Chemical composition and transportation characteristic of trace metals in suspended particulate matter collected upstream of a metropolitan drinking water source, Beijing

Hongbing Ji [a,b,*], Huaijian Ding [a], Lei Tang [a,c], Cai Li [a], Yang Gao [a], Meryem Briki [a]

[a] School of Energy and Environmental Engineering, 0020, University of Science and Technology Beijing, Beijing 100083, China
[b] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[c] Beijing Geological Engineering Design and Research Institute, Beijing 101500, China

ABSTRACT

The impact of mining on environment should get more attention. The Chaobai River is the major source of Miyun Reservoir, a unique surface drinking water storage for Beijing. 11 sampling sites along the Baihe and Chaohe rivers are chosen in June and September 2012 to investigate the distribution, pollution and sources of trace metals in suspended particulate matter. We analyzed 10 trace metals and Sr, as an indicated element of soil weathering. 7 samples of colloidal particles were collected and the characterization of colloids was performed using Transmission electron microscope. The results reveal that most of mean concentrations of metals in suspended particulate matter are higher than the background of Beijing soil and have no significant difference in both seasons. According to the results, a serious contamination with Cd should be discussed and addressed, especially at site B4 on Baihe River close to the gold mine. Statistical analysis suggests that Zn, Pb, Cd and Sb represent anthropogenic sources including industrial mining, atmospheric depositions and vehicle emissions; the Ni, Cu and Ba pollution may have mixed sources of anthropogenic and natural origin. The partitioning coefficient of metals shows that most metals are affected by mines, with the exception of Ni, Cr, Cu and V, which were not significantly affected by gold mine. The source of Cd included mining pollution and other serious Cd pollution sources. The colloidal particles in rivers played important role in trace metals transportation. In this study, iron oxides, organic matter and amorphous clay minerals were important in the removing and transformation of trace metals in water. In conclusion, the analysis and assessment of particulate metals would help control and reduce the pollution of trace metals in Chaobai River and Miyun Reservoir, and consequently contribute to preservation of public health.

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1. Introduction

Trace metals cannot be degraded under natural conditions and trace metal contamination is one of the most ubiquitous and persistent issues in aquatic environment (Fu and Wang, 2011; Varol, 2013). Even trace levels of these metals can do harm to living organisms, including humans, the end of the biological chain (Fargussion, 1990; Blo et al., 2002). Regarding their input, anthropogenic sources, such as mining industry, waste disposal and use of fertilizers or pesticides, which have been greatly influencing the local and global geochemical cycles of trace metals (Viers et al., 2009), play more significant roles than natural sources. Some studies also found that vehicle exhaust deposit, dust particles and soil erosion in mining areas contribute significantly trace metal contamination in rivers (Velleux et al., 2006).

Trace metals do not just remain in river water, but are more likely to be scavenged or removed by the suspended solids or sediments because of adsorption, hydrolysis and co-precipitation (Santsch, 1984; Duan et al., 2007), especially the suspended particulate matter, which acts as sponges adsorbing pollutants directly from the dissolved phase as well as their suspension of sediments and playing a fundamental role in transport of metals in rivers (Hart, 1986; Bibby and Webster-Brown, 2005; Je et al., 2007; Onderka and Pekárová, 2008; Hua et al., 2011).

Suspended particulate matter is ubiquitous in environmental system and mainly consists of inorganic mineral phases and organic matter. Zhang et al. (2004) showed the organic suspended matter accounts for 30% of total suspended matter in Taihu Lake. There is a growing interest in the nature of the binding interactions about trace metals in suspended particulate matter, including those adsorbed to mineral surfaces, associated with carbonates, Fe/Mn oxides and organic matter (Viers et al., 2009; Song et al., 2010; Hua et al., 2011).

Besides that, the accumulation of trace metals in environment is of increasing concern. Some studies have demonstrated the extent of

metal contamination in suspended solids, sediments or soils can be indicated sensitively using the geo-accumulation index (Igeo), enrichment factor (EF) and the potential ecological risk index (RI) (Qu and Kelderman, 2001; Ghrefat et al., 2011). Furthermore, multivariate statistical techniques such as correlation, principal component analysis (PCA) and cluster analysis (CA) have been frequently applied to explore the relationship between constituents, to identify the geochemical behavior and sources of trace metals (Beltrame et al., 2009; Çevik et al., 2009; Yang et al., 2009). Song et al. (2010) studied the spatial changes of As, Cd, Co, Cr, Cu, Ni, Pb and Zn in sediment and suspended solid along the Changjiang River basin. Their results showed that As and Cd had high Igeo values, and mining areas were the main contaminating sources of trace metals by using PCA analysis. Yiğiterhan et al. (2011) analyzed the elements Cu, Cr, Cd, Mo, Re, U, V, Mn, Fe, Ba, Ni, Pb, Zn, Co, Ti, Al and P in suspended matter from the Black Sea, and determined which is influenced by lithogenic input from rivers, biological and geochemical processes, and many studies have been carried out about the transport of metals (Egli et al., 2010; Marchand et al., 2011; Ingelmo et al., 2012).

The Miyun Reservoir, which is the largest reservoir located on Chaobai River, supplies the main source of drinking water for Beijing, the capital of China (Chen et al., 2011). However, numerous mines have been distributed in upper reaches of Miyun Reservoir over time, mainly for the purpose of gold and iron mining (Huang et al., 2012; Qiao et al., 2013; Zhu et al., 2013). Although most of them stopped production in recent year, the soil is still contaminated in some areas (Liao, 2007), furthermore, atmospheric depositions and vehicle emissions are also indispensable factors, all of which can become a source of pollution and have a large and lasting impact on Chaobai River and Miyun Reservoir.

Many researches have been conducted on risk assessment and source of trace metals in Miyun Reservoir and the soils around watersheds (Tian et al., 2009; Wang and Gong, 2010; Zhu et al., 2013), however no published data are available on the metal contamination in suspended particulate matter of Chaobai River. Therefore, the aim of this research is 1) to identify the concentration and distribution of trace metals in suspended particles of Chaobai River; 2) to assess contamination of trace metals in suspended particulate matter; 3) to define

the sources of trace metals in suspended particulate matter. This is the first time that the data on metals in particulate matter of Chaobai River have been collected, quantified and evaluated.

2. Materials and methods

2.1. Study area

The study area is located in the northeast of Beijing, and a map showing a section of the Chaobai River is depicted in Fig. 1, The Miyun Reservoir is situated in the northern part of Beijing, between 40°31′–40°45′N and 115°56′–117°10′E with a watershed area of about 15,788 km^2, which was built in 1960 and has been used as surface drinking water storage for Beijing since 1997. The Chaobai River is the major source of Miyun Reservoir and is divided into two tributaries. The east branch is called Chaohe River including 400 km^2, and the west branch is called Baihe River about 3114 km^2. The Chaohe River originates in Fengning County of Hebei Province, runs south through Gubeikou Village into Miyun County, and then empties into the Miyun Reservoir near Xinzhuang village; The Baihe River originates in Guyuan County of Hebei Province, runs south through Chongli and Chicheng County, and flows into the Baihepu Reservoir in Yanqing County, Beijing and finally empties into the Miyun Reservoir near Zhangjiafen Village (Lu et al., 2013).

Beijing area exposed strata include Archean, the Proterozoic, Paleozoic, Mesozoic and Cenozoic. The main phase consists of Archean to amphibolite grade metamorphic rocks of the granulite facies composition, it is part of the crystalline basement of the North China platform, rich in mineral resources, iron, chromium and gold. The study area is precambrian metamorphic rocks outcrop area, however, there are many metal mines located in the catchment area around the catchment area.

