Analysis and evaluation of the source of heavy metals in water of the River Changjiang

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Abstract In order to analyze and evaluate different trace metals on surface water of the Changjiang River, concentrations of dissolved trace metals (Cu, Ni, Fe, Co, Sc, Al, Zn, Pb, Cd, Se, As, Cr, and Hg), major elements(Ca and Mg), and nutrient(NO_3^-) were measured. Samples were taken at 76 positions along Changjiang River in flood and dry seasons during 2007-2008. Spatial distributions identified two main large zones mainly influenced by mineral erosion (sites 1–22) and anthropogenic action (sites 23-76), respectively. Principal component analysis (PCA) and hierarchical cluster analysis were used to identify the variance distinguishing the origin of water. Four significant components were extracted by PCA, explaining 74.91% of total variable. Cu, Ni, Fe, Co, Sc, Al, Ca, and Mg were mainly associated with the weathering and erosion of various rocks and minerals, while an anthropogenic source was identified for Cd and As. Although erosion was one source of Pb and Zn, they were also input by atmospheric deposition and industrial pollu-

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L. Wang e-mail: wanglan437@163.com tions. NO_3^- and Se were mainly associated with agriculture activities. However, Hg and Cr showed different sources. CA confirmed and completed the results obtained by PCA, classifying the data into two large groups representing different areas. Group 1 referred to the upper reaches which represented samples mainly corresponding to natural background areas. Group 2 referred to the middle and lower reaches including samples under anthropogenic influence. Meanwhile, group 2 was subdivided into three new groups, representing agricultural, industrial, and various artificial pollution sources, respectively.

Keywords Heavy metals · Changjiang River · Water pollution · PCA · HCA

Introduction

Metals are ubiquitous in the environment. Because of their wide application, ubiquity in the environment, bioaccumulation, and high toxicity, heavy metals are considered as one of the most serious pollutants in the environment. They are introduced naturally through the weathering of rocks as well as a variety of human activities such as mining, smelting, electroplating, and other industrial processes that have metal residues in their waste streams (Shine et al. 1995). In addition, agriculture also has been identified as a source of heavy metals via fertilizers (Kidd et al. 2007; Mico et al. 2006; Michel et al. 2000).

Changjiang (Yangtze River) is the largest river in Euro-Asian continent, and is ranked third in length (6,300 km), fifth in freshwater discharge $(924.8 \times 10^9 \text{ m}^3 \text{ year}^{-1})$ in the world (Milliman and Syvitski 1992). The drainage covers an area of 1.80×10^6 km². The Upper Changjiang runs through the Tibetan Plateau, while its middle and lower part runs through one of the most populated areas of the world, and population is unevenly distributed and mainly concentrates in the Sichuan basin. Changjiang suffers anthropogenic pollution over a large surface area. In consequence, the river receives many inputs from both natural and anthropogenic origins, which may cause deterioration of water quality. Besides, about 24% of the national arable land is located in its basin and devoted to agriculture with high production of rice, wheat, and fruits, and with the corresponding environmental effects in the river as well (Xing and Zhu 2002).

In spite of Changjiang's significance in the world, almost no study has been performed about heavy metal pollution in the water of the entire Changjiang. Increasing interests were only shown in the geochemistry of major elements in the water of the Changjiang (Chen et al. 2002; Hu et al. 1982). Most studies on heavy metal pollution of Changjiang basin were mainly concerned with heavy metals' distributions in the estuary area and some polluted sections (Chen et al. 2008; Zhang 1999; Xia et al. 2007; Müller et al. 2008; Shan et al. 2008).

In this work, through a series of more systematic investigations of the Changjiang, including the mainstream, tributaries, and lakes along the river, we focus on the discussions of the distributions of heavy metals (Al, Ni, Sc, Fe, Co, Zn, Cu, Pb, Cd, Se, As, Cr, and Hg) in the river water. Besides, based on the concentrations of nutrient (N–NO₃⁻) and major elements (Ca and Mg) as well as dissolved heavy metals, the chemometrics methods were used to establish the influences of the nature erosion and human activities performed in the river on river water.

