

Elemental Metals in Agricultural Soils Along Two Tributaries of Chaohu Lake: Implication on Soil Erosion Caused Enrichment in Sediments

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ABSTRACT

Agricultural soil as a potential source of input of heavy metals into the lacustrine sediments of Chaohu Lake via soil erosion and weathering has not been well documented. In the present study, rice soil samples along two main tributaries of Chaohu Lake were collected to determine 30 metal elements which were compared with the data on the elements in surface sediments of Chaohu Lake to explore the impacts of soil erosion on the accumulation in the sediments. The results showed that the concentrations of most elements were less than their soil background values of Anhui Province, but Se, Sb, Sn, As, and Ba were greater than the corresponding background values. Furthermore, these elements except for Sc in the soils appeared a low variability in spatial distribution. Enrichment factor (EF) also suggested that most elements were minimally enriched, but Se, Th and As were found with moderate enrichment in the study areas. More than 90% of agricultural soils were not expected with significant contamination by the residual elements based upon the consideration of pollution level index (PLI) combining probabilistic density function. Compared with the residual elements in the surface sediments of Chaohu Lake, most elements (Ti, Mn, Zr, Sr, Zn, Ga, Hf, U, Se, Sn, Nb, Th, V, Cd) appeared depletion in agricultural soils but enrichment in sediments. Specially for Cd, it was not detectable in all soils samples, but it existed at an extreme average content in the lacustrine sediments. These results possibly implied that elements in agricultural soils in Chaohu Lake were depleted because of soil erosion and weathering during long-term agricultural practice, resulting in enrichment in sediments of the lake. The depletion of elements in soils was predominately due to the fact that these metals existed in the soil with a large mobile fraction. While As, Th and Se moderately accumulated in the soils due to their insusceptibility of transport potentials. Because Sr and U are easier to be leached from soils than Rb and Th, respectively, a greater ratio of Rb/Sr and a lower value of U/Th was found in soil samples than in sediments. Therefore, our study implied agricultural soils could play an important role in the input of heavy metals into sediments via soil erosion and weathering.

Keywords: Chaohu Lake watershed, metal elements, agricultural soils, soil erosion and weathering

INTRODUCTION

As well known, some elements are essential to human body and play irreplaceable roles in the functioning of body organs, and all living organisms require varying amounts of metals (Lane and Morel, 2000). It will be toxic at higher concentrations, and certain metals can even lead to a wide range of toxic effects, such as carcinogenicity

(Qu, et al., 2012b, Thomas, et al., 2009). Chronic exposure to those heavy metals and metalloids even at relatively low levels has adverse effects on human body health and other animals (Kamunda, et al., 2016, Qu, et al., 2012b, Tsai and Lee, 2013). Therefore, widespread attention on the heavy metals pollution and related controls strategies has been attracted around the world (Davis, et al., 2009, Hu, et al., 2015, Sun, et al., 2013).

Soil contamination with heavy metals not only threatens the food safety but also damages to the human body health (Breivik, et al., 2004, Chen, 1999, Cheng, 2003, Tsuchiya, 1977, Wang, 2001). However, intake of heavy metals via the soil-crop system has been considered as the predominant pathway of human exposure to these toxic elements (Luo, et al., 2011, Luo, et al., 2012, Luo, et al., 2006, Wei and Yang, 2010). Heavy metals can enter the human body through the chronic low-level intake of soil metals including inhalation of dust, direct ingestion, dermal contact, and consumption of infected animals, farm products which take up heavy metals by absorbing them from contaminated soils or from atmospheric deposition by polluted air (Qu, et al., 2012a, Tsai and Lee, 2013). The rapid urban and industrial development and increasing reliance on agrochemicals over the past decades have been verified as a vital factor on the accumulation of heavy metals in agricultural soils (Chen, et al., 2015, Wong, et al., 2002, Wu, et al., 2016). However, the metals can be removed from soil by crop adsorption, leaching soil erosion and weathering (Quinton and Catt, 2007, Salt, et al., 1995, Sun, et al., 2001). The transport potential of each element varied largely depending on the speciation in soil (Fanfani, et al., 1997).

Soil erosion and weathering are the important environmental processes which can transport heavy metals from agricultural soils into the sediment of receiving water system (Jiao, et al., 2014, Quinton and Catt, 2007, Tang, et al., 2010). However, this issue has not been well documented for Chaohu Lake watershed (Tang, et al., 2010). Therefore, the objectives of this study are to (1) investigate the accumulation and spatial variability of 30 metal elements in the rice soils along two main tributaries of Chaohu Lake; (2) evaluate the accumulation status by pollution indices, (3) explore the potential impacts of metals in agricultural soils on sediments of Chaohu Lake.

MATERIALS AND METHODS

Study area and sample collection

The Chaohu Lake which is located in the middle of Anhui province, between Yangtze River and Huaihe River watershed, with longitude from E117°16'54" to E117°51'46" and latitude from N31°43'28" to N31°25'28" (Zhang,

2008). It is one of five largest fresh water lakes in China, and is surrounded by Chaohu, Hefei, Lujiang, Feidong, and Feixi cities. This study was conducted around two main tributaries (i.e. Tongyang River and Hangbu River, which situated at Northeast and Southwest of Chaohu Lake, respectively). Both areas are characterized by long-term intensive cultivation, and rice is the predominant crop. These both rivers have been found with significant impacts by the non-point source inputs from agricultural activities (Wang, et al., 2016). In the present study, a total of twenty-two surface soil samples were collected in the rice fields. Ten samples were corrected along Tongyang River (defined as N1-N10) and the remaining twelve soils were obtained along Hangbu River (referred as S1-S12) using a plastic sampler in August, 2015 (Fig. 1). Surface soil samples were almost completely comprised by silt. A global positioning system was used to determine the geographical coordinate of all the sampling sites. After sampling, all soil samples were placed in polyethylene zip bags, and immediately transported into the laboratory. Before storage in a refrigerator until laboratory analysis, the samples were subsequently treated by air drying, manual homogenization, trituration in a ceramic mortar to pass through a 100 mesh stainless steel sieve.

