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Speciation and Spatial Distribution of Heavy Metals (cu and Zn) in Wetland Soils of Poyang Lake (China) in Wet Seasons

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Abstract The distribution of heavy metals (Cu and Zn) and their geochemical speciation (exchangeable fraction, carbonate fraction, Fe/Mn oxide fraction, organic fraction and residual fraction) in wetland soils of Poyang Lake were examined by modified Tessier sequential extraction methods. The results showed that the Cu and Zn concentrations in the wetland soils were 6.83–342.54 mg·kg^{-1} and 34.39–195.36 mg·kg^{-1}, respectively. The highest heavy metal concentrations were found in the wetland soils located in the lower reaches of mines and metal smelters. The metal speciation analysis showed that Cu and Zn were mainly linked to the residual fraction in all samples which account for 65.64% and 68.14%, respectively. The content of the exchangeable fraction (Cu 1.00%, Zn 3.60%) and carbonate fraction (Cu 2.09%, Zn 1.53%) was generally lower. Assessments of pollution levels revealed that Cu and Zn were much higher than their background value and heavy metal pollution in the wetland soils located in the lower reaches of mines and metal smelters was often more severe. The sites Duchang and Hukou were least polluted by Cu and Zn.

Keywords Heavy metals · Wetland soil · Poyang Lake · Sequential extraction · Chemical speciation

Introduction

Wetlands play an important role in retaining pollutants and protecting water quality of rivers or/and lakes (Mitsch and Gosselink 2000; Knox et al. 2017; Melly et al. 2017; Cui et al. 2016). Wetlands have long been recognized as an important sink for heavy metals due to a variety of physical, chemical, and biological processes which involve sedimentation, settling, adsorption, precipitation, and absorption and induced changes in biogeochemical cycles by plants and bacteria (Lu et al. 2016; Garg 2015; Oyuela Leguizamo et al. 2017). They are potential sources for the surrounding communities providing a wealth of ecological, social and economic functions to the countries in the region (Matagi et al. 1998; Jiang et al. 2016). Poyang Lake is the largest freshwater lake in China and one of the most important wetlands in the world. It receives a large quantity of water coming from the Ganjiang River, Fuhe River, Xinjiang River, Raohe River and Xiushui River, together with several smaller tributaries such as Xihe River, Zhangtian River and Tongjing River etc., then releases the incoming water into the Yangtze River through a narrow passage regulated at Hukou. These inputs are the most significant contributors of industrial wastewater and domestic sewage to the lake. At the upstream of these rivers especially at the upstream of Raohe River, many non-ferrous metal mines have been exploited for decades, such as Dexing and Yongping copper mines, Yinshan lead-zinc mine and Huaqiao gold mine. In addition, the Guixi metallurgical refinery, are located next to the Poyang Lake. Mining activities and metal smelting have been known to be the main heavy metal sources (Rodríguez et al. 2009; Li et al. 2014; Xiao et al. 2017; Kwon et al. 2017; Hamiani et al. 2010). The exploration and extraction of the vast mineral resources in the surrounding areas of the Poyang Lake catchment has produced a large amount of waste water and residue containing heavy metals dumping into Poyang Lake (Chen et al. 2016;

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Wang et al. 2017). The results from the determination of heavy metals in water and sediments reflect the impacts of industrial activities and urban development (Zhang et al. 2012; He et al. 1997). Cu, Pb, and Zn levels in sediments from Poyang Lake averaged 30.20 mg·kg^{-1}, 68.18 mg·kg^{-1}, and 75.56 mg·kg^{-1}, respectively, values that are significantly higher than their background concentrations of 4.75, 17.57, and 45.75 mg·kg^{-1}, respectively (Zhang et al. 2012).

Although copper and zinc are the essential minerals for humans, overdosing on these beneficial elements can also cause health problems (Gale et al. 2004; Yu et al. 2016). They cannot degrade, and continuously deposited and incorporated into water, sediments, and aquatic organisms (Linnik and Zubenko 2000). The toxicity of the metal particularly depends on their chemical forms rather than on their total contents (Liu et al. 2007), and therefore, measurements of total metal concentrations in soils or sediments may not reveal useful information when assessing the impact and estimation of environmental effects of metals such as bioavailability, mobility, and toxicity (Tüzen 2003; Ahlf et al. 2009) because it is the chemical species that determines the mobility and bioavailability of the metal in soil and sediment to other environmental compartments, such as water and plants, when physical and chemical properties of soil and sediment are favorable (Yang et al. 2014; Zhang et al. 2017). The study of heavy metals in water and sediments in the Poyang Lake watershed has gained considerable interest recently (Luo et al. 2008; Yuan et al. 2011; Zhang et al. 2012). However, few reports have focused on the speciation analysis of heavy metals in the wetland soils of Poyang Lake. It is extremely significant to analyze the heavy metal speciation and to find out the distribution in different speciation.

