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RESEARCH ARTICLE

A comparative study of metal pollution and potential eco-risk in the sediment of Chaohu Lake (China) based on total concentration and chemical speciation

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Abstract Total and extractable concentrations of Cu, Pb, and Zn were determined in surface sediments of west Chaohu Lake (China) by HCl-HNO_3-HF-$HClO_4$ digestion and an optimized BCR sequential extraction procedure, respectively. The metal pollution was evaluated by the enrichment factor approach, and the potential eco-risk was evaluated by the sediment quality guideline (SQG) and risk assessment code (RAC) assessments. The results indicated that both total and extractable metal concentrations were highly variable and were affected by sediment properties, even though the sediments were predominantly composed of <63-μm particles (>89 %). Enrichment factors of the metals based on the total and extractable concentrations all showed higher values in the northern lake area and decreasing values towards the south. This distribution indicated an input of anthropogenic metals via the Nanfei River. Anthropogenic Cu, Pb, and Zn in surface sediments showed comparable values for each metal based on the total and extractable concentrations, suggesting that anthropogenic Cu, Pb, and Zn resided predominantly in the extractable fractions. Sediment Cu had low eco-risk, and Pb and Zn had medium eco-risk by the SQG assessment, whereas the eco-risk rankings of Cu, Pb, and Zn were medium, low, and low–high, respectively, by the RAC assessment. Referencing to the labile (dilute acid soluble) metal concentrations, we deduced that the eco-risk of Cu may be largely overestimated by the RAC assessment, and the eco-risk of Pb may be largely overestimated by the SQG assessment. Overall, sediments Cu and Pb may pose low eco-risk, and Zn may pose low–high eco-risk.

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Keywords Metal · Total concentration · Chemical speciation · Pollution · Eco-risk · Sediment

Abbreviations

EF	Enrichment factor
SQG	Sediment quality guideline
RAC	Risk assessment code
BCR	Community Bureau of Reference
LOI	Loss on ignition
TELs	Threshold effect levels
PELs	Probable effect levels
SEM	Simultaneously extracted metals
AVS	Acid volatile sulfides

Introduction

Human activities are significantly increasing the load of potentially toxic metals to the aquatic environment (Cheng 2003; Pan and Wang 2012). A major proportion of the anthropogenic metals are stored in the bottom sediment by relatively weak physical and chemical bonds (Passos et al. 2010; Lewis et al. 2011; Weber et al. 2013), which may be remobilized and made bioavailable more easily than geogenic metals (Pertsemli and Voutsa 2007; Delgado et al. 2011; Birch and Apostolatos 2013), posing high potential adverse effects on the health of aquatic ecosystems (Lewis et al. 2011; Weber et al. 2013). Therefore, quantifying the magnitude of anthropogenic metals in sediment and determining the potential eco-risk accurately are important facets of sediment quality assessment and aquatic environmental protection.

Total metal concentrations are usually determined in sediment quality assessments; however, these data are strongly influenced by variations in sediment properties (primarily grain size and organic matter content), and concentrations tend to increase as sediment becomes finer due to active scavenging of metals by fine-grained particles (Birch et al. 2008; Yuan et al. 2012). This "grain size effect" on metal concentrations may confuse and even cause misleading interpretation of pollution levels. Consequently, a normalizing procedure to reduce the confusion caused by variable sediment properties is essential for the interpretation of chemical data (Birch 2003; Birch et al. 2008). For coarse-grained estuarine and coastal sediments, physical segregation and analysis of the <63-μm fraction is usually used (Birch 2003; Olivares-Rieumont et al. 2005; Díaz-de Alba et al. 2011). For the fine-grained lake and marine sediments, metal concentrations in the bulk sediments are typically determined, and the chemical data are standardized using a conservative element, wherein an enrichment factor (EF) method is used for the pollution estimation (Birch et al. 2008; Selvam et al. 2012; Yuan et al. 2012). Generally, these approaches reduce the influence of the grain size effect on metal concentrations and improve quantification of pollution levels.

Chemical speciation of metals determined by sequential extraction procedures has also become a common approach in studies of sediment quality. These data can contribute insights into the biological availability and potential mobilization of metals as well as their pollution levels (Sakan et al. 2007; Passos et al. 2010; Velimirovic et al. 2011). Certain studies have indicated that chemical partitioning of metals is also grain-size dependent in coarse-grained sandy sediment (Clark et al. 2000; Pagnanelli et al. 2004; Sutherland and Tack 2007). However, the potential influence of variable sediment texture on the chemical partitioning of metals for fine-grained sediment (i.e., silt and clay) is seldom addressed in studies of sediment quality, and few studies have compared the relationships of anthropogenic metals quantified based on their total concentrations and chemical speciation.

The potential eco-risk of metals in sediment is primarily related to their concentrations and chemical partitioning, in addition to the environmental factors (Simpson and Batley 2009; Campana et al. 2013). To understand the potential eco-risk of metals in sediment, various risk assessment indices have been developed. Sediment quality guideline (SQG) and the risk assessment code (RAC) are two commonly used methods in eco-risk assessment, which are related to the total concentration index and the speciation index (Long et al. 1995; Smith et al. 1996; Burton 2002; Jain 2004). The SQG was developed based on the biological effect database from equilibrium-partitioning models, laboratory-spiked sediment toxicity tests and field investigations on the toxicity, and benthic community composition in sediment (Long et al. 1995; Smith et al. 1996; Burton 2002). The RAC was assigned by considering the percentage of metals associated with sediment in the labile fraction (Jain 2004; Delgado et al. 2011), which may relate more directly to the mobility of metals and their bioavailability (Velimirovic et al. 2011). However, studies indicated that both SQG and RAC might provide inadequate information for the eco-risk of metals (Pertsemli and Voutsa 2007; Simpson and Batley 2009; Velimirovic et al. 2011). It is because that the RAC does not take into consideration the labile concentrations of metals, and the SQG does not take into consideration the toxicity threshold change for different sediment types (Campana et al. 2012). Despite the known potential limitations of the SQG and RAC assessments, a comparative study on eco-risk ranking of metals in sediment using the two assessments has been scarcely performed (Yu et al. 2011).

