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Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China

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ABSTRACT

Surface sediment (0–10 cm) samples were collected from 12 typical sites throughout the Dongting Lake. Samples were detected by inductively coupled plasma–mass spectrometry and atomic fluorescence spectrometry for Cr, Cu, Zn, Pb, Cd, As, and Hg, respectively. Based on geostatistics analyses, generally distributions of these heavy metal contents except that of Hg decreased in the order of the South Dongting Lake > the East Dongting Lake > the outlet of Dongting Lake ≈ the West Dongting Lake. Sediment quality guidelines (SQGs) and Hakanson's method were used to determine potential risk of heavy metal contamination. The results indicated that the mean contents of As and Cd exceeded the probable effect level (PEL), and there were 58% for Cd and 50% for As out of all sampling sites exceeding PEL. The calculated mean potential ecological risk degrees were in the descending order of Cd, Hg, As, Pb, Cu, Cr and Zn. Besides, multivariate statistical analyses revealed that Zn, Pb, Cd and As mainly originated from mining wastewater and industrial wastewater which were probably in the close relationship with characteristics about the Yueyang city and the Xiangjiang River. Cr and Cu mainly derived from natural erosion and nonpoint agricultural sources. However, Hg originated from both sources. Cluster analysis indicated that Cluster 1, S5, S6 and S10 included, were probably taken as the higher polluted sites, and Cluster 2, S7, S9 and S11 included, might be explained as the moderate pollution regions.

1. Introduction

Heavy metal contamination in aquatic environment has drawn particular attentions due to their toxicity, persistence and biological accumulation (Jiang et al., 2012; Varol, 2011). Direct hazardous effects or potential risks to human health and ecosystem stability can be caused by heavy metal residues through multi-exposure pathways owing to their transport and transformation among multi-media such as ambient air, soil, surface water, sediments etc. (Cooke et al., 1990; Mackay, 2001; Zeng et al., 2009).

Heavy metals have low solubility and primarily get absorbed and accumulated on bottom sediments. Bottom lake sediments are sensitive indicators for monitoring pollutants as they act as a sink and a carrier for contaminations in aquatic environment (Bai et al., 2011; Caeiro et al., 2005; Suresh et al., 2012). The only measurements of pollutants in water are not conclusive owing to water discharge fluctuations and short resident time. The same remains true for the suspended matter. The study of bottom lake sediments plays an important role for their longer residence time, and the role is called "the record of history" (Mackay, 2001). Spatial distribution and concentrations of heavy metals in the bottom lake sediments are effected by both natural environment factors and anthropogenic factors (Lalah et al., 2008). Natural environment factors are including benthic agitation, flow changes and natural erosion etc. Anthropogenic factors are including sewage discharge, industrial wastewater discharge, agricultural fertilizer leaching etc. For this reason, bottom lake sediments are not only the sink of heavy metals, but also potential secondary sources of heavy metals in aquatic system (Segura et al., 2006; Yu et al., 2008). Therefore, it is necessary to investigate spatial distributions of heavy metals in sediments from the Dongting Lake and assess risks caused by these heavy metals in order to protect corresponding aquatic ecosystem.

The Dongting Lake, which includes three national wetland nature reserves, is one of the most important inland freshwater lakes in China. Some reports have been published on the heavy metal levels in water and water-area variations in this aquatic system (Ding and Li, 2011; Du et al., 2001), the geochemistry of trace and rare earth elements in red soils from the Dongting Lake area (Mao et al., 2009), the effect of the Three Gorges Dam Project on flood control in the Dongting Lake area (Hayashi et al., 2008), and the numerous ecological studies (Fang et al., 2007; Li et al., 2000). In this paper, we report the first comprehensive study on spatial distributions, source identification

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and potential ecological risks of heavy metals in sediments from the Dongting Lake.

The objectives of this study were (i) to determine spatial distributions of heavy metals in surface sediments from the Dongting Lake using contour maps based on geostatistics method of the inverse distance weighted (IDW) interpolation, (ii) to assess potential environmental risk of these heavy metals by comparison with sediment quality guidelines (SQGs), (iii) to further study potential ecological risk of these heavy metals employing Hakanson's method with consideration of the model uncertainty, and (iv) to define the natural and/or anthropogenic sources of these heavy metals using combined multivariate statistical techniques.

2. Materials and methods

2.1. Study area

The Dongting Lake is the second largest freshwater lake in China, with an extensive catchment area from 28°30′N to 29°38′N and 112°18′E to 113°15′E (Ding and Li, 2011) (Fig. 1). The Lake spans the Hunan and the Hubei province, and has the Xiangjiang River, the Zi River, the Yuan River and the Lishui River as its south and west input, the Miluo River and the Xinqiang River as east input, the Songzi estuary, the Taiping estuary and the Ouchi estuary as three bleeder of Yangtze River water flow. Besides, The Dongting Lake is a typical passing reservoir which adjusts both the inflow from and outflow to the mid-reach of the Yangtze River. It drains a catchment area of 2,820 km^2. The maximum depth of the Dongting Lake is 30.8 m and the average depth is 6–7 m. Because of its key geographic location, the Dongting Lake, which includes three national wetland nature reserves namely the East Dongting wetland, the South Dongting wetland and the West Dongting wetland, plays a key role not only in storing floodwater, agricultural irrigation, water supply and climatic regulation, but also in producing a good deal of marketable grain, freshwater fish and so on (Du et al., 2001; Zhu et al., 2012). Therefore, the environmental quality in aquatic system of the Dongting Lake has direct and significant effects on drinking water safety of the peripheral cities, stability of the wetland ecosystem, biodiversity of the wetlands and so on.

2.2. Samples collection and preparation

Surface sediment samples were collected from 12 typical locations (Fig. 1), which were chosen referring to the current national hydrologic stations (Gao et al., 2008; Hayashi et al., 2008; Yao et al., 2006; Zhu et al., 2008). The 12 typical locations were Nanzui (S1), Muping Lake (S2), Xiaohezui (S3), Wanzi Lake (S4), Zhangshugang (S5), Yugongmiao (S6), Hengling Lake (S7), Lujiao (S8), East Dongting Lake (S9), Yueyang Tower (S10), Jingjiangkou (S11) and Chenglingji (S12), respectively. The sampling locations (Latitudinal and Longitudinal position) were recorded by hand-held Global Positioning System (GPS) unit.