Materials and methods

The geomorphology of the Changjiang Basin is mainly overlain by sedimentary rocks that is Precambrian to Quarternary in age and composed of marine carbonates, evaporites, and continental deposits. Carbonates are widely spread throughout the drainage basin and are particularly abundant in the southern region of the middle reaches. The Jurassic red sandstone is widely distributed in the Sichuan Basin. Evaporites are mainly present in the Upper Reaches of the Changjiang (Chen et al. 2002). At the same time, various minerals resources have been detected in its basin. Chetelat divided the Changjiang basin into three physiographic provinces according to its altitude, the first one, 3,500-5,000 m, is composed of the southern part of the Qinghai province. Then 500-2,000 m, consists of the Qinba mountainous area, the Sichuan basin, and the mountainous regions in Hubei and Guizhou. The last one, below 500 m, covers the Huaiyang mountainous area and the hilly area in the southern Changjiang (Chetelat et al. 2008). Samples were collected at 76 sites representing the different geomorphological reaches (Fig. 1).

Sampling

A total of 76 water samples were collected along the river during two 45-day periods from July to September(summer, wet season) and November in 2007 to February in 2008 (winter, dry season), in which 36 were located in the main stream and 40 others in major tributaries and anabranches of Changjiang River (Fig. 1). Samples for laboratory metal heavy analysis were collected in disposable polyethylene narrow-mouth bottle with screw cap. To provide reliable and accurate metal data, cleansing techniques were used for handing and analyzing samples. All materials coming in contact with the samples were acid washed and stored in double polyethylene bags before used. At the same time, the parallel samples included in these 76 samples were taken at every six sampling sites in order to ensure test results. The samples for dissolved traces metals were acidified with high-purity HNO₃ and then stored at approximately 4°C before analysis.

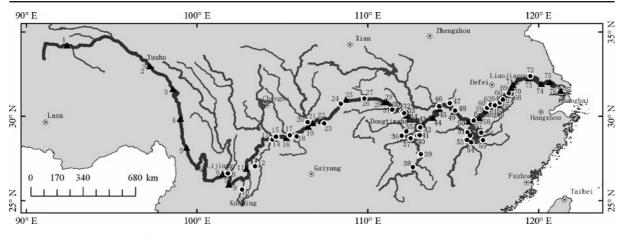


Fig. 1 Study area and sampling locations

Analytical methods

Samples collected were analyzed at the Ministry of Land and Resources P.R.C. Hefei Mineral Resources Supervision and Testing Center. Determination of Al, Ni, Sc, Fe, Co, Zn, Cu, Pb, Cd, and Cr was carried out by inductively coupled plasma-mass spectrometry (ICP-MS, IRIS Advantages, USA), Cin which Al, Sc, and Co were determined by the standard addition methods, while Ni, Fe, Zn, Cu, Pb, Cd, and Cr were monitored by standard sample (multi-elements standard, lot number GBW(E)080194). As, Hg, and Se were determined by atomic fluorescence spectrum (AFS) using standard addition methods. Determination of Ca, Mg, and NO₃⁻ was performed using an ion chromatograph(IC, Dionex ICS3000, USA), employing GBW(E)080112 for Ca, Mg and GBW(E)080416 for NO_3^- as monitoring samples, respectively. The detection limits were 1 μ g/L for Al and Sc; 0.1 mg/L for Ni; 0.05 mg/L for Fe; 0.05 µg/L for Co and Cd; 0.2 µg/L for Zn and Cu; 0.1 μ g/L for Pb and Cr; 2 μ g/L for Se (AFS); 1 μ g/L for As (AFS), 0.1 μ g/L for Hg (AFS); 3 mg/L for Ca and Mg (IC); 0.2 mg/L for NO_3^- (IC). The relative errors for the analysis of standard solution were less than 5%. The recovery of standard addition was greater than 93% for Al, Sc, and Co, and 95% for As, Hg, and Se. Data below analytical detection limits were set to a value of half of the detection limit in constructing all plots and statistic calculation.