Analytic methods

The analytic methods of the surface soil can be found in the previous study (Liu and Shen, 2014) and [GB/T 17138-1997, HJ 491-2009; GB/T 17141-1997]. In the present study, accurately weighted freeze-dried soil samples (0.2000 ± 0.0005 g) were digested by a mixture of acids including 10 mL HCl, 5 mL HF 5 mL HClO₄ and 3 mL HNO₃ in Teflon beakers until the solid residue disappeared and the solution turned into white or light yellow-greenish pasta-like material (Zhang, et al., 2009). After digestion, the samples were then diluted to 50 mL with ultra-pure water. The concentrations of 30 metal elements including Cd, Se, Sb, Hf, U, Dy, Gd, Sc, Sn, Pr, Cs, Th, Co, Nb, Ga, Cu, Ni, La, Pb, Li, Ce, As, Sr, Cr, Zr, V, Zn, Mn, Ba, and Ti in the final solutions were measured by an Agilent 7700X inductively coupled plasma-mass spectrometer (ICP-MS), and analytic data were quantified with an internal standards method (1 mg/L Rh and In as internal standards).

A quality control procedure was also applied throughout the different steps from sampling preparation of analysis. The analytic precision, determined by using two sets of parallel samples while three replicate comprises one set, both two sets were randomly selected from those samples. Furthermore, blanks and standards were regularly run with each series of analyses in order to check the accuracy of data. For every twelve samples, a laboratory blank and a standard was incorporated into the analytic procedure (Zan, et al., 2011).

Statistical analysis

All element concentrations were reported as $\mu\text{g/g}$ dry weight. Normal distribution of individual element was checked using Kolmogorov-Smirnov test (with a significance level at 0.05). A principal component analysis (PCA) was performed in SPSS software package (SPSS 16.0) to assess the possible origins of metals. All statistical analyses were functioned using the SPSS 20.0 software (Chicago, IL, USA). To obtain the pollution degree of elements in agricultural area in Chaohu Lake watershed, enrichment factor (EF) and pollution level index (PLI) were calculated. EF values are used to assess the degree of enrichment of a given element from anthropogenic activities:

$$EF_i = \frac{C_i(\text{soil})/C_R(\text{soil})}{C_i(\text{background})/C_R(\text{background})} \quad (1)$$

where: $C_i(\text{soil})$ and $C_i(\text{background})$ – the concentration and background value of i^{th} element; $C_R(\text{soil})$ and $C_R(\text{background})$ – the concentrations in the soil samples and background value of the reference element.

In the present study, The soil background values for all selected elements in Anhui Province (Chen, et al., 2012) were adopted in the present study. And Ti was selected as the reference element because of the low residual concentration in the soil samples ($3890 \pm 478 \mu\text{g/g}$ for soils in Hangbu River Valley, $4070 \pm 313 \mu\text{g/g}$ for soils in Tongyang River Valley, respectively) and which was closed to the background concentration ($3800 \mu\text{g/g}$). EF_i value less than 1.0 indicates no enrichment; $1 < EF < 3$ means minor enrichment, $3 < EF < 5$ means moderate enrichment, $5 < EF < 10$ means moderately severe enrichment, $10 < EF < 25$ means severe enrichment; $25 < EF < 50$ means very severe enrichment and $EF > 50$ means extremely severe enrichment, respectively (Lu, et al., 2014, Tasmemir and Kural, 2005, Zhang and Liu, 2002).

PLI value was developed to assess the overall pollution level by all observed metal element for a certain given sample:

$$PLI = \sqrt[x]{\prod_{i=1}^x \frac{C_i(\text{soil})}{C_i(\text{background})}} \quad (2)$$

When PLI less than 1.0 means no metal pollution, but it greater than 1.0 do suggests contamination (Varol, 2011).

