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# Assessment of Heavy Metal Pollution in Estuarine Surface Sediments of Tangxi River in Chaohu Lake Basin

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**Abstract:** A total of 30 surface sediments samples from the estuary wetland of the Tangxi River, Chaohu Lake Basin were obtained and tested. Enrichment factor (*EF*) and geoaccumulation index ($I_{geo}$) as well as multivariate statistical analysis methods including Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA) were applied for the assessment of heavy metal pollution in surface sediments. The results of *EF* values show that the pollution of copper (Cu) and cadmium (Cd) occurs in the estuarine sediments, and that zinc (Zn), lead (Pb) and chrome (Cr) may originate from crustal materials or natural weathering process. The mean *EF* values of the five heavy metals are in the decreasing order: Cu>Cd>Zn>Pb>Cr. Based on the $I_{geo}$ of target heavy metals, the surface sediments collected from the study area can be approximately categorized as unpolluted with Zn, Pb and Cr, and moderately polluted with Cu and Cd. The degree of heavy metal pollution decreases in the order of Cu>Cd>Zn>Pb>Cr. Three groups of pollution factors are presented from FA: Zn-TOC, Cu-Cd and Cr-Pb, which respectively accounte for 27.22%, 25.20% and 21.05% of variance. By means of HCA, a total number of seven groups are distinguished from 30 sampling sites. Results indicate that Cu and Cd are the prior controlled pollutants in the estuarine sediments of the Tangxi River.
**Keywords:** heavy metal pollution; sediment; estuary; multivariate analysis; Chaohu Lake Basin

## 1 Introduction

Heavy metals are regarded as serious pollutants of aquatic ecosystems, because of their environmental persistence, toxicity, and ability to be incorporated into food chains (Förstner and Wittman, 1983; Seralathan *et al*., 2008). Their occurrence in the environment results primarily from anthropogenic activities, though natural processes that may enrich waters with trace elements also play a noticeable role (Loska and Wiechuła, 2003). It is well-known that sediments have a great capacity to accumulate and integrate heavy metals and organic pollutants even from low concentrations in the overlying water column (Tam and Wong, 2000). In recent years, the studies of heavy metal pollution in sediments and soils have received increased global attention by investigators (Farkas *et al*., 2007; Abubakr, 2008; Liao *et al*., 2008; Yalcin *et al*., 2008; Amaya *et al*., 2009; N′guessan *et al*., 2009; Sakan *et al*., 2009; Wang and Chen, 2009; Zhang *et al*., 2009). Currently, there are two main aspects in the research of heavy metal pollution in sediments. One is the evaluation of heavy metal pollution, the other is the identification of heavy metal sources. Thus geochemical approaches such as enrichment factor (*EF*) and geoaccumulation index ($I_{geo}$), and statistical methods including Factor Analysis (FA) and Cluster Analysis (CA), have been broadly adopted to assist the interpretation of geochemical data.

It has been well documented that heavy metals can be delivered to estuary from the watershed via fluvial transport, local wastewater discharge, and even atmospheric deposition (Windom *et al*., 1991; Lin *et al*., 2002; Taylor and Mclennan, 1995; Censi *et al*., 2006; Birth, 2003). Therefore, it is essential to gain insights on the concentrations and spatial variations of heavy metals in sediments for ecological remediation and water environment protection of estuarine wetlands. Chaohu Lake Basin, within the geographical range of 30°58′40″–32°06′00″N and 116°24′30″–118°00′00″E, is located in the center of Anhui Province, China. There are more

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than 30 streams and rivers in the basin, and most of them have been seriously polluted by domestic sewage and industrial wastewater. The water pollution of Chaohu Lake Basin has received great attention in recent years, there is, nevertheless, very limited research on pollution levels of heavy metals in the estuarine environment. The Tangxi River, being 19.5 km long and 6 m wide, with a watershed area of about 50 km$^2$, is situated on the northwest of Chaohu Lake Basin, and it flows through Hefei City, the capital of Anhui Province, from northwest to southeast and flows into Chaohu Lake near Tangxi Village. In the past two decades, overpopulation, urbanization and largely uncontrolled pollutant inputs have resulted in the degradation of river water quality and the damage of estuarine aquatic ecosystem (Li, 2007). For understanding the existing and potential effects on aquatic environment and human life from toxic metal pollutants, therefore, it is necessary to investigate the current concentrations and spatial distribution characteristics of metal pollutants in the estuarine wetland.