2.2. Sampling and analytical methods

2.2.1. Suspended particulate matter samples

Suspended particulate matter samples were collected along the Chaobai River, taken at 11 stations, 7 in June (C1, C2, C3, B3, B5, B6
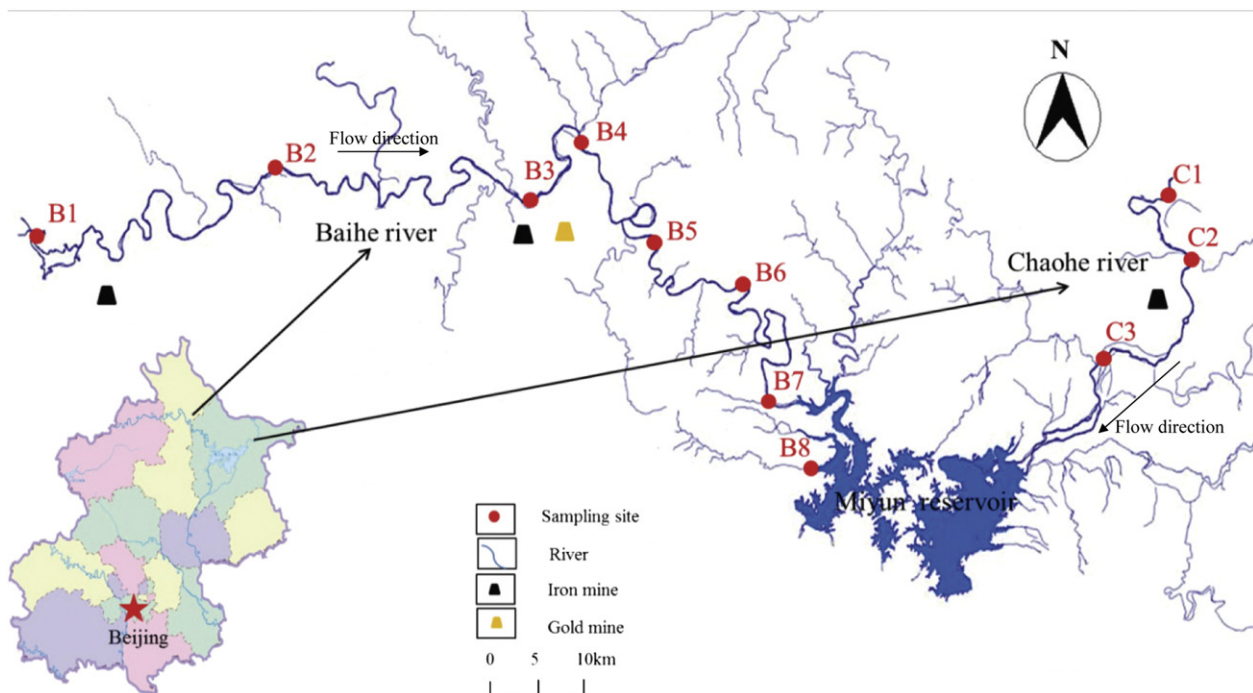

Fig. 1. Schematic map of the study area and sampling points.

Table 1
Seven classes of the geo-accumulation index and EF.

I_{ge} value	Quality	EF value	Quality
$I_{geo} < 0$;	Unpolluted	EF < 1	No enrichment
$I_{geo} < 1$	Unpolluted to moderately polluted	$1 \leq EF < 3$	Minor enrichment
$1 \leq I_{geo} < 2$	Moderately polluted	$3 \leq EF < 5$	Moderate enrichment
$2 \leq I_{geo} < 3$	Moderately to heavily polluted	$5 \leq EF < 10$	Moderately severe enrichment
$3 \leq I_{geo} < 4$	Heavily polluted	$10 \leq EF < 25$	Severe enrichment
$4 \leq I_{geo} < 5$	Heavily to extremely polluted	$25 \leq EF < 50$	Very severe enrichment
$I_{geo} \geq 5$	Extremely polluted	EF ≥ 50	Extremely severe enrichment

and B7) and 10 in September (C1, C2, C3, B1, B2, B4, B5, B6, B7 and B8), respectively. Water was collected from the middle of the stream flow using 1 L high-density polyethylene containers. Immediately after collection, water samples were filtered through 0.45 μm acetate cellulose membranes (Millipore 47 mm) using a pre-cleaned holder. All funnels, tubes, bottles and containers were cleaned by ultrapure HNO_3 and MlliQ water before using. After sampling, the samples were stored in a plastic vessel and frozen at −20 °C.

The suspended particulate samples were washed with Milli-Q water and freeze-dried, then separated in the laboratory. The suspended matter (50 mg) was treated with 0.8 mL of concentrated HF and 1 mL HNO_3 in closed PTFE autoclaves at 180 °C for 33 h, then digested with 0.4 mL HNO_3 and heated until dry. Subsequently, the residue was dissolved in 1 mL Rh, 2 mL HNO_3 and 5 mL Milli-Q water at 140 °C for 4 h, and finally diluted with ultra-pure water.

Water conductivity and pH were measured in situ. Major ions were determined by ion chromatograph (ICS-2000) with an uncertainty of ±2%. Total organic carbon and total nitrogen were measured using total organic carbon analyzer (Element 3000), and the measuring error was ±3%. The pretreated samples were measured by inductively coupled plasma mass spectrometry (ICP-MS Perkin-Elmer ELAN DRC-e) with a laser ablation sample introduction system (LA-ICP-MS, GeoLasPro 193 nm, Coherent). Rhodium was used as an internal standard to correct matrix effects and instrument drift. All of samples were measured in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences with error ≤5%.

2.2.2. Colloids samples

For further analysis of migration and transformation features, additional 7 samples at stations (C1, C2, C3, B3, B5, B6, B7) were collected in previously acid-cleaned high-density polyethylene (HDPE) containers. The collected waters were filtered through 0.45 μm acetate cellulose membranes (150-mm diameter), the first 200–500 mL of the filtrate were discarded, 50–60 mL were stored for major ions and trace metals analysis, and the others were filtered again over 0.22 μm filters. The particles trapped by 0.22 μm filters were applied to Electron microscope analysis. Filtered solutions through 0.45 μm cellulose membranes for total organic carbon and total nitrogen analyses were acidified (pH = 2) with HNO_3 and stored in glass bottles previously washed and burned. The operators were wearing rubber gloves in the whole process.

The characterization of colloids was performed using Transmission electron microscope (TEM, JEOL model JEM-1230).

2.3. Multivariate statistical method

Multivariate statistical methods offer powerful tools for monitoring soil properties. Such methods have been widely applied to investigate the concentration, accumulation and distribution of trace elements in soils (Salman and Ruka'h, 1999; Lin et al., 2002; Qishlaqi and Moore, 2007), as well as the behavior, distribution and interrelationship of trace elements in soils.

Principal component analysis (PCA) can reduce the complexity of large-scale data sets and is broadly used in environmental impact studies (Perona et al., 1999) to elucidate the relationships among variables by identifying common underlying processes (Webster and Oliver, 1990; Farnham et al., 2003). The number of significant principal components was selected on the basis of a Kaiser criterion of eigenvalues higher than 1 (Kaiser, 1960) and a total explained variance equal to or higher than 85%.

Cluster analysis (CA) is often coupled with PCA to check results and group individual parameters and variables (Facchinelli et al., 2001). Cluster analysis (CA) is a group of multivariate techniques that allows the assembly of objects based on their characteristics. CA classifies objects so that each is similar to others in the cluster with respect to a predetermined selection criterion. Hierarchical agglomerative clustering, which is the most common approach, provides intuitive similarity relationships between any one variable and the entire data set and is typically illustrated by a dendrogram.

The data for the abundance of different metals in the samples from the different sample site variables, measured in these samples were also analyzed by canonical correspondence analyses (CCA) (Ter Braak, 1986). In the result of CCA, each metals (variables) and sampling sites (sample) correspond at one point on the factor plane, so that the sample and variables point marked the same factor plane, and adjacent sample points (sample sites) and variable point (metals) classified as a class, which can be preferably and its interpretation and inference.

2.4. Geo-accumulation index

The geo-accumulation index (I_{geo}) introduced by Muller (1969)was used to quantify trace metal pollution in aquatic sediment. The formula of I_{geo} is as follows:

$$I_{geo} = \log_2(C_n/1.5B_n)$$

Where C_n is the measured concentration of metal n, B_n is the background value (average shale) of metal n, and factor 1.5 is the background matrix correlation factor due to lithogenic variation. Seven

Table 2
Grades of potential ecological risk of trace metal pollution.

Value	Potential ecological risk for single regulator	Value	Potential ecological risk index of various metals
$E_r^i < 40$	Low	RI < 150	Low
$40 \leq E_r^i < 80$	Moderate	$150 \leq RI < 300$	Moderate
$80 \leq E_r^i < 160$	Considerable	$300 \leq RI < 600$	High
$160 \leq E_r^i < 320$	High	RI ≥ 600	Significantly
$E_r^i \geq 320$	Significantly		

Table 3
Physiological-chemistry indexes in aquatic system of Chaobai River.

	Baihe River ($n = 4$)				Chaohe River ($n = 3$)			
	Max	Min	Mean	SD	Max	Min	Mean	SD
Ca^{2+}	60.73	48.56	53.08	5.29	75.50	60.29	67.64	7.62
Mg^{2+}	18.56	15.74	17.15	1.22	17.20	15.65	16.26	0.83
$Na^+ + K^{2+}$	28.95	19.75	24.09	4.23	25.64	24.03	24.88	0.81
HCO_3^{-1}	19.69	17.03	18.16	1.18	17.03	15.75	16.31	0.65
Cl^{-1}	13.30	11.42	12.81	0.96	26.38	23.07	25.06	1.75
SO_4^{-2}	47.26	40.32	52.06	15.55	79.06	71.56	75.45	3.76
DOC	2.67	1.79	2.32	0.59	1.77	1.45	1.63	0.17
TN	3.79	2.74	3.21	0.44	11.74	9.12	10.32	1.32
pH	7.69	7.40	7.52	0.13	7.46	7.20	7.35	0.14
EC	404.39	289.00	324.85	53.44	470.32	389.00	425.67	41.04
TDS	188.49	136.97	177.36	44.28	240.81	210.36	225.59	15.41

classes of the geo-accumulation index were suggested by (Muller, 1969): class 0 (unpolluted), $I_{geo} < 0$; class 1 (unpolluted to moderately polluted), $0 < I_{geo} < 1$; class 2 (moderately polluted), $1 < I_{geo} < 2$; class 3 (moderately to heavily polluted), $2 \leq I_{geo} < 3$; class 4 (heavily polluted), $3 \leq I_{geo} < 4$; class 5 (heavily to extremely polluted), $4 \leq I_{geo} < 5$; and class 6 (extremely polluted), $I_{geo} \geq 5$ (Table 1).

