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Original Research

Origin and Risk Assessment of Potentially Harmful Elements in River Sediments of Urban, Suburban, and Rural Areas

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Abstract

The Changjiang Delta Region is a rapidly urbanizing area in China. But this area still reveals different anthropogenic activities and urbanization levels. River sediments from urban, suburban, and rural areas were studied to characterize potentially harmful elements (PHEs) and their ecological risks. Chemical compositions of sediments were analyzed, which revealed pronounced differences in three areas. Al_2O_3, Fe_2O_3, CaO, and MgO were elevated in the urban sediments. Sediments from the rural area showed high organic matter. CaO and TOC of sediments fluctuated significantly in the suburban area. They are associated with the local geological provenance and sediment circumstance. The enrichments of PHEs in sediments of urban rivers were prevalent, among which Cd and As were prominent. Concentrations of PHEs in the suburban area fluctuated significantly. Lead and Cu were obviously enriched in this area. Rural sediments had relatively low concentrations of PHEs, which were also stable in the regional distribution, although As showed a slight enrichment. Based on *RI* values from Hakanson, the urban sediments showed moderate to considerable ecological risk. And the suburban sediments were in moderate ecological risk, except some high-risk samples. The majority of rural sediments revealed low ecological risk. Of these hazardous elements, Cd, Hg, and Pb contribute the largest proportion of the total ecological risk. It is evident that the urbanization level influences the distributions and contamination grades of PHEs for river sediments of the Changjiang Delta Region.

Keywords: potentially harmful element, river sediment, ecological risk, urbanization level, Changjiang Delta Region

Introduction

Potentially harmful elements (PHEs) in sediments are particularly toxic to aquatic organisms. The characteristics of spatial distributions and concentrations of PHEs are useful for identifying sources of sediments [1, 2]. Moreover, they are important for recognizing the characteristics and risks of PHEs in sediments from areas with different urbanization levels. Previous studies indicate that the characteristics of PHEs in different areas vary significantly due to distinct sources, transportation, and deposition of sediments [3-5]. In this research, anthropogenic impacts on sediments have increased the complexity of sediment components.

The Changjiang (Yangtze River) Delta Region consists of major cities, counties, small towns, and rural areas.

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These areas display prominent differences in industrial and agricultural activities, resident density, and land-use. We chose the urban area, suburban area (with mixed characters of village, town and field), and rural area to investigate the characteristics and risks of PHEs in river sediments with the goal of controlling the pollution by improving management. The comparison studies of different compartments for hazardous metals in soils can be seen in the literature [6-8]. However, few papers focus on the characteristics of hazardous metals from river sediments in different urbanization areas, especially the comparison of sediment contamination in urban, suburban, and rural areas. Compared to soils, sediments are prone to remove and reveal composite characters of regional materials and composite properties.

For analysis of spatial distribution, acquiring concentration data of PHEs in sediments may not be enough. Due to the presence of a grain-size effect, data normalization by conservative elements Al, Ti, or Sc is necessary [9]. But the enrichment of the element can only reflect the relative accumulation of elements in the sediment. The evaluation of sources of PHEs and ecological risk needs more study. Correlation analysis and primary component analysis can help us understand the relationship between PHEs and their predominant origins. The distributions of industrial, agricultural, and residential sites lead to different assemblages of PHEs, which show different toxic effects on different organisms. Based on the toxic response factor, the ecological evaluation method is addressed by the index of ecological risk [10, 11]. By means of the evaluation methods, we can determine the pollution levels of PHEs in river sediments from diverse areas of the Changjiang Delta Region.

The objectives of this study are as follows:

1. Characterize the major origins of PHEs in sediments from the urban area, suburban area and rural area of the Changjiang Delta Region.
2. Evaluate the prominent contaminated elements and contaminated levels in different areas.
3. Investigate the relationships between rising PHEs and chemical and mineral components of sediments in different areas.

Materials and Methods

Site Characteristics and Sediment Sampling

The study areas are located in the Changjiang Delta Region, a rapidly urbanizing area in China. Although many large and small cities are distributed in this region, suburban and rural areas are still explicit, particularly in the west of Taihu Lake. Nanjing City, which comprises a large number of businesses, transport, commercial, and living facilities, is chosen as the urban area for this study. Continuous and discontinuous rivers are distributed in the city and accommodate discharges of industrial waste, municipal sewage, and street runoff, although a large quantity of sewage has been treated. The Yixing-Wujin Region located west of Taihu Lake is considered a suburban area where we can find dispersed towns, factories, and farmlands. The netlike rivers flow through these multi-use landscapes. The Changxing-Anji Region is regarded as a rural area, where hilly lands with trees and wide agricultural lands are dominant. Few factories can been found in this area (Fig. 1).

Sediment samples were collected in rivers of three various urbanization areas during 2008-09, using a gravity sampler (24 samples for urban area, 39 samples for suburban area, and 42 samples for rural area). These samples (>500 g) were gathered on the basis of river distributions (Fig. 1). Sediments from the urban area were collected from river monitoring sections in the city. Those from the suburban area were distributed in sites beside inhabitants, factories, or farmlands. Rural sediments were gathered along river sections where forestland, cropland, and barren land were dominant. All samples were collected from the surface at a depth of about 0-10 cm in the bottom sediment.