The present study was conducted as a preliminary survey on sediment pollution of estuarine wetlands in Chaohu Lake Basin. The aims of this study were to: 1) determine the concentration levels of some heavy metals (copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd) and chrome (Cr)) in the estuarine surface sediments of the Tangxi River; 2) evaluate the heavy metals pollution by means of geochemical approaches and statistical methods and; 3) preliminarily analyze the anthropogenic contribution to the heavy metals pollution.

## 2 Materials and Methods

### 2.1 Arrangement of sampling sites

Normally, the estuarine wetland of the Tangxi River is more than 1 000 m long in the west-east direction and 200 m wide in the north-south direction (Li and Shi, 2009), which is about 10 km away from Hefei City and 1.5 km away from Yicheng Town. Considering a majority of the right estuary has been occupied by a pumping station structure and a yacht marina, we mostly chose the left estuary to arrange sampling sites. In the left study area, we set six sampling sections for sample collection, with 50 m apart and perpendicular to the lakeshore from east to west, as shown in Fig. 1. In each section, four sampling sites were set with 50 m apart from north to south. Moreover, as for the river course at the mouth of the Tangxi River, we set a section and its numbering for sampling sites was similar to above sections. In addition, we set a sampling section, including two sampling sites, in the right estuary unoccupied as well. Thus, a total of 30 sampling sites were distributed in the major estuary of the Tangxi River.

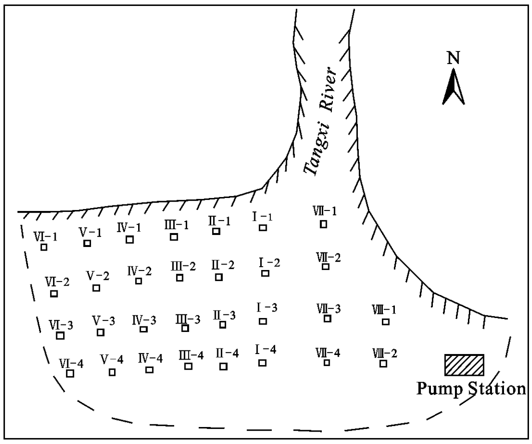


Fig.1 Sketch of sampling sites in the estuary of the Tangxi River

### 2.2 Sample collection and analysis methods

Sediment samples were collected using a polypropylene coring device with 1.0 m long and 5 cm internal diameter. Typically, cores were comprised of a 5 cm sediment surface layer for each sample, and 5 samples were taken at randomly chosen locations within a area of about 1.0 m$^2$ surrounding each site. These samples were thoroughly mixed to create composite samples for each site. A total of 30 composite samples were obtained and transported to the laboratory at –4℃, air-dried prior to screening using a 63-μm nylon sieve.

The concentrations of Al, Cu, Zn, Pb, Cd and Cr and the content of total organic carbon (TOC) in the samples were analyzed. TOC was determined by titration with $FeSO_4$ after digestion with $K_2Cr_2O_7$-$H_2SO_4$ solution (Zhang *et al.*, 2009). For metal analysis, total sediment digestion was performed in Teflon vessels following the classical open digestion procedures (SEPA, 2002). About 0.25 g air-dried sediment sample was weighed into Teflon beakers, in which a mixture of concentrated HF-$HClO_4$-$HNO_3$ (i.e., 10 ml $HNO_3$, 5 ml HF and 5 ml $HClO_4$) was added, a Teflon watch cover was put in place, and the sample was left at room temperature overnight. On the following day the sample was heated to a temperature of about 200℃ on a hot plate and kept under slight boiling state until the solid residue disappeared and the solution turned into white or light yellow-greenish pasta-like material (Zhang *et al.*, 2009). Then, 5 ml $HNO_3$ was added to completely dissolve it and to make a final 50 ml solute with ultrapure water with a Milli-Q system (Millipore, Bedford, USA). Concentrations of metals in solutions were determined using flame atomic absorption spectrometry (FAAS) (Analytikjena AAS vario6, Germany) for Cu, Zn, Pb and Cr, and employing graphite furnace atomic absorption spectrometry for Cd. Al was analyzed using inductively coupled plasma Atomic Emission Spectrometry (ICP-AES) (ICPS-7500, Shimadzu, Japan). The soil reference material (GSD-1, now named GBW07309), issued by General Administration of Quality Supervision, Inspection and Quarantine of the People′s Republic of China, was analyzed along with the samples for quality assurance purpose. The recovery rates for the selected metals from the standard reference material ranged from 96% to 103%.

