

Application of chemometrics methods for the estimation of heavy metals contamination in river sediments

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Abstract: The concentration and speciation of six heavy metals in sediments of eight sampling sites of Haihe River were investigated. The metals, namely Cd, Cu, Co, Ni, Mn and Pb were considered. By using sequential extraction (SE), the total metals were divided into five fractions: exchangeable, carbonate bound, iron/manganese oxide bound, sulfides and organic matter fraction and residual fraction. A multivariate statistical approach (principal component analysis, PCA) was used to evaluate the contamination of heavy metals by the total levels and chemical forms, respectively. The results showed that the total metals concentration (TMC) could not provide sufficient and accurate information because the mobility, bioavailability and toxicity of metals depend not only on their total concentration but also on the physicochemical form in which they occur.

Keywords: speciation; heavy metal; principal component analysis

Introduction

Excessive heavy metals in the environment are toxic to organisms, resulting in disturbance of the ecosystem (Kunito, 1999). As a sink and source, sediment constitute reservoir of the bioavailable trace elements. It is important to investigate the concentration of heavy metals in the sediment. However, the total metals concentration (TMC) cannot provide sufficient and accurate information because the mobility, bioavailability and toxicity of metals depend not only on their total concentration but also on the physicochemical form in which they occur. Examination of toxic heavy metals has special importance in environment samples (Novotry, 2000; Abollino, 2000). Thus, there is a crucial need to develop trace element analysis methods that allow separation of the different element species prior to trace element analysis. It is now widely accepted that the study of metal distribution in different sediment phases, by applying sequential extraction (SE) schemes, may help to predict metal behaviour, giving information about the mobility of metals and the possible transfer from sediment to the aquatic media (Forstner, 1979; Martin, 1998; Akcay, 2003).

Chemical speciation can be defined as the identification and quantification of the different species, forms or phases present in a material, or the description of these. However, the determination of specific chemical species or binding forms is difficult and often hardly possible (Loska, 2002). So, determinations of broader forms can be a good compromise to give information on environmental contamination risks. As a result, single and SE schemes have been designed for the determination of binding forms of trace metals in sediments (Quevauviller, 1994; Lima, 2001).

Many SE methods have been reported, which are variants on the procedure by Tessier (Tessier, 1979) and Kersten (Kersten, 1986). Following the two basic schemes, some modified procedures including the BCR method (Ure, 1993) were developed. According to the proposed method, heavy metals were separated into five different fractions in this paper: exchangeable (F1), carbonate (F2), iron/manganese oxides (F3), sulfides and organic matter (F4),

residue fractions (F5).

Considering the above discussed facts, the primary objectives of the present study were to establish the environmental pollution levels for some major heavy metals (Cd, Cu, Co, Ni, Mn and Pb), to compare the difference of two kinds of results by using the data matrix of TMC and metals distribution in different sediment phases by multivariate statistical approach principal components analysis (PCA). PCA is an important chemometrics tool that seeks to establish combinations of variables capable of describing the principal data tendencies observed. In mathematical terms, PCA relies upon an eigenvector decomposition of the covariance or correlation matrix. The technique has received numerous applications in environmental studies (Morales, 1999; Planquart, 1999; Osún, 2001; Abollino, 2002; Brodnjak-Voncina, 2002; Álvarez-Iglesias, 2003; Farnham, 2003; Beldowski, 2003).

Haihe River is a famous river in north China and locates in Tianjin that has a long history as an industrial city. It receives input of industrial, agricultural and domestic effluents and sends them into the Bohai Sea at Tanggu influx. In our study, eight sampling sites (S1—S8) were selected along Haihe River and the sediment samples were submitted to the proposed SE procedure to obtain the distribution patterns of metals.

1 Materials and methods

1.1 Study sites and sampling

Sediments sampling was carried out on April 8 and 9, 2003. Sampling sites are shown in Fig. 1. Wherein, R1 is located at the estuary of Haihe River, R2, R4 and R5 are located at the area between Tianjin and Tanggu cities, R6 belongs to urban of Tianjin, R3, R7 and R8 are situated in three source rivers, respectively.