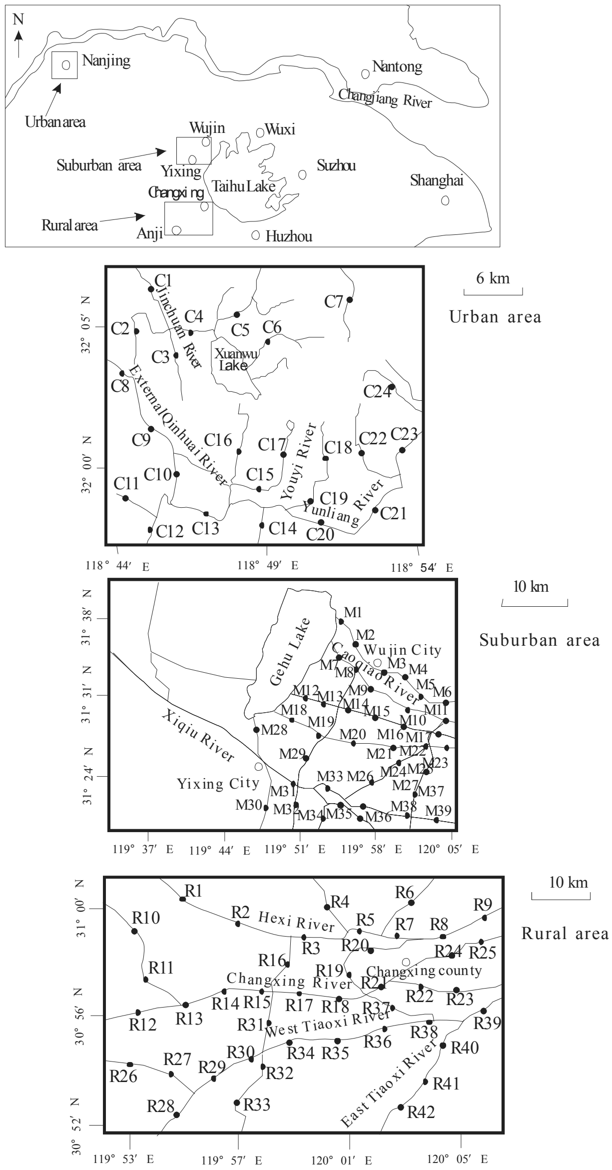

Fig. 1. Map showing research areas and sampling sites.

Table1. Indices and grades of ecological risk of potentially harmful metals in sediments.

Ecological risk of single metal	E_r^i value	Potential ecological risk to the environment	*RI* value
Low risk	E_r^i<40	Low risk	*RI*<150
Moderate risk	40≤E_r^i<80	Moderate risk	150≤*RI*<300
Considerable risk	80≤E_r^i<160	Considerable risk	300≤*RI*<600
High risk	160≤E_r^i<320	Very high risk	*RI*≥600
Very high risk	E_r^i≥320		

Chemical Analysis

Samples were moved to the experiment room soon after collection. They were dried in an oven at 40ºC. Samples were then sieved to remove debris and gravel, and ground for detection through a 0.063 mm sieve. Digestion of samples was done in a microwave digester taking 1 g of sample, 5 mL of HNO_3, 1 mL of HCl, and 4 mL of HF. The concentrations of Si, Al, Fe, Ca, Mg, K, Na, and Mn were determined by inductively coupled plasma atomic emission spectroscopy (ICP6300, Thermo Electron, USA). The concentrations of Cr, Cu, Ni, Pb, Zn, Ni, and Cd were determined by inductively coupled plasma mass spectroscopy (XSERIES, Thermo Electron, USA). Arsenic and Hg were detected by cold atomic fluorescent spectrophotometer (AFS-230E, China). TOC was detected by a colorimeter with potassium dichromate oxidation [12]. Sediment pH was measured in deionized H_2O and 1 M KCl solution with a soil/solution ratio of 1:2.5. They were shaken for 3 h and allowed to settle for 45 min at room temperature, determined by a Sartoris Pb-10 pH meter. A certified reference material (GSD9, China National Standard) was used for quality assurance. Replicate analysis was used for each batch of samples. The results for the standard were within 10% of the certified values.

Statistical and Evaluation Methods

Excel 2007 and SPSS18.0 were employed to process the data. The average values, standard errors, and coefficients of variation of concentrations were calculated using Excel 2007. Factor analysis and correlation analysis were conducted with SPSS 18.0.

The evaluation method of potential ecological risk index (*RI*) is proposed by Hakanson [10]. The *RI* method concerns the pollution index of metals as well as their biological toxicology, which are different for PHEs. The methods for calculating *RI* are listed below:

$$C_f^i = C_d^i / C_n^i \quad (1)$$

$$E_r^i = T_f^i \times C_f^i \quad (2)$$

$$RI = \sum_{i=1}^{n} E_r^i \quad (3)$$

...where C_f^i is the single metal pollution index, C_d^i is the concentration of metal in samples, C_n^i is the reference value for the metal, E_r^i is the monomial potential ecological risk factor, and T_f^i is the metal toxic response factor. The values for the toxic response factor are 10, 30, 2, 5, 40, 5, 5, and 1 for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, respectively. Hakanson has defined five categories of E_r^i and four categories of *RI* for pollution evaluation [10], as shown in Table 1.