Chaohu Lake is the fifth largest freshwater lake in China, playing an important role not only in fishing, industrial and agricultural irrigation water, and flood prevention but also as an important source of drinking water for surrounding cities. Since the 1980s, however, massive economic growth in Chaohu Lake catchment and release of contaminants had induced the sediment pollution by metals, especially in western lake area of Chaohu Lake (termed "west Chaohu Lake") (Liu et al. 2012; Yin et al. 2011). Research also indicated that metal concentrations in the tissue of snails (*Bellamya aeruginosa*) and white shrimp in the west Chaohu Lake were relatively higher than in other lake areas (Du 2009; Yin et al. 2014), implying the potential influence of metal pollution in sediment on the health of aquatic ecosystems and safety of aquatic products in Chaohu Lake. However, limited information is available on the anthropogenic contributions, chemical partitioning, and potential eco-risk of metals in the sediment.

In this study, total and extractable (including dilute acid soluble, reducible, and oxidizable fractions) concentrations of metals (Cu, Pb, and Zn) and sediment properties (grain size composition and organic matter content) of surface sediments from west Chaohu Lake were examined. The objectives of the present study were the following: (1) to examine the spatial distribution of Cu, Pb, and Zn in total concentrations and chemical partitioning in the sediments and the potential influence of the grain size effect on the chemical data, (2) to quantify and compare the pollution features of these metals based on the chemical data, and (3) to evaluate the potential eco-risk of Cu, Pb, and Zn using the SQG and RAC assessments with reference to their chemical partitioning and anthropogenic contributions. We anticipated that our study would provide an improved methodology for evaluating metal pollution and the eco-risk of fine-grained sediment.

Materials and methods

Site description

Chaohu Lake is located in the middle reach of the Yangtze River watershed in China. The lake has a water surface area of 770 km^2 and a mean depth of 2.7 m (Wang and Dou 1998).

Chaohu Lake is recharged primarily by precipitation (996 mm per year) (Wang and Dou 1998). Among the inflow rivers (Fig. 1), the Hangbu River is the largest and accounts for 65 % of the annual runoff, followed by the Nanfei River (11 %) (CCCA 1993). Outflow is via the Yuxi River located in the eastern part of the catchment that feeds the Yangtze River. As a result of rapid economic development and urbanization since the 1980s, a large amount of industrial and domestic sewage was discharged into Chaohu Lake. The discharge was recorded to be 1.4×10^{8} t in 1997, 80 % of which was from Hefei City (Dang 1998), which is the biggest city and the most important economic center in the catchment, with a population of 5.7 million. The high pollutive industries include iron and steel smelting, chemical industry, papermaking, and thermal power industry (Dang 1998). Nanfei River, as the main wastewater discharge channel of Hefei City (Fig. 1), is one of the most severely polluted rivers (Dang 1998; Li et al. 2012).

Sample collection

Twenty-nine surface (0–2 cm) sediments were obtained from the west Chaohu Lake (Fig. 1) in April 2011 using a modified UWITEC gravity corer. Samples were transferred into polyethylene bags, placed into a refrigerating box, and transported to the laboratory. The four samples obtained at a sediment depth of 25, 40, 45, and 50 cm from a core collected in the west Chaohu Lake (Fig. 1) in 2007, which corresponded to preindustrial sediment based on the ^{210}Pb dating (Liu et al. 2012), were determined in this study and used as the reference background.

Laboratory analysis

Surface and background samples were freeze-dried, ground to pass through a 150-mesh sieve, and oven-dried at 105 °C for 2 h prior to analysis.

Accurately weighed samples (approximately 0.12 g) were completely digested with HCl-HNO$_3$-HF-HClO$_4$ in a Teflon beaker. Metal (Al, Cu, Fe, Pb, and Zn) concentrations (termed "total concentrations" relative to the "extractable concentrations" of metals determined by the Community Bureau of Reference (BCR) sequential extraction procedure) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Profile DV).

The optimized BCR sequential extraction procedure, proposed by the European Standard Measurements and Testing program, formerly the BCR (Rauret et al. 1999), was applied to determine the chemical speciation of Cu, Pb, and Zn in sediments of Chaohu Lake. The sequential extraction procedure included the three following extractable fractions: the dilute acid soluble fraction (exchangeable and carbonate-bound, F1 fraction), the reducible fraction (Fe/Mn oxide- and oxyhydroxide-bound, F2 fraction), and the oxidizable fraction (organic matter and sulfide-bound, F3 fraction). Metals in the F1, F2, and F3 fractions were determined, and their sum was defined as the extractable concentrations for each metal. Concentrations of Cu, Pb, and Zn in the extraction solutions were determined by inductively coupled plasma mass spectroscopy (ICP-MS, 7700x).

Grain size distribution in the sediments was measured using a Malvern Mastersizer 2000 instrument following removal of organic matter using 5 % H_2O_2, washing, and ultrasonic dispersion. The instrument accuracy was ±1 % on the DV50 using the Malvern Quality Audit Standard. The organic matter content was measured as loss on ignition (LOI) values at 550 °C for 4 h (Heiri et al. 2001).

Quality control

Data quality during the HCl-HNO$_3$-HF-HClO$_4$ digestion and ICP-AES measuring was ensured using the standard reference material GBW07309 after every tenth sample. Precision, determined by replicate analysis, was <5 % relative standard deviation, and accuracy, expressed as recovery of the reference material, was between 92 and 106 % for all of the metals.