2.5. Enrichment factor

Enrichment factor (EF) was used to assess the level of contamination in sediments and determine whether levels of metals were of an anthropogenic source (Acevedo-Figueroa et al., 2006; Sakan et al., 2009). EF is calculated as follows:

$$EF = \left(\frac{C_i}{C_n}\right)_{sample} / \left(\frac{C_i}{C_n}\right)_{background}$$

Where $\left(\frac{C_i}{C_n}\right)_{sample}$ is the ratio of element i and the proxy element concentrations of the sample, and $\left(\frac{C_i}{C_n}\right)_{background}$ ratio of element i and the proxy element concentrations of the background. EF values were interpreted as according to Acevedo-Figueroa et al. (2006), where: EF < 1 indicates no enrichment, 1–3 is minor, 3–5 is moderate, 5–10 is moderately severe, 10–25 is severe, 25–50 is very severe, and >50 is extremely severe (Table 1). The trace metal concentrations are generally normalized by conservative elements, such as Al, Fe and Sc (Mucha et al., 2003; Amin et al., 2009; Dou et al., 2013), in this study, we select Sc as a conservative tracer.

2.6. Potential ecological hazard index

Hakanson (1980) reflects not only the effects of a single trace element in a particular environment, but also the effects of multiple trace elements. He uses quantitative methods to determine the degree of potential ecological hazard and is widely used in pollution assessments of trace elements in soils and sediments. The calculation includes four steps:

(1) The contamination factor of a single trace element, or C_r^i is determined by:

$$C_r^i = C_{surface}^i / C_n^i$$

Where $C_{surface}^i$ is the measured concentration of trace elements in the soil (or sediment), and C_n^i is the reference value. The reference value is set as the highest background value of trace elements in sediments in modern preindustrial times as suggested by Hakanson, although some scholars use national soil environmental standard values as the reference.

(2) The toxic response factor of trace elements, T_r^i, is used to reflect the response of trace elements in water, sedimentary and biological phases. A standardized trace element toxic response coefficient was taken as the assessment standard as suggested by Hakanson. The toxic response coefficients were Zn = Sr = 1 < Cr = V = Sb = Co = 2 < Cu = Ni = Pb = 5 < Ba = 10 < Cd = 30, the grading standards of potential ecological risk of metals are listed in Table 2 (Abrahim and Parker, 2008; Xu et al., 2008a; Xu et al., 2008b);

(3) The potential ecological risk index, E_r^i can then be calculated for each trace element:

$$E_r^i = T_r^i \times C_r^i$$

Table 4
Trace metal concentrations of river in June and September.

Month	River	Elements	V	Cr	Co	Ni	Cu	Zn	Sr	Cd	Sb	Ba	Pb	Sc
June	Baihe River	Min (µg/g)	62.66	63.94	11.88	38.03	38.39	307.07	173.21	0.91	1.34	488.78	59.00	8.14
		Max (µg/g)	97.00	104.85	15.82	49.88	49.87	485.91	221.15	1.09	1.68	621.25	78.64	13.16
		Mean (µg/g)	80.69	81.45	13.87	44.89	44.08	371.02	198.84	1.01	1.55	566.51	72.46	10.48
		SD	14.13	17.26	1.64	5.02	4.75	81.21	22.96	0.08	0.15	55.90	9.10	2.06
		CV (%)	17.52	21.19	11.85	11.18	10.77	21.89	11.54	8.10	9.58	9.87	12.55	19.69
	Chaohe River	Min (µg/g)	72.90	78.00	17.70	50.00	46.71	138.23	246.00	0.32	0.83	544.00	28.30	10.40
		Max (µg/g)	106.00	82.60	39.70	64.37	137.01	244.08	250.00	0.61	1.06	718.00	38.10	17.90
		Mean (µg/g)	89.10	80.10	27.50	57.71	87.90	191.30	247.67	0.45	0.97	622.33	34.63	14.03
		SD	16.56	2.33	11.19	7.24	45.67	52.93	2.08	0.15	0.12	88.29	5.49	3.76
		CV (%)	18.59	2.90	40.71	12.55	51.96	27.67	0.84	32.88	12.36	14.19	15.86	26.76
September	Baihe River	Min (µg/g)	49.42	60.46	8.64	43.46	51.52	155.72	203.30	0.49	0.83	535.00	41.70	5.89
		Max (µg/g)	77.90	89.72	13.50	62.79	86.22	292.20	283.00	1.35	1.82	686.55	59.30	11.00
		Mean (µg/g)	67.21	78.65	11.45	53.52	72.05	230.57	243.06	0.93	1.31	606.57	50.86	8.63
		SD	11.17	11.72	1.95	6.51	15.18	55.06	25.98	0.33	0.33	59.67	7.16	1.88
		CV (%)	16.62	14.90	17.00	12.15	21.07	23.88	10.69	36.07	24.76	9.84	14.08	21.80
	Chaohe River	Min (µg/g)	73.70	75.00	15.90	54.47	52.96	191.59	264.00	0.51	0.99	580.00	32.60	10.00
		Max (µg/g)	108.00	145.00	30.30	68.24	89.74	208.21	276.00	1.13	1.87	685.00	63.00	17.20
		Mean (µg/g)	91.63	111.33	22.53	59.38	70.48	198.01	269.33	0.76	1.38	645.33	45.83	13.47
		SD	17.20	35.08	7.27	7.69	18.45	8.94	6.11	0.33	0.45	57.01	15.58	3.61
		CV (%)	18.77	31.51	32.25	12.95	26.18	4.51	2.27	42.71	32.60	8.83	33.99	26.79
Average of this study			79.26	85.75	17.14	53.25	67.73	252.22	237.80	0.83	1.32	606.78	52.27	11.01
Background in Beijing soils[a]			77.4	66.7	15	28.2	23.1	97.2	196	0.12	1.08	522	24.7	11.44

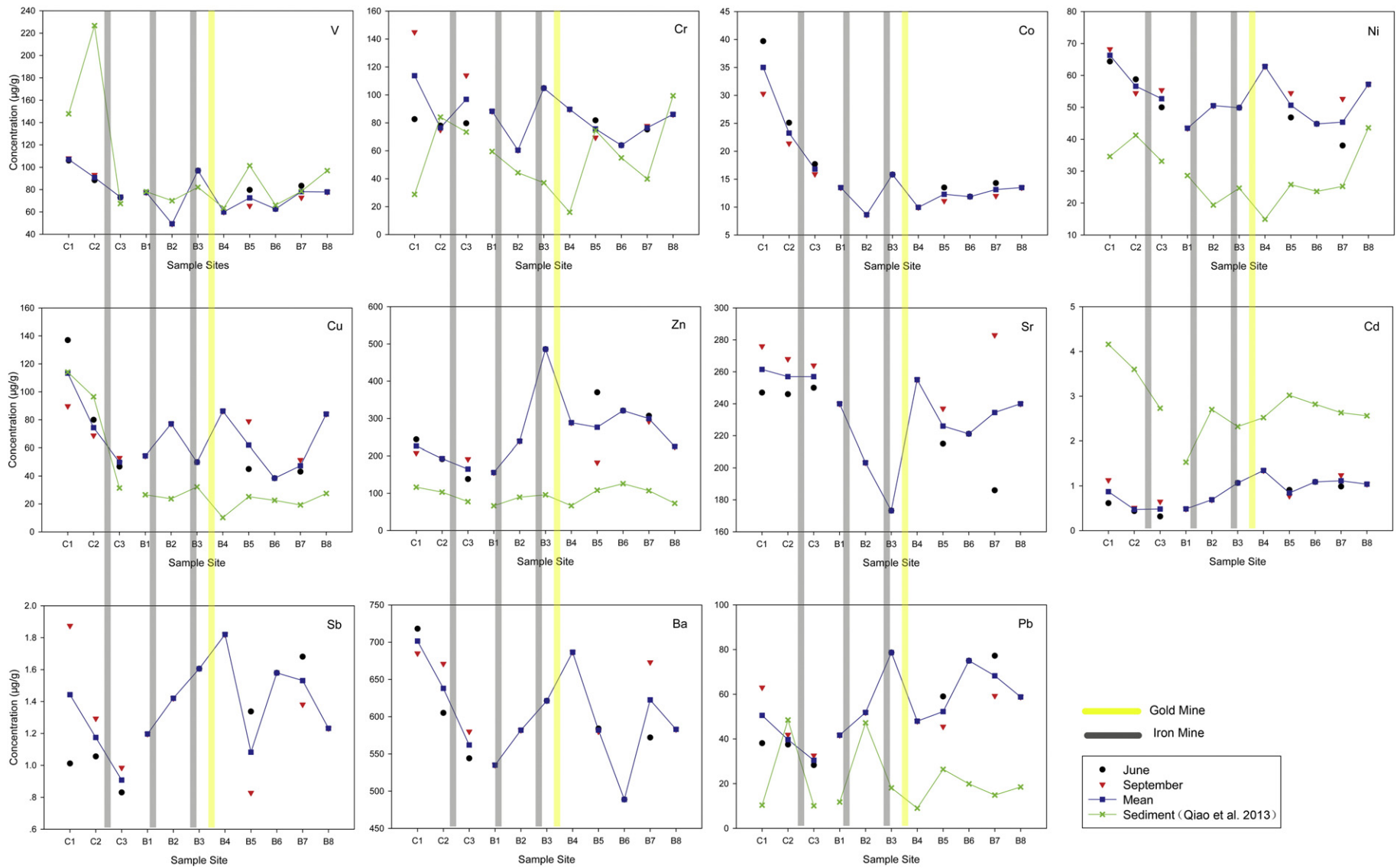[a] (China national environmental monitoring centre; Li and Liu, 1989; Chen et al., 2004).