The upper 0–10 cm depths of sediments were randomly collected using a Van Veen grab in 50 × 50 m area with the center of each sampling location (Fig. 1) and the numbers of collected samples in each area were 5. Afterwards, total 60 samples were put into pre-cleaned aluminum box using stainless steel spoon and freeze drying prior to analyses.

2.3. Analysis and quality control

Sediment samples were firstly dried to a quality of basic stability by a freeze drying machine and then flipped, crushed, and grinded successively. Then all samples were sieved through a 100 mesh nylon sieve to remove stones, dead organisms and coarse debris, and then processed with another 200 mesh nylon sieve. Afterwards, all samples were marked by their corresponding serial numbers. 0.1000 g preprocessed samples were accurately taken by the electronic balance (Sartorius TE124S, Germany), and then moved into different airtight Teflon vessels. Samples were handled under the reference preprocessed steps according to DZ/T0223-2001 (China). The total heavy metal contents of Cr, Cu, Zn, Pb, Cd and As were all detected by inductively coupled plasma-mass spectrometry (ICP–MAS). Besides, atomic fluorescence spectrometry (AFS) was used to analyze the concentrations of Hg at 253.65 nm. Quality assurance and quality control were assessed using duplicates, method blanks, and standard reference materials (GSD-9 and GSD-4, GBW07345), with each batch of samples. The analysis results were reliable when repeat sample analysis error was below 5%, and the analytical precision for replicate samples was within ±10%.

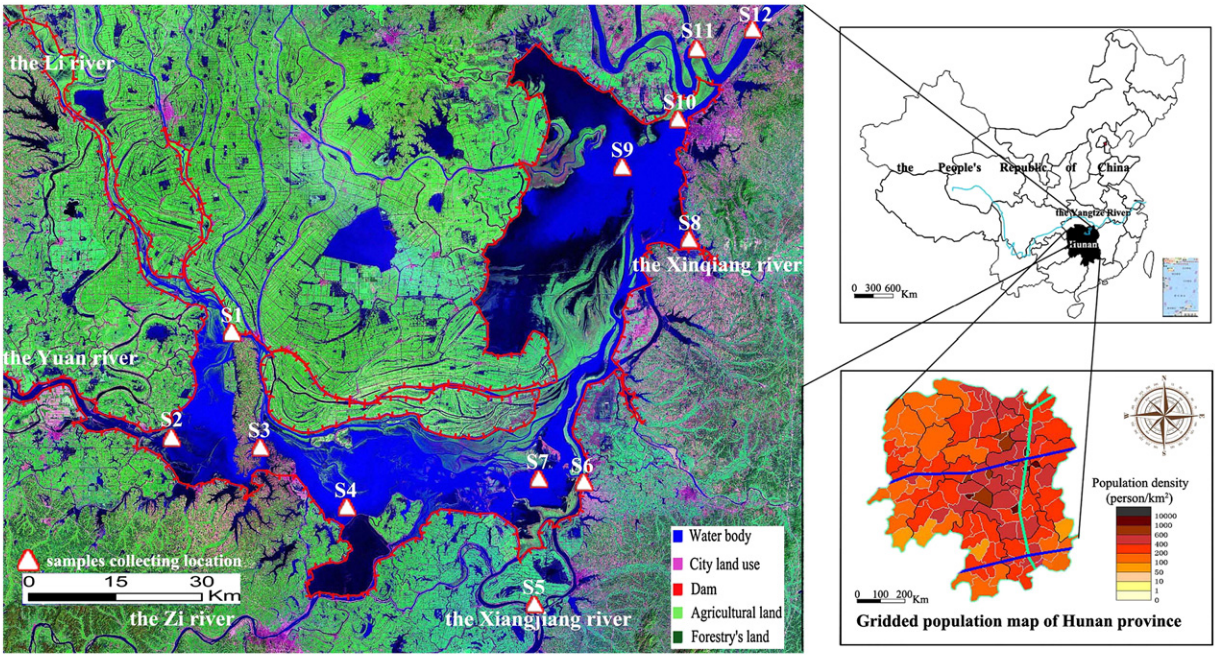

Fig. 1. Map of sediment samples collecting locations along the Dongting Lake.

The results met the accuracy demand of the Chinese Technical Specification for Soil Environmental Monitoring HJ/T 166-2004.

2.4. Assessment method of sediment pollution

2.4.1. Sediment quality guidelines (SQGs)

To screen sediment contamination degree caused by heavy metals, sediment quality assessment guidelines (SQGs) were introduced. SQGs consist of a threshold effect level (TEL) below which adverse biological effects are not expected to occur and a probable effect level (PEL) above which adverse biological effects are expected to occur more often than not. SQGs could evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and were designed to assist in the interpretation of sediment quality (CCME, 1995; Smith et al., 1996). Such SQGs have been successfully used in numerous applications, including designing monitoring plans, interpreting historical data, conducting remedial investigations, and developing sediment quality remediation objectives (Farkas et al., 2007; Zheng et al., 2008).

2.4.2. Potential ecological risk index (PER)

SQGs were developed based on a biological effects database for sediments (BEDS) in which not only data from equilibrium-partitioning models, laboratory spiked-sediment toxicity tests, and field (or co-occurrence) studies that investigated the toxicity and/or benthic community composition in freshwater sediments, but also more than 800 screened publications were considered for inclusion in the database (CCME, 1995; Smith et al., 1996). Model uncertainty, which is mainly caused by model simplified error and model modeling relation error etc., was taken into consideration (Li et al., 2012). To further screen sediment contamination degree caused by heavy metals, potential ecological risk index (PER), which was developed based on sedimentary theory, was introduced to assess the ecological risk degree of heavy metals in present sediments. Potential ecological risk index was originally proposed by Hakanson (1980) and widely used (W.H. Guo et al., 2010; Saeedi et al., 2012). The value of RI can be calculated by the following formulas:

$$C_f^i = C_D^i / C_B^i \tag{1}$$

$$E_r^i = T_r^i \times C_f^i \tag{2}$$

$$RI = \sum_{i=1}^{m} E_r^i \tag{3}$$

where RI is the sum of the potential risk of individual heavy metal, E_r^i is the potential risk of individual heavy metal, T_r^i is the toxic-response factor for a given heavy metal, C_f^i is the contamination factor, C_D^i is the present concentration of heavy metals in sediments, and C_B^i is the pre-industrial record of heavy metal concentration in sediments.