RESULTS AND DISCUSSION

Description statistics of metal pollution

All elements except for Cd were detectable with the mean concentration of Se ($0.97 \pm 0.33 \mu\text{g/g}$) < Sb ($1.45 \pm 0.35 \mu\text{g/g}$) \leq Hf ($1.46 \pm 0.42 \mu\text{g/g}$) \leq U ($1.55 \pm 0.33 \mu\text{g/g}$) < Dy ($1.81 \pm 0.61 \mu\text{g/g}$) < Gd ($2.07 \pm 0.81 \mu\text{g/g}$) \leq Sc ($2.08 \pm 1.39 \mu\text{g/g}$) < Sn ($3.37 \pm 0.87 \mu\text{g/g}$) \leq Pr ($4.03 \pm 1.37 \mu\text{g/g}$) < Cs ($5.24 \pm 1.51 \mu\text{g/g}$) < Th ($6.26 \pm 2.04 \mu\text{g/g}$) < Co ($10.2 \pm 2.17 \mu\text{g/g}$) \leq Nb ($10.6 \pm 1.64 \mu\text{g/g}$) < Ga ($12.6 \pm 2.29 \mu\text{g/g}$) < Cu ($19.5 \pm 4.94 \mu\text{g/g}$) < Ni ($23.3 \pm 5.58 \mu\text{g/g}$) < La ($23.7 \pm 6.43 \mu\text{g/g}$) \leq Pb ($24.3 \pm 2.83 \mu\text{g/g}$) < Li ($33.7 \pm 8.45 \mu\text{g/g}$) < Ce ($41.7 \pm 13.6 \mu\text{g/g}$) < As ($50.7 \pm 12.0 \mu\text{g/g}$) \leq Sr ($54.9 \pm 22.8 \mu\text{g/g}$) \leq Cr ($61.5 \pm 12.1 \mu\text{g/g}$) < Zr ($69.4 \pm 13.1 \mu\text{g/g}$) \leq V ($74.1 \pm 11.7 \mu\text{g/g}$) < Zn ($86.0 \pm 14.2 \mu\text{g/g}$) < Mn ($455 \pm 126 \mu\text{g/g}$) \leq Ba ($514 \pm 174 \mu\text{g/g}$) < Ti ($3989 \pm 397 \mu\text{g/g}$) for all samples. Cd in all samples was undetectable. The concentrations of these elements in soil samples followed normal distributions (Fig. 2), which possibly suggests these elements were from single origin (Hu and Cheng, 2013) or experienced a long-term chemical weathering (Ljung, et al., 2006). Spatially, despite the samples along Hangbu River contained slightly higher concentrations than those along Tongyang River did, all elements except for Sb, Nb, Sr, Ce, Zn, Rb, Mn, and Ba did not appear significant difference between two sampling areas. However, significantly higher concentrations of Nb, Sr, Ce, Zn, Rb, Mn, and Ba were obtained in soil samples along Hangbu River than along Tongyang River (Fig. 1). The concentrations of Hf, U, Dy, Gd, Sc, Pr, Th, Nb, Ga, La, Ce, Sr, Zr, and Zn were lower than their soil background thresholds (Fig. 3), suggesting low accumulation in agricultural soils in Chaohu Lake watershed. But Se, Sb, Sn, As, and Ba significantly accumulated in these areas because of their contents in more