### 2.3 Data analysis

#### *2.3.1 Enrichment factor*

The concept of enrichment factor (*EF*) was developed in the 1970s to evaluate the anthropogenic contribution. Mathematically, *EF* is expressed as follows (Abubakr, 2008):

$$EF = \frac{(C_{\mathrm{EE}}/C_{\mathrm{RE}})_{\mathrm{Sample}}}{(C_{\mathrm{EE}}/C_{\mathrm{RE}})_{\mathrm{Reference\ material}}} \tag{1}$$

where the numerator stands for the ratio of the concentration of the examined element ($C_{\mathrm{EE}}$) to the reference element ($C_{\mathrm{RE}}$) in a sample. The denominator represents the ratio of the concentration of the examined element ($C_{\mathrm{EE}}$) to the reference element ($C_{\mathrm{RE}}$) in a reference material.

Because Al is one of the most abundant elements on the earth and usually has no pollution concerns, it is commonly used for normalization purpose (Susana *et al.*, 2005; Zhang *et al.*, 2009). In addition, other metals such as Li, Cs, Sc, Fe and even organic matter content have also been utilized as reference elements (N′guessan *et al.*, 2009). It should be mentioned that although *EF* is not a function of time in its mathematical expression, it is an index reflecting the status and degree of sediment pollution (Feng *et al.*, 2004).

#### *2.3.2 Geoaccumulation index*

The geoaccumulation index ($I_{\mathrm{geo}}$) has been used since the late 1960s, and has been widely employed in European trace metal studies. Originally used for bottom sediments (Müller, 1969), it has been successfully applied to the measurement of soil pollution (Loska and Wiechuła, 2003) and soil dust in city (Ji *et al.*, 2008). The $I_{\mathrm{geo}}$ enables the assessment of pollution by comparing current concentrations with pre-industrial levels. It can be calculated by the following equation:

$$I_{\mathrm{geo}} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{2}$$

where $C_n$ is the measured concentration of the examined metal n in the sediment and $B_n$ is the geochemical background concentration of the metal. The factor 1.5 is used because of possible variations in background values due to lithological variability.

#### *2.3.3 Cluster analysis*

In this study, Hierarchical Cluster Analysis (HCA) was performed on the normalized data set by means of Ward′s method, and the SPSS software package version 13.0 was used for the multivariate statistical analysis, and for descriptive and correlation analyses.

## 3 Results and Analyses

### 3.1 Concentrations of test elements

Metals concentrations and TOC content in the surface sediments are shown in Table 1. The coefficients of variation (CVs) for Cu, Zn, Pb, Cd and Cr were 30.92%, 47.22%, 35.04%, 23.82% and 32.40%, respectively, and that for Al was 6.05%. Heavy metals concentrations showed significant spatial variations in the study area.

The comparative results (Table 2) showed that the concentrations of most heavy metals studied in the Tangxi River estuary were relatively higher than those in the Huanghe (Yellow) River, China, and Chaohu Lake, China, and slightly lower than that in the Changjiang (Yangtze) River Estuary, China, and the Zhujiang (Peral) River Estuary, China, but significantly lower than those in Taihu Lake, China and other larger industrialized/urban ports in the world such as Izmir Harbor, Turkey, and Bremen Harbor, Germany.

### 3.2 Pollution assessment

#### *3.2.1 Assessment based on enrichment factor*

The use of pre-anthropogenic sediment heavy metal

Table 1 Concentrations of metals and TOC ($n$=30)

| | Al (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Cr (mg/kg) | TOC (%) |
|---|---|---|---|---|---|---|---|
| Maximum value | 77678 | 136.45 | 147.38 | 44.79 | 0.496 | 91.24 | 2.23 |
| Minimun value | 61278 | 40.42 | 15.30 | 11.65 | 0.161 | 27.51 | 0.39 |
| Mean value | 67987 | 76.32 | 65.92 | 25.17 | 0.317 | 54.97 | 1.04 |
| Standard deviation | 4113 | 23.60 | 31.13 | 8.82 | 0.075 | 17.81 | 0.40 |