Results and Discussions

Characteristics of Major and Trace Elements in Sediments

Data for the major elements is shown in Table 2, where differences can be seen in different areas. The concentrations of Fe_2O_3, CaO, and MgO in sediments from the urban area were elevated, while SiO_2 and Na_2O were relatively low. But the urban river sediments showed lower TOC compared to other studied areas. The pH values of sediments from the urban area were higher than those in sediments from the suburban area and the rural area.

The concentrations of SiO_2, Fe_2O_3, Na_2O, CaO, and TOC of sediments in the suburban area showed moderate values in the three studied areas. But Al_2O_3, K_2O, and MgO were lower. The coefficients of variation of CaO, TOC, and Al_2O_3 were significant, particularly for CaO.

The concentrations of Fe_2O_3 and CaO in rural sediments were lower than in the other sites. But rural sediments had higher SiO_2 and Na_2O. Because they generally originated from soils with abundant organic matter, rural sediments had elevated TOC and K_2O.

In most cases, major elements in sediments are associated with the geological setting, especially with local rocks and soils. But river sediments in urban areas are notably influenced by anthropogenic input. Al_2O_3 and Fe_2O_3 in sediments were higher in the urban area of the Changjiang Delta. It is indicated that high Al_2O_3 occurs in the street dust and high Fe_2O_3 occurs in the industrial area [13]. Sediments from the urban area also included higher CaO and MgO, which comes from urban construction material such as lime and cement. The lower TOC in sediments from the urban area is the result of frequent dredging of rivers. In addition to organic matter from soil, the higher TOC in sediments of the rural area is associated with hydrophyte residue, which

Table 2. Major components and TOC of sediments from three studied areas (%, except pH).

Area	Item	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	TOC	pH
Urban area (n=24)	Range	56.31-63.15	11.32-15.68	5.48-7.64	2.20-2.94	0.71-1.33	3.19-6.14	2.02-3.18	1.08-3.19	7.71-8.27
	Average	59.41	14.13	6.81	2.59	0.92	4.40	2.44	2.12	7.99
	CV	0.03	0.09	0.09	0.07	0.20	0.18	0.13	0.27	0.01
Suburban area (n=39)	Range	61.97-75.65	9.81-15.54	3.44-6.48	1.43-2.39	0.72-1.49	0.72-4.64	0.70-1.35	1.20-7.14	7.10-8.46
	Average	68.91	12.60	4.89	1.78	1.10	1.81	0.97	2.36	7.66
	CV	0.05	0.14	0.16	0.13	0.20	0.57	0.17	0.51	0.05
Rural area (n=42)	Range	62.84-74.86	11.51-15.12	2.43-6.02	2.20-3.55	0.75-1.75	0.50-2.20	0.49-1.71	1.15-5.85	6.46-7.96
	Average	68.97	13.21	4.60	2.64	1.39	1.05	1.27	2.78	7.01
	CV	0.05	0.08	0.21	0.14	0.16	0.32	0.30	0.40	0.03

also occurs in the suburban area. The differences in pH value in sediments may result from materials with high CaO and MgO in the architectural area [14].

Results of PHEs with percentage segments were shown in Table 3. There was remarkable variation in levels of PHEs in sediments. Because data from most elements did not show normal distribution by a test of normality, the geometric mean value was employed to calculate mean levels. Usually PHEs of samples from urban rivers showed high concentrations, indicating ubiquitous contamination of rivers in Nanjing City. But the concentrations of most PHEs (Cd, Cr, Cu, Hg, Ni, and Zn) showed a large range in the suburban area. The highest concentrations of PHEs (As, Cd, Cr, Cu, Ni, Pb, Zn) occurred in samples of the suburban area, although the smallest values were lower than those in urban sediments (expect Pb, Cu, and Zn). This showed that some samples had been influenced by industrial and municipal discharge, and other samples had not. PHEs in the rural area showed the lowest concentrations for most samples. Rivers there rarely received deposits of sediments from anthropogenic sources. Concentrations of some elements like As, Cd, Cu, Pb, and Zn in sediments fluctuated significantly in different areas. Among these trace elements, Co, Mn, and Ni showed small regional differences. Compared to the PHE concentrations of soils in similar areas, these elements were enriched in river sediments, which revealed specifically contributions from effluent of industrial wastewater and municipal sewage [15-17].

Cadmium was a prominent toxic metal in urban sediments. The mean concentrations of Cd in urban river sediments (average 1.71 mg/kg) were at least five times higher than those in rural sediments (average 0.32 mg/kg).The concentrations of Cr, As, Hg (average 103 mg/kg, 18.0 mg/kg, and 0.21 mg/kg) also were elevated in the urban area. Apart from industrial effluent, they may derive from atmospheric precipitation in Nanjing City [18].

The highest concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the suburban area (3.26 mg/kg, 431.9 mg/kg, 329 mg/kg, 96.6 mg/kg,344 mg/kg, and 540 mg/kg) exceeded those of the urban area, which is attributed to untreated wastewater discharge from local factories [19, 20]. The mean concentration of Pb in sediments from the suburban area (182 mg/kg) was five times higher than that of rural sediments (34.9 mg/kg), while the mean Cu concentration of suburban sediments (96.8 mg/kg) was two times higher than that of rural sediments (45.3 mg/kg). The Zn concentrations of most samples in the suburban area were also higher (average 182 mg/kg), although the lowest value was lower than those in the urban and rural areas. They reflected the distinctive circumstances (scattered industrial and domestic discharge) in rivers of the suburban area.