Based on the Hakanson's approach, the toxic-response factors for Cr, Cu, Zn, Pb, Cd, Hg, and As are 2, 5, 1, 5, 30, 40, and 10, respectively. In this study area, the pre-industrial concentration records for Cr, Cu, Zn, Pb, Cd, Hg, and As were replaced by their corresponding background values showed in Table 2 (Li et al., 1986). Hakanson defined five categories of E_r^i, and four categories of RI, as shown in Table 1.

2.5. Multivariate and geostatistical methods

Multivariate analyses of heavy metal contents in sediments were performed using Pearson's correlation analysis, Factor analysis (FA) and Hierarchical agglomerative cluster analysis by the software package SPSS version 16.0. The Pearson's correlation analysis is a method measuring the correlativity among heavy metals. FA is a kind of multivariate statistical analysis method and is utilized to reduce some complex variables to a few latent factors for analyzing relationships among the observed variables. In environmental science, FA and derivation methods are widely used to identify pollutant sources of heavy metals in sediments with distinguishing natural versus anthropogenic contributions (Chen et al., 2012; Lu et al., 2010; Yang et al., 2011). Hierarchical agglomerative cluster analysis (CA) classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables (Chen et al., 2012; Lu et al., 2010). In order to explore interrelationship and correlation of analysis data, CA is usually coupled with FA to check analysis results and to group individual parameters and variables. Dendrogram could vividly reflect the proximity and the interrelationship among the heavy metals.

Table 1
Indices and corresponding degrees of potential ecological risk (Hakanson, 1980).

E_r^i value	Grades of ecological risk of single metal	RI value	Grades of potential ecological risk of the environmental
$E_r^i < 40$	Low risk	$RI < 150$	Low risk
$40 \le E_r^i < 80$	Moderate risk	$150 \le RI < 300$	Moderate risk
$80 \le E_r^i < 160$	Considerable risk	$300 \le RI < 600$	Considerable risk
$160 \le E_r^i < 320$	High risk	$RI \ge 600$	Very high risk
$E_r^i \ge 320$	Very high risk		

Geographic information system (GIS) was used to analyze the spatial distribution of heavy metals in sediments from the Dongting Lake. The inverse distance weighted (IDW) method was applied to map the spatial distribution of pollutants based on the ArcGIS 9.3 software. IDW employs a specific number of nearest points that are then weighted according to their distance from the point being interpolated. In this study, the power of 2 and the number of neighboring samples of 12 were chosen to clearly show both spatial variation and spatial patterns of the pollutants.

3. Results and discussion

3.1. Mean heavy metal concentrations in surface sediments

The basic statistics for all heavy metal parameters measured during the sampling period at 12 typical sites as well as background values of the Dongting Lake (Li et al., 1986), and corresponding values based on SQGs (MacDonald et al., 2000; Smith et al., 1996) were summarized in Table 2. According to the background values of heavy metals in the Dongting Lake, it indicated that heavy metal concentrations in surface sediments of this study were all higher than their corresponding background values (Table 2). This was especially true for the cases of Cd and Hg, which were 14.1 and 3.3 times of their background values, respectively. Compared with the corresponding background values in sediments from the Dongting Lake, the degree of enrichment about studied 7 heavy metals decreased in the order of Cd > Hg > Pb > Cu > As > Zn > Cr.

Mean concentrations of 6 heavy metals (Cr, Cu, Zn, Pb, Cd, and As) were higher than their corresponding TEL except that of Hg. Further, mean concentrations of As and Cd exceeded the PEL at 1.75 and 1.32 times, respectively. Mean concentrations of Cr, Cu, Zn and Pb were between the corresponding TEL and PEL. Thus the adverse biological effects were probable due to the concentrations of As and Cd.

Comparing the sediment heavy metal data of the Dongting Lake with the published data of other freshwater lakes at home and abroad (Table 3), it revealed that the sediment heavy metals from the Dongting Lake were in relatively severe pollution degree, especially Cd and As. Generally concentrations of heavy metals in sediments from the freshwater lakes in the developing countries (including India, China and Tanzania) were in higher pollution degree than that in the developed countries (including USA and Greece). Obviously, the concentrations of Zn, Cd, Hg, and As in sediment from Dongting Lake were higher than that of Poyang Lake and Taihu Lake which are as top 5 freshwater

Table 2
Summary statistics of heavy metal contents in surface sediments from the Dongting Lake and guideline values of freshwater sediment quality mg/kg.

	Cr	Cu	Zn	Pb	Cd	Hg	As
Minimum	67.13	29	104	9.89	0.329	0.016	7.44
Maximum	110	79	329	180	12.5	0.461	104.9
Average	88.29	47.48	185.25	60.99	4.65	0.157	29.71
S.D.[a]	12.88	15.81	78.84	50.83	4.25	0.145	27.70
Background[b]	44	20.2	83.3	23.3	0.33	0.047	12.9
TEL[c]	37.3	35.7	123.1	35	0.596	0.174	5.9
PEL[d]	90	196.6	314.8	91.3	3.53	0.486	17

[a] S.D.: standard deviation.

[b] Background: the back ground values of heavy metals in sediments from the Dongting Lake.

[c] TEL: threshold effect level, dry weight (Smith et al., 1996).

[d] PEL: probable effect level, dry weight (Smith et al., 1996).

lakes as the Dongting Lake in China. Detailed comparisons were clearly presented in Tables 2 and 3.