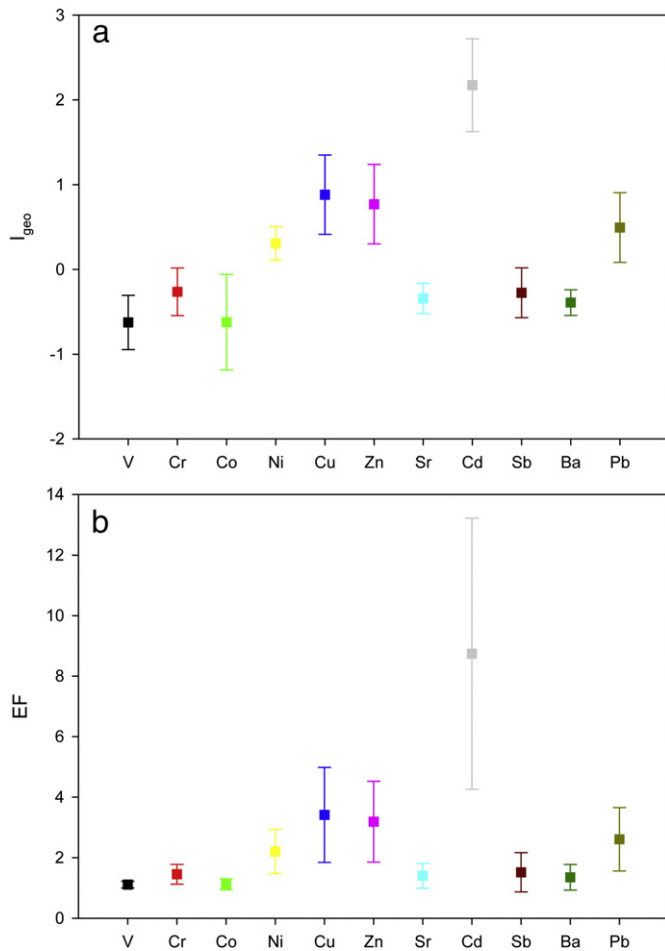**Fig. 2.** Metal distributions in suspended matter and sediment at different sites.

Fig. 3. Geo-accumulation indexes and enrichment factors of metals in investigated suspended particulate matter: a. geo-accumulation index (I_{geo}); b. enrichment factor (EF).

(4) The potential ecological risk index of various trace elements, or RI, can be divided into five levels such that the potential ecological harm is:

$$RI = \sum_{i=1}^{n} E_r^i$$

3. Results

3.1. The major ions chemistry characteristics of Chaobai River

Table 3 lists the major components of Chaobai River. The studied water was weakly basic with pH between 7.4–7.69 at Baihe and 7.2–7.46 at Chaohe. The conductivity of Chaohe ranged between 389.00 and 470.32 μs·cm^{-1}, higher than Baihe (289.00–404.39 μs cm^{-1}). The total dissolved solids (TDS = [Ca^{2+} + Mg^{2+} + Na$^+$ + K$^+$] + [HCO$_3^-$ + SO$_4^{2-}$ + Cl$^-$]) in both rivers ranged from 136.97 mg·L^{-1} to 240.81 mg·L^{-1}, with the average concentrations of 225.59 mg·L^{-1} in Chaohe and 177.36 mg·L^{-1} in Baihe, respectively. The conductivity not only reflected strength and concentration of ions, but also displayed TDS. The percentage contribution of Ca^{2+} and Mg^{2+} in cations was >70%, while Na$^+$ and K$^+$ were low, almost all of the anions were SO$_4^{2-}$, which may be due to the acid waste water caused by some mining activities and mining wastes.

3.2. Concentration of trace metals in SPM

Minimum, maximum and mean concentrations as well as the coefficient of variation of trace metals (V, Cr, Co, Ni, Cu, Zn, Cd, Sb, Ba and Pb) and Sr determined in suspended particulate matter in June and September are presented in Table 4.

During the study period, all the studied metals show low CV % values among the sampling sites except for Co, Cu, Zn, Cd and Pb, the concentrations of these metals have skewed distributions and moderate variations, which would have a higher possibility of being influenced by some extrinsic factors (Wang and Lu, 2011).

When taking into account the seasonal variations of metals, no significant difference in the concentrations of V, Cr, Co, Ni, Cu, Zn, Sr, Cd, Sb, Ba and Pb is observed in both seasons (Fig. 2).

Characteristics about distribution of metals (V, Cr, Co, Ni, Cu, Zn, Sr, Cd, Sb, Ba and Pb) at all the sites are also described in Fig. 2. Generally speaking, mean concentrations of V, Cr, Co, Ni, Cu, Sr and Ba reach the highest values at C1, especially for Co, the concentrations are found to be relatively higher in Chaohe than those collected in Baihe. Yu et al. (2013) also found higher concentrations of Cr, Cu and Ni in soils surrounding the Chaohe River. This could be a consequence of mining mineral resources, frequent mining production transportation and dust particles from these activities in Chaohe area. Cd and Sb show similar distribution, and Zn and Pb show similar distribution, with the highest value at B3 and B4, respectively, and then followed by B6 and B7, suggesting similar sources and/or enrichment mechanisms for these metals in Baihe area.

Table 5
Trace metals ecological risk indexes of Chaobai River.

| Sites | E_r^i | | | | | | | | | | | RI |
	V	Cr	Co	Ni	Cu	Zn	Sr	Cd	Sb	Ba	Pb	
C1	2.76	3.41	11.67	11.76	24.54	2.33	1.33	217.88	13.36	2.69	10.23	301.96
C2	2.35	2.29	7.75	10.04	16.09	1.98	1.31	118.00	10.88	2.44	8.04	181.18
C3	1.89	2.90	5.60	9.35	10.79	1.70	1.31	120.63	8.41	2.15	6.16	170.89
B1	2.00	2.65	4.50	7.71	11.78	1.60	1.22	121.25	11.08	2.05	8.44	174.28
B2	1.28	1.81	2.88	8.96	16.69	2.46	1.04	172.19	13.15	2.23	10.50	233.19
B3	2.51	3.14	5.27	8.84	10.79	5.00	0.88	266.45	14.87	2.38	15.92	336.06
B4	1.55	2.69	3.32	11.13	18.66	2.97	1.30	336.29	16.85	2.63	9.71	407.12
B5	1.88	2.27	4.10	8.98	13.41	2.84	1.15	210.38	10.03	2.23	10.58	267.83
B6	1.62	1.92	3.96	7.95	8.31	3.30	1.13	272.44	14.62	1.87	15.18	332.30
B7	2.02	2.29	4.38	8.04	10.24	3.08	1.20	278.38	14.18	2.39	13.82	340.01
B8	2.01	2.58	4.50	10.15	18.21	2.31	1.22	260.00	11.41	2.23	11.90	326.53
Mean	1.99	2.54	5.27	9.35	14.50	2.69	1.19	215.81	12.62	2.30	10.95	279.21

Table 6
Correlation coefficient matrix of trace metals in suspended matter.