Table 2 Comparison of heavy metal concentrations in study area with those in other regions (mg/kg)

| Region | Cu | Zn | Pb | Cd | Cr | Reference |
|---|---|---|---|---|---|---|
| Tangxi River Estuary, China | 76.32 | 65.92 | 25.17 | 0.317 | 54.97 | This study |
| Zhujiang River Estuary, China | 39.00 | 111.00 | 99.40 | 0.340 | 56.00 | Liu *et al*. (2002) |
| Changjiang River Estuary, China | 30.70 | 94.30 | 27.30 | 0.261 | 78.90 | Zhang *et al*. (2009) |
| Liaodong Bay, China | 17.64 | 105.28 | 23.94 | 1.155 | - | Zhou *et al*. (2004) |
| Huanghe River, China | 21.81 | 57.68 | 21.42 | 0.310 | 51.34 | Yuan *et al*. (2008) |
| Chaohu Lake, China | 17.29 | 114.79 | 15.13 | 0.180 | 37.48 | Cheng *et al*. (2008) |
| Taihu Lake, China | 97.50 | 223.10 | 72.50 | 0.490 | 96.20 | Hua *et al*. (2006) |
| Izmir Harbor, Turkey | 182.00 | 182.00 | 97.00 | 6.200 | 108.00 | Filibeli *et al*. (1995) |
| Bremen Harbor, Germany | 87.00 | 790.00 | 122.00 | 6.000 | 131.00 | Hamer and Karius (2002) |

concentration of the same study area may allow us a better approach of the enrichment levels due to the anthropogenic activity (Ridgway and Shimmield, 2002). In the Tangxi River Basin, however, there were no data about the background concentrations, especially for pre-anthropogenic, of the tested metals. Based on the geographic location, the soil background values of Anhui Province, proposed by China National Environmental Monitoring Center (1990), were taken as the reference values to calculate the enrichment factors. In this study, Al was taken to be the reference element, and the mean concentrations of Al, Cu, Zn, Pb, Cd and Cr were 67 200, 20.4, 62.0, 26.6, 0.097 and 66.5 mg/kg, respectively. According to Equation (1), the *EF* values could be calculated, as shown in Table 3.

The *EF* values were interpreted as the levels of heavy metal pollution that were suggested by Birth (2003) and the assessment criteria were generally based on the *EF* values. Birth suggested that $EF<1$ indicated no enrichment, $1<EF<3$ minor enrichment, $3<EF<5$ moderate enrichment, $5<EF<10$ moderately severe enrichment, $10<EF<25$ severe enrichment, $25<EF<50$ very severe enrichment and $EF>50$ extremely severe enrichment. In order to better evaluate anthropogenic influences on the sediments, Zhang and Liu (2002) recommended using $EF=1.5$ as an assessment criterion, i.e., *EF* values between 0.5 and 1.5 suggested that the trace metals might be entirely from crustal materials or natural weathering process，while *EF* values greater than 1.5 suggested that a significant portion of trace metal was delivered from non-crustal materials or non-natural weathering processes. Han *et al*. (2006) divided the pollution into different categories based on *EF* values. If $EF\leq 2$, it suggested deficiency to minimal metal enrichment, and if a value of *EF* was greater than 2, it suggested various degrees of metal enrichment.

From Table 3, it could be seen that the mean *EF* values of Zn, Pb and Cr were less than 2, showing a minimal anthropogenic impact on the heavy metals concentration levels in the estuary. Therefore, it could be deduced that Zn, Pb and Cr pollution in the studied estuary might entirely come from crustal materials or natural weathering process according to the scale proposed by Han *et al*. (2006). As a result, these three heavy metals pollution should not be currently a major concern.

In comparison, the mean *EF* values of Cu and Cd were almost greater than 2 in the 30 samples, showing a moderate to moderately severe anthropogenic enrichment. Compared with the assessment criteria proposed by Birth (2003), since the mean *EF* values of Cu and Cd in the sediments were larger than 3, the anthropogenic inputs of Cu and Cd were moderately significant. In fact, moderately severe enrichment were revealed in several sampling stations, such as sites Ⅱ-1, Ⅲ-1, Ⅲ-3, Ⅴ-1, Ⅵ-3, Ⅵ-4, Ⅶ-4 and Ⅷ-2 for Cu ($EF>4$) and Ⅰ-4, Ⅱ-1, Ⅲ-1, Ⅳ-1 and Ⅵ-1 for Cd ($EF>4$). In the meanwhile, the *EF* value for Cu even approached 6.86 in site Ⅵ-3. It indicated that the pollution of Cu and Cd really occurred in the Tangxi River estuary. Compared Table 3 with Fig. 1, it could be found that the sampling sites with higher *EF* values of Cu and Cd were concentrated on three sections, namely on the verge of lake waters, in the Tangxi River course at the mouth, and adjacent to the lakeshore. While other sampling sites, especially in the central region of the left estuarine wetland, were not so seriously polluted. It implied that the pollution of Cu and Cd in the estuary might be correlated to the industrial activities and municipal sewage discharges from Hefei City, and the local domestic waste water from Tangxi Village. Pollution of other three heavy metals Pb, Zn and Cr presented the same levels and similar spatial variation. In summary, the mean *EF* values of the five heavy metals decreased in the order of Cu>Cd>Zn>Pb>Cr.