3.2. Spatial distributions of heavy metals in surface sediments from the Dongting Lake

Spatial distribution patterns of Cr, Cu, Zn, Pb, Cd, Hg, and As in surface sediments from the Dongting Lake were showed in Fig. 2(A) to (G) using contour maps based on IDW method. These maps illustrated the distinct zones of lower or higher concentrations in the Dongting Lake. In order to characterize the spatial distributions of heavy metals in sediments effectively, the Dongting Lake was divided into the East Dongting Lake (including S8, S9 and S10), the South Dongting Lake (including S5, S6 and S7), the West Dongting Lake (including S1, S2, S3 and S4) and the outlet of the Dongting Lake (S11 and S12).

According to Fig. 2(a), average concentrations of Cr from each sampling site decreased in the order of S7 > S11 > S10 > S3 > S4 > S6 > S5 > S2 > S1 > S12 > S9 > S8. Based on SQGs, there were 23% out of all sampling sites exceeding PEL. Spatial enrichment degree of Cr in sediments was the lowest among all 7 heavy metals relatively. The upper South Dongting Lake and the outlet of the Dongting Lake were the parts of higher enrichment.

Cu and Zn are two micronutrients for aquatic life in all natural water and sediments. Although both of them are minor nutrients at low concentrations, they can become toxic to aquatic life at higher concentrations than the threshold required contents (Hall et al., 1997). Based on Fig. 2(B) and (C), there were a similar spatial distribution between them in the East Dongting Lake, the South Dongting Lake and the outlet of the Dongting Lake. However, there was a relatively higher enrichment for Cu in the West Dongting Lake which was different from Zn. Average concentrations of each sampling site of Cu concentration decreased in the order of S11 > S1 > S5 > S10 > S7 > S9 > S6 > S2 > S4 > S3 > S12 > S8 and there were 83% out of all sampling sites exceeding TEL with none exceeding PEL. By comparison, average concentrations of each sampling site of Zn concentration decreased in the order of S5 > S10 > S6 > S7 > S11 > S9 > S2 > S4 > S3 > S1 > S8 > S12 and there were 75% out of all sampling sites exceeding TEL with only S5 exceeding PEL.

As and Cd are proved carcinogen to human being and have potential damage to the ecological communities from environmental protection agency of USA (USEPA). Sadip et al. (2003) reported that low concentrations of Pb still might pose a threat to life in a marine environment in comparison with other heavy metals. Spatial distribution of As was similar with that of Cd, Pb and Zn, namely their concentrations decreased in the order of the South Dongting Lake > the East Dongting Lake > the outlet of the Dongting Lake ≈ the West Dongting Lake. Average concentrations of each sampling site for As, Cd, and Pb were in the descending order of S5 > S10 > S9 > S6 > S7 > S8 > S4 > S3 > S1 > S2 > S11 > S12, S5 > S10 > S7 > S9 > S6 > S2 > S3 > S4 > S8 > S11 > S12 > S1 and S5 > S10 > S11 > S8 > S6 > S9 > S7 > S12 > S1 > S4 > S2 > S3, respectively. Moreover, there were 58% and 50% out of all sampling sites exceeding PEL for As and Cd, respectively. And for Pb, there were 67% out of all sampling sites exceeding TEL with S5 and S10 exceeding PEL. The similar spatial distribution pattern of the concerned heavy metals in sediments from the Dongting Lake might be closely related to the similar geological enrichment characteristics, which also showed that they might come from the same input sources.

Hg is violent in toxicity and has a very low concentration in natural water which is beneath 0.1 μg/L (Acquavita et al., 2012). Spatial distribution of Hg, compared with spatial distributions of other heavy metals, was in special distribution (Fig. 2(F)). Spatial distribution of Hg was in a general distribution pattern of the upper South Dongting Lake > the West Dongting Lake > the outlet of the Dongting Lake > the East Dongting Lake. Besides, average concentrations of each sampling site for Hg decreased in the order of S6 > S2 > S3 > S7 > S5 > S4 > S10 > S9 > S1 > S11 > S8 > S12, and there were 25% out of all sampling sites exceeding TEL with none exceeding PEL.

3.3. Potential ecological risk assessment of heavy metals and risk mapping

Potential ecological risk assessment was applied to detect the potential ecological risk level of heavy metals in sediments from the Dongting Lake. Calculated single element pollution factor, potential

Table 3
Summaries of measured elements in freshwater lake sediments from different countries at home and abroad.

Name of the lakes	Metal concentration (mg/kg)						
	Cr	Cu	Zn	Pb	Cd	Hg	As
Poyang Lake, China[a]	70.77	27.711	65.778	48.67	0.56	0.08	10.67
Taihu Lake, China[b]	41.5	14.03–39.22	32.5–111.06	29.2–74.48	0.2–2.88	NA	5.94
Yilong Lake, China[c]	39.65–125.49	15.37–66.95	29.6–121.68	30.71–88.96	0.32–1.62	NA	7.77–25.93
Western Lake Erie basin, USA[d]	64.9	34.3	162.6	98.7	3.6	NA	13.2
Veeranam Lake, India[e]	40–150	65–125	69–599	20–41	0.2–3.9	NA	NA
Doirani Lake, Greece[f]	1–17	1–13	6–66	1–6	0.1–0.4	NA	NA
Lake St. Clair, USA[g]	3.7–20	2.2–25.8	8–84.7	1–29.1	NA	NA	5–14.5
Lake Victoria, Tanzania[h]	11–12.4	21.6–24.0	36.4–38.2	29.6–31.2	2.5–3.0	0.1	NA

NA: not available.

[a] Yuan et al., 2011.

[b] Jiang et al., 2012; Bing et al., 2011.

[c] Bai et al., 2011.

[d] Opfer et al., 2011.

[e] Lalah et al., 2008.

[f] Anthemidis et al., 2002.

[g] Gewurtz et al., 2007.

[h] Kishe and Machiwa, 2003.

ecological risk of individual element and comprehensive potential ecological index were presented in Table 4 and Fig. 3, respectively. The calculated mean potential ecological risk degrees decreased in the order of Cd > Hg > As > Pb > Cu > Cr > Zn. The corresponding potential ecological risk degrees of Cd and Hg were at very high risk and considerable risk, respectively. And that of other 5 heavy metals were at low risk level (Table 4). As a consequence, Cd and Hg in sediments might lead to higher potential risk than other heavy metals.