Statistical methods

The application of different multivariate statistical techniques can allow us to identify the possible sources that influence water systems and offer a valuable tool for reliable management of water resources as well as rapid solution to pollution problems (Reghunath et al. 2002; Simeonov et al. 2004; Mendiguchia et al. 2004; Chen et al. 2007). The techniques, such as principal component analysis (PCA), hierarchical cluster analysis (HCA), and factor analysis (FA) have been used by a number of investigators to examine multivariate environmental data sets (Singh et al. 2004; Laaksoharju et al. 1999; Alberto et al. 2001; Shrestha and Kazama 2007). In this paper, PCA and CA were applied to the measure data from the Changjiang to assess relationship between variables and possible patterns in the distribution. MATLAB 6.5 for windows was used for the multivariate statistical calculations, and the program was written by us.

Results and discussion

Spatial variance

The spatial variance of the studied variables along the course of Changjiang River was shown in Figs. 2, 3, and 4 in the form of error bar plots. As observed, the curves for Cu, Ni, Fe, Co, Sc, and Al (Fig. 2) were very similar, whose high concentration were all in the upper reaches, from its source to sample site 22, where not anthropogenic activities but nature events are the predominant factors. The highest concentration of Ni, Fe, Co, and Al were all measured between 10 and 12, Cu was measured in 14, and Sc was in source site. It shows that rare earth elements such as, Ti, Al, Sc, Nb, and Th are stable in a hypergene environment and may represent the whole composition of source rocks (Taylor and McLennan 1985; Fralick and Kronberg 1997). Aluminum is also important as a tracer of aluminosilicate content in environment and concomitant background crustal levels of metals. Meanwhile, Co and Ni have been shown to have similar geochemistries (Shine et al. 1995). Although some experts have associated the increase of Ni in rivers with sewage effluents, the concentrations were about 0.3 μ g/L (Yang et al. 2002), and the results reported for agriculture zones were about 1.46 μ g/L (Markich and Brown 1998; Cenci and Martin 2004). The lowest concentration of Ni measured in Changjiang River and

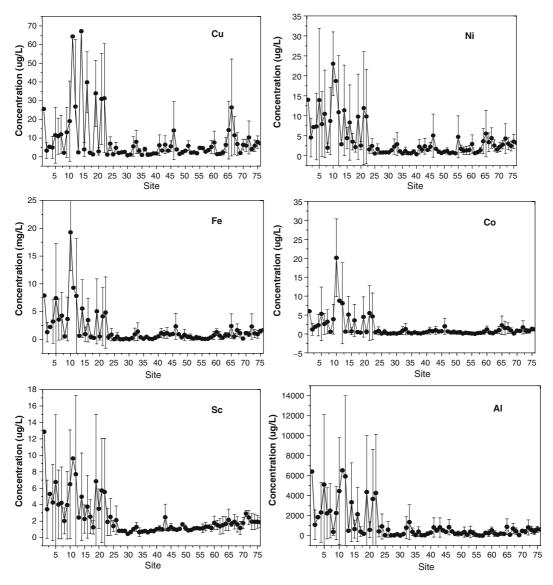


Fig. 2 Spatial variance of Cu, Ni, Co, Sc, Al (μ g/L), and Fe (mg/L) concentrations in the sampling stations of Changjiang River