1.2 Analytical techniques

Elements were determined by graphite furnace atomic absorption spectrometry using a Hitachi Z5700 Polarized Zeeman spectrometer, equipped with single element hollow-cathode lamps and autosampler. Zeeman background correction was used for all analyses in the experiment.

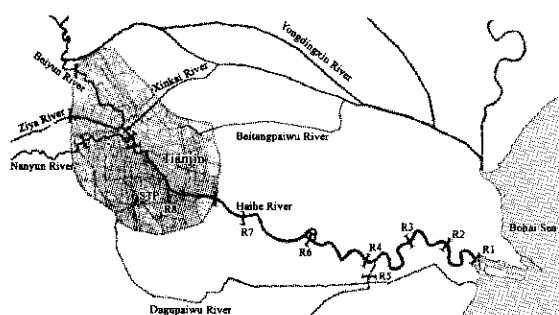


Fig.1 Map of study area and sampling sites

Palladium modification (200 mg/L) was preferred for the determination of cadmium and lead. Analytes were determined at the following wavelengths (nm): Cd 228.8; Cu 327.4; Co 240.7; Ni 232.0; Mn 280.1; Pb 283.3.

The analytical quality assurance can be seen in our previous work (Yuan, 2004). The SE procedure is illustrated as follows:

F1: 20 ml 1 mol/L NH_4OAc at initial pH 7 was added to 0.5 g dry sediment in a 50 ml centrifuge tube. The mixture was shaken for 2 h at room temperature. 20 ml volume 1 mol/L NaOAc buffered to pH 5.0 with HOAc was added to the residue from the above step and stirred for 5 h at room temperature.

F2: The residue from step two was extracted with 20 ml 0.1 mol/L $\text{NH}_4\text{OH}\cdot\text{HCl}$ (adjusted to pH 2 with HNO_3). The tube was then shaken for 16 h at room temperature.

F3: 5 ml 30% H_2O_2 (pH 2.0 adjusted with HNO_3) was added to the residue from step three. The digestion procedure lasted for 1 h at room temperature with occasional manual shaking. Then the centrifuge tube was put into an 85°C water bath for 1 h. A second 5 ml aliquot of H_2O_2 was added and the tube was again heated to 85°C for 1 h. 20 ml 1 mol/L NH_4OAc (adjusted to pH 2.0 with HNO_3) was added to the cool, moist residue. Then the tube was shaken for 16 h at room temperature.

Metals bound to iron/manganese oxide fraction are unstable under reducing (anoxic) conditions. These conditions result in the release of metal ions to the dissolved fraction.

F4: The residue from step four was freeze-dried and 0.1000 g(dw) of residue was weighted into a 30 ml Teflon container with seal and then 2 ml concentrated HNO_3 , 0.5 ml HF were added in sequence. The container was heated at 180°C for 8 h.

F5: At the end of each extraction step, the extract was separated by centrifugation and 10 ml deionized water was used to wash the residue by shaking for 15 min. Then the tube was centrifuged, and the supernatant was decanted. To obtain TMC in the samples, the total digestion procedure similar to the fifth step was applied. Compared to the fifth step extraction, 2 ml hydrogen peroxide was added to accelerate destruction of organic components in samples during the total digestion procedure.

1.3 Statistical analysis

Principal component analysis (PCA) on the analytical data was executed in order to obtain a visual representation of the main characteristics and of metal distribution in the

sediments, which would be more difficult to detect just observing the numbers in the tables. It is an unsupervised multivariate technique in which new variables (called principal components (PCs)) are calculated as linear combinations of the olds ones. When most of the variation is explained by the first two or three components, a two or three-dimensional scattergram, plotting the values for the first two or three principal components of the data points, gives essential features of the multidimensional scatter. So, it is possible to show the information by plotting the first two or three PCs (in this case, usually PC1 and PC2 which eigenvalues are > 1 , are considered to represent the main examined objects and variables). The combined plot of scores and loadings allow us to recognize groups of samples with similar behaviour and the existing correlation among the original variables. In this paper, PCA and correlation analysis were performed with SPSS 12.0 for Windows Release 12.0.0(4 Sep. 2003, SPSS Inc., 1989—2003).