In a comparison of the *EF* values of Cu, Zn, Pb, Cd and Cr in the Tangxi River estuarine sediments with another polluted estuary systems, for example the Zhujiang River Estuary (Liu *et al*., 2002), and the Changjiang River Estuary (Zhang *et al*., 2009), it could be found that, although the values of the *EF* in the Tangxi River estuarine sediments were lower, nevertheless they showed the existence of pollution. Therefore, the Tangxi River estuarine sediments served as a repository for heavy metal accumulation from adjacent urban and industrial areas. Here it should be emphasized that the calculated enrichment factors varied with the choice of reference values. In actual applications, the local background concentrations are always proposed as reference values for investigated heavy metals (Sakan *et al*., 2009; Yu *et al*., 2008). For further investigation, we can determine the background concentrations of the study area by using the modified method proposed by Rubio *et al*. (2000).

#### *3.2.2 Assessment based on geoaccumulation index*

To understand current environmental status and heavy metal pollution extent with respect to natural environment, other approaches should be also applied. A common criterion to evaluate the heavy metal pollution in sediments is the geoaccumulation index. It can be more correctly evaluated if complementary information based on metal baseline values is considered using the geoaccumulation index (Yu *et al*., 2008). In this study, we did not obtain the background concentrations of heavy metals in the sediments. Therefore, $I_{geo}$ was calculated by using the soil element background values of Anhui Province. The results of $I_{geo}$ values are shown in Table 3.

Müller (1981) distinguished seven classes of geoaccumulation index, as shown in Table 4, the highest class (class 6) reflects 64-fold enrichment over the background values (Singh *et al*., 1997). From the classification criteria (Table 4), all the sediments collected from the study area could be approximately categorized as practically unpolluted with Zn, Pb and Cr (mean $I_{geo}<0$ for each heavy metal), and moderately polluted with Cu and Cd ($1<$mean $I_{geo}<2$ for both heavy metals). While, according to these extremes of $I_{geo}$ values (Table 3), the sediments in sampling sites Ⅵ-3, Ⅵ-4 and Ⅶ-4 could be considered as moderately to heavily polluted with Cu ($2<$mean $I_{geo}<3$). Furthermore, above three stations are all located in the outer marginal of the estuarine wetland but close to the lake waters, and site Ⅶ-4 even lies in the course of the Tangxi River at the mouth. Therefore, it could be concluded that the relatively serious pollution in such three sites might be attributed to a considerable industrial wastewater and municipal sewage discharged from Hefei City. On the basis of the mean values of $I_{geo}$, the degree of heavy metal pollution in the surface sediments yielded the following ranking: Cu>Cd>Zn>Pb>Cr. The result was consistent with that based on enrichment factors.

### 3.3 Factor analysis

In order to explore the possible associations between these variables, we performed simple statistical analysis, namely factor analysis on the measured concentrations of heavy metals (Cu, Zn, Pb, Cd and Cr) and Al and TOC. Logarithmic transformation was conducted on Al data before the analysis to ensure a normal distribution (Zhang *et al*., 2009). Varimax rotation was utilized to maximize the sum of the variance of the factor coefficients. The statistical results of factor analysis are list in Table 5.

The pearson′s correlation coefficient matrix among the selected heavy metals, Al and TOC showed that Zn had statistically significant correlation with TOC, and the rest of heavy metals concentrations had a low positive correlation with TOC content. It suggested that except Zn, other heavy metals had not been introduced to the system attached to organic materials. The results endorsed that the organic matter of sediment acted as a carrier for Zn. Moreover, there were slightly significant correlations between Cu and Pb ($r=0.511$), Cu and Cd ($r=0.514$), Pd and Cr($r=0.509$), which indicated that