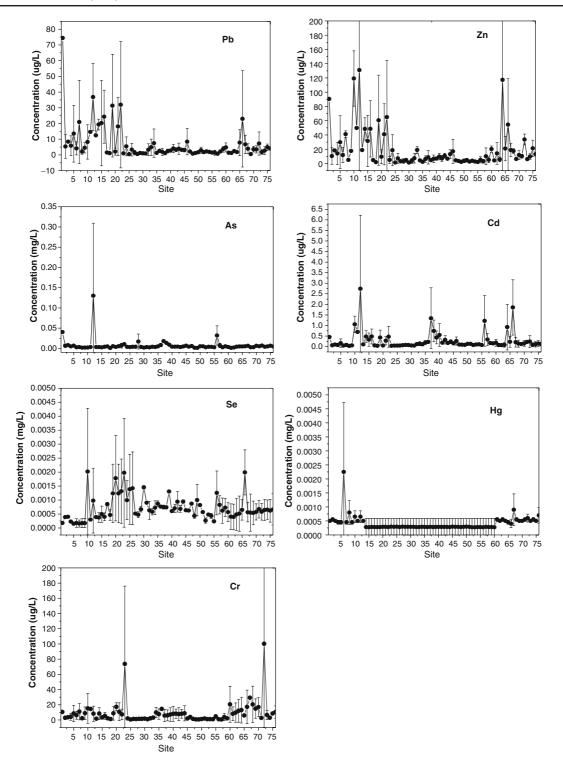


Fig. 3 Spatial variance of Pb, Zn, Cd, and Cr (μ g/L) and As, Hg, and Se (mg/L) concentrations in the sampling stations of Changjiang River

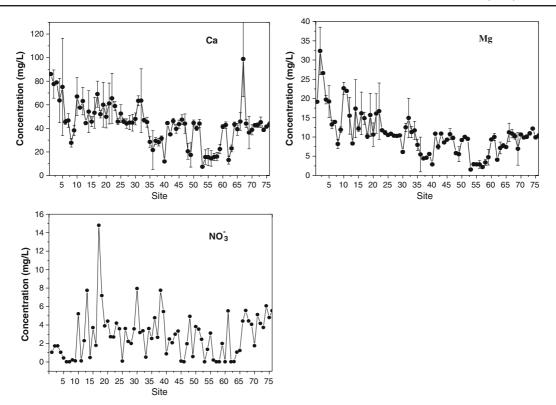


Fig. 4 Spatial variance of Ca, Mg, and NO_3^- (mg/L) concentration in the sampling stations of Changjiang River

its tributaries was 0.36 μ g/L, mean concentration 3.69 μ g/L, which indicated neither industry nor agriculture was its source. Moreover, evaporites and various ore deposits are ubiquitous in the upper reaches of Changjiang and undergoing strong chemical weathering (Mendiguchia et al. 2007; Chen et al. 2002), which suggests that high concentrations of these elements was due to weathering of rocks and minerals. Concentrations of these elements decreased from site 22 to estuary due to different geological background in basin, dilution by joining of tributaries, and adsorption of suspended matter.

The highest concentrations of Pb (Fig. 3) was measured at the first site, the source of Changjiang River, and the concentration was about two or three times higher than that of the upper reaches (between 5 and 22), which were also high concentrations regions of Pb in the basin. The profile of Pb showed that Pb did not have only one source. The fact that the source region of Changjiang River is scarcely populated shows that atmospheric deposition and weathering were its origin. The other high concentrations zone of Pb was in the 64–66, where the Tongling Mine Area was located, thus suggesting strong anthropogenic local inputs. The trend observed for Zn (Fig. 3) was similar to that for Pb, with high concentrations in the upper reaches and 64–66, which showed these two metals were consistent with a non-point and point source in different sections and its tributaries. Atmospheric deposition and stormwater runoff in upper reaches and 67–76 were mainly due to different geological background in basin and dilution effect.

The As and Cd (Fig. 3) showed highest concentration in 12, where a power plant was located. Then these two elements showed some similar high-value regions along the Changjiang basin, such as the sites 37–40 and 56, Cd also showed high values between 65 and 67. These sampling sites are generally in the middle and lower reaches of the Changjiang River. However, this zone is a place where the industry becomes dense. Higher concentration of Cd and As might be attributed to the effluent of the different plants, whereas the low concentration sections of Cd and As in basin were mainly due to dilution effect. The concentration of Se (Fig. 3) increased from the site 10 to estuary, although some low concentrations can also be found between 27 and 55. Highest concentrations mainly appeared in 10 and 19-26, most of which are densely populated and agriculture areas. The NO_3^- profiles (Fig. 4) matched the Se profiles in that there was a distinct rise in concentrations after the site 10, with highest concentrations in the intermediate zone (nature to agriculture), corresponding to extensive agricultural zones previously reported for Ganga River, India (Jain 2002). Meanwhile, Se and NO_3^- behaviors identified Changjiang River as a source of both metal and nutrients to East China Sea, as Garcia-Luque suggested that Cu in Guadalquivir River was a source to the Atlantic Ocean (Garcia-Luque et al. 2003). It was regrettable that only the wet season values of NO₃⁻ concentrations were obtained. In this study, NO_3^- has significantly higher concentrations along the course of river compared with the average in world rivers (1 mg/L; Levinson 1974), mean concentration is 3.45 mg/L. This was mainly attributed to non-point pollutants, i.e., agricultural fertilizers (Müller et al. 2008; Xing and Zhu 2002).