2 Results and discussion

2.1 Metal concentration

Six heavy metal levels in the sediment of eight sampling sites are outlined in Table 1. The results of the Haihe River sediment samples were obtained from the proposed SE scheme.

Table 1 Results for the total metals concentration (TMC) of the sediment samples ($\mu\text{g/g dw}$)

Site	Cd	Cu	Co	Ni	Mn	Pb
1	1.62	45.72	18.64	35.66	897.96	35.77
2	1.13	29.85	16.66	36.85	742.70	29.00
3	0.98	27.75	13.85	35.44	719.24	17.71
4	1.62	36.12	13.70	29.04	744.29	18.26
5	0.86	33.25	17.66	38.13	753.71	45.58
6	2.01	33.06	16.17	31.61	675.95	35.82
7	0.79	29.60	15.86	35.66	479.82	30.36
8	1.35	37.51	19.63	43.93	910.90	33.14

From Table 1 it can be seen that TMC of six metals of S3 and S7 (which locate the branch rivers of Haihe River) are lower than other sampling sites, which show that Ziya River and Machangjian River do not affect the heavy metal contamination levels of Haihe River.

The chemical speciation data showed that the sum metal concentration of F1, F2, F3 and F4 (S_{F1-F4}) that have more pollution risk are not significant in TMC.

Table 2 Correlation matrix (using the total metal concentration (TMC))

	Cd	Cu	Co	Ni	Mn	Pb
Cd	1.000					
Cu	0.533	1.000				
Co	0.055	0.569	1.000			
Ni	-0.436	0.075	0.759*	1.000		
Mn	0.365	0.697	0.564	0.406	1.000	
Pb	-0.034	0.299	0.742*	0.414	0.157	1.000

Note: Correlation is significant at the 0.05 level

Comparing with other heavy metals, the mean percentage of nonresidual fractions of Cd and Ni of eight sampling sites are the highest (46.31% and 41.47%). The amount of Cd and Ni in each fraction followed the order: residual > exchangeable > carbonate > Fe-Mn oxide bound > organic, which is similar to the previous study (Ma, 1997).

While the mean Cu concentration of sum of nonresidual fraction of eight sampling sites is the lowest (only 9.35%).

This means that there is no pollution risk and the fractionation pattern is correlation with other literature data (Boughriet, 1992; Akcay, 2003).

The percentage of Co- S_{F1-F4} is changed between 19.11% and 39.22%. This is different from the study of the heavy metal pollution in Buyak Menderes River and Gediz River sediments by Akcay et al. (the first three fractions(F1 + F2 + F3) amount $\geq 57\%$ for Gediz River and $\geq 68\%$ for Buyak Menderes River) (Akcay, 2003). The same information is also for Mn since the mean Mn- S_{F1-F4} is 38.11% (in the reference(Akcay, 2003), F1 + F2 + F3 of Mn is 67%).

Our study for Pb is similar to the study by Akcay et al, which shows that the sediment Pb is found in the last two fractions(F4 + F5) in Buyak Menderes River. But this study is different from the Gediz River sediment (it is found abundantly in the first three fractions(F1 + F2 + F3 $\geq 52\%$) which means that Gediz River has a Pb pollution risk) as the mean percentage of Pb- S_{F1-F4} is 16.94%.

2.2 Multi-element data treatment

Because metals in the residue fraction(F5) are safer to environment for their lowest mobility and bioavailability, the data measured in this experiment are analyzed by using the data matrix of TMC and metals distribution in different sediment phases (S_{F1-F4}), respectively. The purpose is to compare the difference by using the two kinds of data to evaluate environmental pollution levels for multivariate analysis.