Heavy metals in soils can be classified as adsorptive and exchangeable species, bond to carbonate phases, bond to Fe/Mn oxide, bond to organic matter and sulfides, and detrital or lattice metals. Tessier et al. (1979) set up the five-step sequential extraction method to separate five metal fractions in soil and sediment samples. The main objective of the present study were: (1) to investigate the Cu and Zn concentrations and distributions in the wetland soils from Poyang Lake (China); (2) to analysis the different geochemical fractions of Cu and Zn in the wetland soils; (3) to assess the level of selected metals pollution in the wetland soils using the geoaccumulation index (I_{geo}).

Material and Methods

Study Area

Poyang Lake is located in the north part of Jiangxi province, lying on the south bank of the middle and lower reaches of Yangtze River (Fig.1). The Lake, with an area of 3583 km^2 and a volume of 27.6 km^3, is about 173 km in length from north to south and 74 km width from east to west (Xu et al. 2001). Poyang Lake receives annual mean precipitation of 1636 mm, typical of the subtropical humid monsoon climate. Temperatures are highly seasonal, with June–August average of 27.3 °C and December–February average of 7.1 °C, and annual average of 17.6 °C. The annual potential evapotranspiration is 1049 mm·year^{-1}, with the highest rates during May to September. The lake is divided into two parts by the Songmenshan Mountain in the middle of the lake. The northern part is the water channel joining the Yangtze River, with the length of 40 km and the width of 3-5 km (the narrowest point is 2.8 km or so). The southern part is the main lake, with the length of 133 km and the furthest width of 74 km.

The surrounding Poyang Lake area is a typical water-land transition zone and represents a unique lake ecosystem in the world. Its seasonal variations in inundation regimes along with water level fluctuations generate a unique landscape of marshlands in winter and flood plains in summer, which are dominantly controlled by the water balance between the Yangtze River and five major tributaries (Ganjiang River, Fuhe River, Xinjiang River, Raohe River and Xiushui River) (Shankman et al. 2006; Hui et al. 2008). During the wet seasons, water recharges from Jiangxi basin and the Yangtze River increase the lake coverage to the peak of approximately 4000 km^2, whereas during the low-water dry months, the lake becomes a complex assembly of hydrological distinct rivers and shallow waters interspersed with meadows (Jia et al. 2013). This unique hydrologic rhythm in the Poyang Lake area has formed many types of wetlands and provides a suitable habitat to breed rich biodiversity.

Sample Collection and Pre-Treatment

Fifteen soil samples were collected from the top 20 cm at various locations in each quadrant (Fig. 1) to offer a composite sample using a manual soil auger in September, 2013. There was a sampling point at the each main branch flow into the Poyang Lake, and about every 10 km in the main channel set a sampling point. The soils were placed in polythene bags, stored in cooled boxes and transported to the research laboratory. Soil samples were air-dried at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris. The fresh soils were oven dried at 105 °C for 24 h and weighed for soil moisture (Ministry of agriculture, animal husbandry and fishery, People's Republic of China 1987).

Soil organic matter (SOM) was estimated by measuring the loss of weight on ignition at 550 °C (Díaz-de Alba et al. 2011). Soil pH was measured using a pH meter (soil: water =1: 5). The dry samples were ground with a pestle and mortar until all particles passed a 200 mesh nylon sieve and used for determining chemical properties of soils.

Ultrapure water with 18 MΩ·cm (supplied from a Millipore Milli-Q system) resistivity was used for extraction, solution preparation, and rinsing during the analytical studies. All