The concentrations of Cr and Hg presented different profiles (Fig. 3), suggesting their different origins. A strong Hg pollution was in the site 6 and significant Cr contamination in 72 and 23. The high concentrations of Cr were also found in 1–22, 34–43, and lower reaches. The lowest concentrations of Hg were measured between 14 and 60. The irregular profiles implied the complexity of pollution sources.

Finally, Ca and Mg showed almost same profile (Fig. 4). The major element composition of river water (such as Ca and Mg) reveals the nature of weathering and a variety of other natural processes on basin (Zhang et al. 1990). Moreover, concentrations of Ca were about three or four times higher than that of Mg in the river water of the Changjiang. This was because the major element chemistry of Changjiang was mainly controlled by rock weathering, with the Ca^{2+} dominating the major ion composition (Chen et al. 2002).

Mean metal concentrations in Changjiang River were summarized in Table 1 and compared with concentrations in home (Li and Zhang 2010) and abroad rivers (Sakai et al. 1986; Krishna et al. 2009) and world averages (Klavinš et al. 2000). The mean metal concentrations in Changjiang River were evidently higher than the estimated world averages, the mean value of an unpolluted river in Japan and even higher than assumed metal background concentrations (Lithner 1989) determined for industrially developed countries. Our results showed that Changjiang is almost a lower polluted river compared with the rivers in industrial areas.

In Table 1, the mean values obtained by our study showed that the Al concentration was about 32 times as high at background concentrations, Fe was 16 times, Co was 19 times, and Cu was 12 times as high at background concentration. The highest concentrations of Al, Fe, Co, and Cu in Changjiang water appeared in the upstream regions, where there was almost no influence of anthropogenic activities. At the same time, studies had shown that Changjiang basin was characterized by high Fe group and Cu group elements with high background levels of Fe, Ni, Sc, Cu, Co, Pb, and Zn (Qiao et al. 2007). This shows that the high concentrations of Al, Fe, Co, and Cu of the Changjiang water might be associated with intense weathering and erosion over the drainage basin (Rojas and Vandecasteele 2007). The concentrations of other metals such as Pb, Cd, Cr, As, and Hg were also several times or even several tens of times higher than background and unpolluted river. Concentration of the Pb and Cu was lower than Han River but higher than two abroad rivers, Cr was exactly opposite to Pb and Cu in home and abroad rivers, Co was almost the same, while Zn, Cd, and As were all lower for both home and abroad rivers. Considering the priority toxic pollutants, i.e., As, Cd, Cr, Pb, and Se presented in US EPA, 2006 for aquatic life protection [US EPA 2006], much greater attention should be paid to As and Pb.

Metal	Present work	Background concentrations, world average ^a	Background concentrations, Sweden ^b	Han River ^c	Nakkavagu ^d	Rhine River ^a	Japan ^e
Ni	3.69	0.30	0.50	1.71	26.7	2.00	
Al	974		30	188			
Sc	2.23						
Fe	1,660		100	30.6	162		
Со	1.55	0.08	0.20	2.24	2.8	0.34	
Cu	8.40	1.00	0.70	13.35		3.40	1.50
Pb	6.40	0.2	0.40	9.26	2.1	5.70	1.00
Zn	18.75	10	3.00		98.6	33.0	20
Cd	0.28	0.02	0.03	2.31		5.30	0.02-0.1
As	7.04		0.30	14.2	29.2		
Se	0.73			9.56			
Hg	0.04		0.001				
Cr	8.90		0.30	8.14	16.8		1.00