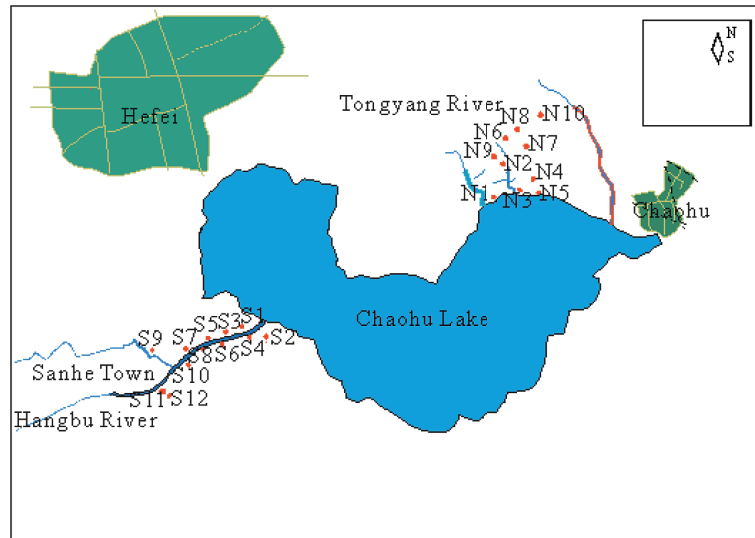


Fig. 1. Location of sampling sites and map of Chaohu Watershed

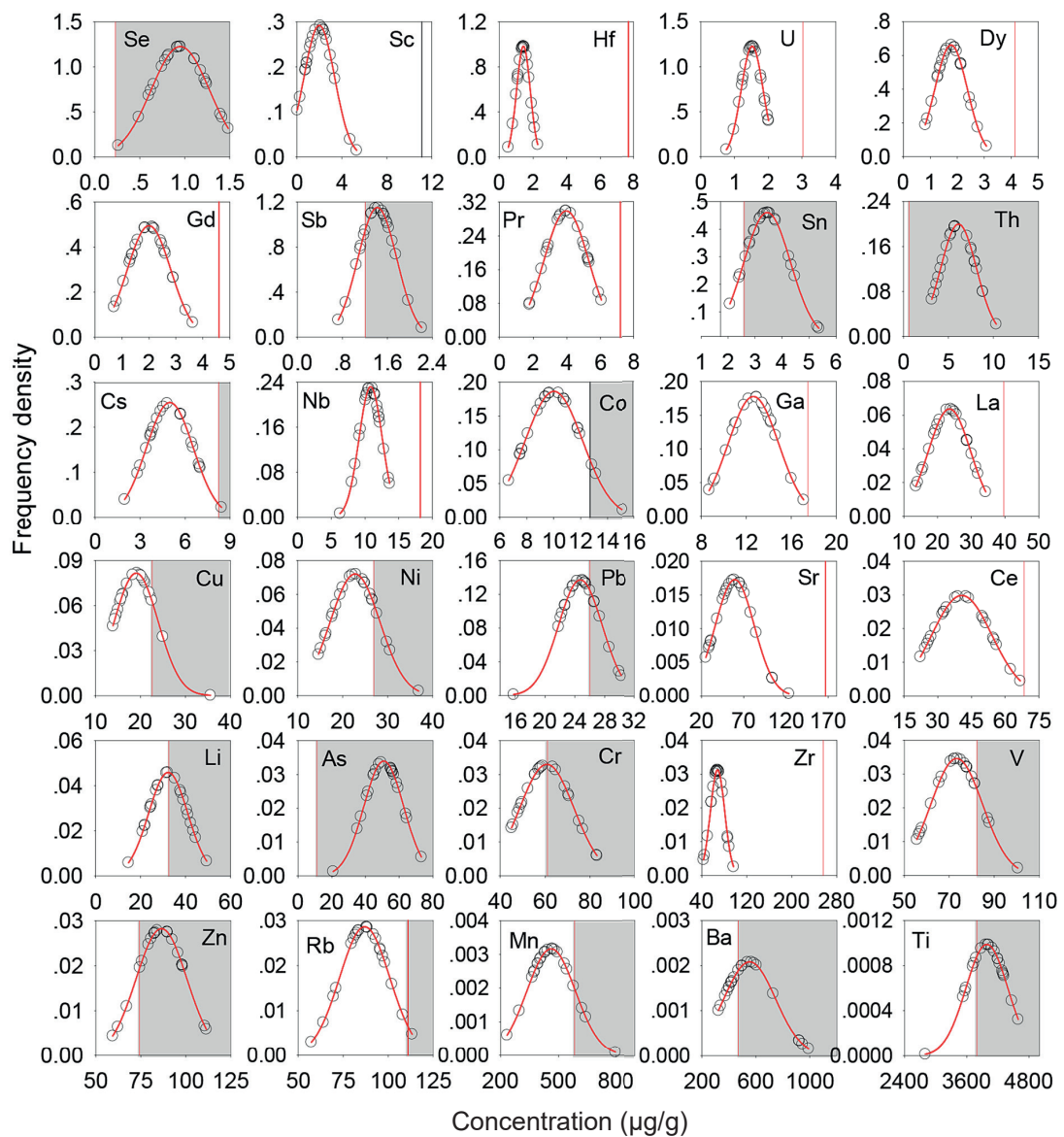


Fig. 2. The normal distribution of all selected metals in agricultural soils along two main tributaries of Chaohu Lake

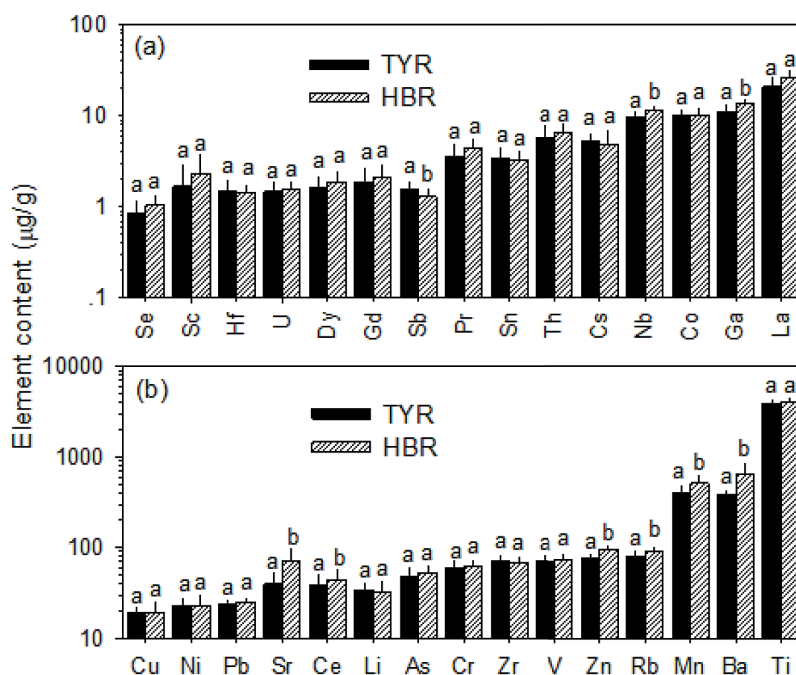


Fig. 3. Distribution of 30 metal elements in soil samples collected in Hangbu River valley and Tongyang River Valley, Chaohu Lake watershed

than half samples greater than the corresponding background values (Table 1). Especially for As, the concentration in all samples exceeded its background value, approximately 4.55 ± 1.55 times higher than its background value. It should be noted that the content of Ba exceeded its background value in all samples collected along Hangbu River, but was less than the background value in all samples along Tongyang River.

The coefficient of variation (CV) is usually used to understand the degree of variability for the concentrations of metal in the soil. If CV less than 20% generally suggests low variability, $20\% < CV \leq 50\%$ means moderate variability, while higher than 50% indicates high variability (Karimi Nezhad, et al., 2015). In the present study, only Sc was characterized by high variability, elements of Ti, Rb, Zn V, Zr, Cr, Pb, Ga, and Nb were showed low variability (Fig. 4), and the remaining elements were moderate variability. These results suggested Ti, Rb, Zn V, Zr, Cr, Pb, Ga, and Nb were less influenced by human activities or were impacted by intensive weathering processes (Jiao, et al., 2014).

Evaluation of enrichment

EF of individual element in soils was calculated to distinguish the metals derived from anthropogenic activities and those from natural origin.

Results showed that Th was mostly enriched element amongst all metals with a mean EF value of 9.35 ± 2.90 (5.62–15.9) (Table 1). The average EF values of Se and As were 3.09 ± 0.97 (1.22–4.98) and 4.29 ± 0.81 (2.52–6.20), indicating

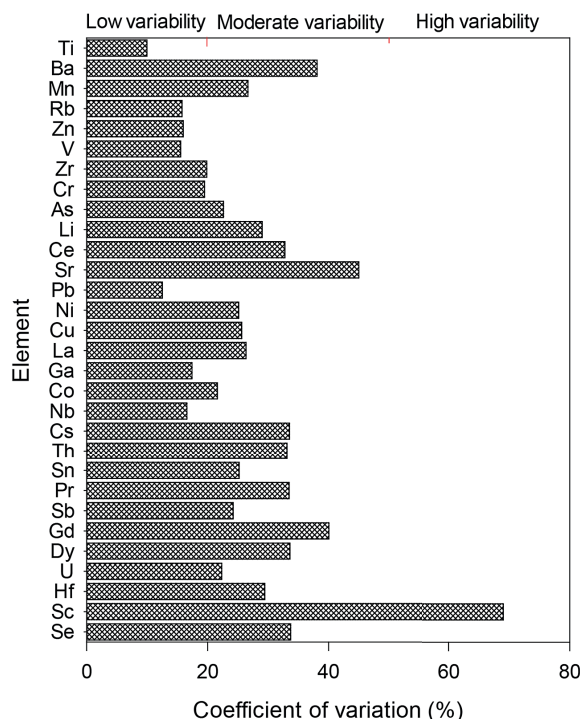


Fig. 4. The coefficient of variation for each metal element in agricultural soils along two main tributaries of Chaohu Lake