From the viewpoint of pollution level in every sampling site, the sampling sites at the highest risk degree caused by each heavy metal were S5 for Cd, S6 for Hg, S7 for Cr, S11 for Cu, S5 for Zn, S5 for Pb and S5 for As, respectively (Table 4). Detailed comparisons were clearly presented in Table 4.

The calculated RI values of every sampling site were in the descending order of S5, S10, S7, S6, S2, S9, S3, S4, S8, S11, S1 and S12 (Fig. 3). The calculated RI values of S1 and S12 were in low risk level, and the calculated RI values of S8 and S11 were in moderate risk level. Further, the calculated RI values of S3 and S4 were in considerable risk level, and the calculated RI values of S2, S5, S6, S7, S9 and S10 were in very high risk level. From viewpoint of the whole Dongting Lake, the mean RI (611.24) belonged to very high risk level with higher contributions to RI of Cd, Hg and As, especially RI of Cd. Compared with the assessment results of SQGs, there was similar assessment conclusions for Cd and As. However, these different conclusions on the contamination level of Hg proved that it was essential to synthesize different assessing methods to reduce the uncertainty among these assessing models and to supply more comprehensive information for policy-makers.

3.4. Sources identification based on multivariate statistical analyses

3.4.1. Correlation matrix

The correlation among heavy metals can provide some information on the sources and pathways of heavy metals. The Pearson's correlation analysis needs all analysis variations according with the normal distribution. Therefore, test of normality was done, and results showed that Cr, Cu, Zn, Pb and Cd were above 0.005 (Sig.) by Shapiro–Wilk test. However, Hg (Sig. = 0.003) and As (Sig. = 0.001) were below the threshold and needed data conversion. In this study, the Ln function was used and the transformed results were in accordance with the normal distribution. Then, Pearson's correlation coefficients of heavy metals in sediments from the Dongting Lake were done and the results were showed in Table 5.

The elements pairs Cr – Cu and Cu – Pb had a significantly positive correlation at $P < 0.05$ significance level (Table 5). The element pairs Zn – Pb, Zn – Cd, Zn – As, Pb – Cd, Pb – As and Cd – As had a significantly positive correlation at $P < 0.01$ significance level (Table 5). Based on the researches of published studies (Lu et al., 2010; Saeedi et al., 2012), if the correlation coefficient between the heavy metal factors is positive, these factors may have common source, mutual dependence and identical behavior during the transport.

3.4.2. Factor analysis (FA)

Firstly, to examine the suitability of the data for FA, Kaiser–Meyer–Olkin (KMO) and Bartlett's Sphericity tests were performed. KMO is a measure of sampling adequacy that indicates the proportion of variance

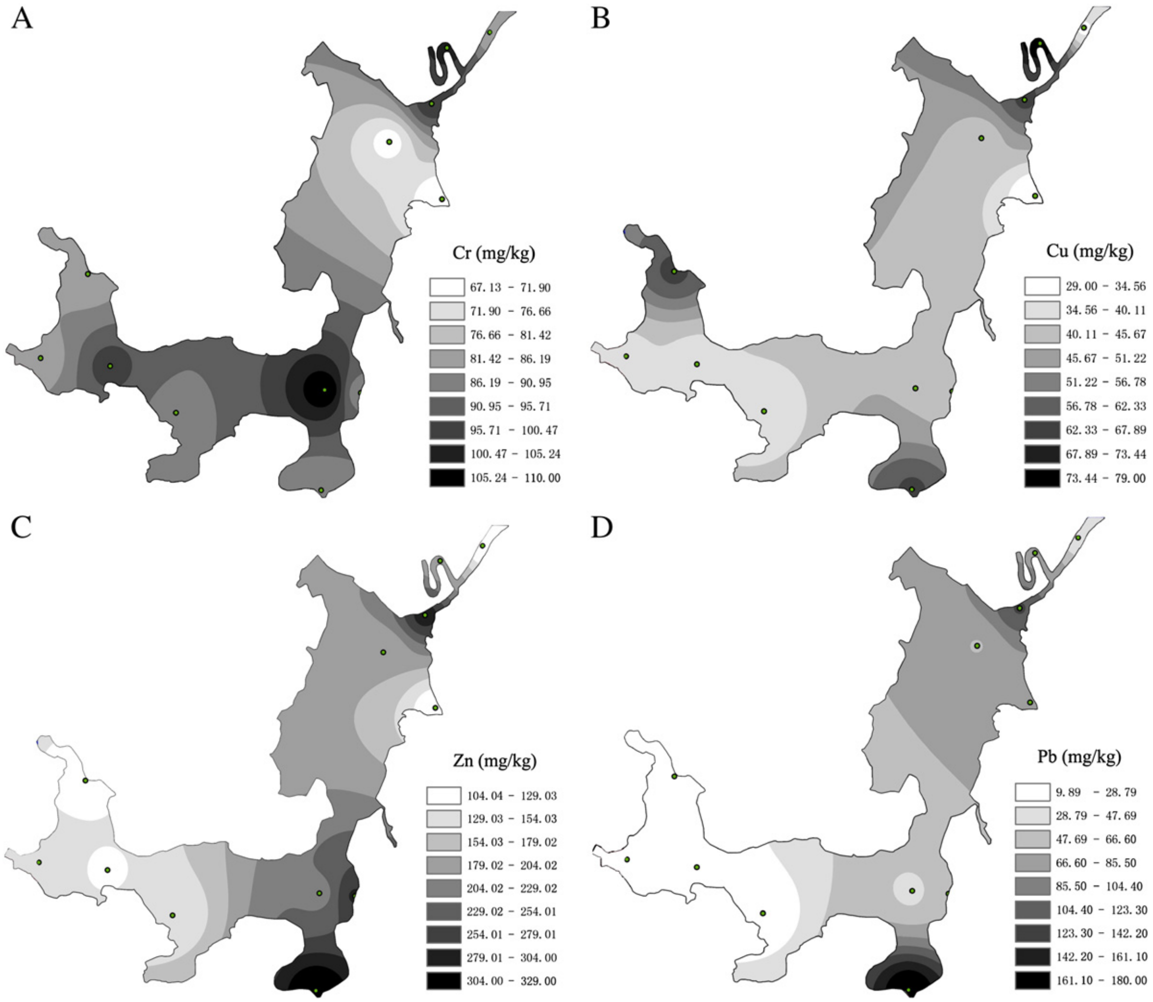

Fig. 2. Spatial distributions of Cr (A), Cu (B), Zn (C), Pb (D), Cd (E), Hg (F) and As (G) in surface sediments from the Dongting Lake.