2.2.1 Correlation analysis

In order to establish inter-element relationships in sediment samples, correlation coefficients for the six metals were calculated. Table 2 and Table 3 are the correlation coefficients for the six metals. In Table 2, a significant correlation was found between Co—Ni ($R = 0.759, P < 0.05$) and Co—Pb ($R = 0.742, P < 0.05$), while in Table 3, a significant correlation was found between Co—Ni ($R = 0.712, P < 0.05$) and Co—Mn ($R = 0.870, P < 0.05$). No other metals were significantly correlated with each other. The significant correlation between the metals that have synergy effects indicates a common source for these metals.

Table 3 Correlation matrix(using the data of S_{F1-F4}).

	Cd	Cu	Co	Ni	Mn	Pb
Cd	1.000					
Cu	0.626	1.000				
Co	0.682	0.622	1.000			
Ni	0.645	0.522	0.712*	1.000		
Mn	0.467	0.470	0.870*	0.678	1.000	
Pb	0.439	0.199	-0.150	0.367	-0.327	1.000

Note: Correlation is significant at the 0.05 level

2.2.2 Principal component analysis by TMC

A Varimax with Kaiser Normalization rotation was used performed to secure increased PCs significance(Kaiser, 1958). Fig.2 is the combined plot obtained by PCA for TMC. The results (Fig. 2a) show that PC1 is positive by the total concentration of Co, Ni and Pb(loadings 0.91, 0.91 and 0.73 for Co, Ni and Pb, respectively) and negatively by the total concentration of Cd. It accounts for 49.2% of the total variance. PC2 accounts for 29.8% of the total variance and is characterized by Cd, Cu and Mn(loading 0.85, 0.88 and 0.72 for Cd, Cu and Mn, respectively). In the plot of PC1 vs. PC2

(Fig.2b), it is interesting that it is possible to note one group of S1 and S8, which locates headwater and downriver of the section of Haihe River we select. It is evident by Fig.2b that S1 and S8 are characterized by high percentages of Co, Ni and Pb(S1 is also characterized by high percentages of Cd, Cu and Mn). From Fig.2b it can be seen S7 is not characterized by any heavy metal, which shows that by using TMC, as the branch of Haihe River, the contamination of heavy metal is seemly not serious in Ziya River.

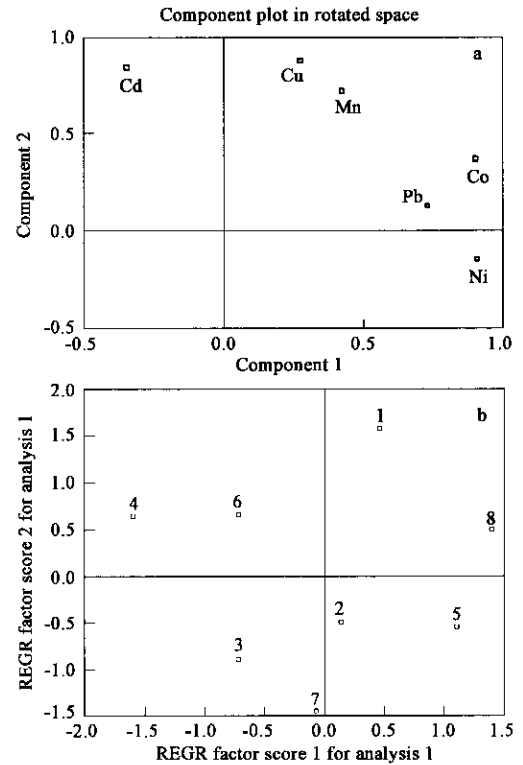


Fig.2 Biplot of the principal component analysis by using TMC a. PC1 vs. PC2; b. the loading point on PC1-PC2

2.2.3 Principal component analysis by the data of speciation

It is interesting to note that in the plot of the loading points on PC1-PC2 from the data matrix of the concentration of extracted metals in five SE procedures(Fig.3). The points of metals concentration are obviously divided into two groups: one is F1, F2, F3 and F4 and the other is F5 of eight sampling sites. This also shows that F5, depending on the

