BioTechnology

An Indian Journal

Determination of heavy metals in inner continental shelf near the Pearl River estuary by BCR sequential extraction method

LinglongCao[1,2], Ping Shi[1]*, JianXie[1], HaitaoTian[1], LiangWang[1]

[1]South China Sea Marine Engineering and Environment Institute, SOA, Guangzhou Guangdong 510300, (P.R.CHINA)

[2]School of Earth Sciences and engineering geology, Guangdong Provincial Key Laboratory of Geological Processes and Mineral Resource Exploration, SunYat-sen University, Guangzhou Guangdong 510275, (P.R.CHINA)

E-mail : pshisoa@163.com

ABSTRACT

Utilizing the sequential extraction procedure(acid soluble, reducible, oxidizable, and residual) proposedby The European Community Bureau of Reference (BCR),the metals present in the sediments of the inner continental shelf nearthe Pearl River Estuary (IPRE)were determined. The sediment sampleswere collected from 22 sampling sites and analyzed toidentify the concentrations ofCr, Ni, Cu, Pb Zn, Cd and As. Results show the contents of selected metals decreases from land to sea as the water depth increase. As the results of BCR sequential extraction showed in the area, Cr,Ni,Cu and As appear mainly as the residual form and thus of low bioavailability, Cd appears mainly in acid-soluble formand thus of high potential mobility, Pb appears mainly as reducible form, Zn appears mainly in residual form and acid-soluble form. The order of migration and transformation sequence was Cd >Pb> Zn> Cu>Ni>As>Cr and the same order as the degree of pollution. Correlation and principal component analyses indicate that most ofthe metals primarilyoriginate from natural sources, and then from anthropogenic activities.

KEYWORDS

Heavy metal; Speciation; BCR; Source analysis; Inner continental shelf.

INTRODUCTION

With high geochemical availability, heavy metals easily migrate among waters, suspended matter, and sediments through absorption and desorption of suspended particles, biological uptake, and exchange reactions between the water-sediment interface[1-3]. The environmental behavior, bioavailability, and toxicity of metals in surface sediments are not only correlated with total concentration but with speciation, which is an important index indicating the toxic and ecological risk of heavy metals[4,5]. Different speciation has different activity, biological toxicity, and migration characteristics[6]. Therefore, the sequential extraction procedures havebeen designed for the selective extraction of metalsbonded to the soil and sediments in different fractions[7]. Thus, spatial surveys of metal concentrations in the sediments are useful to assess pollution in themarine environment and to provide basic information for the judgment of environmental health risks.

MATERIALS AND METHODS

Sampling and sediment pretreatment

22 surface sediment samplings were takenin the inner continental shelf nearthe Pearl River Estuary(IPRE)from May 2011, and collected inbrown glass bottles and polyethylene bags and stored at low temperature (-20°C) for further experiments. Upon analysis, samples were defrosted and air-dried in an oven at 60°C to constant weight, then ground to a powder using an agate mortar and pestle, and sieved to collect the <63 um grain size fraction for homogenization. Approximately 0.5 g of dried and homogenized sediment samples were weighed and placed into an acid washed PTFE digestion, using the established US EPA method 200.2 protocols[8].
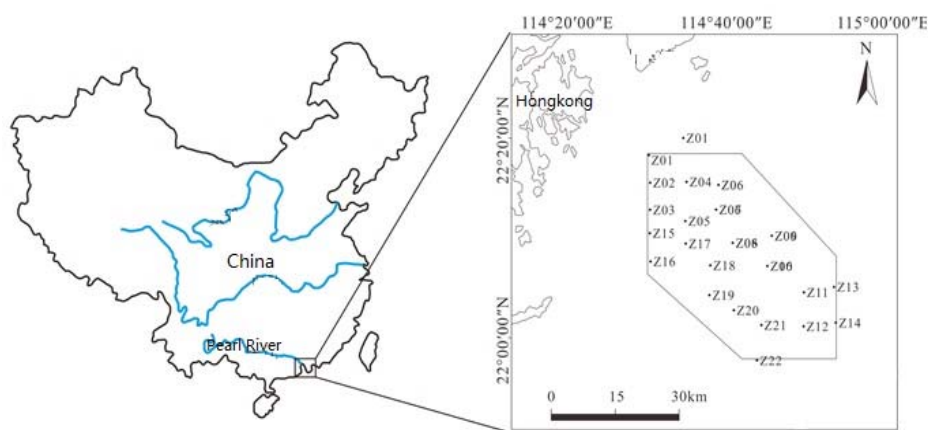