	V	Cr	Co	Ni	Cu	Zn	Sr	Cd	Sb	Ba	Pb
V	1										
Cr	0.745**	1									
Co	0.835**	0.638*	1								
Ni	0.332	0.520	0.575	1							
Cu	0.277	0.376	0.552	0.889**	1						
Zn	0.132	0.096	−0.195	−0.152	−0.286	1					
Sr	0.125	0.201	0.434	0.508	0.438	−0.765**	1				
Cd	−0.121	0.040	−0.260	0.179	0.069	0.664*	−0.230	1			
Sb	−0.110	0.003	−0.155	0.133	0.113	0.640*	−0.307	0.807**	1		
Ba	0.462	0.538	0.524	0.794**	0.726*	0.112	0.296	0.278	0.351	1	
Pb	0.065	−0.133	−0.217	−0.327	−0.317	0.848**	−0.702*	0.690*	0.626*	−0.131	1

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

3.3. Assessment of trace metal pollution

3.3.1. Geo-accumulation index and enrichment factor

Fig. 3 show I_{geo} and EF of metals in suspended particulate matter. The mean I_{geo} values of the trace metals in suspended matter decrease in following order: Cd > Cu > Zn > Ni > Pb > Cr > Sb > Ba > Co > V, and V, Cr, Co, Sr, Sb and Ba showed no pollution; The I_{geo} values for Ni (0.31), Cu (0.88), Zn (0.77), Pb (0.15) are below one, suggesting that the study area is unpolluted to moderately polluted with these metals. In contrast, the mean I_{geo} for Cd reaches 2.17, suggesting that the study area is moderately to heavily polluted with Cd. Generally, the result shows low pollution as a whole, but also indicates the existence of some anthropogenic influences, especially for Cd.

The mean values of EF decrease in the order: Cd > Cu > Zn > Pb > Ni > Sb > Cr > Ba > V > Co. The mean EF values for V, Cr, Co, Ni, Sr, Sb, Ba and Pb are less than three with minor enrichment, indicating very limited input from anthropogenic sources and these metals may be entirely from naturally weathered crustal materials. The metals Zn and Cu show moderate enrichment, with EF values slightly less than five. Highest EF value was found for Cd (8.74) among all the metals studied, which indicates the presence of anthropogenic pollution with Cd in the study area.

3.3.2. Potential ecological hazard index

The potential ecological risk of metals in suspended particulate matter of the Chaobai River is calculated based on RI method. Spatial distribution of E_r^i value is shown in Table 5. The single risk indices of metals are ranked in the order of Cd > Cu > Sb > Pb > Ni > Co > Zn > Cr > Ba > V. The main element causing ecological risk is Cd, with the average E_r^i of 215.81. Cd has low potential ecological risk at sites of C2, C3 and B1, but highest values at B4 (336.29), suggest a high potential ecological risk of Cd in this area. The E_r^i values of other metals are lower than 40, indicating slight potential ecological risk of these metals at 11 stations.

In order to quantify the overall potential ecological risk of metals in suspended particulate matter, the values of RI are also shown in Table 5, which ranges from 170.89 to 407.12 in all the sampling sites, with an average of 279.21, attributing to moderate potential ecological risk level. The lower and the higher RI values are observed at C3 and B4, respectively. 54.5% of the sampling sites posed moderate risk, 45.5% high risk, and this higher value may be due to the presence of Cd. Generally, metal mining, waste disposal, transportation activities and atmospheric depositions are the main anthropogenic sources of Cd in the environment of the Chaobai River.

3.4. Application of multivariate statistical method

The data obtained from analytical methods were analyzed using SPSS (Statistical Package for Social Science) version 19.0 for Windows. Pearson's correlation coefficient analysis, PCA, and cluster analysis (CA) were performed to identify the relationships between metals and their possible sources.

As shown in Table 6, highly significant positive correlations ($P < 0.01$) are found between V and Cr, V and Co, Cr and Co, Ni and Cu, Ni and Ba, Cu and Ba, Zn and Sr, Zn and Pb, Sr and Pb, Cd and Sb, Cd and Pb, Sb and Pb, suggesting that they had similar geochemical behaviors and an apparent common source.

Due to the complexity of the relationship between metals, it is difficult to draw more clear conclusions directly. So PCA analysis is performed for suspended particulate matters to further discern relationships and grouping among the trace metals in different seasons. Table 7 shows the results obtained in this case. There are three eigenvalues higher than one and these three factors explain 85.49% of the total variance. The first principal component (PC1) explains 40.32% of the total variance and higher contributions of Co, Ni, Cu and Sr. The second principal component (PC2) reveals higher contributions of Zn, Cd, Sb and Pb, accounting 30.60% of the total variance, and the third principal component explains 14.75% of the total variance, having strong negative loading on V and Cr. The relations among the metals based on the principal components are illustrated in Fig. 4a by three-dimensional space. This result coincides with the conclusion of correlation analysis and which demonstrated that these metals probably originate from a common source.

The result of Cluster analysis are reported in Fig. 4b, which reveal three clusters of elements: the first cluster (C1) includes metals Ni, Cu, Sr and Ba, the second cluster (C2) contains V, Co and Cr, the third cluster (C3) includes Zn, Pb, Cd and Sb.

Table 7
Initial eigenvalues and Rotated component matrix of trace metals in suspended matter.

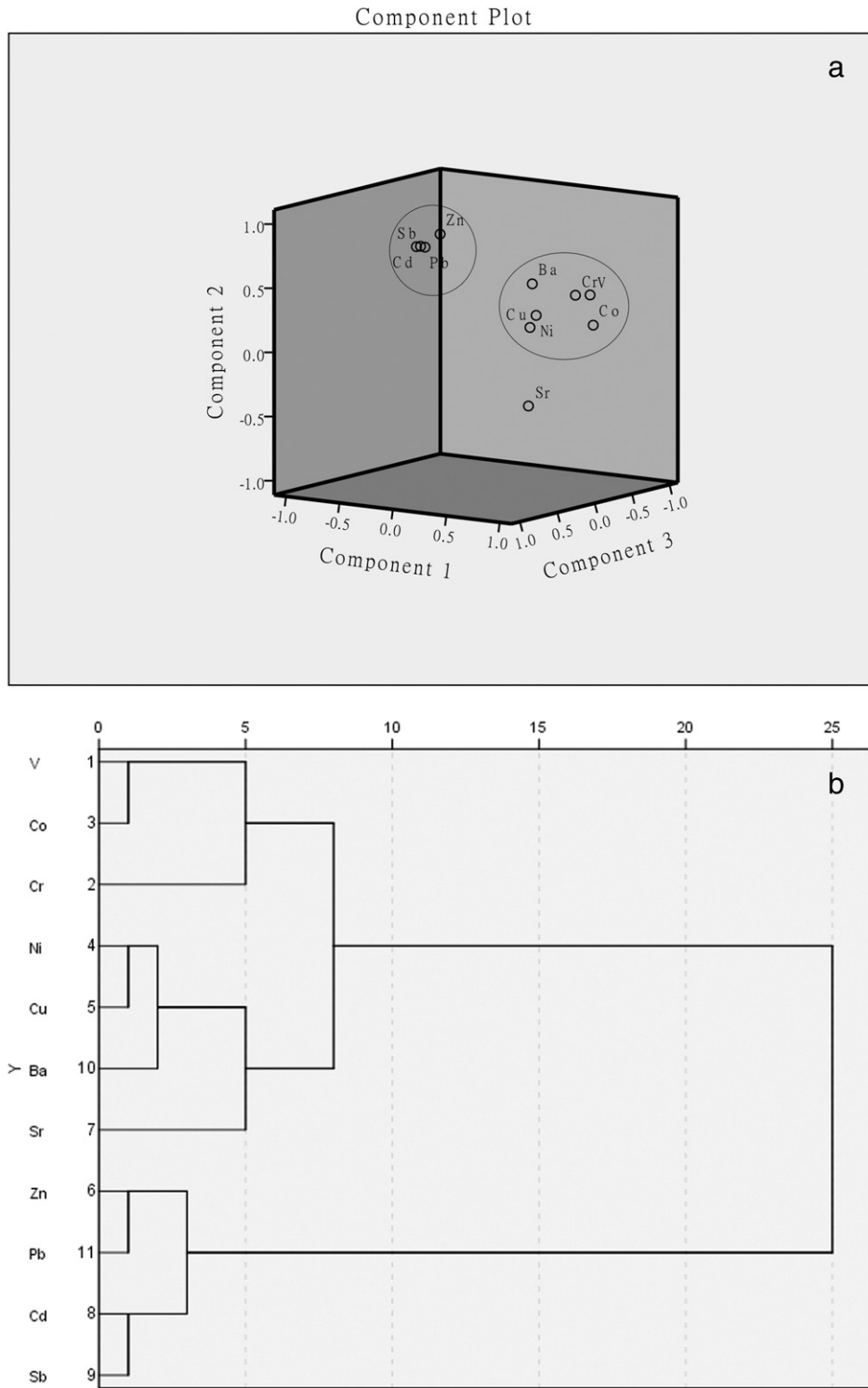| Elements	Component		
	PC1	PC2	PC3
Eigenvalue	4.435	3.366	1.603
% Total variance	40.320	30.598	14.570
Cumulative variance %	40.320	70.918	85.488
V	0.581	0.358	−0.694
Cr	0.638	0.401	−0.418
Co	0.815	0.189	−0.402
Ni	0.807	0.372	0.348
Cu	0.775	0.280	0.385
Zn	−0.507	0.787	−0.244
Sr	0.721	−0.346	0.329
Cd	−0.298	0.799	0.371
Sb	−0.272	0.803	0.354
Ba	0.670	0.583	0.205
Pb	−0.621	0.679	−0.206

Component Plot

Fig. 4. PCA and CA results of metals in suspended matter: a. PCA results in the three-dimensional space; b. cluster analysis of trace metals in SPM.