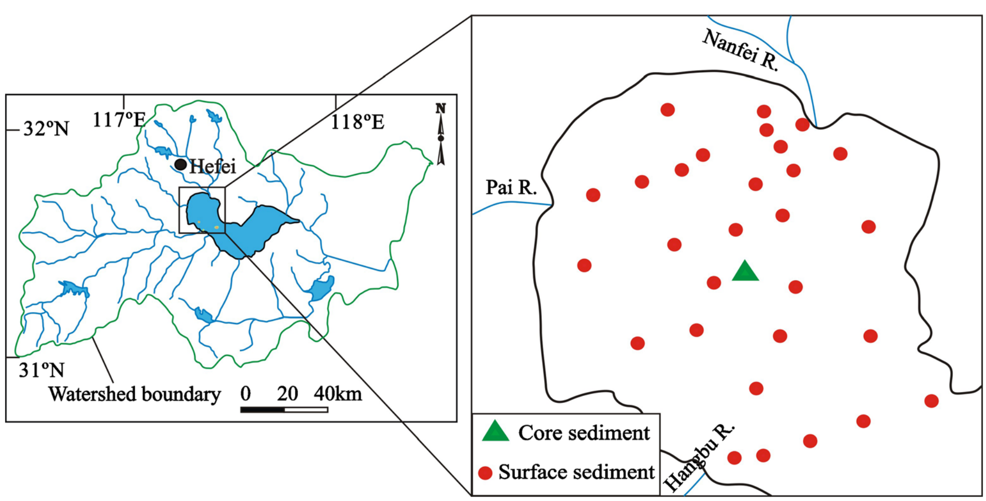

Fig. 1 Location of the Chaohu Lake and sampling sites of the sediments

No contamination was detected in the laboratory or in the procedural blanks.

During the sequential extraction analysis, accuracy control was performed with duplicates of the GBW07436 standard reference material. The replicate analyses of GBW07436 indicate relative standard deviations <13 % for the metals in each fraction except for oxidizable Zn (21 %). Nearly all of the determined values of Cu, Pb, and Zn in the extractable fractions (F1, F2, and F3) were within the certified ranges (Table 1), which indicated a high precision of the sequential extraction analysis.

Indices of pollution evaluation

Pollution of Cu, Pb, and Zn in surface sediments of west Chaohu Lake was evaluated with reference to the EF approach (Birch et al. 2008; Selvam et al. 2012; Yuan et al. 2012), wherein Al was selected as the reference element for chemical data standardization, and the preindustrial concentrations of the metals in a sediment core collected in west Chaohu Lake were used as the background.

EFs of Cu, Pb, and Zn based on the total metal concentrations were calculated following Eq. (1):

$$EF_{\mathrm{n}} = (C_{\mathrm{ns}}/Al_{\mathrm{s}})/(C_{\mathrm{nb}}/Al_{\mathrm{b}}) \quad (1)$$

where EF_{n} is the enrichment factor of element n, C_{ns} and C_{nb} are the concentrations of element n in surface and background sediments, respectively, and Al_{s} and Al_{b} are the concentrations of Al in surface and background sediments, respectively.

Table 1 Comparisons of the determined and reference values of the GBW07436 standard reference material

Speciation	Parameters	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
F1	R.D. (n=9)	2.3–2.5	1.2–1.3	18–20
	M.D. (n=9)	2.5	1.2	19
	R.R. (n=7–9)	2.4–2.8	1.1–1.8	16–25
	M.R. (n=7–9)	2.6	1.5	20
F2	R.D. (n=9)	9.0–11	50–55	27–32
	M.D. (n=9)	9.9	51	29
	R.R. (n=8–9)	7.4–9.6	44–55	16–32
	M.R. (n=8–9)	8.5	49	24
F3	R.D. (n=9)	1.9–2.4	5.4–6.4	15–22
	M.D. (n=9)	2.1	5.9	19
	R.R. (n=9)	1.6–3.3	3.1–7.7	12–24
	M.R. (n=9)	2.4	5.4	18

R.D. ranges of determined values, *M.D.* means of determined values, *R.R.* ranges of reference values, *M.R.* means of reference values

EFs of Cu, Pb, and Zn based on the extractable concentration were calculated following Eq. (2):

$$EF'_{\mathrm{n}} = (C'_{\mathrm{ns}}/Al_{\mathrm{s}})/(C'_{\mathrm{nb}}/Al_{\mathrm{b}}) \quad (2)$$

where EF'_{n} is the enrichment factor of element n, and C'_{ns} and C'_{nb} are the extractable (F1+F2+F3) concentrations of element n in surface and background sediments, respectively.

Anthropogenic Cu, Pb, and Zn based on the total and extractable concentrations and corresponding EFs were estimated following Eqs. (3) and (4), respectively, assuming that the EF >1 indicates the presence of pollution. Anthropogenic Cu, Pb, and Zn based on the total concentrations are expressed mathematically in the following equation:

$$M_{\mathrm{n\text{-}anthro}} = C_{\mathrm{ns}} \times ((EF_{\mathrm{n}}-1)/EF_{\mathrm{n}}) \quad (3)$$

Anthropogenic Cu, Pb, and Zn based on the extractable concentrations are expressed mathematically in the following equation:

$$M'_{\mathrm{n\text{-}anthro}} = C'_{\mathrm{ns}} \times ((EF'_{\mathrm{n}}-1)/EF'_{\mathrm{n}}) \quad (4)$$

Indices of eco-risk assessment

The SQG was used for the potential eco-risk assessment of Cu, Pb, and Zn in surface sediments of west Chaohu Lake based on the total concentrations. The freshwater ecosystem SQG used in Canada was used as a reference to provide threshold effect levels (TELs) and probable effect levels (PELs) (Smith et al. 1996). The metals had no or low eco-risk when concentrations were <TELs (36, 35, and 123 mg kg^{-1}for Cu, Pb, and Zn, respectively) and high or very high eco-risk when concentrations were >PELs (191, 91, and 315 mg kg^{-1} for Cu, Pb, and Zn, respectively) (Smith et al. 1996). The metals pose medium eco-risk when concentrations were between the TELs and PELs.