Table 3 *EF* and $I_{geo}$ values of heavy metals in sediment samples

| Sites | *EF* | | | | | $I_{geo}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cd | Cr | Cu | Zn | Pb | Cd | Cr |
| Ⅰ-1 | 3.28 | 0.81 | 0.81 | 2.53 | 0.91 | 1.09 | –0.93 | –0.93 | 0.71 | –0.76 |
| Ⅰ-2 | 3.69 | 0.81 | 0.76 | 3.05 | 0.40 | 1.34 | –0.85 | –0.94 | 1.06 | –1.86 |
| Ⅰ-3 | 2.81 | 2.23 | 1.00 | 2.90 | 0.70 | 0.92 | 0.59 | –0.58 | 0.96 | –1.09 |
| Ⅰ-4 | 3.82 | 1.13 | 1.15 | 4.01 | 0.91 | 1.28 | –0.48 | –0.45 | 1.35 | –0.79 |
| Ⅱ-1 | 6.19 | 1.33 | 1.08 | 5.45 | 1.09 | 1.95 | –0.27 | –0.57 | 1.77 | –0.55 |
| Ⅱ-2 | 3.39 | 0.93 | 0.69 | 2.92 | 1.20 | 1.35 | –0.51 | –0.94 | 1.13 | –0.14 |
| Ⅱ-3 | 3.00 | 1.22 | 0.46 | 2.00 | 0.56 | 1.10 | –0.20 | –1.60 | 0.52 | –1.33 |
| Ⅱ-4 | 2.11 | 1.52 | 1.02 | 2.40 | 1.04 | 0.40 | –0.08 | –0.65 | 0.59 | –0.62 |
| Ⅲ-1 | 4.07 | 0.89 | 0.99 | 4.46 | 0.53 | 1.54 | –0.66 | –0.50 | 1.67 | –1.39 |
| Ⅲ-2 | 2.45 | 0.59 | 0.47 | 1.62 | 0.48 | 0.75 | –1.31 | –1.64 | 0.14 | –1.59 |
| Ⅲ-3 | 4.26 | 1.04 | 0.91 | 2.76 | 0.90 | 1.39 | –0.64 | –0.84 | 0.76 | –0.86 |
| Ⅲ-4 | 3.86 | 1.00 | 0.82 | 3.36 | 0.64 | 1.46 | –0.48 | –0.77 | 1.26 | –1.12 |
| Ⅳ-1 | 3.88 | 1.08 | 0.75 | 4.16 | 0.85 | 1.34 | –0.50 | –1.04 | 1.43 | –0.85 |
| Ⅳ-2 | 3.08 | 0.43 | 0.57 | 3.17 | 0.48 | 1.02 | –1.83 | –1.42 | 1.05 | –1.65 |
| Ⅳ-3 | 3.20 | 0.26 | 0.46 | 2.71 | 0.69 | 1.03 | –2.60 | –1.78 | 0.79 | –1.19 |
| Ⅳ-4 | 2.84 | 0.68 | 0.96 | 2.01 | 0.64 | 0.91 | –1.15 | –0.65 | 0.41 | –1.24 |
| Ⅴ-1 | 4.01 | 1.43 | 0.97 | 3.24 | 0.65 | 1.35 | –0.14 | –0.70 | 1.04 | –1.29 |
| Ⅴ-2 | 3.97 | 0.92 | 1.12 | 3.32 | 0.79 | 1.52 | –0.59 | –0.31 | 1.26 | –0.81 |
| Ⅴ-3 | 3.07 | 1.09 | 1.19 | 3.36 | 0.78 | 1.07 | –0.42 | –0.30 | 1.20 | –0.90 |
| Ⅴ-4 | 2.78 | 1.28 | 1.67 | 3.23 | 1.39 | 0.76 | –0.36 | 0.02 | 0.97 | –0.24 |
| Ⅵ-1 | 2.75 | 0.46 | 0.71 | 4.17 | 0.97 | 0.81 | –1.77 | –1.14 | 1.40 | –0.70 |
| Ⅵ-2 | 3.09 | 0.85 | 0.75 | 2.77 | 1.38 | 1.03 | –0.82 | –1.00 | 0.88 | –0.13 |
| Ⅵ-3 | 6.86 | 1.27 | 1.57 | 3.28 | 1.23 | 2.16 | –0.27 | 0.03 | 1.09 | –0.32 |
| Ⅵ-4 | 5.23 | 0.88 | 1.46 | 3.51 | 1.11 | 2.01 | –0.55 | 0.17 | 1.44 | –0.22 |
| Ⅶ-1 | 3.48 | 0.56 | 0.97 | 3.05 | 0.54 | 1.30 | –1.34 | –0.54 | 1.11 | –1.38 |
| Ⅶ-2 | 3.02 | 0.46 | 0.50 | 3.76 | 0.68 | 1.05 | –1.66 | –1.53 | 1.36 | –1.10 |
| Ⅶ-3 | 3.02 | 0.72 | 0.84 | 3.19 | 0.49 | 1.07 | –1.01 | –0.78 | 1.15 | –1.56 |
| Ⅶ-4 | 5.99 | 1.47 | 1.15 | 3.63 | 0.73 | 2.08 | 0.06 | –0.30 | 1.36 | –0.96 |
| Ⅷ-1 | 4.42 | 1.97 | 1.56 | 3.41 | 0.94 | 1.58 | 0.41 | 0.07 | 1.20 | –0.66 |
| Ⅷ-2 | 3.03 | 2.19 | 0.73 | 3.43 | 0.88 | 1.13 | 0.66 | –0.92 | 1.31 | –0.65 |
| Minimum | 2.11 | 0.26 | 0.46 | 1.62 | 0.40 | 0.40 | –2.60 | –1.78 | 0.14 | –1.86 |
| Maximum | 6.86 | 2.23 | 1.67 | 5.45 | 1.39 | 2.16 | 0.66 | 0.17 | 1.77 | –0.13 |
| Mean | 3.69 | 1.05 | 0.94 | 3.23 | 0.82 | 1.26 | –0.66 | –0.75 | 1.08 | –0.93 |
| Standard deviation | 1.11 | 0.49 | 0.33 | 0.77 | 0.27 | 0.41 | 0.72 | 0.52 | 0.36 | 0.47 |

