1967). Most elemental concentrations or log-transformed concentrations show bimodal or multimodal distributions, which indicates the mixed sources of the elemental residue (Hu and Cheng 2013). Therefore, these results imply that the 25 elements accumulated in the surface sediment from different sources.

Tables S2, S3, and S4 summarizes the minimum, maximum, and mean concentrations of 15 elements (Ba, Cr, Cu, Mn, Ni, Sr, Ti, V, Co, Pb, Zn, Cd, Rb, Zr, and Mo) in the

sediments collected from Chaohu Lake in different studies compared with our results. In total, the concentrations of Cr, Cu, Mn, Ni, Ti, V, Co, Pb, and Rb in the present study are comparable to their previously reported concentrations. The concentration of Ba in the present study was slightly lower than the value observed in the core sediments collected from the western lake (Jia et al. 2009), and Cr, Cu, Mn, Ni, Ti, Co, and Rb contents in our study were comparable to their respective contents reported in other studies. But for Sr, Zn, Zr, and Mo, our data were higher than their respective contents in other studies (Chen and Li 2007; Han et al. 2011; Jia et al. 2009). Our result for Cd was 1–2 orders of magnitude higher than the published data (Cheng et al. 2008; Li et al. 2010; Zan et al. 2011). To confirm our results, four sediment cores at four main estuaries of Chaohu Lake were collected in August 2012 to analyzed Cd. The results show the concentration of Cd in core sediments ranged from 4.36 to 10.1 $\mu\text{g/g}$, with an arithmetic mean of 7.03 (Fig. S7), which was 2.5 times less than the mean concentration observed in the surface sediment but much larger than the previously reported concentrations. A recent study also found high enrichment of Cd in the bottom sediment of limnetic ecosystems in Eastern China (Tang et al. 2014).

Spatial variation

Hierarchical cluster analysis suggested that two clusters existed (Fig. S8). The elements in cluster 1, including Cd, Pb, Zr, Hf, U, Sr, Zn, Th, Rb, Sn, Cs, Tl, Bi, Ba, Ga, and Ta, had large CV values compared with those (V, Cr, Co, Ti, Ni, Cu, Nb, Mn, and Mo) found in cluster 2 (Table S1). Large CV values indicate considerable spatial variation and imply significant input from external sources (Li et al. 2013). A low CV suggests that nonpoint input or natural occurrence is predominant (Yao and Li 2004). Because metal elements are essential components of the Earth’s crust, the natural occurrence of elements in a lacustrine system tends to show weak spatial variation (Roussiez et al. 2005).

The spatial distribution of individual elements is illustrated in Figs. S9 and S10. In total, for all of the elements in cluster 1 except Ga, the concentrations were significantly higher in the eastern lake than in the western lake (all $p < 0.01$); however, the elements in cluster 2 did not show significant spatial variance (Fig. 2). Additionally, the concentrations of the elements in cluster 1 were poorly correlated to the urban-oriented contaminants, including LABs and PAHs (Table S5). These results suggest that the contribution of municipal and industrial sewage was negligible and that agricultural cultivation was the major exterior source because the western lake was affected by the urban and industrial sewage from Hefei City (Wang et al. 2012a, b; Wang et al. 2011). Furthermore, the concentrations of Cd in the core sediments collected from Hangbu River and Tangyang River, which are mainly associated with

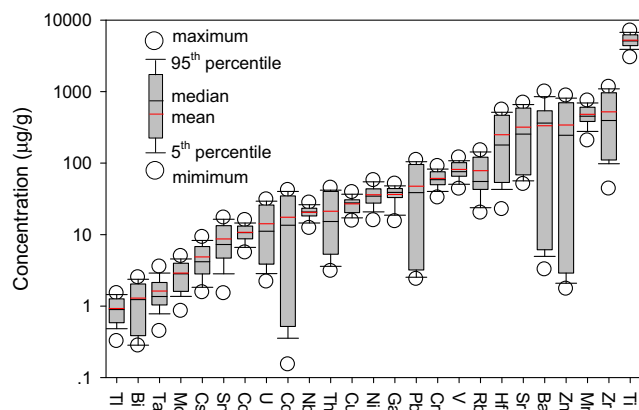


Fig. 1 Metal elemental concentrations in the surface sediment of Chaohu Lake. The results are presented on a log scale