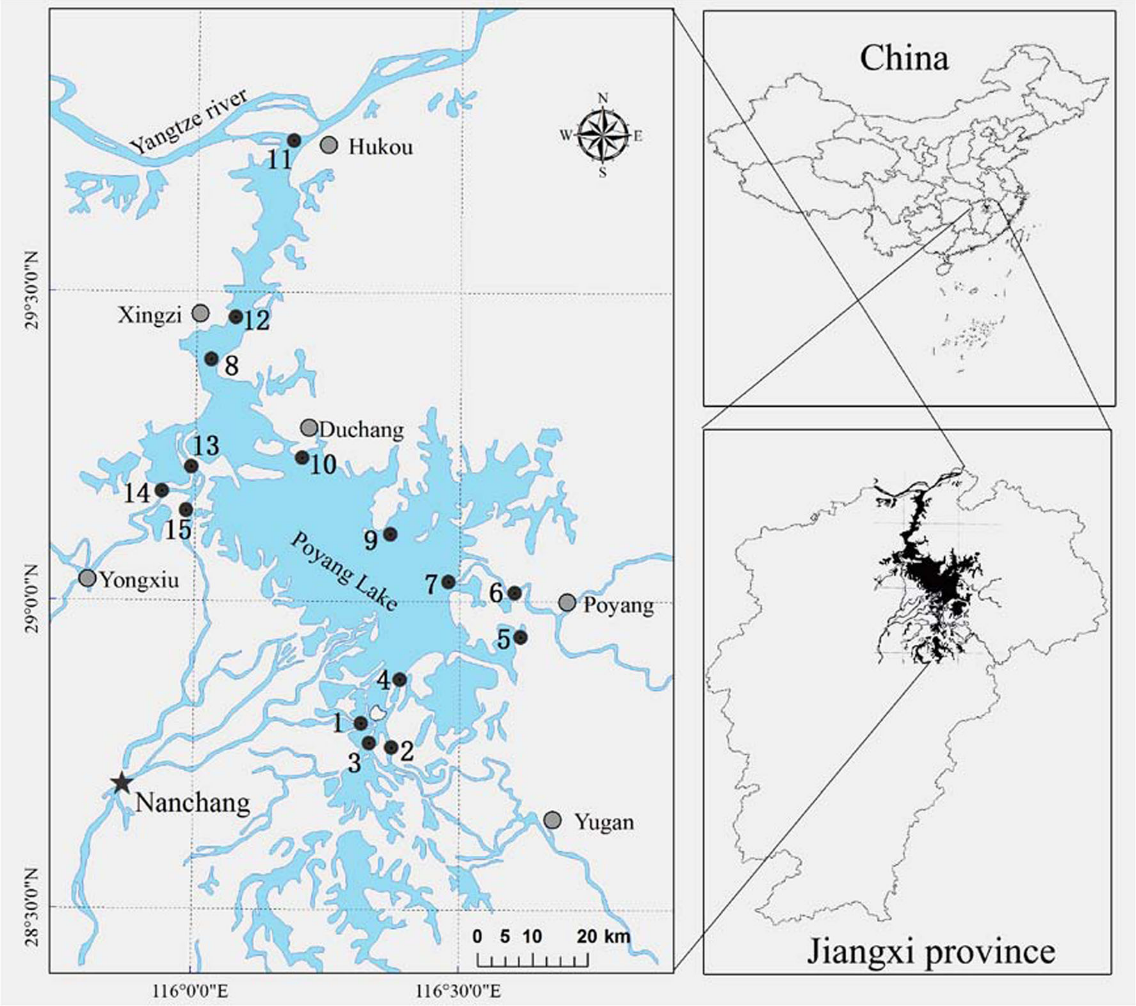


Fig. 1 Sampling sites of wetland soils taken from Poyang Lake. Notes: 1-the entrance of Ganjiang River south branch 2-the entrance of Xinjiang River 3- the entrance of Fuhe River 4-Kangshan 5-Caijiawan 6-the entrance of Raohe River 7-Longkougang 8-Laoyemiao 9-Zhouxi 10-Duchang 11-Hukou 12-Xingzi 13-Wucheng 14- the entrance of Xiushui River 15- the entrance of Ganjiang River north branch

chemicals and standard solutions used in the experiments were guarantee reagent grade. All glassware and plastic containers were cleaned using a nitric acid (20%, *v*/v) bath overnight and rinsed with ultrapure water before they were used for analyses.

The Sequential Extraction Procedure

Chemical fractionation of metals in the soil samples was completed using the modified Tessier five-step sequential extraction procedure described by Akcay et al. (2003). A detailed description of this procedure is provided below.

The first fraction (F1) that contains exchangeable species of the trace metals is obtained by the following procedure: each soil sample is extracted at room temperature for an hour with 10 ml of magnesium chloride solution (1 M $MgCl_2$) adjusted to pH 7.0 with ammoniac with continuous agitation.

The second fraction (F2) contains the species bound to carbonates. The residue from the first extraction is leached for 5 h at room temperature with 10 ml of NaOAc (1 M) adjusted to pH 5.0 with acetic acid (HOAc) plus agitation.

The residue from the second extraction is extracted with 20 ml $NH_2OH{\cdot}HCl$ (0.004 M) dissolved in 25% (*v*/v) HOAc heated for 6 h at 95 °C with occasional agitation. This third fraction (F3) includes trace metal species bound to Fe and Mn oxides (third fraction).

3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 are added to the residue from the third extraction. Samples were heated at 85 °C for 2 h with occasional agitation. A second 3 ml aliquot of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 is then added and the sample is heated again to 85 °C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20% (*v*/v) HNO_3 is added and the sample is diluted to 20 ml and agitated continuously for 30 min. The addition of NH_4OAc prevents adsorption of the extracted metals onto the oxidized sediment. The fourth extract (F4) thus involves the trace metal species bound to organic matter (fourth fraction).