The concentrations of PHEs in rural sediments were lower in the studied area, especially for Cr, Pb, Cu, and Zn (average 85.8 mg/kg, 34.9 mg/kg, 45.3 mg/kg, and 102 mg/kg). Their coefficients of variation also were small, indicating less contamination and single provenance of river sediment. But the majority of PHEs in sediments displayed significantly elevated values compared to lacustrine deposits and loess in this region (Table 4). We infer that anthropogenic materials (like fertilizer, atmospheric deposit) have changed the background levels of metals in soils.

Enrichment of PHEs

The grain size normalization approach has been shown to be a useful technique for detecting the presence of elevated concentrations of metals in sediments. In particular, metals like Cu, Cr, Pb, Zn, Ni, and As have shown strong linear relationships with a grain size normalizer Al [21-23]. Aluminum is commonly used as a proxy of clay content as it is notably correlated with the finer fraction of sediments, as well as hazardous elements [24, 25]. The enrichment factor (EF) was calculated to characterize the accumulation levels of PHEs in sediments by Al normalizing. Ten hazardous elements were normalized by Al. Then their enrichment factors were calculated.

The enrichment factor for a given element i is defined as:

Table 3. Data statistics of potentially harmful elements of sediments in different areas (mg/kg).

Area	Item	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Urban area (n=24)	Minimum	9.77	1.18	16.4	91.5	33.7	0.09	747	39.0	35.6	90.9
	10th percentile	12.3	1.34	17.4	94.8	45.0	0.11	767	41.0	45.2	113
	25th percentile	13.7	1.37	17.7	97.7	48.1	0.13	824	41.6	51.4	115
	50th percentile	18.4	1.66	19.2	104	60.3	0.17	978	45.4	64.6	154
	75th percentile	24.6	2.09	20.7	109	67.4	0.29	1115	48.0	91.6	200
	90th percentile	27.8	2.58	21.5	113	76.0	0.45	1216	50.6	242.0	228
	Maximum	38.3	2.85	25.2	114	77.2	0.97	1279	51.0	326.0	236
	Mean	18.0	1.71	19.5	103	59.1	0.21	995	44.7	74.8	163
	Std	7.72	0.51	2.10	7.21	12.5	0.19	167	4.07	67.5	45.0
	CV	0.43	0.30	0.11	0.07	0.21	0.90	0.17	0.09	0.90	0.28
Suburban area (n=39)	Minimum	6.4	0.01	9.37	43.3	42.9	0.01	211	24.1	113	63.1
	10th percentile	8.3	0.05	10.7	56.9	55.5	0.04	304	27.0	134	92.7
	25th percentile	9.9	0.18	12.6	67.1	66.5	0.06	354	34.1	146	115
	50th percentile	11.2	0.33	15.6	86.62	94.6	0.13	528	47.7	171	181
	75th percentile	12.1	0.56	16.6	136.7	127	0.23	687	61.6	195	266
	90th percentile	13.2	0.86	17.2	184	158	0.28	884	74.3	302	328
	Maximum	21.0	3.26	24.3	431.9	329	0.46	1324	96.6	344	545
	Mean	11.0	0.31	14.6	101	96.8	0.11	517	46.9	182	182
	Std	2.54	0.66	3.23	73.1	57.2	0.11	266	18.6	59.7	106
	CV	0.23	2.11	0.22	0.72	0.59	1.02	0.51	0.40	0.33	0.59
Rural area (n=42)	Minimum	7.5	0.12	14.0	72.2	35.9	0.07	617	33.2	22.9	85.7
	10th percentile	9.0	0.26	14.8	77.0	40.2	0.09	658	36.3	27.8	89.1
	25th percentile	9.7	0.29	15.1	78.2	42.2	0.09	705	37.7	32.4	92.4
	50th percentile	10.5	0.34	16.3	86.0	45.8	0.11	796	40.5	35.4	102
	75th percentile	10.9	0.36	17.2	91.9	47.9	0.14	871	43.7	38.3	109
	90th percentile	11.7	0.39	18.8	100	50.1	0.18	999	48.0	41.4	111
	Maximum	13.5	0.71	20.5	108	58.7	0.34	1176	49.3	46.1	132
	Mean	10.3	0.32	16.5	85.8	45.3	0.12	803	40.7	34.9	102
	Std	1.19	0.09	1.60	9.18	4.59	0.06	129	4.11	5.2	10.3
	CV	0.11	0.28	0.10	0.11	0.10	0.47	0.16	0.10	0.15	0.10
	Lacustrine deposit	10.60	0.12	—	71.2	24.90	0.08	—	—	22.60	77.60
	Xiashu Loess	9.40	0.27	9.25	79.3	18.9	0.11	411.1	19.5	19.5	59.2

$$EF_{(i)}=(C_i/C_{Al})_{sample}/(C_i/C_{Al})_{crust}$$

...where C_i sample and C_{Al} sample are the concentrations of element *i* and Al, respectively, in the collected sediment sample, and C_i crust and C_{Al} crust are the mean composition of the element *i* and Al, respectively, in the continental crust [26]. It is generally accepted that EF< 2 reflects the natural variability of mineralogical composition of the sample [27, 28]. Results showed PHEs were enriched in most sediment from different areas, but significant differences presented. The EFs of Co and Mn showed less or close to 2 in three areas (Mn was mean 2.05 in the urban area). The two elements are considered as natural origin, although Mn reveals a little anthropogenic input in the urban area.