The cumulative proportion of Inertia in Canonical correspondence analysis of this study reached 0.825. As shown in Fig. 5, Zn, Sb, Cd and Pb obviously gathered around several sampling points (B3, B6 and B7).

3.5. The morphology and mineralogical composition of colloidal particles

TEM-EDS was used to understand the difference in terms of morphology (shapes and sizes) and chemical composition of colloidal particle samples and to further link them to the sources and transportation of pollutants. Our observations suggest the present of three forms of minerals in colloidal particles, and the metals Fe, Mn, Pb, Zn, Cd, Cr, Ni and Ti were the major constituents of minerals in colloids.

According to Figs. 8 and 9, the main three forms of colloidal particles are: (1) oxides or hydroxides, mostly iron oxides (Fig. 6), other oxides in colloidal particles were proved, such as rutile and quartz; (2) silicate minerals, mostly clay minerals, plagioclase, albite, and potassium feldspar; (3) other minerals, such as barite, calcite, gypsum, apatite and magnesite.
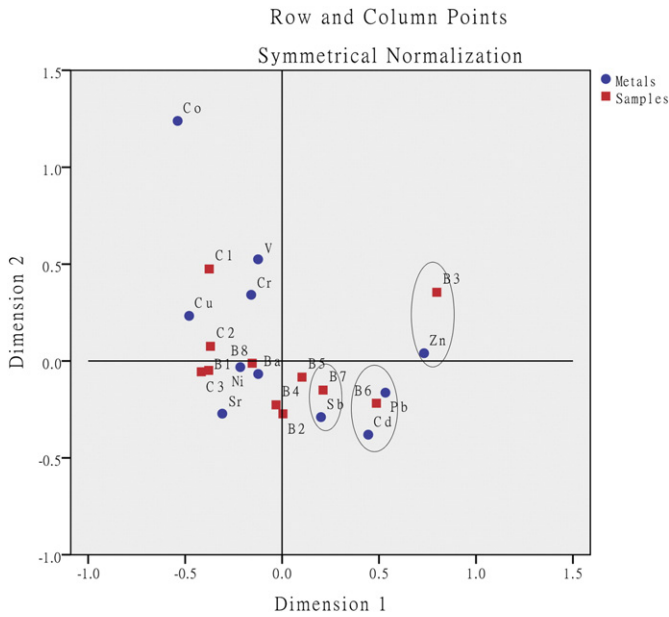
Fig. 5. Canonical correspondence analysis of trace metals in suspended matter.

4. Discussion

4.1. Pollution degree and source identification

4.1.1. Pollution degree

To assess the trace metal contamination in this region, the concentration of metals in this study are compared with the background value of Beijing soil (Table 4), the average concentrations of trace metals in suspended particulate matter of Chaobai River are much higher, this is particularly evident for Cd (6.9 times).

With the exception of Ni in flood season, the concentrations of each of these trace metals were lower in the Chaobai River than in the Changjiang River (Song et al., 2010). With the exception of Zn, the concentrations of each of these trace metals were lower in the Chaobai River than in World River (Viers et al., 2009).

Some of previous studies proved most metals we studied in suspended matter of Chaobai River are relatively higher than in sediments of Miyun Reservoir (Fig. 2) (Qiao et al., 2013; Zhu et al., 2013). It is most likely a result of adsorption by Fe/Mn oxides or organic matter, and further precipitation in the river. This process also reduced the pollution of Miyun Reservoir. Chen et al. (2012) studied the trace metals of surface sediments in three reservoirs in Huizhou, the average contents of Cr, Cu, Zn, Cd, and Pb were lower than that in our study.

Overall, as the main rivers flowing into the reservoir with drinking water, the trace metals in suspended particulate matter of Chaobai River are higher when compared with the sediments of reservoirs, and more attention should be paid to it.

4.1.2. Partition coefficient of metals between SPM and sediment

The interaction relationship of distribution of SPM and sediment can be described by the partition coefficient (K_d) for individual metals. To further investigate the correlation of K_d between various metals, we analyzed the K_d of metals by PCA. Fig. 7 shows the result of K_d and the PCA.

$$Kd = C_{SPM}/C_{sediment}$$

Fig. 7 (Qiao et al., 2013) shows that the mean K_d values for seven metals were all exceeded 1 except Cd and V. The K_d of most metals appeared significantly increased downstream of mines, suggesting that the mining or related operations has significant input to the trace metal concentration in SPM. There seem to be minor differences in distributions of these metals, so PCA was used to data dimensionality reduction for more information. The result showed there were two principal components, explaining 80.05% of the total variance. The first principal component (PC1) explains 60.64% of the total variance and higher contributions of all the metals. Fig. 7d shows that the scores of PC1 showed the K_d values of most metals reached a peak at B4, but the metals related to PC2 highly peaked at B3. The K_d values at the next downstream sample site after the peak decreased significantly, followed by a rising trend towards site B7. We conclude that metal pollutants from mine area will first affect the metal content in SPM, and
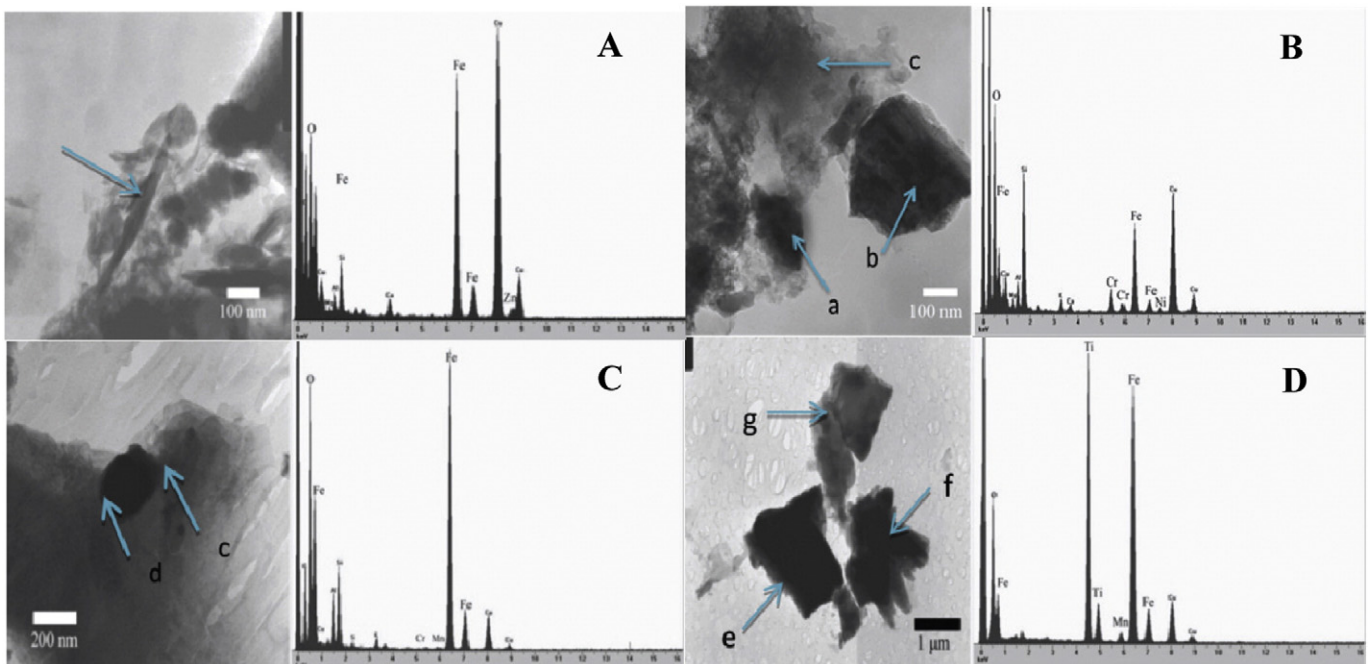