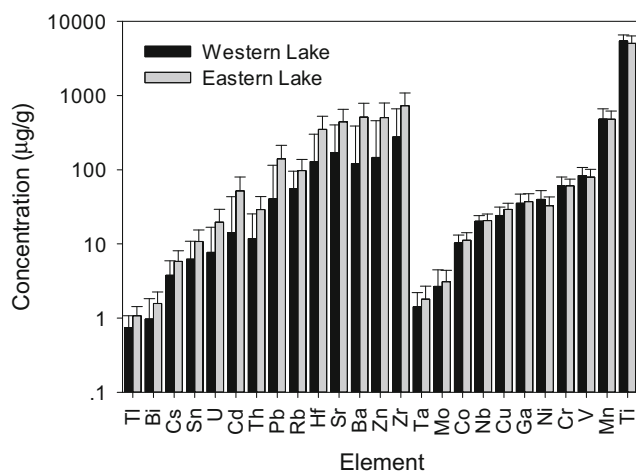


Fig. 2 Spatial variation of individual elements. The left part of the figure shows significantly higher concentrations of these elements in the eastern lake than in the western lake, but the right part of the figure shows that there is no spatial variation in these elements. Elemental concentrations are presented on a log scale

farmlands, were significantly higher than those in the samples collected from Nanfei River and Yuxi River ($p < 0.01$). It was further confirmed that Cd potentially originated from agricultural cultivation. Previous studies have demonstrated high residues of Pb in sediment in the estuaries of Tongyang River (Gan 2008; Huang 2009) and Zhogao River (Cao et al. 2004; Sun et al. 2008), which are located in the eastern lake and are predominantly related to agricultural cultivation. Evidence of agriculture-dominated Pb and Cd in the sediment of the ten valleys around the southwestern and northern lake was verified by the significant positive correlation between the concentrations of the total phosphorus and heavy metals (Tang et al. 2010). Thus, the significant accumulation of Cd and Pb in Chaohu Lake was due to the application of phosphate fertilizer containing Pb and Cd (Chen et al. 2009; Mar and Okazaki 2012) during agricultural cultivation around the study area (Zhang and Shan 2008). Hence, Cd, Pb, Zr, Hf, U, Sr, Zn, Th, Rb, Sn, Cs, Tl, Bi, Ba, and Ta were from agricultural nonpoint sources.

V, Cr, Co, Ti, Ni, Cu, Nb, Mn, and Mo were evenly distributed, and there were no significant differences in the average concentrations between the western and eastern parts of the lake (Fig. 2). The concentrations of V, Cr, Cu, Ni, and Mn were significantly correlated with sediment TOC (Table S5). The lake suffered from long-term eutrophication; as a result, sediment TOC mostly originated from internal sources (e.g., plankton decomposition) (Liu et al. 2008; Yao and Li 2004; Zan et al. 2011). Therefore, these elements reflect the natural occurrence in the lacustrine system.

Some previous studies have suggested that the western lake was more severely affected by heavy metals than the eastern lake was (Cheng et al. 2008; Kong et al. 2015; Liu et al. 2012; Zheng et al. 2011) based on the limited numbers of samples

and elemental species. For example, Zheng et al. analyzed the Cr, Pb, Cu, Co, Zn, and Ni in nine surface sediment samples with four from the western lake and five from the eastern lake (Zheng et al. 2011). The results showed higher mean concentrations of Cr and Pb and lower mean values of Cu and Zn in the western lake, and the concentrations of Co and Ni were comparable between the western and eastern lake. Their data supported our conclusions because our results also indicate that Zn and Cu were found at higher concentrations in the eastern lake (Fig. 2) and that Co and Ni did not show significant spatial variation. Conversely, Pb was found in higher concentrations in the eastern lake in our study. A minimal value of Pb, approximately one order of magnitude lower than the mean concentration, was obtained in the eastern lake in the previous study (Zheng et al. 2011).