Finally, the residue from the fourth extraction was digested with a mixture in a ratio of 3:1:1:1, of HNO_3: HF: H_2O_2: HCl for 3 h in a water-bath. The residue (F5) dissolved entirely and it was diluted with 100 ml ultra-pure water.

After each successive extraction, separation was performed by centrifuging the sample at 5000 rpm for 30 min. The supernatant was then removed with a micropipette and analyzed for trace metals, whereas the residue was once again washed in 10 ml of ultra-pure water, after centrifugation for an hour, this second supernatant is discarded. Concentrations of Cu and Zn in the digests acquired at each stage were determined using a flame atomic absorption spectrometer (PerkinElmer, AA800). The calibration line method was used to quantify selected metals and the digests were appropriately diluted whenever required (Radojevic and Bashkin 1999). All the measurements were made in triplicates. The calculated relative standard deviations (RSD) of total contents for Cu and Zn were below 10%.

Determination of Metal Concentrations

The total heavy metal concentrations of the prepared soils (0.5 g) were determined by an atomic absorption spectrometer fitted with flame or graphite furnace atomization (PerkinElmer, AA800) after microwave digestion (SEM, Mars5) in a mixture of HNO_3 (6 ml), HCl (2 ml), HF (2 ml) and H_2O_2 (2 ml). Laboratory blanks were analyzed for the same elements to control for heavy metal contamination during the digestion process. Reagent blanks were prepared in the same manner as the samples and the blanks were used to correct instrument readings. Quality control was provided by a duplicate analysis of standard reference materials (GBW08301) from the Chinese Academy of Measurement Sciences. And it was also employed in the chemical extraction. The recoveries of heavy metals in the certified samples ranged from 95 to 105%.

Internal Check Recovery

An internal check was performed on the sequential extraction by comparing the total amount of metal extracted by different reagents during the sequential extraction procedure with the results of the total metal concentration (Nemati et al. 2011). The recovery of the sequential extraction method was calculated as follows:

$$\text{Recovery}(\%) = \frac{C_{\text{ex}} + C_{car} + C_{ox} + C_{org} + C_{res}}{C_{\text{total}}} \times 100$$

The results shown in Table 1 indicate that the sums of the five fractions are in good agreement with the total digestion results at all sites, with satisfactory recoveries (99.48–103.02%). In addition, the modified Tessier five-step sequential extraction procedure is reliable and can be repeated.

Geoaccumulation Index (I_{geo})

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and pre-industrial concentrations of the metals in earth crust (Muller 1969). It can also be applied to the assessment of soil Contamination (Iqbal and Shah 2011). It is computed using the following mathematical formula: $\mathrm{I_{geo}} = \log_2\left(\frac{C_n}{1.5B_n}\right)$, where C_n is the measured concentration of the metal in the soil samples and B_n is the geochemical background value in earth crust. The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to geogenic variations. The I_{geo} values were interpreted as: $I_{\text{geo}} \leq 0$ - practically uncontaminated, $0 < I_{\text{geo}} \leq 1$ - uncontaminated to moderately contaminated, $1 < I_{\text{geo}} \leq 2$ - moderately contaminated, $2 < I_{\text{geo}} \leq 3$ - moderately to heavily contaminated, $3 < I_{\text{geo}} \leq 4$ - heavily contaminated, $4 < I_{\text{geo}} \leq 5$ - heavily to extremely contaminated and $I_{\text{geo}} > 5$ - extremely contaminated (Muller 1969).

Statistical Analysis

Correlation relationships between heavy metals and physicochemical characterization was performed using the software packages of Sigmaplot 6.0 and SPSS statistics 17.0. Differences were considered significant when $p < 0.05$.

Results

Physicochemical Characterization of Wetland Soils

Soil physicochemical characterization such as pH, SOM and moisture can impact the accumulation of heavy metals in wetland soils (Bai et al. 2012; Yao et al. 2016), so it is essential to analyze their levels and distributions in different soils. The pH, SOM and moisture of wetland soils at various sites were summarized in Table 1. The pH values ranged from 4.9 to 8.4, with the highest value observed in Hukou (site 11) and the lowest value in the entrance of Ganjiang River north branch (site 15). The pH values in the wetland soils of the main channel showed an increasing trend from upstream to the outlet of the Lake (range 5.6–8.4). Alkaline soils were found in the northern part of Poyang Lake with pH values ranging from 7.3–8.4 (i.e., within the normal range of lake waters), which suggests that lake water intrusion impacts on the pH conditions of the soils. The acidic soils appeared associated to the others remaining sampling sites. The moisture content ranged from 6.0% to 24.3% with mean values of 17.9%, the highest content appeared in Hukou and the lowest content was found in Duchang. The lower soil moisture in Duchang is due to the sandy soil with low water retention capability. The organic matter contents varied between 1.51% and 6.76%, with a