Table 1 Mean metal concentrations in surface waters of Changjiang River (μ g/L)

^aFrom Klavinš et al. (2000)

^bFrom Lithner (1989)

^cFrom Li and Zhang (2010)

^dFrom Krishna et al. (2009)

^eFrom Sakai et al. (1986)

Correlation between variables

The relationships between variables were analyzed by Pearson correlation matrix. The results were shown in Table 2. Only those with correlation values higher than 0.50 were considered and expressed in bold. In general, the high degree of correlation between element concentrations suggested either a common or a similar geochemical behavior origin (Kucuksezgin et al. 2008). From Table 2, it could be observed that Al, Fe, Ni, Co, Sc, Cu, Pb, and Zn exhibited significant correlation. Hakanson and Jansson (1983) suggested that even metals with quite different chemical properties 'in the laboratory' may appear with similar distribution patterns in nature, e.g., due to the fact that they are linked to the same type of 'carrier particles' with similar sedimentological properties. High positive correlations also existed between trace elements Al and chemical weathering elements Ca and Mg. The significant correlation between Al and the other variables (except As, Se, Cd, Cr, NO_3^- , and Hg) confirmed that these elements were associated with aluminosilicate minerals and other weathering effects (Rubio et al. 2000).

The correlation matrix between variables and major elements (Ca and Mg) showed that those variables are mostly due to industrial, agricultural, and other uncertain sources (Cd, As, Hg, Cr, Se, and NO_3^-) did not present any correlation with major elements. As' high positive correlations with Zn and Cd indicates anthropogenic activities as its sources. The absence of strong correlation among other variances suggests that the concentrations of these variances are not controlled by a single factor, such as Hg, Cr, Se, and NO_3^- (Jain et al. 2005).

Principal component analysis

PCA is a linear analysis technique used to reduce the dimensionality of a data set while attempting to preserve relationships present in the original data. It is often employed in data representation and data compression tasks, where representing a large data set in a smaller number of dimensions might be desirable. This method generates a new set of variables named principal component (PCs) as linear combination of the initial variables. The largest variance in the data set is described by PC1, while PC2, orthogonal to PC1, has the

Tabl	Table 2 Pearson correlation coef	n correlatio	on coefficient	fficient matrix of analyze variables for 76 samples	analyze v;	ariables fo	r 76 sample	es							
	As	Se	AI	Pb	Zn	Cu	Cd	Fe	Cr Ni	Ni	Hg Co	Co	Sc	NO_3^- Ca	Ca
As	1.000														
Se	0.080	1.000													
Al	0.414^{**}	-0.052	1.000												
Pb	0.461^{**}	-0.025	0.761^{**}	1.000											
t															

	\mathbf{As}	Se	Al	Pb	Zn	Cu	Cd	Fe	Cr	Ni	Hg	Co	Sc	NO_3^-	Ca	Mg
\mathbf{As}	1.000															
Se	0.080															
Al	0.414^{**}		1.000													
\mathbf{Pb}	0.461^{**}		0.761**	1.000												
Zn	0.502^{**}		0.718**	0.686**	1.000											
Cu	0.170		0.749^{**}	•**609*0	0.593**	1.000										
Cd	0.723**		0.379^{**}	0.402^{**}	0.664**	0.372^{**}	1.000									
Fe	0.259^{*}	0.102	0.845**	0.532**	0.747**	0.617**	0.384^{**}	1.000								
C	0.027		0.056	0.048	0.154	0.085	0.064	0.107	1.000							
ïŻ	0.208		0.910^{**}	0.617**	0.732**	0.737**	0.332^{**}	0.940^{**}	0.098	1.000						
Hg	0.056		0.097	-0.005	0.136	0.035	0.127	0.175	0.105	0.175	1.000					
Co	0.261^{*}		0.798**	0.485^{**}	0.758**	0.613**	0.429^{**}	0.987**	0.099	0.916**	0.160	1.000				
Sc	0.375		0.946**	0.802**	0.693**	0.685**	0.312^{**}	0.782**	0.087	0.872**	0.118	0.728**	1.000			
NO_3^-	-0.052		-0.194	-0.093	-0.063	-0.165	-0.015	-0.103	0.096	-0.134	-0.067	-0.062	-0.145			
Ca	0.170		0.537**	0.521**	0.459^{**}	0.422^{**}	0.225^{*}	0.454^{**}	0.130	0.540**	0.126	0.441^{**}	0.567**	0.182	1.000	
Mg	0.107	-0.021	0.653**	0.447^{**}	0.439^{**}	0.483^{**}	0.073	0.598**	0.060	0.689**	0.125	0.571**	0.677**		0.827**	1.000
> <i>d</i> **	$p < \check{C}0.01; *p < \check{C}0.05$	<Č0.05														