In addition, the RAC was used for the potential eco-risk assessment of Cu, Pb, and Zn in surface sediments of west Chaohu Lake based on the chemical partitioning. According to the RAC (Jain 2004; Delgado et al. 2011), there is no eco-risk when the metal in the labile fraction (i.e., F1 fraction) is lower than 1 % of the total concentration; there is a low eco-risk from 1−10 %, a medium eco-risk from 11−30 %, a high eco-risk from 31−50 %, and a very high eco-risk for higher F1 fraction percentages.

Data processing

Correlation analysis was used to elucidate the interrelationship among the sediment indices, which was conducted using the SPSS 12.0 software for Windows. Spatial distributions of the metals were depicted through the Kriging method using Surfer 10 software (Golden Software Inc.).

Results

Sediment property

Surface sediments in west Chaohu Lake were predominantly composed of fine-grained particles (<63 µm), which ranged from 90 to 100 %, with high values in the central lake area (Fig. 2a). The LOI value ranged from 3 to 12 % and exhibited higher values in the central lake area (Fig. 2b). The background sediments of the core were exclusively composed of <63-µm particles and have a mean LOI of 4 %.

Total metal concentrations

The total concentrations of Al, Fe, Cu, Pb, and Zn in surface sediments of west Chaohu Lake were highly variable (Table 2). The chemical data showed generally high values in the central lake area (Fig. 2c–g), similar to the spatial distributions of the LOI values (Fig. 2b) and the percent composition of the <63-µm particles (Fig. 2a). Zinc also exhibited high concentrations in the northern lake area near the Nanfei River mouth (Fig. 2g). Most of the metals showed positive correlations ($p \leq 0.05$) with the LOI values and the percentage of the <63-µm particles (Table 3). Compared with background sediments, surface sediments were 1.1-fold higher in concentrations for Al and Fe and were 1.6- to 3.9-fold enriched with Cu, Pb, and Zn, on average (Table 2).

Chemical partitioning of the metals

Spatially, Cu and Pb in the three extractable fractions and Zn in the reducible and oxidizable fractions exhibited high values in the central lake area (Fig. 2h–i, k–p). Dilute acid soluble Zn showed higher concentrations in the northern lake area near the Nanfei River mouth and decreased values towards the south (Fig. 2j). The concentrations of extractable Cu and Pb

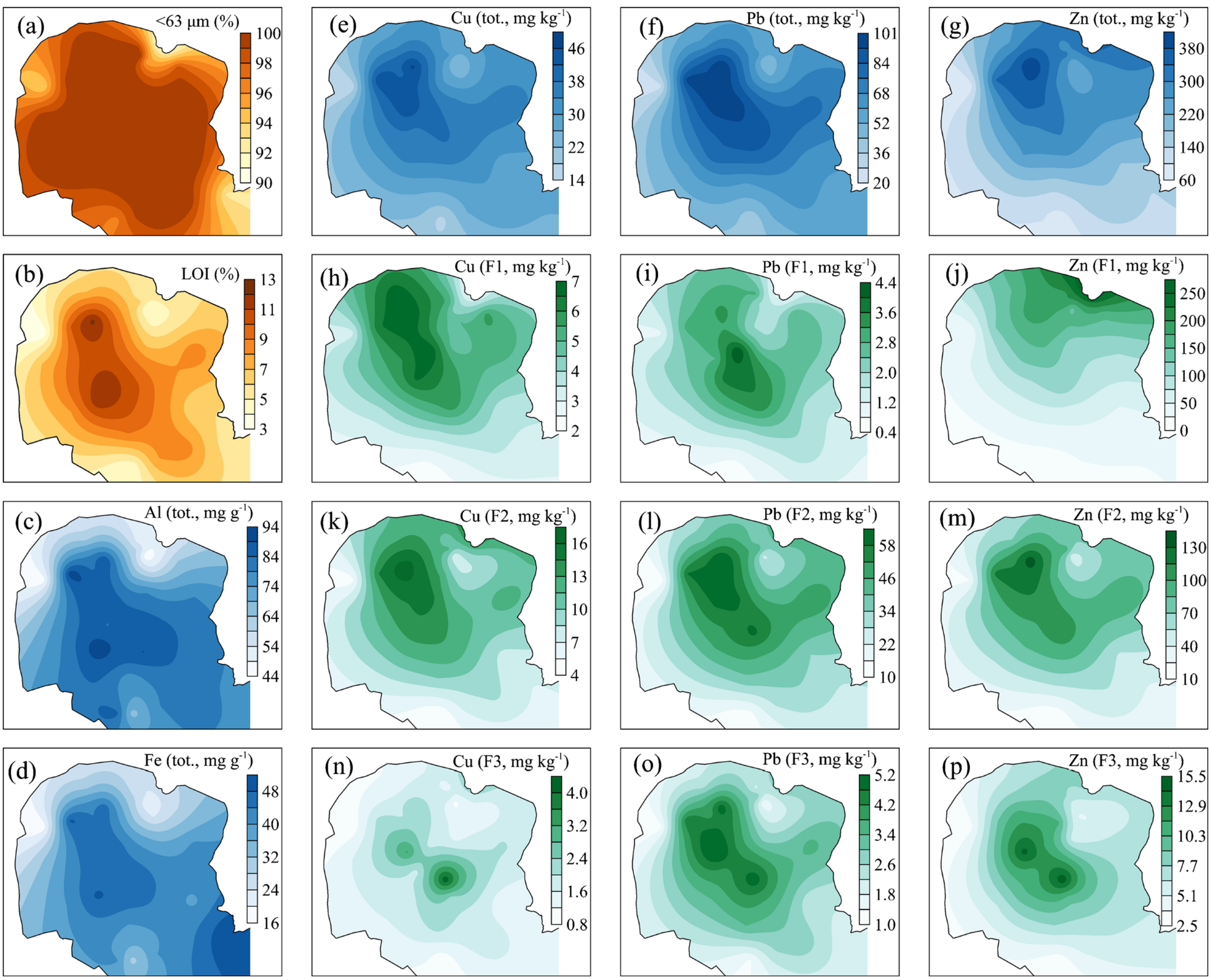

Fig. 2 Spatial variations of the <63-µm particles, LOI values, total (tot.) and extractable (F1, F2, and F3) concentrations of the metals in surface sediments of west Chaohu Lake

Table 2 Total metal concentrations of surface and background (preindustrial) sediments of west Chaohu Lake

		Al (mg g^{-1})	Fe (mg g^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
Surface sediments (*n*=29)	means	74	37	31	68	244
	ranges	46–93	17–52	15–47	26–101	70–428
Background sediments (*n*=4)	means	69	33	19	30	63
	ranges	65–74	29–37	16–22	29–31	58–69

showed positive correlations (p=0.01) with LOI values, and that of extractable Pb also exhibited a positive correlation (p=0.05) with the percentage of the <63-μm particles (Table 3).