Table 1 Metal concentrations (mg/kg) by five-step sequential extraction method and the physicochemical parameters in the wetland soils

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Cu	F1	0.039	0.574	0.040	1.411	2.356	2.260	0.751	0.042	0.047	0.069	0.003	0.074	0.037	0.019	0.762
	F2	0.61	0.51	1.15	0.70	4.01	0.49	1.31	0.65	0.36	0.44	0.43	0.46	0.44	1.06	0.45
	F3	2.60	7.39	22.08	1.69	59.23	5.41	5.53	8.46	4.05	1.95	2.71	2.68	1.54	1.71	1.89
	F4	7.54	7.55	26.51	17.52	67.06	11.51	6.62	21.14	6.59	0.46	1.34	4.74	4.41	2.08	5.08
	F5	20.09	13.56	65.16	39.45	210.14	58.99	5.99	50.35	30.20	4.12	7.60	28.07	26.38	45.44	33.62
	Sum	30.88	29.58	114.93	60.76	342.79	78.65	20.20	80.64	41.25	7.04	12.08	36.03	32.81	50.31	41.80
	Total metals	30.60	29.72	113.94	59.54	342.54	78.59	19.83	79.58	40.25	6.83	11.98	35.03	32.71	49.31	40.80
	Recovery(%)	100.92	99.56	100.87	102.05	100.07	100.08	101.90	101.34	102.48	103.02	100.84	102.85	100.30	102.03	102.45
	Bio	0.65	1.09	1.19	2.11	6.37	2.75	2.06	0.69	0.41	0.51	0.43	0.54	0.47	1.08	1.21
	Nbio	30.23	28.50	113.74	58.65	336.42	75.91	18.14	79.95	40.84	6.53	11.65	35.49	32.34	49.23	40.58
Zn	F1	3.30	6.23	4.35	8.38	5.06	10.61	2.75	7.00	3.33	1.51	1.50	0.99	4.01	2.05	7.29
	F2	1.78	1.65	2.77	2.36	1.87	1.12	4.05	1.05	0.27	0.97	1.13	1.03	1.49	1.13	1.96
	F3	14.31	36.76	26.82	14.46	25.82	61.56	12.83	52.91	11.14	8.78	18.60	21.56	10.33	3.58	14.42
	F4	7.89	8.00	15.72	19.64	21.31	23.66	7.73	19.99	6.58	1.75	3.50	8.88	6.83	2.83	8.54
	F5	71.98	50.75	115.70	146.49	91.08	100.40	59.64	90.48	80.17	22.37	40.89	60.40	140.56	94.20	85.57
	Sum	99.26	103.40	165.36	191.33	145.14	197.36	87.00	171.42	101.49	35.39	65.62	92.86	163.22	103.79	117.79
	Total metals	98.26	102.90	164.36	190.33	144.14	195.36	86.00	170.42	100.49	34.39	63.87	92.85	163.06	102.80	118.41
	Recovery(%)	101.02	100.49	100.61	100.53	100.69	101.02	101.17	100.59	101.00	102.91	102.73	100.02	100.10	100.96	99.48
	Bio	5.08	7.88	7.12	10.74	6.93	11.74	6.81	8.05	3.61	2.49	2.63	2.01	5.51	3.18	9.25
	Nbio	94.18	95.52	158.24	180.60	138.21	185.62	80.20	163.38	97.89	32.90	62.99	90.85	157.71	100.61	108.53
pH		6.5	5.0	5.4	5.0	5.6	5.6	6.6	6.4	5.6	7.7	8.5	7.3	5.1	5.7	4.9
SOM (%)		6.44	6.5	5.51	3.06	6.43	5.72	1.51	6.76	5.46	2.11	1.65	6.27	2.97	5.46	4.64
Moisture (%)		16.5	24.2	19.5	17.9	15.7	20.8	11.3	11.8	19.1	6.0	24.3	22.3	18.5	17.5	23.4

Bio: bioavailable fraction, *Nbio:* nonbioavailable fraction mean value of 4.70%, obtaining the highest percentages in soils from Hukou site and the entrance of Xinjiang River. The studied soils contained high organic matter contents that could decrease the metal availability by complexing.