Among the PHEs of the urban area, Ni, Cr, Zn, Hg, and Cu showed moderate enrichment (2< EF <5). Cadmium, As, and Pb had a higher enrichment (EFs were 18.4, 9.8, 5.3, respectively). These elements are associated with road dust, municipal pipeline, and industrial wastewater of the city [29].

EFs of PHEs in the suburban area showed obvious changes from 1.3 to 13.5, among which Cd, Cu, Pb, and Zn displayed wide ranges. The elements of high EFs were Pb, Cu, and As in this area (13.5, 8.8, and 7.2). Some studies indicated that, in the rural soils around a city, Cu usually shared a common source with Pb and Zn, such as atmospheric deposition and inorganic fertilizers [30, 31]. Mercury, Ni, Cr, Cd, and Zn showed moderate EF values (2 <EF <5). These enriched metals resulted from dispersive industrial discharge and municipal discharge without treatment [20].

The enrichment factors of most PHEs in the rural area were relatively low (EF <3.3), except As. Arsenic was evidently enriched in the rural area (5.3). This result is similar to that found in other studies [28, 29], because As is generally used in many pesticides to strengthen insecticidal efficacy [32]. Most elements showed normal fluctuations related to the mineralogical composition of the soil. Rural river sediments revealed an apparent provenance character of ambient soil.

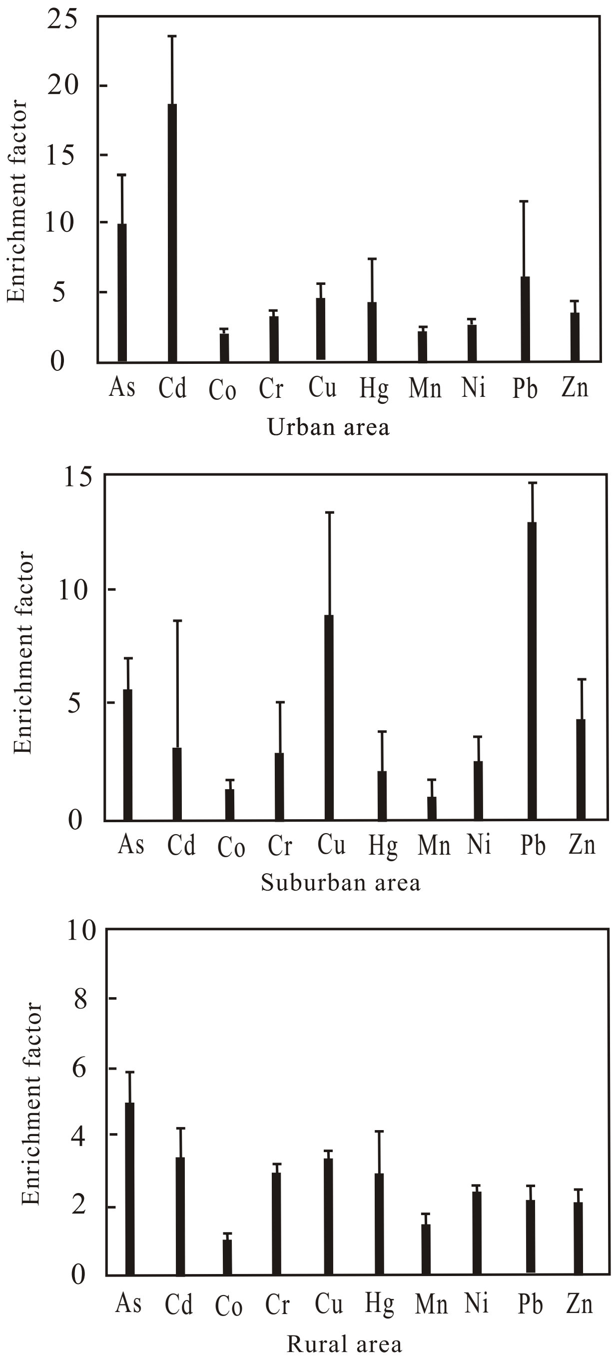

Fig. 2. Charts of enrichment factors for hazardous elements of sediments.

Multivariate Statistical Analysis

Correlation Analyses

Correlations between hazardous elements can show the relationships between these metals in sediments, although it is difficult to classify these metals into specific contamination sources. These elements will exhibit good internal relations if they have the same source. The correlation between hazardous elements in rural sediment was better than that of urban sediments, and the suburban sediment showed the weakest correlation (Table 4).

Copper, Mn, Zn, Ni, and Co showed a strong correlation with other metals in the urban sediments (r=0.416~0.910). But Pb was negatively correlated with other metals except As (r=-0.085~ -0.552). Obvious correlation was not present between Cd and other metals except Hg and As (r=-0.085~0.312). These results differ from other studies of soil in this area [16]. Copper in sediments of the suburban area showed a strong correlation with Cr, Ni, Zn, and Pb (r=0.442~ 0.907), especially with Cr. There were also significant correlations between Ni and Co, Cu, Cr, Pb, and Zn (r=0.522~0.731). But only weak relationships or no relationship present among other metals. Apart from Cd and As, most hazardous elements in rural sediments showed significant positive correlations. Mercury, which showed weak or no correlation with other hazardous elements in urban and suburban sediments, had significant correlation with Co, Pb, Cr, Mn, Ni, and Cu (r=0.332~0.564) in rural sediments. These results indicate those samples from rural rivers had similar geochemical properties in this area [31].