Table 1. The soil background values in Anhui Province, the concentrations in agricultural soils along two main tributaries, the contents in surface sediments of Chaohu Lake, and the enrichment factor in the soil samples of all selected metal elements

Background ^a		Soil (µg/g)		Sediment (µg/g)		Enrichment factor (EF)	
		Range	Mean ±RSD	Range	Mean ±RSD	Range	Mean ±RSD
Cd		0.045–1.48 ^b	0.226±0.245 ^b	0.08–84.7 ^b	34.7±34.0 ^b	–	–
Se	0.29	0.26–1.49	0.95±0.32	–	–	1.22–4.98	3.09±0.97
Sc	11.1	0.01–5.30	1.97±1.36	21.9–469 ^b	257±104 ^b	0.00–0.41	0.17±0.11
Hf	7.72	0.53–2.28	1.43±0.42	5.48–571 ^b	249±206 ^b	0.09–0.26	0.17±0.04
U	3.03	0.76–2.01	1.52±0.34	1.00–31.7 ^b	14.2±11.1 ^b	0.32–0.63	0.48±0.08
Dy	4.13	0.82–3.08	1.77±0.59	1.96–21.8 ^b	11.3±6.80 ^b	0.21–0.64	0.41±0.12
Gd	4.6	0.71–3.62	2.00±0.80	0.63–61.1 ^b	33.1±14.4 ^b	0.16–0.70	0.41±0.15
Sb	1.21	0.73–2.21	1.42±0.34	–	–	0.57–1.75	1.13 ±0.27
Pr	7.17	1.77–6.05	3.96±1.33	2.71–105 ^b	43.9±24.1 ^b	0.26–0.81	0.52 ±0.16
Sn	2.6	2.07–5.37	3.45±0.87	0.41–19.6 ^b	8.69±5.13 ^b	0.86–1.87	1.26 ±0.28
Th	0.62	3.15–10.3	6.11±2.03	0.24–46.4 ^b	21.2±16.5 ^b	5.62–15.9	9.35 ±2.90
Cs	8.24	1.96–8.43	4.98±1.67	1.32–10.0 ^b	4.87±2.42 ^b	0.24–0.89	0.58 ±0.18
Nb	18.2	6.29–13.7	10.8±1.79	8.49–29.2 ^b	20.5±4.26 ^b	0.45–0.75	0.57 ±0.08
Co	12.7	6.66–15.12	10.0±2.16	4.42–16.7 ^b	10.8±2.92 ^b	0.54–1.01	0.75 ±0.13
Ga	17.5	8.74–17.12	12.6±2.20	10.7–56.8 ^b	36.4±10.9 ^b	0.49–0.83	0.69 ±0.09
La	39.7	13.6–34.3	23.5±6.20	5.62–237 ^b	128±65.5 ^b	0.35–0.76	0.56 ±0.13
Cu	22.6	13.9–35.6	19.1±4.88	12.6–41.8 ^b	26.9±7.10 ^b	0.59–1.42	0.80 ±0.18
Ni	26.9	14.6–36.9	22.7±5.71	14.8–59.1 ^b	36.0±11.8 ^b	0.54–1.17	0.80 ±0.18
Pb	26	15.8–30.2	24.7±3.09	3.13–225 ^b	94.8±88.4 ^b	0.76–1.17	0.91 ±0.09
Sr	167	25.1–124	59.4±26.7	42.5–768 ^b	318±257 ^b	0.14–0.74	0.34 ±0.15
Ce	68.4	22.3–66.7	40.7 ±13.3	49.1–1219 ^b	7267±2851 ^b	0.35–0.93	0.56 ±0.17
Li	32.5	14.6–49.4	32.3±9.35	–	–	0.45–1.36	0.94 ±0.25
As	11.2	20.8–73.2	50.8±11.5	3.88–12.7 ^c	8.02±2.91 ^c	2.52–6.20	4.29 ±0.81
Cr	61	45.0–83.1	60.7±11.8	28.7–91.1 ^b	61.0±16.2 ^b	0.74–1.33	0.95±0.17
Zr	256	43.2–96.6	68.1±13.5	10.3–1192 ^b	521±431 ^b	0.18–0.33	0.25±0.04
V	82.4	55.6–100	73.3±11.4	42.3–140 ^b	81.5±22.5 ^b	0.71–1.04	0.85±0.10
Zn	74.2	59.3–111	86.5±13.8	1.50–907 ^b	341±347 ^b	0.86–1.51	1.11±0.15
Rb	111	57.2–113	86.9±13.7	8.13–162 ^b	78.3±45.1 ^b	0.59–0.93	0.75±0.09
Mn	583	233–797	462±123	168–887 ^b	482±157 ^b	0.50–1.24	0.75±0.16
Ba	469	323–991	554±211	1.88–1113 ^b	333±335 ^b	0.68–2.12	1.12±0.41
Ti	3800	2805–4595	3989±397	1715–8412 ^b	5247±1229 ^b	–	–

Note: a – the soil background values (µg/g) of Anhui Province was adopted in the present (Chen et al. 2012); b – Cd concentration in agricultural soil in Chaohu Lake watershed was cited in the literature (Zhang 2007); c – the concentrations in sediment of Chaohu Lake were obtained from the literature (Wang et al. 2016); d – the concentration of As in sediment of Chaohu Lake was from the reference (Zheng et al. 2010).