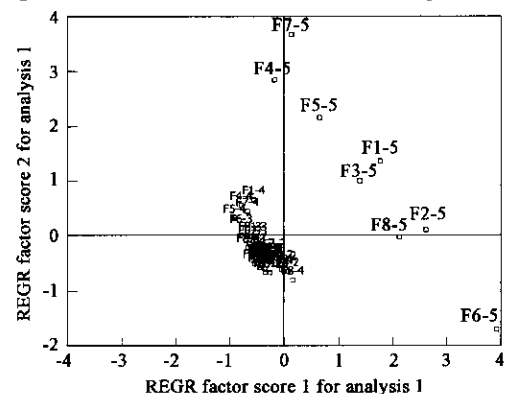


Fig.3 The loading points on PC1-PC2 from the data of the percentages of extracted metals in the five SE procedures

mobility and bioavailability, which is safer to the environment, is different from F1, F2, F3, and F4.

Further statistical analysis was carried out by using the data matrix of S_{F1-F4} and concentration of F5 to evaluate the correlations among the metals distribution in different sediment phases. Fig. 4 shows the relationships between S_{F1-F4} and concentration of F5. It can be seen that Cd-F5 and Cu-F5 are correlated with Cd- S_{F1-F4} and Cu- S_{F1-F4} ,

respectively ($R = 0.729, P = 0.04$; $R = 0.759, P = 0.03$ (Fig. 4a and Fig. 4b)). The significant correlations between the two kinds of fraction of Cd and Cu indicate that there is a synergy effect with each other. However there is a negative correlation coefficient between Ni-F5 and Ni- S_{F1-F4} in Fig. 4d, which shows that the possible existence of Ni-F5 and Ni- S_{F1-F4} is "antagonistic".

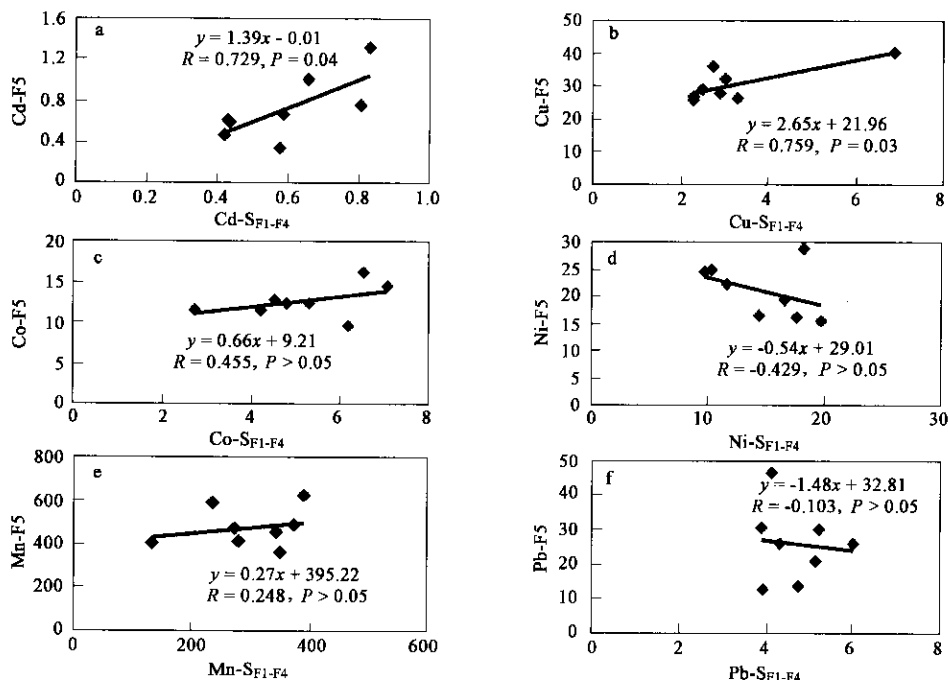


Fig.4 The relationships between the sum of concentration of F1, F2, F3 and F4(S_{F1-F4}) and concentration of F5

Also, PC1 vs. PC2 and the scores of eight sampling sites on the first two PC basing on the data matrix of S_{F1-F4} are plotted as a scatter diagram in Fig.5. The results show that PC1 is positively determined by Cd, Cu, Co, Ni and Mn (loading 0.78, 0.74, 0.95, 0.84 and 0.87 for Cd, Cu, Co, Ni and Mn, respectively), and it accounts for 59.2% of the total variance; PC2 accounts for 24.6% of the total variance and is characterized by Pb (loading 0.98 for Pb) (Fig.5a). In Fig.5b, S1 is characterized by percentages of Cd, Cu, Co, Ni and Mn, which is similar with Fig. 2b. Then it can be seen that S1 is the most contaminated site by heavy metals among eight sampling sites no matter what analytical method we use.