Fig. 6. TEM micrographs with EDS spectra of goethite (A), chromite (B), magnetite (C) and ilmenite (D) in colloidal particles: a point, Ni element; b point, calcite debris; c point, some amorphous clays; d point, Cr and Mn adsorbed by magnetite; point e, Mn element; point f, Plagioclase; point g, calcite.
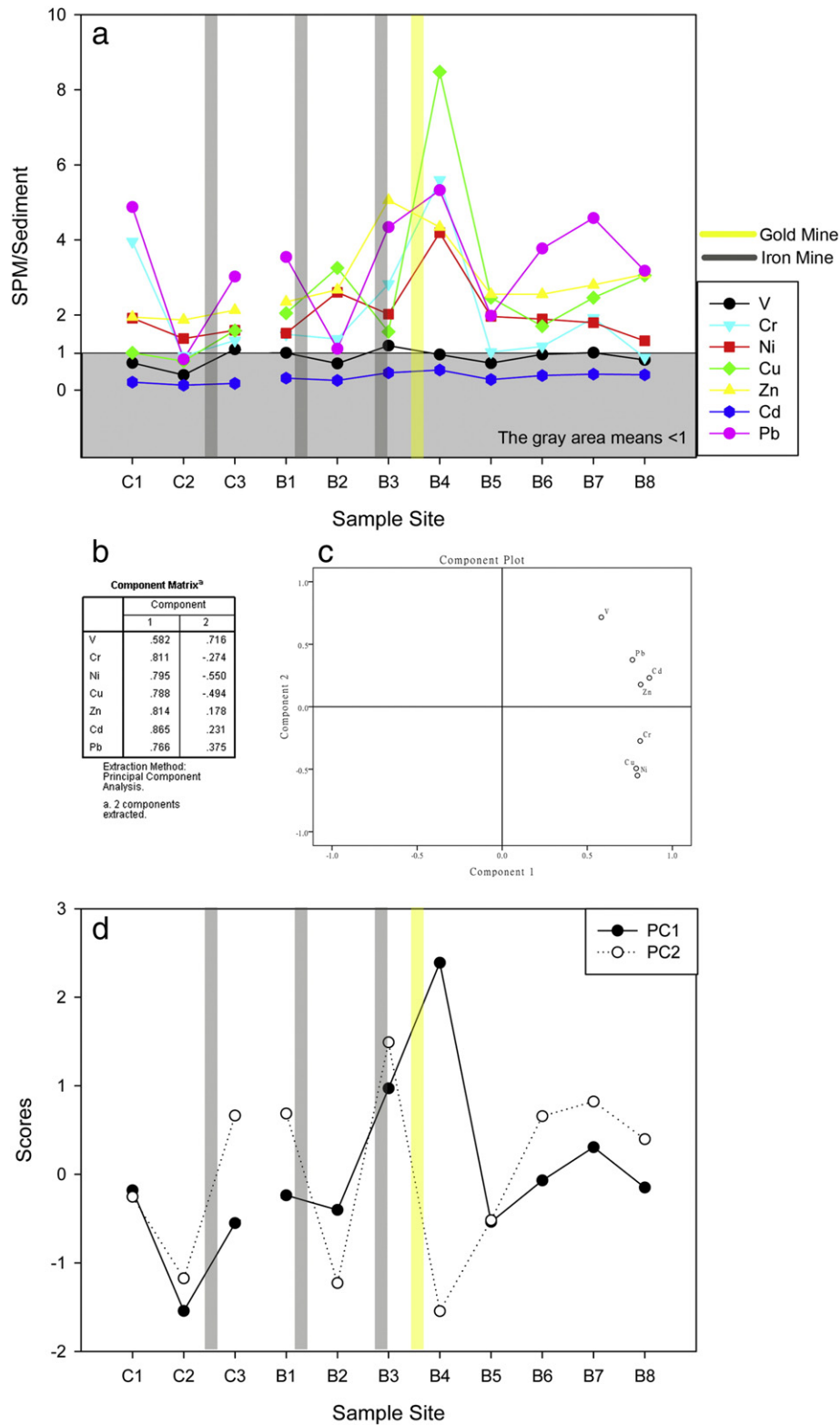
Component Matrix[a]

	Component	
	1	2
V	.582	.716
Cr	.811	-.274
Ni	.795	-.550
Cu	.788	-.494
Zn	.814	.178
Cd	.865	.231
Pb	.766	.375

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Fig. 7. Distribution and the PCA result K_d of seven metals in study area: a. K_d of metals in Chaobai River; b. the component matrix of PCA; c. loading plot of PCA; d. scores plot of PCA.

then, some of the metal will enter the sediment (K_d value decrease). Then the metal contents in SPM which easily enter sediment, gradually decrease, which leads to a decreasing phenomenon of K_d values. We can see in Fig. 7, the K_d values of Cr, Ni, Cu and Zn increased downstream of gold mine. We hypothesized that these metals were significantly affected by gold mine and iron ore, which is consistent with the result of previous studies (Huang et al., 2013; Qin et al., 2014).

In addition, while previous results show a higher degree of pollution with Cd, its K_d distribution shows it has no dramatic changes in the entire basin. The results show that the source of Cd included mining pollution and other serious Cd pollution sources, such as agricultural pollution from upstream. These other sources of pollution made the K_d values of Cd in Chaobai River show no dramatic changes. K_d values of Pb were >1, and
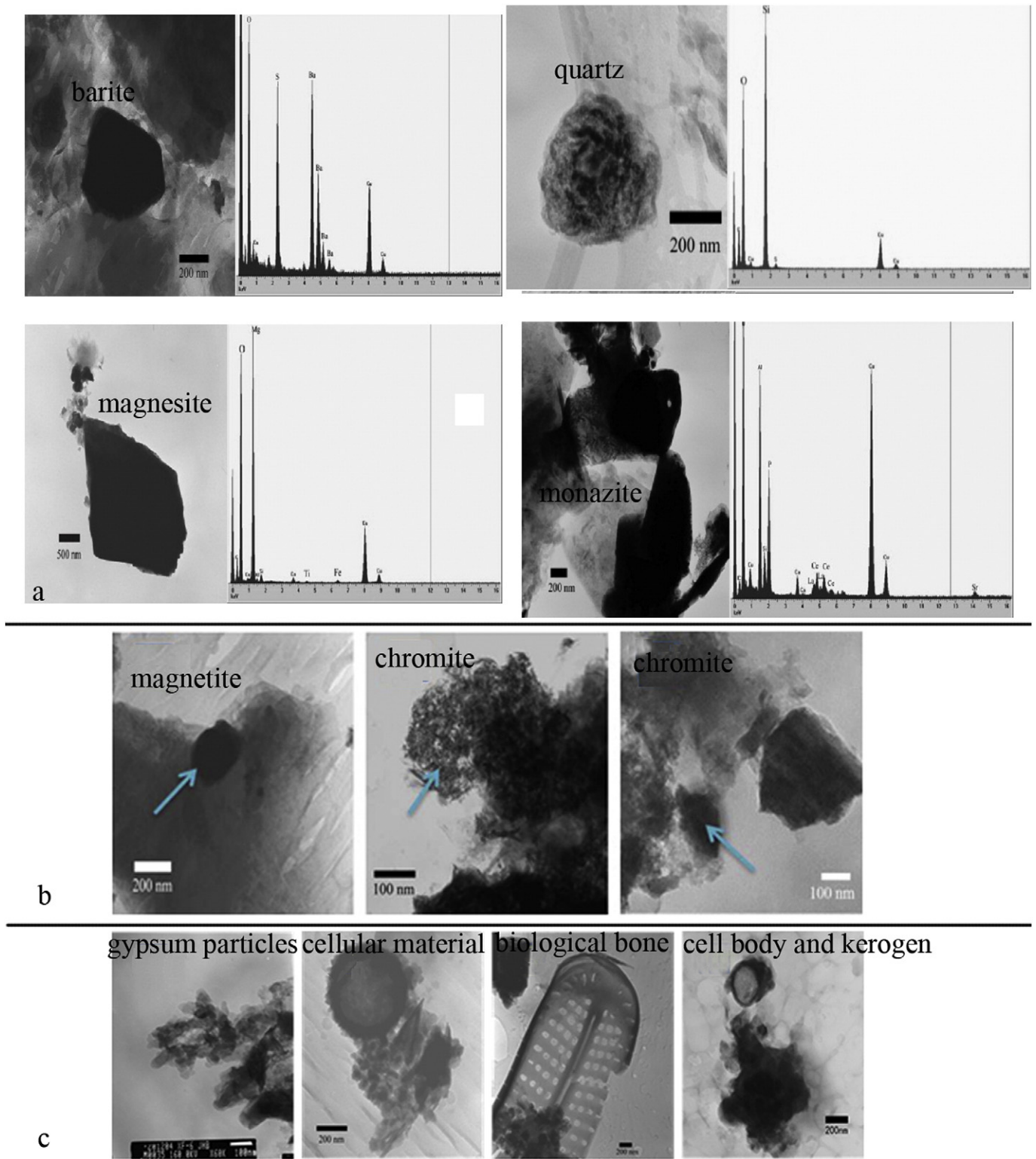
Fig. 8. TEM images of main three forms of colloidal particles of: (a) Fe-oxide/hydroxide of geogenic origin, (b) anthropogenic origin (c) biogenic origin.

compared to other elements, its content of SPM has a greater input in B5–B7.