moderate enrichment in the agricultural soils in Chaohu Lake watershed. Half of these samples were investigated with EF value of Se less than 3.0, suggesting these sampling sites were slightly contaminated by Se. However, only one sample was found the EF value of As less than 3.0, four samples had EF value of As greater than 5.0. Thus a portion of sampling sites were moderately influenced by enriched As. Moderate accumulation of

Th, Se and As were possibly due to the significant contribution of sewage of poultry farming (Han, et al., 2004, Zhang, et al., 2006). Furthermore, these metals are generally thought as immobile elements (Virtanen, et al., 2013), resulting in low loss from soil. The remaining elements including Sc, Hf, U, Dy, Gd, Sb, Pr, Sn, Cs, Nb, Co, Ga, La, Cu, Ni, Pb, Sr, Ce, Li, Cr, Zr, V, Zn, Rb, Mn, Ba were minimally enriched in the surface soil

in the study areas. The EF values of Pb, Li and Ba in the soils along Hangbu River were significantly greater than those along Tongyang River ($p < 0.05$), suggesting that Pb, Li and Ba were significantly enriched in soils along Hangbu River.

PLI value was calculated to assess multiple metals pollution. PLI values for all sampling sites varied 0.405 to 1.08 with a mean of 0.78 ± 0.15 (Fig. 5). Two sampling sites (site 7 and 9 in Hangbu River valley) had PLI greater than 1.0. The distribution of PLI value was tested using Monte Carlo simulations (10000 times). Results showed PLI value followed a normal distribution. The probability of PLI higher than 1.0 could be estimated to predict the contamination of the study areas based upon the probabilistic density function. Results showed that 8.2% of sampling areas had PLI greater than 1.0. Thus, most surface soils (representing 92% of study areas) were not significantly contaminated by mixture of elements, approximate 8.2% of the areas was predicted to be polluted by the mixture of metals.

Source evaluation

PCA was performed to reduce the high dimension of the variable space, and further to identify the potential sources of elements in the present study. Totally, five factors were obtained (Table 2), which could explain a total variance of 88.6%. Of them, only the fifth factor (F5) appears to be associated with natural source, because this factor was dominated by Hf, U, and Zr, whose levels were lower than the background values (Fig. 2). First factor (F1) which explained 46.5% of total

variance was highly loaded by Se, Sc, Dy, Gd, Pr, Th, La and Ce. Of them, Th was highly enriched in the soils of the study areas, indicating anthropogenic origins. Sc was considered as a marker of agroindustry such as sugar and alcohol production (Fernandes, 1993). As a member of lanthanide family, Ga is usually found the coexistence with Sc in the environment (Py, et al., 2011). The second factor (F2) which might suggest fertilizer-associated source (Quinton and Catt, 2007). Some phosphate fertilizer has potentially toxic As, Cd, Cr Hg, Ni, and V (Mortvedt, 1996). Both sampling areas were located in agricultural fields, industrial and mining sources of Ni, Li, Cu, and Cr could be ignored. For the third factor which was characterized by high loading of Cu, Pb and As, it might imply poultry farming related sources (Cang, et al., 2004). The fourth factor (F4) was highly loaded by Sb, Sr and Ba. Sb can be used to trace the emission of coal burning (Cao, et al., 2014, Tang, et al., 2017), and Ba is widely used in manufactured materials such as tiles, brick and glass (McBride, et al., 2014). In the study areas, little manufactures of tiles, brick and glass were generally operated in the villages or towns which were surrounded by agricultural land. Therefore, this factor possibly implied the influence from little manufacture in rural areas.

A comparison between soil and sediment: implication on soil erosion and weathering

Elements in arable soils are generally associated with organic matter or other charged material (Tipping, et al., 2003). Thus soil weathering and

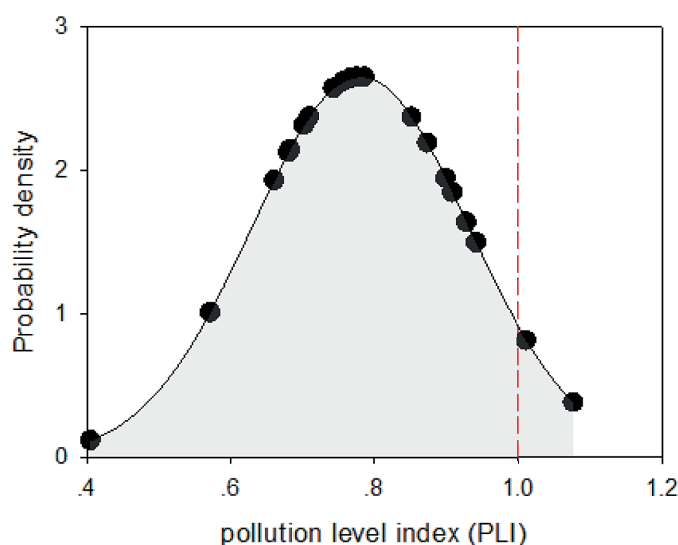


Fig. 5. Probability distribution of pollution level index (PLI) for soils collected in Chaohu Lake watershed