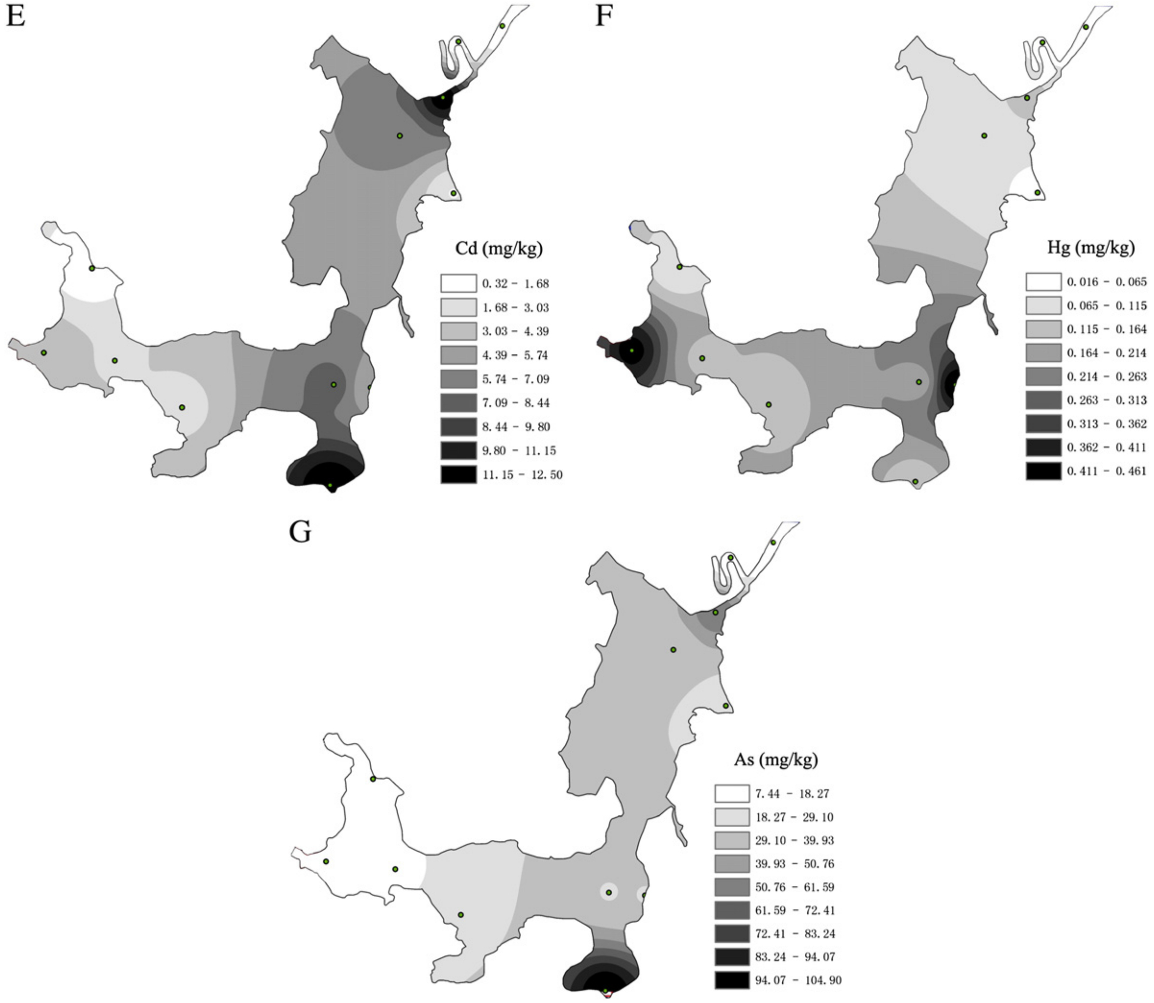

Fig. 2 (*continued*).

which is common variance, i.e., which might be caused by underlying factors. The KMO test value (0.631) showed that the heavy metal concentration data in sediments from the Dongting Lake are suitable for FA (Chen et al., 2012; Varol and Şen, 2009). Similarly, Bartlett's test of sphericity indicates whether correlation matrix is an identity matrix, which would indicate that variables are unrelated. The significance level which is 0 in this study (less than 0.05) indicates that there are significant relationships among variables. FA was applied to the data sets (7 variables) separately for the 12 typical sampling sites to identify sources of heavy metals in sediments from the Dongting Lake by employing varimax rotation with Kaiser Normalization. By extracting the eigenvalues (>1) and eigenvectors from the correlation matrix,

Table 4
Basic statistic of potential ecological risk assessment (PER) of heavy metals in surface sediments from the Dongting Lake.

Sampling sites	E_r							RI
	Cr	Cu	Zn	Pb	Cd	Hg	As	
S1	3.76	15.79	1.37	5.51	29.91	55.32	11.94	123.60
S2	3.77	9.36	1.72	2.74	368.18	368.51	10.00	764.28
S3	4.45	8.84	1.49	2.12	264.45	127.66	12.58	421.59
S4	4.07	8.86	1.58	2.98	226.36	119.15	14.81	377.81
S5	3.96	15.69	3.95	38.63	1136.36	122.55	81.32	1402.46
S6	3.97	10.20	3.39	14.18	396.36	392.34	22.25	842.69
S7	5.00	11.26	2.63	8.93	709.09	151.49	22.17	910.57
S8	3.05	7.18	1.32	15.19	148.18	39.15	16.74	230.81
S9	3.16	10.42	2.16	14.14	582.73	61.28	25.43	699.32
S10	4.50	15.67	3.51	26.82	1100	115.74	47.13	1313.37
S11	4.73	19.55	2.32	18.24	80.82	40.85	6.28	172.79
S12	3.73	8.22	1.25	7.55	35.36	13.62	5.77	75.50
Average	4.01	11.75	2.22	13.09	423.15	133.97	23.03	611.24
Maximum	5.00	19.55	3.95	38.63	1136.36	392.34	81.32	1402.46
Minimum	3.05	7.18	1.25	2.12	29.91	13.62	5.77	75.5