On average, Cu and Pb were primarily associated with the reducible fraction in the surface sediments (Fig. 3a), which averaged 11 and 40 mg kg^{-1}, respectively, and accounted for 34 and 59 % of their total concentrations, respectively. Zinc was primarily present in the dilute acid soluble fraction (mean value of 107 mg kg^{-1}) followed by the reducible fraction (mean value of 74 mg kg^{-1}) (Fig. 3a), which accounted for 44 and 30 % of the total concentration, respectively. The oxidizable fraction of Cu, Pb, and Zn averaged 1.8, 3.0, and 7.7 mg kg^{-1}, respectively (Fig. 3a), and accounted for 6, 4, and 3 % of their total concentrations, respectively. The concentrations and percentages of oxidizable Cu, Pb, and Zn in surface sediments of west Chaohu Lake were low compared with other studies (Olivares-Rieumont et al. 2005; Pertsemli and Voutsa 2007; Passos et al. 2010), which may be due to the low organic matter content.

Compared with the background sediments (Fig. 3b), concentrations of Cu, Pb, and Zn were 2.8- to 38-fold, 1.7- to 7.2-fold, and 1.6- to 2.0-fold higher in the dilute acid soluble, reducible, and oxidizable fractions, respectively, in surface sediments of west Chaohu Lake. The most significant increase was in the dilute acid soluble Zn, which increased 38-fold.

Discussion

Pollution determination

Positive correlations (p=0.05) between most of the chemical data and the grain size and LOI values in surface sediments of west Chaohu Lake (Table 3) suggested that variations in the total and extractable concentrations of the metals were influenced by sediment properties. Therefore, a normalizing procedure to reduce the confusion on the chemical data caused by variable sediment properties should be used for the pollution determination. The low concentrations of oxidizable Cu, Pb, and Zn (Fig. 2n–p) and the low LOI values (Fig. 2b) in surface sediments of west Chaohu Lake suggested that variations in organic matter content should have less influence on Cu, Pb, and Zn concentrations. Thus, concentrations of Cu, Pb, and Zn should be influenced primarily by the grain size composition. Based on the systematic correlation analysis between the chemical data and the grain size fractions (Fig. 4), the >16-μm particles should play a dilution role in the metal concentrations, and the <12-μm fraction should contribute to metal enrichment. Theoretically, the <12-μm particles should be analyzed if the physical segregation was used to compensate for the grain size effect; however, this laboratory procedure is difficult and time-consuming. Consequently, the EF method

Table 3 Correlation coefficients between total (tot.) and extractable (extract.) concentrations of metals and sediment proxies in surface sediments of west Chaohu Lake

	$Al_{(tot.)}$	$Fe_{(tot.)}$	$Cu_{(tot.)}$	$Pb_{(tot.)}$	$Zn_{(tot.)}$	$Cu_{(extract.)}$	$Pb_{(extract.)}$	$Zn_{(extract.)}$	LOI
$Fe_{(tot.)}$	0.948[a]								
$Cu_{(tot.)}$	0.644[a]	0.654[a]							
$Pb_{(tot.)}$	0.696[a]	0.695[a]	0.980[a]						
$Zn_{(tot.)}$	0.177	0.211	0.835[a]	0.801[a]					
$Cu_{(extract.)}$	0.397[b]	0.426[b]	0.922[a]	0.906[a]	0.899[a]				
$Pb_{(extract.)}$	0.521[a]	0.545[a]	0.961[a]	0.961[a]	0.880[a]	0.970[a]			
$Zn_{(extract.)}$	−0.069	−0.021	0.683[a]	0.637[a]	0.962[a]	0.825[a]	0.773[a]		
LOI	0.756[a]	0.756[a]	0.829[a]	0.857[a]	0.531[a]	0.786[a]	0.820[a]	0.358	
<63 μm	0.527[a]	0.353	0.416[b]	0.474[a]	0.122	0.340	0.395[b]	0.012	0.541[a]

[a] Correlation is significant at the 0.01 level (two-tailed test)

[b] Correlation is significant at the 0.05 level (two-tailed test)

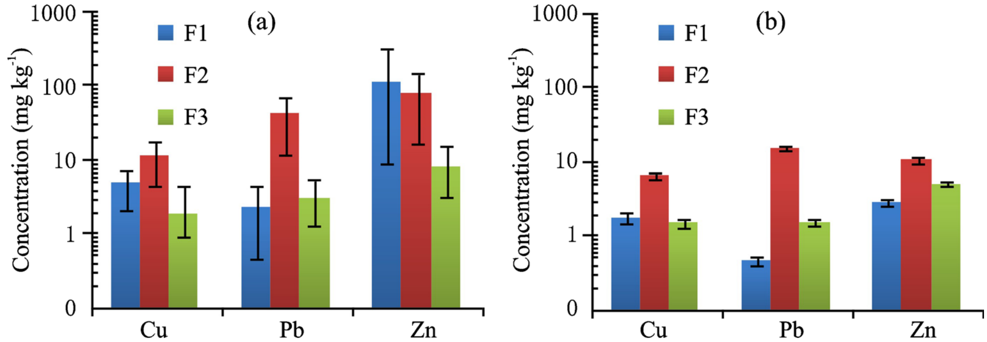

Fig. 3 Concentrations of Cu, Pb, and Zn in each chemical fraction (F1, F2, and F3) in (**a**) surface and (**b**) background sediments of west Chaohu Lake

was referenced to establish a value estimating the anthropogenic input of Cu, Pb, and Zn in surface sediments of Chaohu Lake (Birch et al. 2008; Selvam et al. 2012; Yuan et al. 2012). The conservative element Al exhibited a positive correlation (r>0.67, p<0.01) with the <12-μm fractions (Fig. 4), suggesting that Al can be used as a normalizer for the chemical data standardization in EF calculations.