 Table 3 Loadings corresponding to the first four principal
components for PCA and contribution of each to the variable of the original data set

	Compone	ent		
	VF1	VF2	VF3	VF4
Ni	0.936	0.132	-0.086	0.180
Al	0.913	0.274	-0.151	0.001
Sc	0.907	0.212	-0.118	-0.012
Fe	0.853	0.219	-0.024	0.256
Co	0.817	0.254	0.042	0.266
Cu	0.750	0.199	-0.104	-0.016
Pb	0.708	0.398	-0.055	-0.223
Zn	0.680	0.572	0.055	0.150
Cd	0.212	0.886	0.139	0.121
As	0.165	0.848	-0.012	-0.070
Se	-0.022	0.257	0.775	0.090
Hg	0.083	0.012	-0.184	0.796
Cr	0.062	0.027	0.333	0.541
NO_3^-	-0.083	-0.097	0.758	-0.058
Ca	0.718	-0.056	0.441	-0.021
Mg	0.840	-0.207	0.149	0.005
Eigenvalue	6.765	2.402	1.619	1.200
Contribution	42.28%	15.01%	10.12%	7.50%
to total				
variance				

second maximum variance and so on. The elements of the eigenvectors in the PCA method are called weights; the eigenvalues represent the amount of original variance in each eigenvectors (Lu et al. 2007).

The results of PCA for total variable concentrations were shown in Table 3. Four rotated principal components (varifactors) with eigenvalues

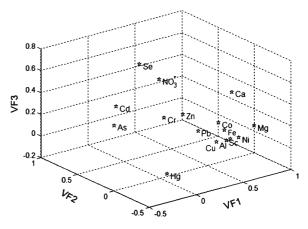


Fig. 5 Plot of loadings of the first three rotated principal components

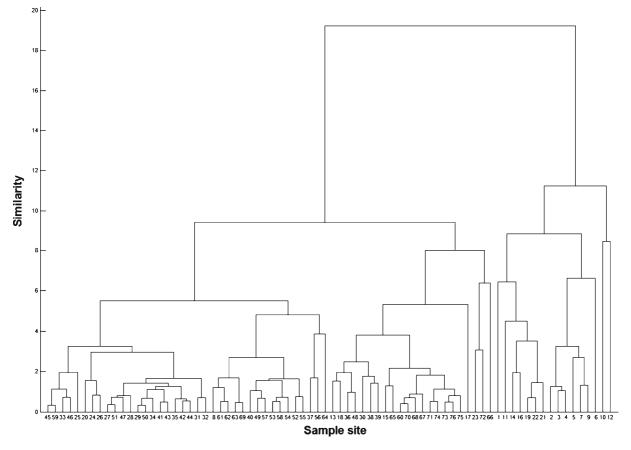


Fig. 6 Dendrogram obtained with the HCA for the 76 sampling sites in the Changjiang River (*Y*-axis indicates the relative similarity of different cluster groups; the lesser the distance, the greater the similarity between objects)