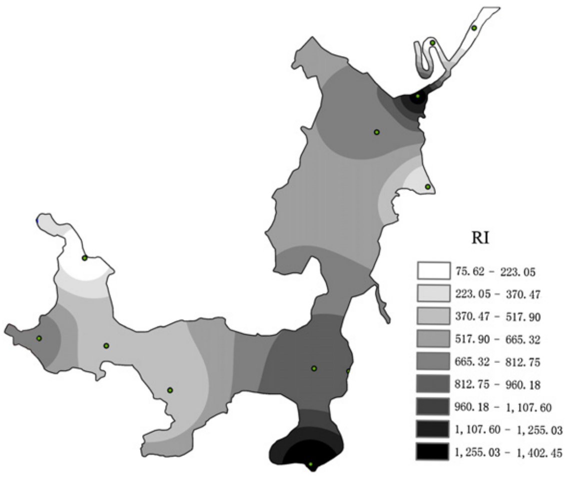

Fig. 3. Spatial risk mapping based on RI of heavy metals in surface sediments from the Dongting Lake.

Table 5
Pearson correlation matrix for heavy metal concentration in surface sediments from the Dongting Lake.

	Cr	Cu	Zn	Pb	Cd	Hg	As
Cr	1.000						
Cu	0.562*	1.000					
Zn	0.392	0.517	1.000				
Pb	0.137	0.585*	0.813**	1.000			
Cd	0.328	0.360	0.844**	0.741**	1.000		
Hg	0.219	−0.073	0.445	−0.029	0.388	1.000	
As	0.189	0.335	0.778**	0.744**	0.905**	0.352	1.000

* Correlation is significant at $P < 0.05$ (two-tailed).
** Correlation is significant at $P < 0.01$ (two-tailed).

the number of significant factors and the percent of variance explained by each of them were calculated.

Total variance of heavy metals contents and rotation component matrix for heavy metal contents were showed in Table 6. The results indicated that three components were extracted which explain 90.8% of total variance. First component explained 50.1% of the total variance loaded heavily on Zn, Pb, Cd and As. Factor 2, dominated by Cr and Cu, accounted for 23.2% of the total variance. Factor 3 was dominated accounting by Hg for 17.5% of total variance. The results of FA were well matched with the results of Pearson correlation analysis.

3.4.3. Cluster analysis

Data of the variables were standardized and Euclidean distance for similarities among variables were calculated. Then hierarchical clustering was performed on standardized data applying Ward's method. Firstly, CA was applied to group the analyzed parameters (data of the heavy metal concentration) (Fig. 4). Fig. 4 showed three statistically significant clusters: (1) Cd–As–Hg, which were identified in the higher contamination level, (2) Cu–Pb–Cr, which were identified in the moderate contamination level, and (3) Zn, which was in the relatively low pollution degree.

Similarly, CA calculated by sampling sites was also organized and the dendrogram obtained was showed to identify the spatially geochemical groups (Fig. 5). Fig. 5 showed three statistically significant clusters: (1) S5, S6 and S10, which belonged to the Cluster 1, were probably taken as the higher polluted sites, (2) S7, S9 and S11, which belonged to the Cluster 2, might be explained as the moderate pollution regions, and (3) S1, S2, S3, S4, S8, S12, and S13, which belonged to the Cluster 3, were the sites at relatively low pollution level.

3.4.4. Heavy metals sources identification

Three main sources of the studied heavy metals in sediments from the Dongting Lake could be identified according to the spatial distribution maps, correlation coefficient analysis, FA and CA, i.e. (1) Zn, Pb, Cd and As mainly originated from discharging excessive pollutants from mining wastewater and industrial wastewater. (2) Cr and Cu mainly derived from natural sources and nonpoint agricultural sources. (3) Hg mainly originated from mining wastewater, industrial wastewater and natural sources.

Table 6
Rotation component matrix for heavy metals in surface sediments from the Dongting Lake.

Elements	Component		
	PC1	PC2	PC3
Cr	0.063	**0.928**	0.185
Cu	0.395	**0.771**	−0.300
Zn	**0.866**	0.329	0.279
Pb	**0.924**	0.160	−0.231
Cd	**0.893**	0.184	0.194
Hg	0.075	0.012	**0.965**
As	**0.969**	0.055	−0.019
Eigenvalue	3.507	1.627	1.224
% of variance explained	50.1	23.2	17.5
% of cumulative	50.1	73.3	90.8

Extraction method: principle component analysis; rotation method: varimax analysis. Bold data are the main contribution elements to component.

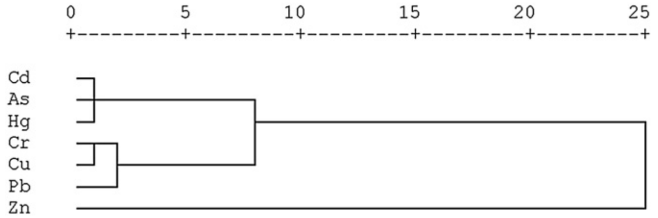

Fig. 4. Dendrogram of the elemental concentrations in surface sediments from the Dongting Lake.