Table 4 Müller's classification for geoaccumulation index

| $I_{geo}$ | Class | Pollution status |
|---|---|---|
| >5 | 6 | Extremely polluted |
| 4–5 | 5 | Heavily to extremely polluted |
| 3–4 | 4 | Heavily polluted |
| 2–3 | 3 | Moderately to heavily polluted |
| 1–2 | 2 | Moderately polluted |
| 0–1 | 1 | Unpolluted to moderately polluted |
| <0 | 0 | Unpolluted |

these heavy metals perhaps had the same or similar source input (Windom *et al*., 1991; Lin *et al*., 2002). In most cases, however, there were no significant correlations among the selected heavy metals (Table 5), suggesting that these heavy metals were not associated with each other and their identical behavior during transport in estuarine environment (Yu *et al*., 2008).

Here three factors were obtained by FA, as shown in Table 5. The first three factors with eigenvalue greater than 1.0 accounted for 73.47% of the total variance. As a result, these three factors played a significant role in explaining heavy metal pollution in the study area. Individually, factor 1, which had the highest loadings of Zn and TOC and accounted for 27.22% of variance, could be considered mainly as Zn-TOC factor. It further interpreted that Zn was bound closely with the organic matter (Zhang *et al*., 2009). In other words, factor 1 revealed the concentration of municipal or domestic sewage to the estuarine sediment pollution. Factor 2, which

Table 5 Statistical results of factor analysis (*n*=30)

| Matrix to be factored | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Al | Cu | Zn | Pb | Cd | Cr | TOC |
| Al | 1.000 | | | | | | |
| Cu | 0.072 | 1.000 | | | | | |
| Zn | 0.006 | 0.196 | 1.000 | | | | |
| Pb | –0.103 | 0.511 | 0.445 | 1.000 | | | |
| Cd | –0.069 | 0.514 | 0.115 | 0.289 | 1.000 | | |
| Cr | –0.245 | 0.247 | 0.261 | 0.509 | 0.193 | 1.000 | |
| TOC | 0.222 | 0.267 | 0.654 | 0.311 | 0.278 | 0.086 | 1.000 |

| | Rotated loading matrix (VARIMAX Gamma=1.000) | | | Percent of total variance explained | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| Zn | 0.905 | 0.011 | 0.173 | 27.22% | 25.20% | 21.05% |
| TOC | 0.849 | 0.215 | –0.195 | | | |
| Cu | 0.169 | 0.860 | 0.060 | | | |
| Cd | 0.032 | 0.834 | 0.045 | | | |
| Al | 0.232 | 0.105 | –0.776 | | | |
| Cr | 0.238 | 0.228 | 0.745 | | | |
| Pb | 0.476 | 0.469 | 0.493 | | | |

had the high loadings of Cu and Cd and accounted for 25.20% of variance, could be considered as Cu-Cd factor. It disclosed the contribution of industrial wastewater to the heavy metals pollution in the estuarine sediments. Factor 3, which had superior loading of Cr and moderate loading of Pb, accounted for 21.05% of variance and it might be considered as Cr-Pb factor. From above analysis, it indicated that factor 3 exhibited the contribution of natural background to the originations of heavy metals in sediments.