Source apportionment

The results of the PCA analysis indicate that three eigenvectors-factors could explain the majority of the variance (87.9 %). Factor 1 was mostly associated with Cu, Zn, Rb, Sr, Zr, Cd, Sn, Cs, Ba, Hf, Ta, Tl, Pb, Bi, U, and Th, with high CV values (Fig. S11), and the loading of the rotated component matrix was logically correlated to the coefficients of variation of individual elements (Fig. 3), which indicated that they were predominately derived from exterior sources. Factor 2 was mostly explained by Ti, V, Cr, Mn, Co, and Ni, and the factor 2 loading was negatively correlated with the CV value of the individual elements (Fig. 3), which indicated that factor 2 represents the natural occurrence (interior source) of these metals. These results also suggest that the origins associated with the spatial variation were the major controlling factor for the classification by PCA analysis. Factor 3 was contributed by Ga. Because urban and industrial sewage was not a major contributor to the enrichment of these sediment-associated

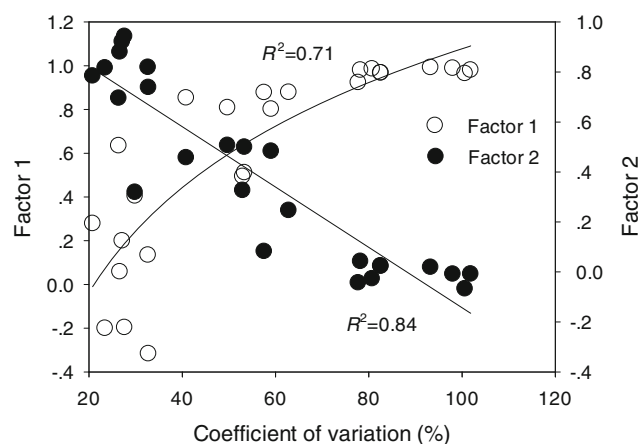


Fig. 3 The logical correlation between CV and factor 1 by PCA (circle) and the negative correlation between CV and factor 2 (black circle)

metals in Chaohu Lake, factor 1 was mostly contributed by agriculture cultivation, and factors 2 and 3 potentially represented the natural background.

Figure 4 shows the predicted concentrations of elements by PCA-MLR; Fig. 4a shows that the concentrations were perfectly modeled with the measured values for each element. The linear correlation between the predicted and observed concentrations for all elements had an $R^2=1.0$. For Tl, Bi, Ta, Cs, Sn, U, Cd, Th, Pb, Rb, Hf, Sr, Ba, Zn, and Zr, the contributions from exterior sources were significantly higher than from interior sources (Fig. 4b). The average contribution of agricultural cultivation ranged from $59.0\pm 24.5\%$ for Rb to $92.7\pm 17.7\%$ for Cd. However, Mo, Co, Nb, Ni, Cu, Ga, Cr, V, Mn, and Ti in the sediment of Chaohu Lake were expected to be authigenous in origin, with the average contributions of exterior sources ranging from $0.45\pm 1.31\%$ for Co to $44.7\pm 33.9\%$ for Cu.

The sedimentation rate in Chaohu Lake was estimated to be ~ 0.25 cm/year (Du et al. 2004); thus, the elemental sedimentary flux for the whole lake from agricultural cultivation was estimated from 8.3 kg/year for Co to 109,000 kg/year for Zn (Fig. S12). The individual elemental sedimentary rate was from 0.01 mg/m²/year for Co to 128 mg/m²/year for Zn. The average sedimentary rates of Cu, Zn, and Pb from anthropogenic sources were estimated at 16.2, 246, and 47.8 mg/m²/year in a previous study (Du et al. 2012). The reason for the variations of Cu, Zn, and the sedimentary rates between the previous and present studies was due in part to the scale of the study area. The estimated elemental sedimentary rates were