higher than 1 were extracted, which described 74.91% of the overall variance and revealed some strong trends of these elements. The varimax rotation was performed to address the problem of variables loading moderately (or equally) on one or more of the axes (Bengraine and Marhaba 2003). The graphic representation of the three former components was also shown in Fig. 5, where the associations between these variances could be seen. The first varifactor (VF1) showed that 42.28% of the total variance was correlated with Ni, Al, Sc, Fe, Co, Cu, Pb, Zn, Mg, and Ca. Parent rock and weathering conditions might be the source of this factor. The second varifactor (VF2) explained 15.02% of the total variance was mainly participated by Pb, Zn, Cd, and As and was considered as representing "anthropogenictoxic" pollutions from metal activities/industrial effluents. It was noteworthy that both Pb and Zn had high load in VF1 and VF2, indicating that mineral and rock erosion and anthropogenic pollution were all their sources. In addition, the high contents of these metals found in some samples confirmed a point pollution source, especially for Cd and As. The third varifactor (VF3) was mainly contributed by NO_3^- and Se, which might be related to the effects caused in the river by agriculture activities. Finally, Hg and Cr loaded in the fourth varifactor (VF4) presented different behavior without relation with any other variable.

Hierarchical cluster analysis

HCA was performed to identify the analogous behavior between the different sampling stations or between the measured variables. It is an unsupervised classification procedure that involves measuring either the distance or the similarity between the objects to be clustered. The resulting clusters of objects should then exhibit high internal (within cluster) homogeneity and high external (between clusters) heterogeneity (Kazi et al. 2009). The information of HCA results reflected in a two-dimensional plot called dendrogram which can be used to provide information on chemical behavior and verify the results obtained by PCA. In this study, HCA was performed on the normalized data set by means of the Ward's method, using squared Euclidean distances as a measure of similarity.

The results obtained with the HCA analysis were displayed in the dendrogram as shown in Fig. 6. As can be seen from this figure, all sites were first divided into two large groups. One includes the upper reaches sites and the other the middle and lower reaches sites. The upper group included waters with the highest concentrations of Cu, Ni, Fe, Co, Sc, Al, Ca, and Mg and high concentrations sites of Pb and Zn as well. The concentrations of this variance were two to three times high than that of the middle and lower reaches. At the same time, the concentrations of As, Cd, Se, Hg, and Cr also had one or two high sites in this group. This showed that the waters of this reaches was mainly affected by geological background, and the elements mainly come from weathering and erosion and followed by some other pollution sources such as atmospheric deposition and industry and agriculture point pollution.

The middle and lower reaches group was subdivided into three new groups. Group one presented the highest concentrations in variances with NO_3^- , Se, and Cr, which had an agricultural source. Group two included waters of regions with high concentrations of Pb and Zn, which presented some industry sources. Finally, As, Cd, Zn, Pb, Hg, and Cr had some high sites in group three, which indicated that this river reach had different pollution sources, including anthropogenic, industrial, and other factors. Group three mainly included the lower reaches of the Changjiang where industry and shipping developed rapidly. Meanwhile, there was also dense population in basin area, indicating various artificial pollutions.

Conclusions

In this study, the water quality of Changjiang River was established by analyzing dissolved heavy metal, as well as other parameters such as major elements (Ca and Mg) and nutrient (NO_3^-) . PCA helped to identify that Cu, Ni, Fe, Co, Sc, Al, Ca, and Mg were mainly associated with the weathering and erosion. As and Cd were isolated in another principal component, indicating anthropogenic origin, and the highest concentration were all measured in the vicinity of power plant and industrial zone. While the sources of Pb and Zn can be attributed to both geological background and anthropogenic factors. Pb, in particular, was possibly input through aerial deposition. Meanwhile, NO_3^- and Se showed the influence of agriculture activities. But Hg and Cr show different sources. Cluster analysis was used to identify those sampling points which were most affected by background and many other sources (including industrial or agricultural influence). It grouped together those samples (sites 1-22) with highest levels of Cu, Ni, Fe, Co, Sc, Al, Ca, and Mg which represents sites where erosion of rocks and minerals were quite important. The other group was industrial and agricultural zones, which was subdivided into three groups. Group one with high concentration of NO₃⁻, Se, and Cr was affected by agriculture; while sites with high concentration of As, Cd, Zn, Pb, Hg, and Cr were in the other two subgroups, where urban and industrial wastewaters and other pollution sources were the origin of the river pollution.

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