However, characterizations of S6, S7 and S8 are different from Fig.2b(in Fig.5b, S6 is characterized by high percentage of Pb, S7 by percentage of Pb and S8 is not significantly contaminated by heavy metals; while in Fig. 2b, the contamination of S6 and S7 is not serious and S8 is characterized by Co, Ni and Pb). We suggest that when evaluating the contamination of heavy metals, speciation analysis is more effective than only using TMC.

3 Conclusions

TMC in eight investigated sampling sites of Haihe River are determined. The results show that the contamination of heavy metals, namely Cd, Cu, Co, Ni, Mn and Pb, are not very serious. Of course the results of this study apply to only a limited zone of the considered river, because of the

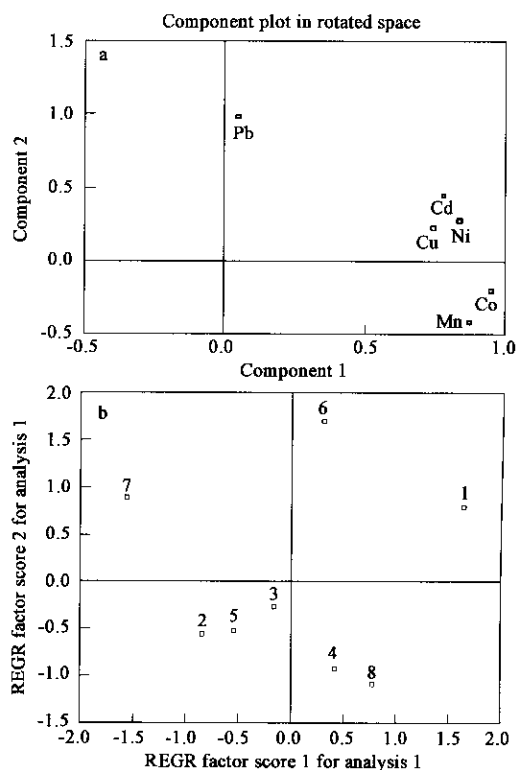


Fig.5 Biplot of the principal component analysis by using the sum metals concentration of F1 to F4(S_{F1-F4}) a. PC1 vs. PC2; b. the loading points on PC1-PC2

restricted number of samples. The main goal of the investigation is to compare the difference of using TMC and using metals distribution in different sediment phases to evaluate the heavy metals pollution levels of Haihe River.

For this reason metal speciation and mobility are studied with Tessier's SE procedure. The mobility of these metals is related to their solubility and geochemical forms, and it decrease in the order of extraction sequence: exchangeable > carbonate bound > iron/manganese oxide bound > sulfides and organic matter fraction > residual fraction. This order is just a generalization and offers only qualitative information on metal mobility. PCA and correlation analysis based on the data of TMC and metals distribution in different sediment phases are used, respectively. It indicates characterizations of the same sampling sites are different by using two evaluated methods. However, R1 is contaminated most by heavy metals among eight sampling sites no matter what analytical method we use though it is characterized by high percentages of Cd, Cu, Co, Ni, Mn and Pb in Fig. 2 and by Cd, Cu, Co, Ni and Mn, since there is a Dagupaiwu River which discharge industrial effluent to Haihe River.

For all these reasons above, it seems that speciation analysis is more effective than only using TMC for helping in understanding geochemical processes and it also allows one to assess the potential for remobilization with changes in surrounding chemistry, the bioavailability of an element and the signature of multiple sources (Tack, 1995; Hall, 1996).

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