Table 2. Rotated principal component loadings

Element	F1	F2	F3	F4	F5
Se	0.864	0.173	0.344	0.040	0.247
Sc	0.695	0.285	0.397	0.140	0.361
Hf	0.354	0.318	0.331	-0.113	0.782
U	0.469	0.418	0.252	0.085	0.686
Dy	0.906	0.376	0.124	-0.012	0.031
Gd	0.927	0.316	0.118	-0.064	0.084
Sb	0.237	0.463	0.248	-0.658	0.183
Pr	0.964	0.131	0.103	0.134	0.120
Sn	-0.020	0.280	0.854	-0.147	-0.021
Th	0.911	0.203	0.049	-0.029	0.283
Cs	0.160	0.862	-0.073	-0.356	0.198
Nb	-0.006	-0.005	0.713	0.535	0.224
Co	0.240	0.834	0.041	0.093	0.251
Ga	0.251	0.610	0.215	0.696	0.088
La	0.916	0.061	0.073	0.302	0.181
Cu	0.152	0.825	0.364	-0.247	0.067
Ni	0.235	0.933	-0.044	-0.067	0.093
Pb	0.180	-0.037	0.833	0.353	0.133
Sr	0.420	-0.367	0.218	0.709	-0.168
Ce	0.947	0.099	0.004	0.018	0.170
Li	0.309	0.826	-0.044	-0.361	0.191
As	0.365	-0.034	0.739	0.073	0.403
Cr	-0.006	0.789	0.198	0.000	0.159
Zr	0.360	0.295	0.174	-0.120	0.822
V	0.300	0.878	0.175	0.190	0.129
Zn	0.158	0.195	0.439	0.463	0.199
Rb	0.205	0.690	0.429	0.486	0.060
Mn	0.395	0.399	0.609	0.305	0.203
Ba	0.038	-0.167	0.264	0.927	-0.039
Ti	0.317	0.348	0.537	0.313	0.496

erosion are frequently expected as the important pathways to transport metals from soil to receiving water (Quinton and Catt, 2007). Sediment will be a key sink of these pollutants derived from soil particles. Under the supposition that chemical components in a given sediment sample have a strong correspondence to the chemical composition of donor soil. A comparison of elements in soils from Chaohu Lake and in sediments in the lake was made (Fig. 6). Results clearly showed that As, Cu, Cr and Ba tended to accumulate in soil rather than in sediment. The mobility of these elements is predominantly responsible for the differences on the accumulation potential in soil and sediment. Despite chemical speciation of metals in soils of Chaohu Lake watershed is scarce, Cu, Cr and As in sediment of Chaohu Lake mainly existed in residual fraction (Chen and Li, 2007, Kong, et al., 2015).

Elements in residual fractions are insusceptible to be lost during chemical weathering or soil erosion, resulting in high accumulation in soils. However, many elements (including Cd, U, Se, Hf, Sn, Th, Zr, Mn, Sr, Ga, Nb) appeared higher accumulation in sediment than in soil. Especially for Cd, it was undetectable in all soils in the present study. Similar study also demonstrated that low concentration of Cd was also observed in soil samples from Chaohu Lake watershed (Zhang, 2007, Zhong, et al., 2015). For example the average value of Cd was $0.226 \pm 0.245 \mu\text{g/g}$ with a range of 0.045–1.478 $\mu\text{g/g}$ for Daxing town, and was $0.145 \pm 0.075 \mu\text{g/g}$ with a range of 0.054–0.432 $\mu\text{g/g}$ for Yicheng Town (Zhang, 2007). Zhong et al. reported a mean concentration of Cd was $0.44 \pm 0.05 \mu\text{g/g}$ for the soil samples collected in Chaohu city (Zhong, et al., 2015). Thus soils in Chaohu Lake

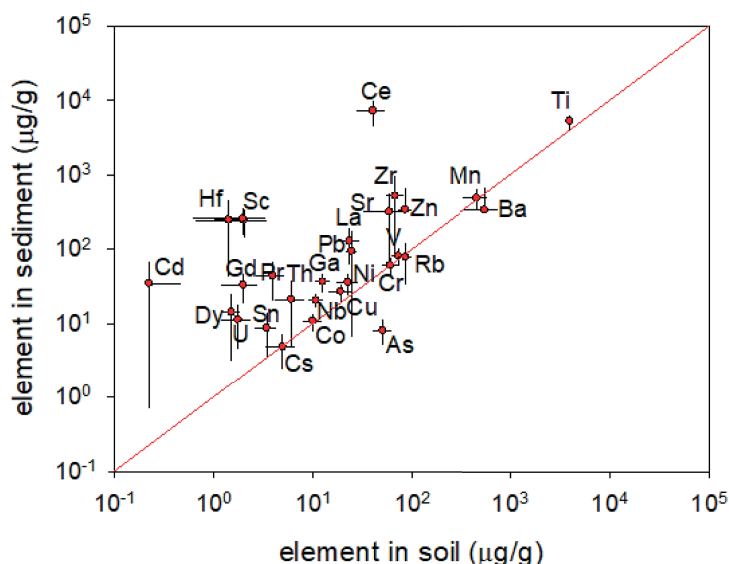


Fig. 6. Comparison of metal concentrations in the soils from Chaohu Lake watershed to sediments in Chaohu Lake. The data of Cd in soils was obtained from the literature (Zhang, 2007), and the concentrations of metals in sediments of Chaohu Lake were obtained from the literatures (Wang, et al., 2016, Zhang, et al., 2007)

watershed contained Cd content much lower than the lacustrine sediments did (Tang, et al., 2010, Tang, et al., 2014, Wang, et al., 2016a) The depletion of metal element in soil was predominantly caused by soil erosion or weathering due to long-term agricultural cultivation (Jiao, et al., 2014). A previous study on the metal accumulation in sediments caused by soil erosion also indicated that the concentrations of selected elements were much lower in soils than in sediment (Quinton and Catt, 2007), which in part supported our statement on the accumulation of elements in the sediment due to the soil erosion.