Total Metal Concentrations

Total heavy metal concentration in the soil reflect natural differences in soil genesis and properties and the degree of contamination. The concentrations of selected metals at fifteen sampling sites are listed in Table 1. The total heavy metal contents in the Poyang Lake wetland soils ranged from 34.39 to 195.36 mg·kg^{-1} Zn; 6.839 to 342.54 mg·kg^{-1} Cu. The entrance of the Raohe River was the most contaminated area by Zn and the most contaminated by Cu was in Caijiawan. The Duchang and Hukou sites were the least contaminated by Cu and Zn. The non-parametric Spearman correlation analysis in this study showed significantly negative correlation between these heavy metals and pH ($p < 0.01$; Table 2), suggesting that the metal concentrations will increase with the decrease of pH value. There were significant correlations among the Zn and Cu ($p < 0.01$), implying that the Zn and Cu shared the same source of contamination. However, no significant correlations between these heavy metals and soil moisture were identified. SOM exhibited a positive linear relationship with Cu ($p < 0.01$). But Zn was not significantly correlated with SOM, which might be due to lower SOM levels in the study area.

Table 2 Spearman correlation matrix between heavy metals and selected soil properties in all samples ($n = 15$)

	Cu	Zn	pH	TOM	Moisture
Cu	1.000				
Zn	$.804^{**}$	1.000			
pH	$-.482^{*}$	$-.689^{**}$	1.000		
TOM	$.490^{*}$	.391	−.175	1.000	
Moisture	−.046	.089	−.271	.066	1.000

*Significant correlation at the level of $p < 0.05$

**Significant correlation at the level of $p < 0.01$

Metal Speciation

Chemical speciation differentiates metals of natural origin and/or derived from anthropogenic sources. Metal fractionation is of critical importance to their potential toxicity and mobility (Islam et al. 2015; Pejman et al. 2017). Results of speciation of heavy metals in different sampling sites are shown in Fig. 2. The percentage of metal extracted was calculated from the ratio between the concentration of the element in each fraction, and the sum of concentrations in all fractions. Orders of different fractions of heavy metals in wetland soils of Poyang Lake were:

$$\text{Cu}: \text{residual fraction} > \text{organic fraction} > \text{Fe/Mn oxide fraction} > \text{carbonates fraction} > \text{exchangeable fraction}$$

$$\text{Zn}: \text{residual fraction} > \text{Fe/Mn oxide fraction} > \text{organic fraction} > \text{exchangeable fraction} > \text{carbonates fraction}$$

The highest portion of Cu was obtained in residual fraction at all sites expect the Longkouguang site where Cu was obtained mainly in the organic fraction followed by the residual fraction. The highest residual fraction of Cu was found in the Xiushui River site. The lowest residual fraction of Cu was found at Xinjiang River site with 45.82%. The lowest levels of Cu occurred in exchangeable fractions with an average of 1.00%, followed by carbonates fraction (2.09%).

The lowest levels Zn occurred in carbonates fractions with an average of 1.53%, followed by exchangeable fraction (3.60%). The highest levels Zn occurred in residual fraction with a range from 49.06% to 90.76%, followed by Fe/Mn oxide fraction (average 18.51%). The lowest residual fraction of Zn was found in the Xinjiang River site with 49.09%.

Geoaccumulation Index (I_{geo})

I_{geo} is the quantitative measure of the pollution index in soils. Any increase in the current levels is viewed to be anthropogenic. The background of Cu and Zn in the Poyang Lake are 4.75 mg·kg^{-1} and 45.75 mg·kg^{-1} respectively (Zhang et al. 1988). As shown in Fig.3, the I_{geo} values for the metals revealed that the studied soils were characterized as extremely contaminated at the site 5 (Caijiawan), heavily contaminated at sites 3, 4, 6 and 8, moderately to heavily contaminated at sites 1, 2, 9 and 12–15, moderately contaminated at site 7, uncontaminated to moderately contaminated at site 11, and practically uncontaminated at site 10 by Cu. The soils were practically uncontaminated at sites 10–11,