EFs of Cu, Pb, and Zn based on the total and extractable concentrations are shown in Fig. 5. These factors varied from 0.8 to 23 and showed similar spatial trends for each metal, with higher values in the northern lake area and decreasing values towards the south. This spatial variation in EFs indicated the input of anthropogenic Cu, Pb, and Zn to Chaohu Lake via the Nanfei River, which is consistent with the monitoring results of the water (Li et al. 2012). Anthropogenic Cu, Pb, and Zn in surface sediments of west Chaohu Lake, calculated according to Eq. (3) and (4) based on the total and extractable concentrations, showed similar spatial variations, with high values in the central lake area and in the north (Fig. 6). The enrichment of anthropogenic Cu, Pb, and Zn in the central lake area should be due to the preferential deposition of pollutant combining with fine-grained particles (Birch et al. 2008). Anthropogenic Cu, Pb, and Zn averaged 11, 35, and 177 mg kg^{-1}, respectively, based on the total concentrations, which were comparable to the values of 7.2, 28, and 169 mg kg^{-1}, respectively, based on the extractable concentrations, suggesting that anthropogenic Cu, Pb, and Zn resided predominantly in the extractable fractions. Specifically, anthropogenic Zn was primarily concentrated in the dilute acid soluble fraction, followed by the reducible fraction, and anthropogenic Cu and Pb were primarily present in the reducible fractions by comparing the difference in the chemical data between the surface and background sediments (Fig. 3a, b). The chemical partitioning of anthropogenic Cu, Pb, and Zn in surface sediments of west Chaohu Lake was in agreement with other studies (Delgado et al. 2011; Díaz-de Alba et al. 2011; Velimirovic et al. 2011).

The above discussions highlighted that normalization on both total and extractable concentrations of metals should be performed in pollution quantification in the fine-grained sediment (i.e., silt and clay) in view of the potential influence of sediment properties on the chemical data. The conservative element normalization may be considered a candidate.

Potential eco-risk of the metals

The potential eco-risk classifications of Cu, Pb, and Zn in surface sediments of west Chaohu Lake according to the SQG and RAC assessments are presented in Fig. 7. Generally, Cu had a low eco-risk, and Pb and Zn posed a medium eco-risk according to the SQG assessment (Smith et al. 1996). Cu was categorized as a medium eco-risk, Pb posed a low eco-risk,

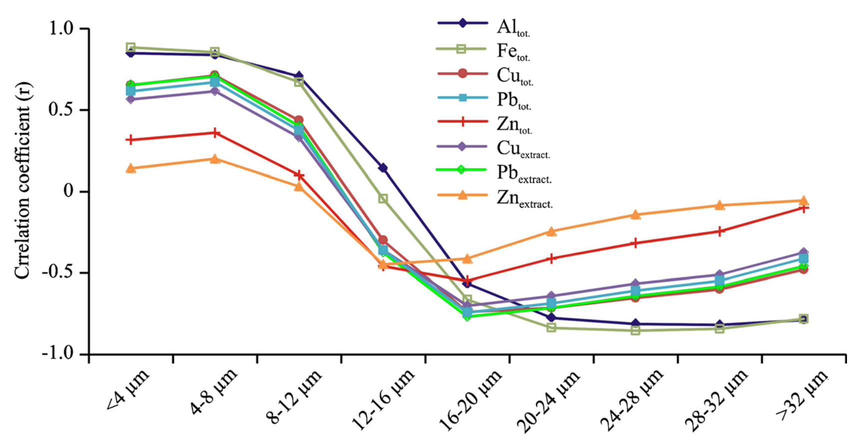

Fig. 4 Correlation coefficients between total (tot.) and extractable (extract.) concentrations of the metals and grain size fractions in surface sediments of west Chaohu Lake (R^2≥0.25, correlation is significant at the 0.01 level; R^2≥ 0.18, correlation is significant at the 0.05 level)