There were significant differences in correlations between TOC and hazardous elements in the three areas. TOC in urban sediments was significantly correlated with Zn, Mn, As, and Cu (r=0.466~0.588). TOC in suburban sediments was weakly correlated with Zn and Pb (r=0.282~0.340). But no significant correlations between TOC and hazardous elements occurred in rural sediments (r <0.100). This may be attributed to uneven distribution of hydrophytes in rivers. The transportation and deposition of hazardous elements are influenced by physiochemical properties such as pH and Eh [33]. These elements are associated with more effects of anthropogenic manners in urban and suburban rivers.

Table 4. Correlation coefficients among hazardous elements in sediments of three areas.

		As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	TOC
Urban area	As	1										
	Cd	0.474**	1									
	Co	0.186	0.137	1								
	Cr	0.282	0.037	0.705**	1							
	Cu	0.574**	0.233	0.583**	0.839**	1						
	Hg	0.190	0.500**	0.034	0.086	0.231	1					
	Mn	0.460*	0.128	0.684**	0.666**	0.706**	0.263	1				
	Ni	0.157	0.069	0.752**	0.766**	0.543**	0.085	0.774**	1			
	Pb	0.016	-0.085	-0.445*	-0.552**	-0.497**	-0.360	-0.375*	-0.430*	1		
	Zn	0.707**	0.312	0.536**	0.683**	0.910**	0.245	0.668**	0.392*	-0.460*	1	
	TOC	0.499**	0.187	0.229	0.265	0.466*	0.258	0.537**	0.170	0.392*	0.588**	1
Suburban area		As	Cd	Co	Cr	Cu	Hg	Mn	Ni	-0.337	Zn	TOC
	As	1										
	Cd	0.702**	1									
	Co	0.675**	0.479**	1								
	Cr	0.068	-0.299	0.148	1							
	Cu	-0.068	0.292	0.045	0.907**	1						
	Hg	0.770**	0.547**	0.493**	-0.042	-0.141	1					
	Mn	0.162	0.598**	0.240	-0.356*	-0.333*	0.174	1				
	Ni	0.266	-0.069	0.522**	0.731**	0.686**	0.129	-0.343*	1			
	Pb	0.020	0.011	0.144	0.243	0.442**	0.179	-0.267	0.536**	1		
	Zn	-0.05	-0.335*	0.006	0.534**	0.551**	0.114	-0.335*	0.563**	0.477**	1	
	TOC	0.144	0.015	0.013	-0.041	-0.039	0.258	-0.220	0.008	0.282*	0.340*	1
Rural area		As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	TOC
	As	1										
	Cd	0.767**	1									
	Co	0.119	0.003	1								
	Cr	0.080	-0.010	0.928**	1							
	Cu	0.521**	0.482**	0.702**	0.676**	1						
	Hg	-0.480**	-0.271*	0.564**	0.486**	0.332*	1					
	Mn	-0.083	-0.030	0.550**	0.305*	0.329*	0.495**	1				
	Ni	0.180	0.104	0.915**	0.952**	0.718**	0.475**	0.321*	1			
	Pb	0.220	0.309*	0.538**	0.521**	0.639**	0.518**	0.130	0.594**	1		
	Zn	0.651**	0.627*	0.390**	0.389**	0.840**	0.062	0.167	0.459**	0.490**	1	
	TOC	0.081	0.054	0.020	0.031	0.065	-0.015	-0.095	0.116	0.075	0.128	1

**Correlation is significant at $p<0.01$, *Correlation is significant at $p<0.05$.

Factor Analysis

To reduce the high dimensionality of variable space and better understand the relationships among PHEs and major elements, factor analysis was applied to the transformed data matrixes. The parameters of factor analysis for element contents were listed in Table 5. According to the results of the initial eigenvalues in Table 5, four factors were extracted from the available data set, which account for 87.4%, 84.8%, and 91.9% of the total variations of sediment components for the urban, suburban, and rural rivers, respectively. The first factors of the urban and rural sediments accounted for high proportions (51.1% and 49.3%, respectively) of the total variations. But that of the suburban sediment only

Table 5. Total variance explained for trace element contents of three investigation areas.

	Urban area					
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	Variance%	Cunulative%	Total	Variance%	Cunulative%
1	5.107	51.066	51.066	5.107	51.066	51.066
2	1.728	17.28	68.346	1.728	17.28	68.346
3	1.147	11.475	79.821	1.147	11.475	79.821
4	0.756	7.559	87.381	0.756	7.559	87.381
5	0.506	5.056	92.437			
6	0.289	2.894	95.331			
7	0.246	2.461	97.792			
8	0.133	1.331	99.123			
9	0.046	0.46	99.583			
10	0.042	0.417	100,00			
	Suburban area					
Component	Initiao Eigenvalues			Extraction Sums of Squared Loadings		
	Total	Variance%	Cunulative%	Total	Variance%	Cunulative%
1	3.677	36.77	36.77	3.677	36.77	36.77
2	3.08	30.798	67.568	3.08	30.798	67.568
3	0.942	9.425	76.992	0.942	9.425	76.992
4	0.78	7.8	84.792	0.78	7.8	84.792
5	0.61	6.101	90.894			
6	0.476	4.765	95.658			
7	0.237	2.365	98.024			
8	0.098	0.975	98.999			
9	0.063	0.633	99.632			
10	0.037	0.368	100,00			
	Rural area					
Component	Initiao Eigenvalues			Extraction Sums of Squared Loadings		
	Total	Variance%	Cunulative%	Total	Variance%	Cunulative%
1	4.933	49.332	49.332	4.933	49.332	49.332
2	2.605	26.05	75.382	2.605	26.05	75.382
3	0.872	8.718	84.1	0.872	8.718	84.1
4	0.78	7.8	91.9	0.78	7.8	91.9
5	0.346	3.459	95.359			
6	0.22	2.201	97.56			
7	0.109	1.086	98.646			
8	0.074	0.741	99.387			
9	0.042	0.425	99.812			
10	0.019	0.188	100,00			