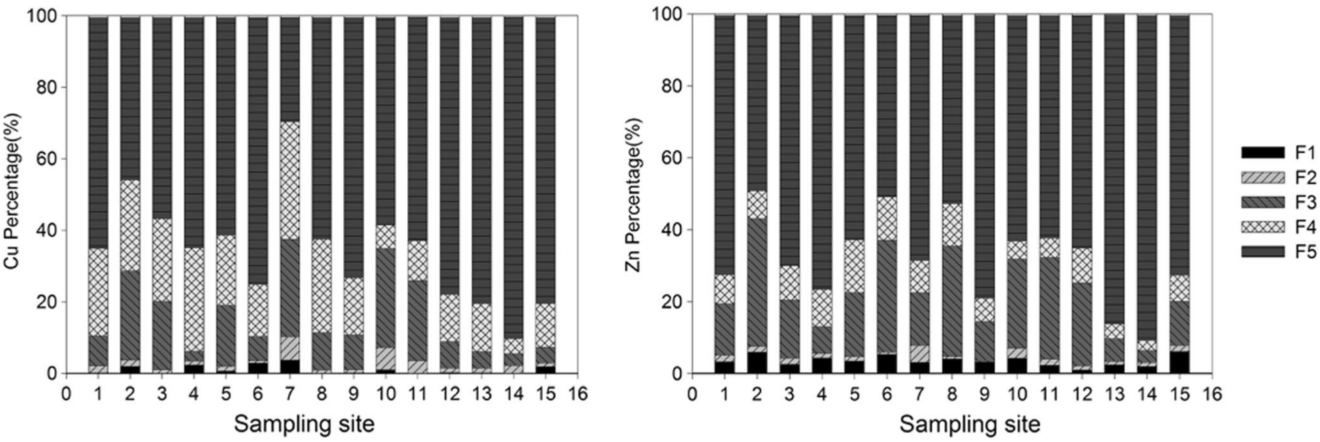


Fig. 2 Percentage of metal fractionation in the wetland soils at different sites

uncontaminated to moderately contaminated at most sites (1, 2, 7, 9, 12, 14, 15), and moderately contaminated at sites 3–6, 8 and 13 by Zn.

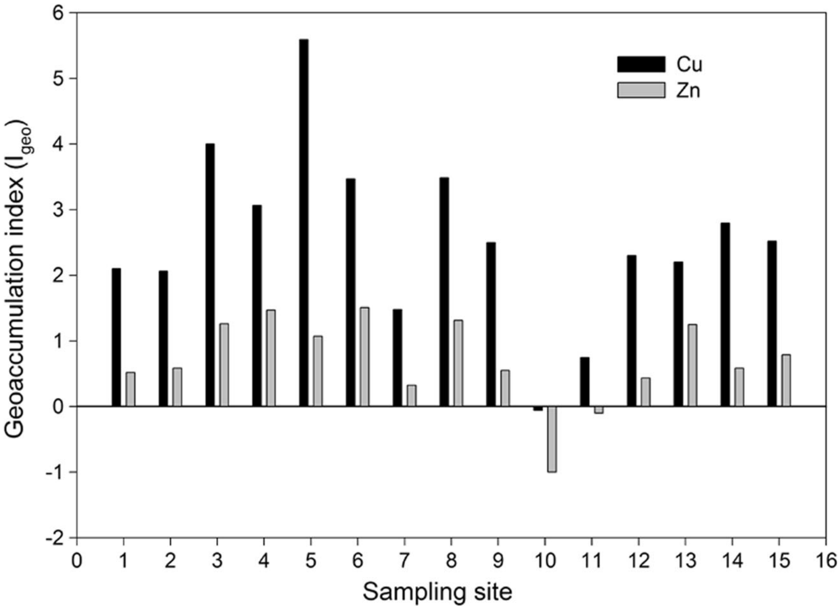
Discussion

Correlation Analysis

The soil pH is known to play an important role in controlling the mobilization–immobilization processes of heavy metals (Huang et al. 2017). The lower pH may promote the remobilization of the metals depending on the buffering capacity of the existing alkalinity (Batchman et al. 2001; Chen and Lin 2001). The negative correlation between pH and heavy metal concentration demonstrated it. Stability of Cu in soil is strongly pH dependent – the mobility increases with decreasing pH (Kumpiene et al. 2008). Kumpiene et al. (2008) also concluded that leaching of Cu, Zn, and Pb was strongly pH dependent, with lowest mobility being around neutral to slightly alkaline conditions. Their mobility is usually the lowest in these soils with slightly alkaline pH (Bai et al. 2011; Rennert et al. 2010) and the lowest mobility would favor metal accumulation in the soil (Kashem and Singh 2001).

Soil organic matter can act as a major sink for heavy metals due to its strong complexing capacity for metallic contaminants (Bai et al. 2011; Laing et al. 2009). Association of the metals with SOM can be explained by the high affinity of the metals for the humic substances that comprise much of this material. This is due to the formation of the stable metal complexes and in soluble metal sulfides that are important sinks for trace metals in the soils (Passos et al. 2010). There was no

Fig. 3 Description of geoaccumulation index (Igeo) of Cu and Zn at different sites



significant correlation between Zn and SOM, which suggested that SOM was not considered to represent the main carrier of Zn in the Poyang Lake wetland soils. Cu exhibited significantly correlated with SOM ($p < 0.01$). This result as supported by Bai et al. (2011) and Laing et al. (2009). They reported that SOM can keep Cu mobility low in soil by chemisorption.