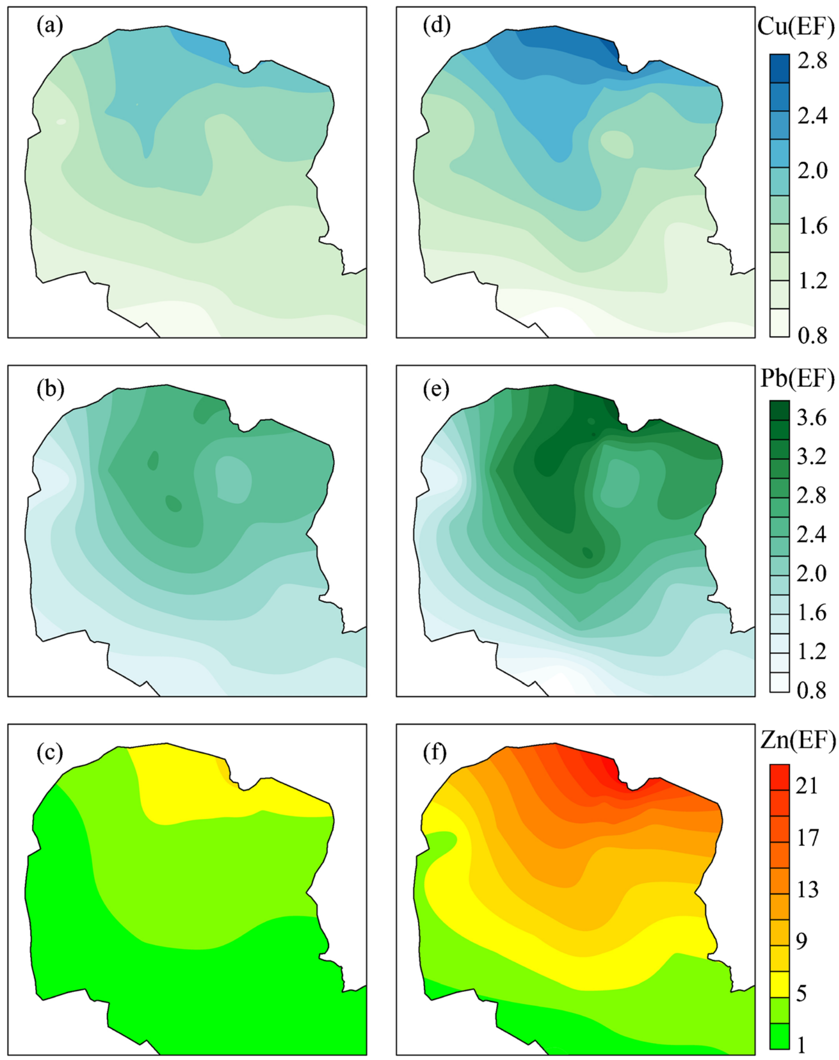

Fig. 5 **a**, **b**, **c** Enrichment factors of Cu, Pb, and Zn based on total concentrations. **d**, **e**, **f** Enrichment factors of Cu, Pb, and Zn based on extractable concentrations in surface sediments of west Chaohu Lake

and Zn exhibited a high eco-risk in the northern lake area and a decreased to low eco-risk towards the south according to the RAC assessment (Jain 2004).

Studies have shown that the measured and predicted toxicities for Cu, Pb, and Zn in the SQG have a high internal reliability (>95 %) when metal concentrations are lower than the TELs (Smith et al. 1996), which indicates that the TELs provide a more reliable upper boundary for the low eco-risk rank assignment and will be protective for the aquatic species. The internal reliability between the predicted and measured toxicity is generally low (<50 %) when metal concentrations are above the PELs (Smith et al. 1996), suggesting that the adverse biological effects may not occur when metal concentrations are above the PELs. In surface sediments of west Chaohu Lake, concentrations of total Cu were generally lower than the TEL boundary and were enriched by <two-fold (Fig. 5a). The dilute acid soluble fraction concentrations (Fig. 2h) and the anthropogenic Cu (Fig. 6a, d) were generally low (mean values <11 mg kg^{-1}), although the percentage of Cu in the dilute acid soluble fraction was relatively high (mean value of 15 %). Therefore, the eco-risk of Cu should be low, as indicated by the SQG assessment. Although the total Pb concentrations exceeded the TEL value in 97 % of the sediments (Fig. 7b), a less proportion (mean value of 3 %) and low concentrations of Pb were presented in the dilute acid soluble fraction (Fig. 2e). Because of the low internal reliability between the predicted and measured toxicity for Pb when its concentrations were above the PEL boundary (Smith et al. 1996), we deduced that the SQG assessment may overestimate the eco-risk of Pb, and Pb should have a low eco-risk as indicated by the RAC assessment. The eco-risk degree for Zn in surface sediments of west Chaohu Lake according to the RAC was higher than the corresponding result given by the SQG, especially in the northern lake area (Fig. 7c, f). Because of the dominant presence (ranging from 9 to 80 %, mean value of 40 %) and high concentrations (mean value of 107 mg kg^{-1}) of Zn in the dilute acid soluble fraction (Fig. 2j), the eco-risk of Zn defined by the RAC may be more

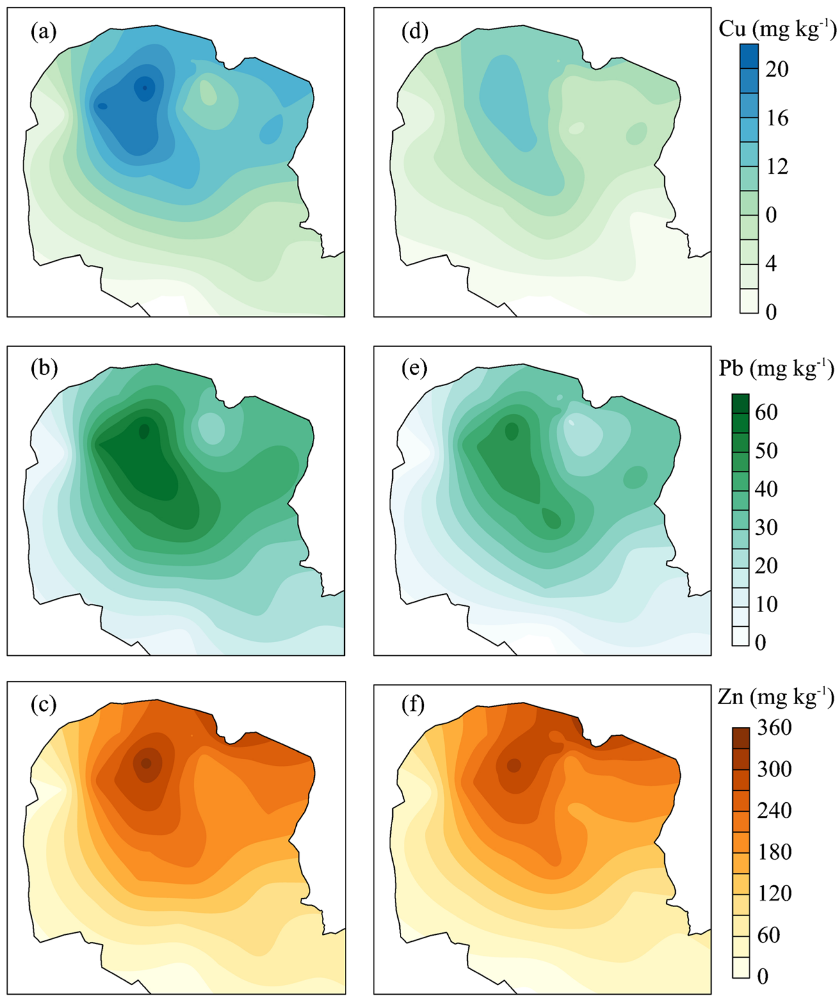

Fig. 6 Concentrations (mg kg^{-1}) of anthropogenic metals in surface sediments of west Chaohu Lake (**a**, **b**, **c**) based on total concentrations, and (**d**, **e**, **f**) based on extractable concentrations