One group of elements, including Zn, Pb, Cd and As, had a similar spatial distribution with the higher polluted sites mainly located at the South Dongting Lake and part of the East Dongting Lake near the Yueyang city (Fig. 2). In this studied region, the area with city land use was intensively distributed among the east bank of the Dongting Lake, and the most of these city land belonged to the Yueyang city (Fig. 1). Agriculture land use was dominant in other bank (Fig. 1). Further, the inputs of these heavy metals could be interpreted that they were imported mainly by Xiangjiang River and the discharge of Yueyang city. According to the published researches (Yao et al., 2006; Zhu et al., 2008, 2012), Xiangjiang River has been the most polluted river by heavy metals in China and heavy metals mainly come from industrial manufacturing and refined mineral mining (Chai et al., 2010; Z.H. Guo et al., 2010; Peng et al., 2011). The Zhuzhou smelting group, the Shuikoushan group, the salt plant chemical group, the Hunan Hayley chemical group, the Xiangtan electrochemical group, the Hualing steel enterprise and lots of small smelting workshops, chemical enterprises and printworks locate along the Xiangjiang River. According to the environmental protection bureau of the Hunan province, the emission load of Hg, Pb, Cd and As from Xiangjiang River was accounted for 54.5%, 37.0%, 6.0% and 14.1% in the national emissions of year 2007, respectively. Besides, the Yueyang city, with a population of 5.43 million, is one of the most important mining cities in the Hunan province. The Yueyang city has rich mineral resources with more than 200 mineral mines including 11 large scale deposits, 16 medium scale deposits and 27 small scale deposits. And there are distributed a batch of large enterprises based on outlet of the Dongting harbor industrial zone around 30 km along the Yangtze river, including the Changling refining corporation, the Baling petrochemical corporation, and the Huaneng power plant of the Yueyang paper factory. According to the general mineral resource planning of the Yueyang city (2008–2015), the mining industry (including corresponding industries of mining, beneficiation, smelt and machining) of the Yueyang city made a contribution of the gross output value 74.67 billion Chinese RMB which accounted for 58.87% of the gross industrial output value in the city in 2007. Further, total annual

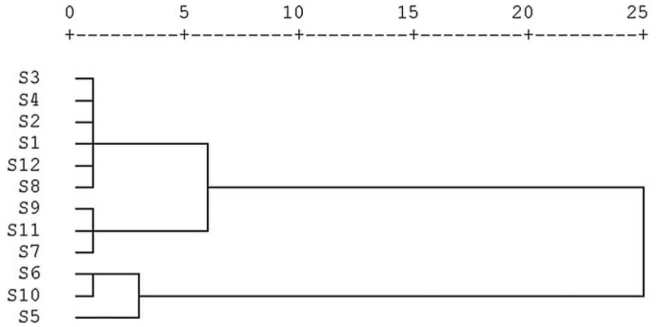

Fig. 5. Dendrogram of the sampling sites from the Dongting Lake.

produced mining waste residue of 10.09 million tons with the 58.93% multipurpose utilization, and total annual produced mining effluent emissions of 2.91 million tons with the 36.24% multipurpose utilization have led to different extent environmental pollutions to the corresponding ecosystem, geomorphologic landscape, and soil, water environment, especially the water environment. Besides, part of the East Dongting Lake near Yueyang city was in a higher polluted degree due to not only wastewater discharge from the mining industries, the papermaking plant, chemical enterprise and petrochemical company but also the coming water of the Yangtze River enhancing the suspended particles of flocculation and precipitation. However, different from published researches (Yao et al., 2006; Zhu et al., 2008), the Zhangshugang (S5) and the Yueyang Tower (S10) instead of the Chenglingji (S12) were the most polluted sites in this study.

A second group of elements consisting of Cr and Cu mainly originated both from natural erosion and nonpoint agricultural pollution due to Cr and Cu were clearly separated from other heavy metals in Pearson correlation analysis and FA (Tables 5 and 6). And among heavy metals studied, Cr and Cu shared relatively lower pollution level and their spatial contents both own low spatial variation which were probably in relationship with the spatial distribution characteristics of agriculture land (Figs. 1 and 2). Further, according to literatures (Zhu and Wang, 2012) and the Hunan statistical yearbook 2007, applying all kinds of pesticide content were above 6000 tons merely in the South Dongting Lake during annual April to October in order to prevent agricultural hazards to reed, rice and vegetables. Further, most of the pesticide chemical composition contains the heavy metals such as Cr, Cu and Hg.

A third group of elements consisted of Hg might have a mixed source of natural source and sources of mining wastewater, industrial wastewater. From Fig. 2, the spatial distribution of Hg was different from that of other heavy metals. The spatial distribution of Hg showed its higher polluted sites primarily located at the part of the West Dongting Lake where the Yuan River was as the main input and the upper South Dongting Lake where the lower course of Xiangjiang River was as the main input (Fig. 2(F)). The Yuan River spans the Guizhou and the Hunan province with a drainage area of 89163 km^2. Further, Hg resource reserves and product production of the Guizhou province rank in the first all over the Asia and the third all over the world, and the Guizhou province is known as the Hg is in China. Therefore, Hg partly had same sources with Zn, Pb, Cd and As and another source from the natural factor mainly because of the higher background level of Hg in the Yuan River (Yao et al., 2006). As the interaction of Li River and Yuan River, it also enhanced the suspended particles of flocculation and precipitation of heavy metals in sediments from the lake delta which made the delta trailing edge own higher contents of heavy metals than delta front edge.

4. Conclusions

In this work, 7 heavy metals in surface sediments from the Dongting Lake were investigated. Then spatial risk assessment at the screening level and source apportionment of these heavy metals were studied based on geostatistics methods, SQGs, Hakanson's method and integrated multivariate statistical methods (Pearson's correlation analysis, FA and CA included). The mean concentrations of studied heavy metals all exceeded the geochemical background values of the Dongting Lake. According to the results based on SQGs and Hakanson's method, Cd and As were identified as the priority metal pollutants of concern. As a whole, the Dongting Lake currently faces the moderate anthropogenic pollution risk. Based on geostatistics analyses, the South Dongting Lake, the East Dongting Lake and the outlet of Dongting Lake were identified as the priority regions of environmental monitoring and management. Multivariate statistical analyses showed Zn, Pb, Cd and As mainly originated from mining wastewater and industrial wastewater. Cr and Cu mainly derived from natural erosion and nonpoint agricultural sources. However, Hg might originate from both sources. The spatial characteristics of heavy metals pollution were found in the close relationship with characteristics about the input rivers and cities around the Dongting Lake, especially the Xiangjiang River and the Yueyang city. Therefore, the measures, to develop strategies of contamination control and management with the comprehensive consideration of the entire basin and to optimize industrial structure of the corresponding cities, are required for aquatic system/human health protection and future restoration of the Dongting Lake.

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