In order to further verify that soil erosion and weathering were the vital reasons on the metal depletion in soil and accumulation in sediment in Chaohu Lake watershed, the ratio of Rb to Sr was used because it has been widely proposed to reflect the degree of pedogenesis and weathering (Jin, et al., 2006, Xu, et al., 2010, Zeng, et al., 2012). Generally Rb coexists with K but Sr tends to be dispersed in Ca – bearing minerals. Weathering can leach Sr much easier than Rb, as a result, Rb tends to be enriched in the parent soil comparing with Sr. Due to the different geochemical behaviors Rb and Sr are easily fractionated, which leads to a different ratio of Rb/Sr. A higher degree of weathering usually is characterized by a greater ratio of Rb/Sr, while a lower degree of weathering is commonly related to a lower ratio value. Furthermore, a low ratio value of Rb/Sr will often be observed in weathering products compared

with parent materials. When weathering materials are eventually transported into lake, resulting in low Rb/Sr ratio for sediments. Therefore, the ratio of Rb/Sr has been considered as a useful tool to identify the intensity of soil weathering and erosion. The ratio of Rb/Sr for soil samples varied between 0.78 to 3.5 with a mean of 1.8 ± 0.73 (Fig. 7a), which is significantly greater than that in sediment of Chaohu Lake (between 0.16 to 0.85 with a mean of 0.38 ± 0.23). Furthermore, Rb/Sr ratio in appeared significant correlation against 1/Sr for soils and sediments in Chaohu Lake watershed ($p < 0.01$). Thus these results indicated sediments in Chaohu Lake were significantly impacted by soil erosion and weathering. Previous studies also demonstrated that Cd was largely associated with mobile fractions of sediments in Chaohu Lake (Chen and Li, 2007, Xu, et al., 2008), possibly implying Cd was easily depleted in soils and accumulated in sediments due to intensive soil erosion and weathering after long-term agricultural practices. Non-residual Sr and Cd are easily to be lost during soil erosion and weathering, thus the residual concentrations of both elements should appear similar trends in soils and sediments. Sr and Cd in sediments of Chaohu Lake displayed a significant correlation (Fig. 7b), but the relationship for soils was not investigated because Cd was under detectable in all samples in the present study. Therefore, these results suggested that soil erosion and weathering could be the key reasons on undetectable Cd in soils of study areas.

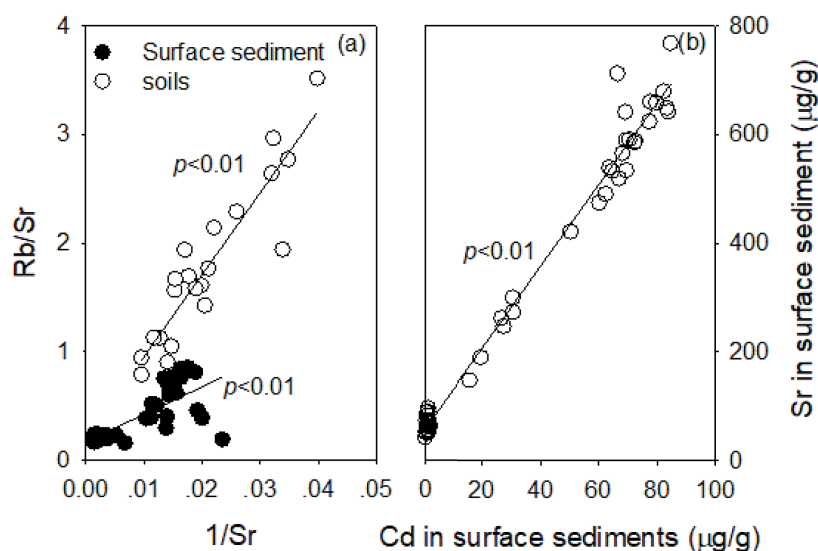


Fig. 7. Correlations of Rb/Sr ratio against 1/Sr in soils and sediments (a) and of Sr against Cd in surface sediments (b) from Chaohu Lake watershed

Ratio of U/Th is proposed to estimate the anthropogenic contribution of U in the agricultural soils (Takeda, et al., 2004). Generally, higher ratio value of U/Th was found in the agricultural soils, but lower value was obtained in the non-agricultural soils. In the present, the ratio of U/Th varied from 0.18 to 0.46 with a mean of 0.27 ± 0.07 for all soil samples, which was significantly lower than those found in lacustrine sediments of Chaohu Lake (varying from 0.34 to 0.95 with a mean of 0.68 ± 0.12). These results clearly suggested that soils in Chaohu Lake watershed were less impacted by phosphatic fertilizers, while sediments of Chaohu Lake were strongly influenced by agrochemicals. This phenomenon could be explained by the fact that U was easier to be leached from soil than Th. As a result, U was depleted in the soils but was enriched in the sediments due to long-term soil erosion and weathering. Correspondingly, the ratio of U/Th was reduced in soils, but was elevated in sediments.

CONCLUSIONS

Intensive cultivation has been considered as an important factor that causes heavy metal pollution in agroecological system. These heavy metals could be depleted by soil erosion and weathering, resulting in the accumulation in the sediment of receiving aquatic system. In the present study, surface soil samples in the

typical agricultural areas along Hangbu River and Tongyang River, the main inflowing tributaries of Chaohu Lake, were collected to investigate 30 metal elements. The results were further compared with previously published data on the heavy metals in surface sediments of Chaohu Lake. For those elements (Cd, Sr, Hf, Sc, U, etc.) with large portion of non-residual fractionation, they were found to be depleted in the soils but be accumulated in the sediments. As a result, the ratio of Rb/Sr was significantly higher in the soil than in sediment, but the ratio of U/Th appeared an opposite trend. As, Se and Th moderately accumulated in the soils due to their weak mobility. These results clearly suggested that high degree of soil erosion and weathering could lead to the loss of heavy metals in the agricultural soils but accumulation in the sediments. Thus, negligible of the ecological risk caused by most of the selected heavy metals in the agricultural soils in Chaohu Lake watershed could be predicted.

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