accounted for 36.8% of the total variation. The second factors of the urban and rural sediments accounted for 17.3% and 26.1%, which were remarkably lower than the first factors. The second factor of components for the suburban area accounted for 30.8%, similar to the first factor. These results indicate that the metal contaminants of the suburban area were diffused while those of the urban area were concentrated in the Changjiang Delta Region [34].

The component plot in rotated space of the urban sediment (Fig. 3a) showed that Fe_2O_3, Al_2O_3, and TOC were associated with most PHEs (As, Hg, Cd, Zn, Cu, Cr, and Ni). Al_2O_3 and TOC were correlated with As, Hg, Zn, and Cd. Fe_2O_3 was closely correlated with Ni, Co, Cr, Mn, and Cu. They illustrate that PHEs mainly originated from urban soil, street deposit, and organic matter-bearing wastewater.

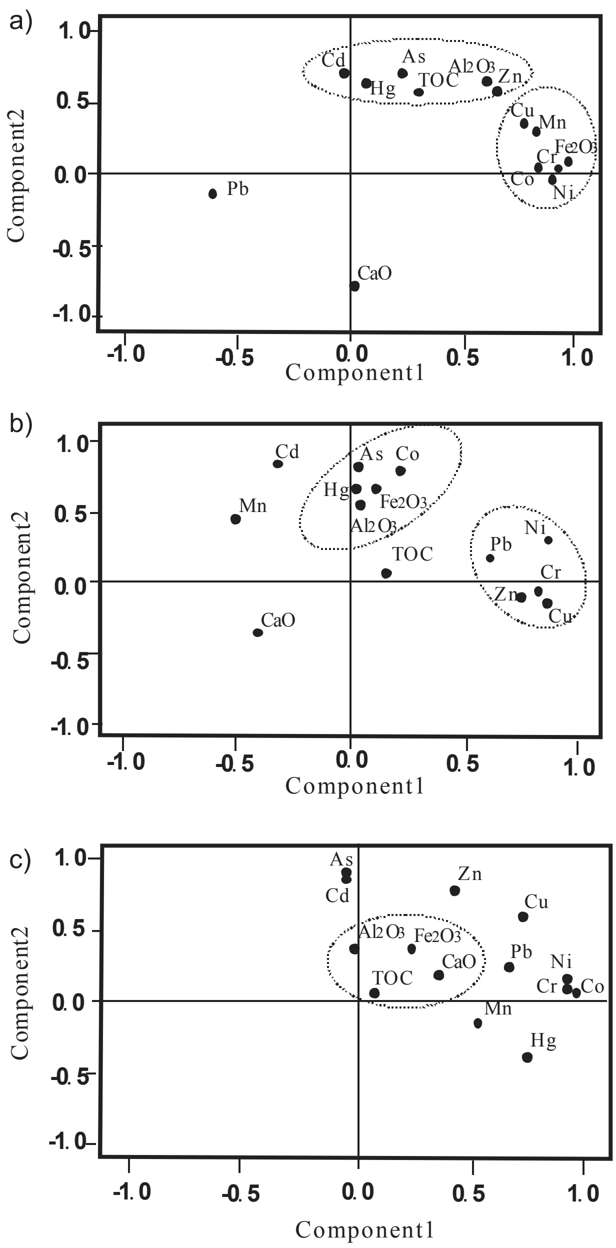

Fig. 3. Component plots of sediments in rotated space of PCA. (a) Urban area, (b) Suburban area, (c) Rural area.

But two components were relatively independent in the plot. CaO reflected the source of constructive material in sediment. Lead mainly came from the deposition of vehicle emissions in the city.

The distribution of components was dispersive in the primary component plot of the suburban sediment (Fig. 3b). The major components Al_2O_3 and Fe_2O_3 were related to As, Hg and Co. Copper, Cr, Zn, Pb, and Ni were agglomerated in the plot. CaO was still a separated component denoting construction fragments. TOC was also an independent component, perhaps due to scattered domestic discharge. Cadmium and Mn were separated from other PHEs, indicating different input sources of river sediments in the suburban area [35, 36].

The components of rural sediments had high extraction factors. Most components were found in the second quadrant of the component plot (Fig. 3c). Al_2O_3, Fe_2O_3, CaO, and TOC were close to each other in the plot. PHEs were associated with these mineral components (representing clay, Fe-oxides, carbonates, and organic matter). Therefore, we concluded that river sediments in the rural area mainly originated from the local soils, which were associated with weathering material of the parent rock.