4.1.3. Source identification

From the results of correlation analysis, PCA and CA, highly significant correlations are found for the metals Cr, V, Co, Ni, Cu, Ba, Pb, Cd, Sb and Zn, considering their similar geochemical behaviors and apparent common sources. Three groups of elements can be distinguished:

(A) Trace metals Zn, Pb, Cd and Sb, the mean concentrations of which are clearly higher than the background values in Beijing soil. Among these the Cd is obviously enriched and enrichment on the basis of I_{geo}, EF and RI indices is mainly a consequence of anthropogenic sources, such as industrial mining, atmospheric sedimentation and vehicle emissions. The concentrations of these metals are greater in Baihe River at sites B4, B7, B6 and B3, and this is probably related with the historical mining and smelting activities along Baihe River. Similar
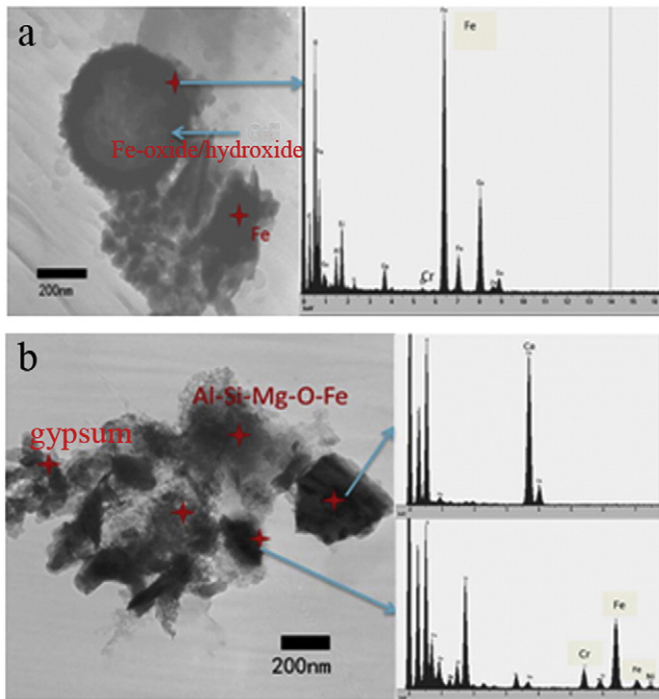
Fig. 9. TEM images of trace metals adsorbed on colloidal particles: (a) biogenic origin, (b) clay and Fe-oxide/hydroxide and Ca-carbonates.

was also observed at contaminated sites in Finland (Åström and Nylund, 2000; Gosar and Miler, 2011). The results of CCA also shows the correlation between the mining sites and these metals. B3 is located downstream of the two iron ore mining areas. According to Fig. 5, Zn and B3 showed a significant cluster; Pb, Cd and B6, located 15 km downstream of the mining area, show a significant cluster; Sb and B7 show a significant cluster at a discharge of the Baihe River into Miyun Reservoir. We can infer that the mining activities near the river are an important source of trace metals in suspended matter. Moreover, the rapidly increasing population of motor vehicles in china is an expanding contributor to air pollution, and then to the soil and water environment from atmospheric sedimentation. Duan et al. (2012) studied the size distributions of elements at curbside, residential and rural sites in Beijing and found high levels of Mn, Ni, Cd and Pb in particulate matter of street sediment. Several investigations at home and abroad had proved traffic is a major source of toxic elements such as Pb and Zn (Chillrud et al., 1999; Chen et al., 2010), which remains high in Chinese urban dusts even after abandonment of the use of leaded gasoline in 1997 (Millman et al., 2008; Qiao et al., 2013).

(B) Elements Ni, Cu and Ba have mixed sources of natural and anthropogenic origin, all of which reach the highest concentrations at C1 of Chaohe River, where there are emissions from industrial mining, gold tailings and frequent transport. Lin et al. (2005) and Al-Momani (2003) also related high contents of trace metals (Ni, Cu, Ba, etc.) in the suspended matter with vehicle emissions.

(C) The elements V, Co, Cr and Sr have the similar concentrations as the background of Beijing soil. Low I_{geo}, EF and RI values suggest they may derive from rock weathering and soil erosion in upper reaches of the Chaobai River. Zhu et al. (2013) found the same origin of V and Cr in sediment of Miyun Reservoir.

4.1.4. The influence of colloidal particles on trace metal transportation

The generation of colloids is a complex process and can be influenced by many factors. According to the TEM/EDS analyses, the trace metals Pb, Zn, Cd, Cr, Ni, Ti and Ba were present in samples of colloids from Chaobai River. They mainly occur bound in particles or adsorbed on the surface of colloidal particles in a variety of mineral forms.

Metal-bearing colloids were identified and classified into three source groups on the basis of their chemical composition and morphology from TEM-EDS: (a) geogenic group (Fig. 8a), (b) anthropogenic group (Fig. 8b) (c) biogenic group (Fig. 8c).

The factors affecting the migration and transformation of trace metals were extremely multivariate and complex. In this research, iron oxides or hydroxides, clay minerals and some organic matter were found to be important regulatory substances and the primary controlling factor for trace metals removal and transformation in water environment system, which was also showed by Turner et al. (2004) and Wu et al. (2007).

This study shows that some trace metals of colloids, such as Pb, Zn, Ni, Cr, Mn and Ti, were absorbed by iron oxides, which is in accordance with trace metals in suspended particles.

The organic matter was the important metal adsorbent, and this conclusion had reported in the previous studies (Sauve et al., 2000). The organics of colloids contained some dead microorganisms or decomposition. In water environment system some Extracelluler Polymer Substances (EPS) may be secreted from microbial cells, which can obtain and accommodate trace metals or nutrient elements in water, being main factor affecting the effects of environment biochemical characters (Gagnon et al., 2009). In our study, we find that in Fig. 9a, S and P were probably biological components, Fe and small amounts of Cd and Zn were adsorbed surrounding the cells under the microbial activities. Moreover, considerable quantities of Fe were found, this result suggest that EPS was important in the removing and transforming of Fe in water.

Lots of amorphous clay minerals were seen in this study, such as kaolinite and montmorillonite according to the test about independent clay particles. In mobile phase their size was about 100–300 nm, while the clay particles of 700 nm to 1 μm in size were regarded as the matrix (Fig. 9b), keeping trace metals adsorbed in surrounding and also transfer with them. Clay minerals were formed by weathering of aluminosilicates, which are very complex and most important in colloids. The sorption mechanism can explain in two ways, the particles of clay minerals passed through the hydroxyl hydrogen in layer shape structure and the ion of M^+, and then exchanged the trace metalion from the water, and in another way, the trace metalions were Hydrolysis first, and then combined with hydroxyl in surface of clay minerals particles to adsorbed easily.

4.2. Risk assessment

According to the results above, the I_{geo} value of Cd reaches 2.17, suggesting a moderate to heavy pollution with Cd in the study area; The EF values show moderate enrichment of Zn and Cu, and moderate severe enrichment of Cd. High values of RI are observed due to the presence of Cd, especially in B4 site. Overall, Cd is consistent with the study reported by Shang et al. (2011). Cd in sediments of Chaobai River also had the highest I_{geo} and E_r^i, values, which may due to the main anthropogenic sources of mining activities, transportation activities and atmospheric depositions. While the other metals show low pollution as a whole in the study area. It should be paid more attention to moderate to heavy pollution of the study area with Cd.

5. Conclusions

As the upstream of the Miyun Reservoir, which is the only one major source of drinking water in the metropolis with >20,000,000 population, drinking water safety is the top priority of urban development. The average concentrations of trace metals are higher than the background values of Beijing soil, sediments of Chaobai River and some reservoirs. No significant difference is observed in June and September. The results of I_{geo}, EF and RI exhibit similar distribution and show low pollution as a whole, but also indicate the existence of some anthropogenic influences, especially Cd, which is obviously elevated, enrichment

with high potential ecological risk. Statistical analysis suggests that Zn, Pb, Cd and Sb represent anthropogenic sources including industrial mining, atmospheric depositions and vehicle emissions; the Ni, Cu and Ba pollution may have mixed sources of anthropogenic and natural origin. The partitioning coefficient of metals show that most metals were affected by mines, Ni, Cr, Cu and V were not significantly affected by gold mine, while the source of Cd included mining pollution and other serious Cd pollution sources. The colloidal particles in rivers played important role on trace metals transportation. In this study, iron oxides, organic matter and amorphous clay minerals were important in the removing and transforming of trace metal in water.

Acknowledgments

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