### 3.4 Cluster analysis on sediment samples

Although performing HCA on variables rather than on cases was preferred in most research studies, HCA was used in this study on sediment samples in order to identify the similarities in heavy metal contents between the analyzed sediment samples. The examined data matrix included the concentrations of heavy metals in the sediments against site number in the study area. The result was presented in a dendrogram, as shown in Fig. 2.

Obviously, a total number of seven groups were distinguished in the dendrogram, performed with the Ward method, which used the squared Euclidean distance as a similarity measure. They were group 1 (including nine sampling sites: Ⅶ-1, Ⅶ-3, Ⅰ-2, Ⅶ–2, Ⅱ-3, Ⅴ-2, Ⅴ-3, Ⅲ-1 and Ⅲ-4), group 2 (including four sites: Ⅳ-2, Ⅳ-3, Ⅲ-2 and Ⅳ-4), group 3 (including two sites: Ⅱ-2 and Ⅵ-2), group 4 (including eight sites: Ⅳ-1, Ⅵ-1, Ⅰ-4, Ⅴ-1, Ⅰ-1, Ⅲ-3, Ⅱ-4 and Ⅴ-4), group 5 (including two sites: Ⅵ-3 and Ⅵ-4), group 6 (including two sites: Ⅰ-3 and Ⅷ-2) and group 7 (including three sites: Ⅶ-4, Ⅷ-2 and Ⅱ-1), respectively.

Compared with the real sites, however, sediments from different sampling sites didn't show apparent trend for grouping sites. It might be attributed to the complicated impacts, including the various originations of heavy metals and the disturbance of human activities. As above explained, Tangxi Village stands on the embankment of Chaohu Lake and is adjacent to the studied estuary. As a result of the lack of drainage systems, great quantities of pollutants (including heavy metals) were usually washed down the bank and transported into the underside wetland by the rain. Except for the runoff pollution, in the field investigations, several vegetable plots and fenced enclosures for poultry scattering were found in the left estuary wetland. In addition, due to the estuary is close to Yicheng Town, for the sake of convenience, a great number of transport ships are preferred to berth in the estuary of the Tangxi River, although there has no formal freight dock. Thus, the human activities inevitably raised the pollution risk and uncertainty of heavy metals in the surface sediments. Consequently, it could be concluded that human activities in the estuarine wetland had made important influence on the pollution and spatial variations of heavy metals in sediments, except for the municipal and industrial wastewater from Hefei City. Perhaps these were the reasons why the relationship between the different sampling sites and the heavy metal concentrations didn't show the apparent regularity.

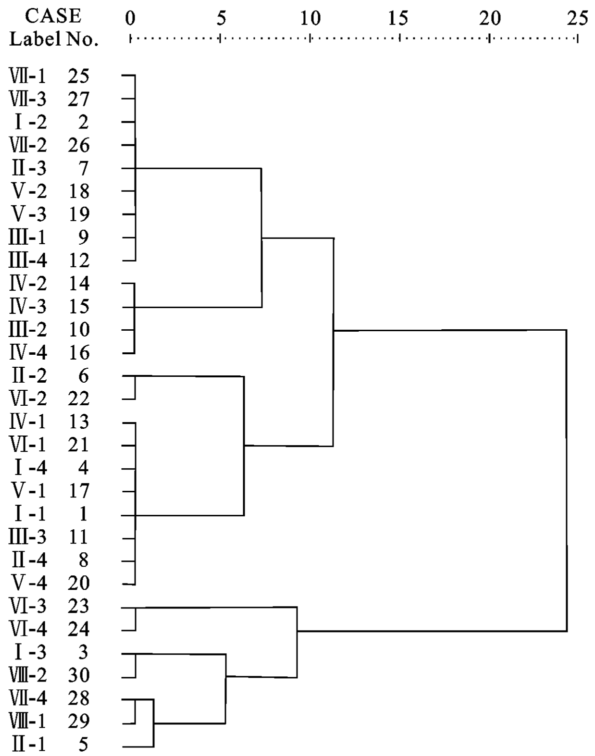


Fig. 2 Dendrogram of the sediment samples

## 4 Conclusions

Heavy metals concentrations showed significant spatial variations in estuarine surface sediments of the Tangxi River in Chaohu Lake Basin. Concentrations of Cu and Cd were above background levels of soils in Anhui Province, and those of Zn, Pb and Cr were generally within the range of background concentrations.

Three groups of pollution factors were presented from FA: Zn-TOC, Cu-Cd and Cr-Pb. Only Zn concentration was closely related to the TOC content. Sediments from different sampling sites didn′t show apparent trend for grouping sites due to the multiple originations of heavy metals and the disturbance of human activities.

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