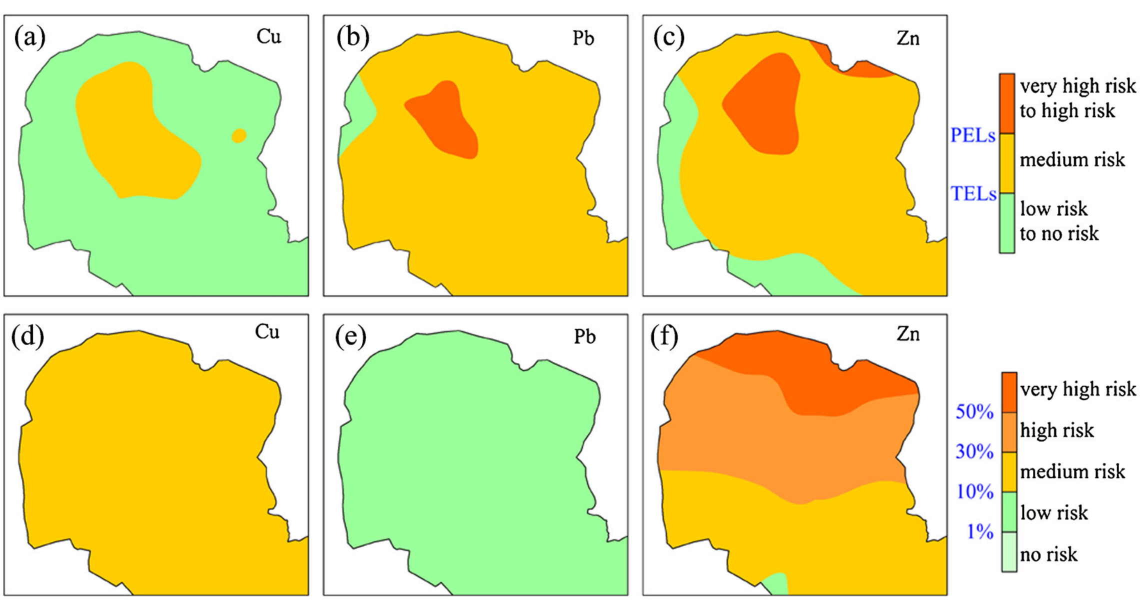

Fig. 7 Potential eco-risk ranks of Cu, Pb, and Zn in surface sediments of west Chaohu Lake with reference to the (**a**–**c**) SQG and (**d**–**f**) RAC assessments

exact than that by the SQG. The higher potential eco-risk of Zn than other metals was related to its high anthropogenic input (Fig. 6c, f).

Sediment properties, such as grain size and organic matter content, may also have an influence on the eco-risk ranking of metals (Campana et al. 2012; Simpson and Batley 2009; Yu et al. 2011). However, this effect was not significant for eco-risk classifications of Cu, Pb, and Zn in surface sediments of west Chaohu Lake, possibly due to the generally low variance in the sediment properties. Our data also implied that the simultaneously extracted metals (SEM) and acid volatile sulfides (AVS) model (Velimirovic et al. 2011) might not be suitable for the eco-risk ranking of metals in sediment, such as that in Chaohu Lake, with low metal concentrations in the oxidizable fraction.

Our study emphasized that referencing only the SQG or the RAC assessment is not sufficient in eco-risk classifications of metals in sediment; instead, a combination analysis combining the SQG and RAC assessments and the chemical partitioning of metals is recommended. More accurate and universal assessment methods and/or SQG combining the concentration of metals, chemical partitioning, and the sediment properties should be developed (Campana et al. 2012, 2013).

Conclusions

This study represents the first examination of the grain size effect on the chemical partitioning of metals in fine-grained sediment (i.e., silt and clay), which were commonly observed in the total metal concentrations. The <12-μm fraction should contribute to metal (Cu, Pb, and Zn) enrichment in the sediments of west Chaohu Lake. The conservative element normalization may be considered a candidate to compensate this grain size effect, and the EF approach was effectively used to provide a reference differentiating the anthropogenic input of metals. The decreasing EFs of Cu, Pb, and Zn from the northern lake area near the Nanfei River mouth towards the south suggested that input of anthropogenic Cu, Pb, and Zn was mainly via the Nanfei River. Similar anthropogenic contributions were characterized for each metal in surface sediments of west Chaohu Lake based on the total and extractable concentrations, suggesting anthropogenic Cu, Pb, and Zn occurred predominantly in the extractable fractions. Anthropogenic Zn was primarily concentrated in the dilute acid soluble fraction, followed by the reducible fraction, and anthropogenic Cu and Pb were primarily present in the reducible fractions. The eco-risk assignments of Cu, Pb, and Zn in surface sediments of west Chaohu Lake differed when referenced to the SQG and RAC assessments. The potential eco-risks of Cu may be largely overestimated according to the RAC assessment, whereas the eco-risks of Pb may be largely overestimated according to the SQG assessment. A combined analysis based on the SQG and RAC assessments and the chemical partitioning of Cu, Pb, and Zn demonstrated that Cu and Pb posed a low eco-risk and Zn posed a low to high eco-risk in surface sediments of west Chaohu Lake. More accurate and universal eco-risk assessment code and/or SQG combining the concentration of metals, chemical partitioning, and the sediment properties should be developed.

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