Risk Assessment of PHEs

As mentioned in the section concerning the contamination evaluation method above, RI was calculated to quantify the overall potential ecological risk of the PHEs (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn). The descriptive statistics of ecological risk factors were summarized in Table 6. Levels of ecological risk for urban sediments were obviously higher than suburban and rural sediments. About 50 percent of *RI* values in urban sediments were between 300 and 600, indicating considerable potential ecological risk. One sample showed very high risk (Site C13, *RI*=736). It was shown that Cd accounted for most of the total risk, the percentages ranged from 36.2% to 60.1%, with a mean of 53.3%. Mercury ranked second among the hazardous metals (average 25.2%). The remaining average values of total risk were Pb (7.0%), As (5.9%), Cu (4.3%), Ni (3.1%), Zn (0.8%), and Cr (0.7%). Cadmium and Hg contributed nearly 80% of the total potential ecological risk in urban sediments.

About 67% of *RI* values in suburban sediments were between 150 and 300, indicating moderate potential ecological risk for most samples. The *RI* values of four samples (Sites M3, M16, M21, M33) were more than 300, meaning considerable potential ecological risks in some places. Cadmium and Hg accounted for the majority of the total risk, the percentages ranged from 9.5% to 59.9% (average 27.1%) and 6.9% to 38.5% (average 24.4%), respectively. Lead also was a major potential risk element in the suburban area, which accounted for 10.4% to 34.7% (average 21.7%). The average values of total risk were followed by Cu (12.8%), Ni (5.8%), As (5.4%), Zn (1.6%), and Cr (1.3%). The three toxic elements Cd, Hg, and Pb contributed more than 70% of the total potential ecological risk.

Table 6. Ecological risk assessment results of PHEs in sediments from different areas.

	Parameter	E_r^i								RI
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
Urban area	Average	20.66	197.13	2.61	15.99	93.23	11.50	25.89	2.85	369.86
	S.D	8.21	56.19	0.18	3.3	69.54	1.04	20.21	0.76	109.83
	Minimum	7.48	96.67	2.30	8.92	33.82	9.21	9.13	1.54	236.26
	Maximum	40.74	316.67	2.88	20.42	352.73	13.08	83.59	3.99	736.08
Suburban area	Average	12.02	60.71	2.94	28.56	54.64	12.86	48.59	3.49	223.8
	S.D	2.71	72.83	1.84	15.13	40.86	4.76	15.31	1.80	104.74
	Minimum	6.81	10.00	1.09	11.36	3.64	6.17	29.00	1.07	105.68
	Maximum	22.34	362.22	10.89	87.12	167.27	24.76	88.31	9.20	625.21
Rural area	Average	11.06	36.52	2.18	12.04	45.54	10.49	9.04	1.72	128.59
	S.D	1.26	9.90	0.23	1.22	20.24	1.05	1.33	0.17	22.45
	Minimum	7.98	12.82	1.82	9.50	25.45	8.51	5.87	1.45	96.85
	Maximum	14.37	78.89	2.72	15.53	124.75	12.64	11.82	2.23	201.81

Most *RI* values in rural sediments were less than 150, indicating the low potential ecological risk. Only four samples (Sites R1, R2, R3, R24) had *RI* values between 150 and 300, which were mainly influenced by Cd and Hg. The percentages of ecological risk for Hg and Cd ranged from 26.3% to 66.3% (average 35.4%) and 10.0% to 39.1% (average 28.4%), respectively. The average values of total risk followed the order of Cu (9.3%), As (8.6%), Ni (8.2%), Pb (7.0%), Cr (1.7%), and Zn (1.3%). Mercury and Cd contributed about 64% of the total potential ecological risk in rural sediments.

No sample showed low ecological risk in the urban area. Sediment samples had low ecological risks in the rural area as a whole. And the risk values of the suburban sediment ranged from low to considerable grades. These differences should be attributed to urbanizing patterns, including industrial and resident distributions, land use manner, and anthropogenic discharge in the Changjiang Delta Region.

Conclusions

River sediments of different urbanization levels show differences both in major and trace components in the Changjiang Delta Region. PHEs are related to the provenance of sediment in the studied areas. Urban sediments show more characteristics of anthropogenic materials such as construction material and street dust. Sediments from the suburban area are influenced by the untreated discharge of industrial and municipal sources. Soils beside rivers in the rural area are the source of most sediments in this area, with the specialty of rock weathering in the watershed. Most PHEs in sediments are enriched in the three areas of different urbanization levels, in the order of urban sediment > suburban sediment > rural sediment.

PHEs of sediments are evidently associated with their mineral components such as Al_2O_3 and Fe_2O_3, which are dependent on the sources in different sites. But TOCs of suburban and rural sediments are not closely correlated with hazardous elements, which indicates that hydrophyte residuals may contribute to sediments in some sites.

The urban sediments have high concentrations of PHEs and pose considerable ecological risk. The concentrations of PHEs in suburban sediment fluctuate largely and some samples show high risk, but most show moderate ecological risk. The majority of rural sediments display the low ecological risk in rivers. Of the hazardous elements, Cd, Hg, and Pb contribute the greatest proportions of total ecological risk. It is indicated that urban sediments are significantly influenced by anthropogenic material and rural sediments do not encounter significant contamination in the Changjiang Delta Region. From these recognitions, we can alleviate the river contamination by improving strategy and management in the developing areas of eastern China.

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