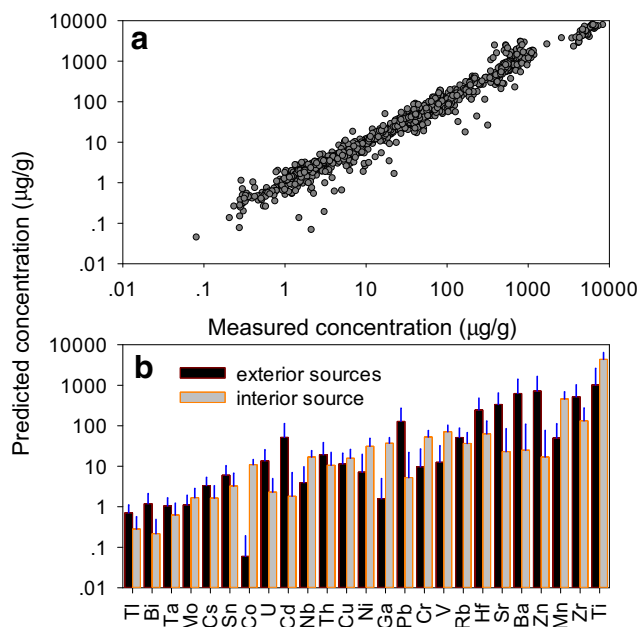


Fig. 4 The correlation between the measured and predicted elemental concentrations (a) and the predicted concentrations from the exterior and interior sources of individual elements (b). The results are shown on a log scale

obtained based on one sampling site in the previous study, but the estimates were made for the whole lake in the present study. The concentrations of individual elements in the riverine runoff and in eroded soils were from 0.0020 µg/L for Co to 26.5 µg/L for Zn and from 0.003 µg/g for Co to 128 µg/g for Zn, considering the annual total volume of riverine runoff and eroded soil at 4.12×10^9 m³ and 2.6×10^6 t, respectively.

Pollution assessment

Table S6 illustrates the CF value of individual elements in the surface sediment samples collected from Chaohu Lake. CF ranged from 0.59 ± 0.29 for Cs to 334 ± 327 for Cd (Table S6 and Fig. 5). Sediment was weakly affected by Cr, Co, Cs, and Ba because more than 30 samples showed low contamination by the four metals. Furthermore, more than 50 % of the samples exhibited low pollution levels of Ti, V, Mn, and Rb. For Ni, Cu, Ga, Nb, Ta, and Tl; the samples had moderate contamination. The sediment contained high levels of Zn, Sr, Mo, Cd, Hf, Pb, Bi, and U. The CF values of Sr, Bi, Pb, Zn, U, Mo, Hf, and Cd were greater than 6.0 in 9, 16, 19, 21, 21, 22, 42, and 44 of the 48 samples, respectively. A total of 87.5 and 91.7 % of the samples had high contamination by Hf and Cd; therefore, special attention should be given to the contamination of Cd and Hf in the sediment of Chaohu Lake. The low pollution of the bottom sediments by Ti, V, Cr, Mn, Co, and Ni supported the hypothesis of the autogenetic origins for these elements inferred above. The PLI values ranged from 0.34 to 4.02, with an arithmetic mean of 2.01 ± 1.25 , and 29 of the 48 samples were observed with PLI values greater than 1.0, which suggests that metal pollution occurs in the bottom sediment of Chaohu Lake because a PLI value greater than 1.0 indicates the existence of contamination (Varol 2011). Despite the highest PLI value being observed at site L9, which was located in the western lake, the mean PLI in the eastern lake was significantly higher than in the western lake ($p<0.01$), thus indicating that the eastern lake was more strongly polluted by metal elements (Fig. 5).