Metal Speciation

The residual fraction is bound with mineral lattice and can only be released during the weathering process, so it is basically biological unavailable because the weathering process is much longer than the life period (Teasdale et al. 2003). The metal present in the detrital and primary mineral phases indicated that soils were relatively unpolluted and that the metals were derived mainly from geogenic origin (Davutluoglu et al. 2010). In the residual fraction, metals are bound to silicates and are therefore unavailable to the aquatic system (Tüzen 2003). The relative content of a metal in the residual phase can be construed as a measure of the contribution of natural sources, and also of the degree of contamination of the fluvial system, with a higher percentage indicative of lower levels of pollution (Singh et al. 2005). High levels of heavy metals (Cu: 65.64% and Zn: 68.14%) in residual phase reveals that these metals are relatively insensitive to any change of surrounding conditions in wetlands of Poyang Lake.

The Fe/Mn oxide phase has been proved to be sensitive to anthropogenic inputs (Modak et al. 1992). Fe/Mn oxides fraction is difficult to release due to strong ionic bonding. However, if the Eh in soil decreased, it may deoxidize and cause secondary pollution. The Fe/Mn oxides fraction of Zn is significant higher than Cu suggested the Zn is more likely to be affected by human activities.

Exchangeable fraction refers to the metals directly adsorbed on soil. The heavy metals bound to exchangeable fractions were absorbed in clay and humus, which are sensitive to environmental changes, easy to migrate and transform, and have high bioavailability and toxicity. This fraction is usually used to represent the environmentally available components (Anju and Banerjee 2010). A high percentage of clay and organics in the soil phase may possibly act as an adsorbent, retaining metals through ion exchange processes with a net result of increased levels of trace metals in the exchangeable phase. So a low percentage of organics may result in the decreased levels of trace metals in the exchangeable phase. The results of this article just confirmed it. The SOM in the wetlands soil of Poyang Lake was obvious low, and the levels of Cu and Zn in the exchangeable phase was also low.

The heavy metals bound to carbonate fractions coprecipitated with carbonate minerals and are easily released under acidic conditions. The fractions introduced by man's activity include the exchangeable and bound to carbonates fractions. These are considered to be weakly bonded metals which may equilibrate with the aqueous phase and thus become more rapidly bioavailable (Salomons and Förstner 1980; Pardo et al. 1990). Level of bioavailability (exchangeable + carbonate-bound) (Sundaray et al. 2011) and non bioavailability fractions of heavy metals in each soil samples of studied area are presented in Table 1. The bioavailable fraction represents the fraction that when the right pH and redox conditions are favorable, the metal will be soluble and can be taken up by aquatic biota causing environmental toxicity (Sundaray et al. 2011). The higher percent of exchangeable and carbonate fractions the soils contain, the easier heavy metals can be released into water and the higher bioavailability heavy metals have. The average concentration in the bioavailable fraction of Cu and Zn was very low (1.44 $\mathrm{mg \cdot kg^{-1}}$ and 6.20 $\mathrm{mg \cdot kg^{-1}}$, respectively) in the wetland soils of Poyang Lake. It was indicated that the Cu and Zn were not easy to release into water and have lower bioavailability in the study area. Generally, the percentage of the bioavailable metals in soils in present study followed the order: Zn > Cu. Results of this study showed that Zn was more mobile which would render them more dangerous for the studied area. The concentration in the bioavailable fraction is a serious environmental concern. The speciation studies of Cu and Zn in these wetland soils indicated that there was very low risk of metal contamination (from the percent distribution of the fractions).

Conclusions

The modified five-step sequential extraction procedure was used to investigate the chemical speciation and distribution patterns of copper and zinc in the wetland soils of the Poyang Lake, China. The highest content copper and zinc of concern, came from the copper mine and lead-zinc mine exploitation, but its main chemical fraction was the residue, which had little effect on environment and humans. The area of least contaminated by copper and zinc was found at the Duchang and Hukou sites. The content of the exchangeable fraction and carbonate fraction was generally low. The wetland soil of the northern part of Poyang Lake was alkaline soil (pH 7.26–8.45). I_{geo} revealed that most of the sampling sites were heavily contaminated and moderately to heavily contaminated by Cu. And most of the sampling sites were uncontaminated to moderately contaminated and moderately contaminated by Zn. Overall, sites 10 and 11 were least polluted by Cu and Zn. The effectiveness of the modified Tessier five-step sequential extraction procedure for heavy metal chemical species analysis was demonstrated. The important and reliable information obtained describe the heavy metal chemical fractionation and their pollution level of wetland soils in Poyang Lake. It has been shown that the mining activities surrounding the Poyang Lake are affecting this ecosystem. The research results provided useful information to local managers and decision makers. The results provided a strong data support for the prevention and control of heavy metal pollution in the wetland soil of Poyang Lake.

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