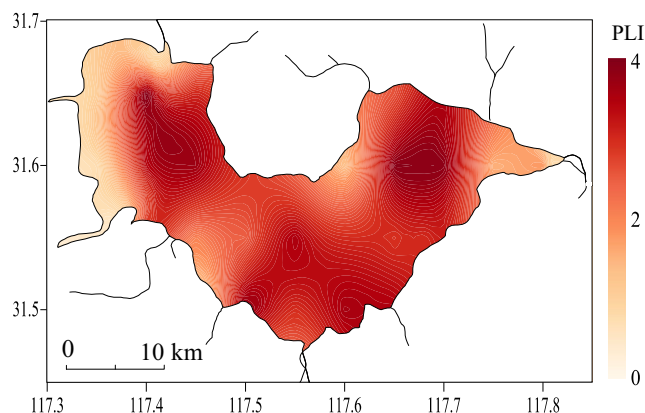


Fig. 5 The spatial distribution of the pollution level index

The arithmetic means of I_{geo} for Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Zr, Nb, Cs, Ba, Ta, Tl, Pb, and Th were less than 0, which suggested that the sediments of Chaohu Lake were lowly polluted by these elements (Table S7). However, the overall sediment samples were freely to moderately polluted by Ga, Sr, and Sn because the means of I_{geo} were 0.61 ± 0.54 , 0.43 ± 1.51 , and 0.41 ± 1.13 , respectively. Mo, Bi, and U showed moderate to heavy pollution in the sediments. Hf and Cd had heavy and extreme contamination in the bottom sediments. All sediment samples were lowly to moderately polluted by Ti, V, Cr, Mn, Co, Ni, Cu, Ga, Rb, Zr, Nb, Sn, Cs, Ba, Ta, Tl, and Th. Overall, 43.8, 18.8, 45.8, 33.3, 41.7, 39.6, 33.3, and 43.8 % of the sediment samples were moderately to heavily affected by Zn, Sr, Mo, Cd, Hf, Pb, Bi, and U, respectively, because their I_{geo} values were less than 4.0 but greater than 2.0. A total of 23 and 27 of the 48 samples were heavily to extremely polluted by Hf and Cd, respectively. These results also reveal that autogenetic elements had weak pollution and that Hf and Cd severely threatened the bottom sediment of Chaohu Lake.

The results of the EF values also indicate V, Cr, Mn, Co, Ni, Cu, Rb, Nb, Cs, Ba, Ta, and Tl were weakly accumulated in the bottom sediment samples (Table S8). More than 40 % of the samples were moderately to moderately severely enriched in Sr, Mo, Sn, Pb, and Bi. Zn, Sr, Mo, Cd, Hf, Pb, Bi, and U had severe enrichment in 19, 2, 3, 5, 4, 3, 2, and 19 of the 48 bottom sediment samples, respectively. Four samples exhibited very severely accumulated Hf; in addition, 27 and 20 samples demonstrated extremely severely accumulated Cd and Hf. Therefore, the EF values also demonstrate that the bottom sediment of Chaohu Lake is extremely severely enriched in Cd and Hf.

Conclusion

Despite numerous studies that set out to examine the contamination of sediment-associated heavy metals around Chaohu Lake, the insufficient number of samples and element species prevented any precise and comprehensive conclusions. In the present study, surface sediment from 48 sites covering the whole lake and three main estuaries of rivers were collected to determine 25 metal elements. Element accumulation, spatial distribution, source appointments and pollution status were investigated using multivariate statistical techniques combined with pollution indices. The following conclusions can be made:

1. Cd, Pb, Zr, Hf, U, Sr, Zn, Th, Rb, Sn, Cs, Tl, Bi, Ba, and Ta had significant spatial distributions, with higher residual concentrations in the eastern lake than in the western lake, but Ga, V, Cr, Co, Ti, Ni, Cu, Nb, Mn, and Mo were

evenly distributed in the bottom sediment within the whole lake.

2. Cu, Zn, Rb, Sr, Zr, Cd, Sn, Cs, Ba, Hf, Ta, Tl, Pb, Bi, U, and Th were predominately from agricultural activities, whereas Ti, V, Cr, Mn, Co, and Ni were potentially endogenous elements
3. Sediments in the eastern lake were more heavily affected by metal elements compared with the western lake, and Hf and Cd posed extremely high risks to Chaohu Lake.

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