Figure 1 : Distributions of sampling stations

Analysis

Total concentrations and phase partitioning of metals

The concentrations of Cr, Ni, Cu, Pb, Zn, Cd and As were all detected by inductively coupled plasma-mass spectrometry (ICP-MAS). The optimized BCR sequential extraction procedure reported by Rauret[9] was used to partition the metals into four geochemical parts as acid-soluble (F1), reducible (F2), oxidizable (F3) and residual (R) fractions. The detailed procedures for the sequential extraction used in this study have been described elsewhere[10].

Particle size and total organic carbon

The analysis ofgranularity was performed using Malven Laser Mastersizer 2000 Particle Size Analyzer-MS 2000 (0.02-2,000um). Total organic carbon (TOC) content of the sedimentsamples was determined by loss on ignition method using a CHENS Elemental Analyzer -Varia EL.

Quality control

The analysis results were deemed reliable when repeat sample analysis error was below 5%, and the relative standarddeviation of samples was within ±10%. The recovery rates for all of the metals between 83-116%. The results of standardsubstance samples all met the standard values.

RESULTS AND DISCUSSION

Distribution of total metals

The spatial distribution variation of metals in surface sediments in IPRE is widely distributed and presentedin Figure 2, which shows a descend trend from the land to seaas the water depth increase. Except forAs, other metals appearsunusual enrichment area in the southwest of the study area, speculating that the sampling station may fall dumping dredged area. The total amount of Cd distribution fragmented in this area, with no apparent regularity.
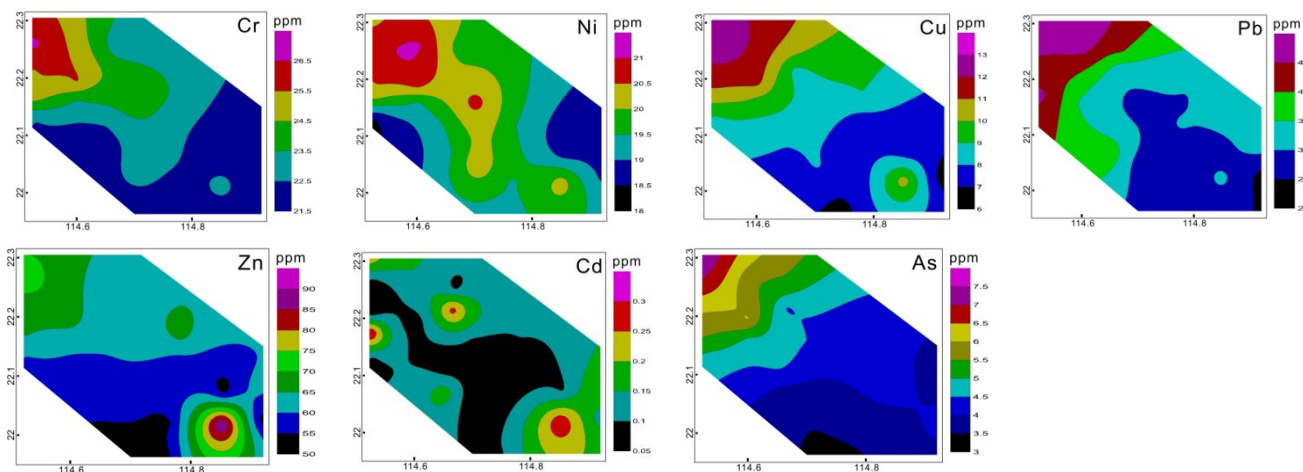

Figure 2 : Content of the heavy metals in study area

The percentages of metals from each extraction step are presented in Figure 3. The residual fraction (R) was the main speciation for Cr, Ni, Cu, As. In addition, for Pb, the amount bound to reducible fraction (F2). Cd was dominated by acid-soluble fraction (F1), andZn mainly between R and F2. The R behavior is the most stable, mainly bound with the crystal lattices of silicate, can only be released during the weathering process, so it is basically biological no bioavailability because the weathering process is much longer than the life period. The F2 fraction is the part of the heavy metals bindingstate of Fe/Mn oxide or hydroxide precipitation, which is difficult to release due to strong ionic wrapping. However, if the Eh and oxygen in seawater decreased, it may deoxidize and cause secondary pollution, also reflecting the pollution of the human activities to the environment. The heavy metals bound to exchangeable fractions in F1includes water soluble, ion exchange and carbonate binding state were absorbed in clay and humus, which wassensitive to environmental changes and easier migration and transformationunder acidic conditions. Based on the concentrations of fractions in each step of extraction, the sequence form is in decreasing order, as follows:

Cr:R(58.69%)> F2(28.04%)>F3(12.52%)> F1(0.75%)
Ni:R(46.86%)> F2(30.24%)>F3(14.04%)> F1(8.86%)
Cu:R(46.35%)> F2(38.19%)> F3(10.74%)> F1(4.72%)
Pb:F2(64.42%)>R(15.33%)> F3(10.19%)> F1(10.06%)
Zn:F2(46.61%)>R(40.91%)> F3(6.92%)> F1(5.56%)
Cd:F1(52.72%)>F2(27.43%)>R(19.98%)> F3(6.87%)
As:R(53.07%)> F2(34.99%)> F1(6.32%)> F3(5.63%)

Therefore, the order of heavy metals migration ability in IPRE surface sediments was Cd >Pb> Zn> Cu>Ni>As>Cr.
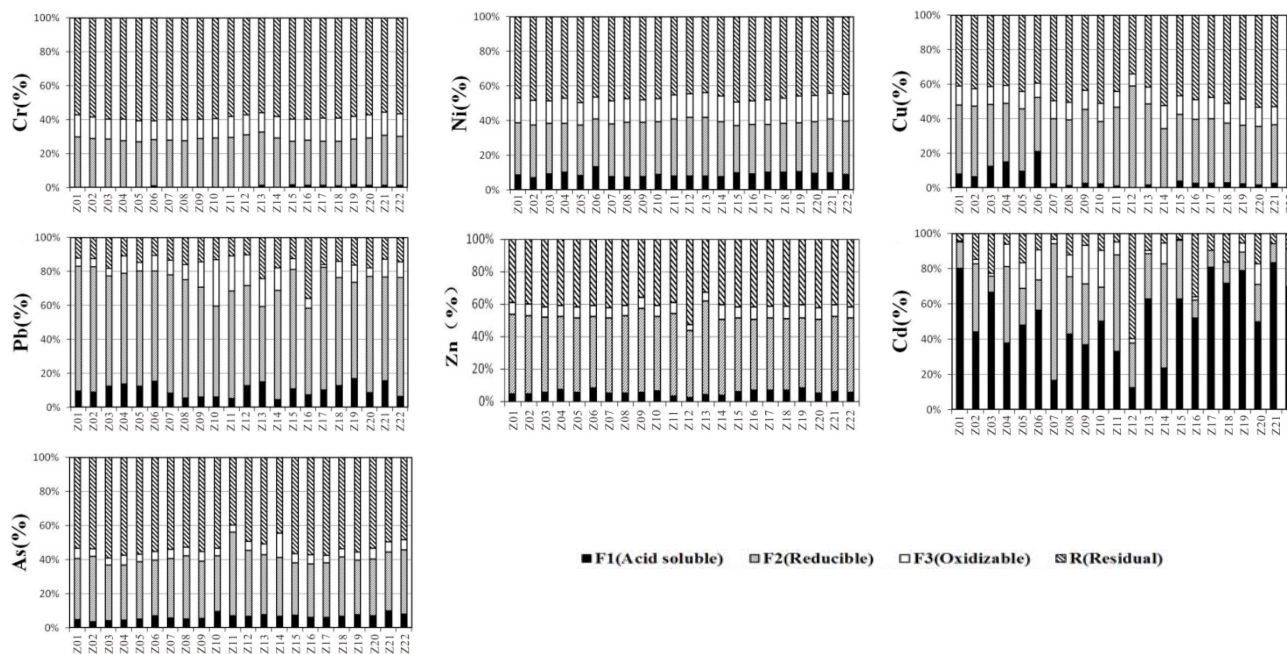

Figure 3 : The distribution in different geochemical fractions of surface sediments

It is widely known that the higher percent of non-residual (F1+F2+F3) fractions the sediments contain, the easier heavy metals can be released and the higher bioavailability heavy metals have. In traditional geochemistry, the primary mineral in particles was called the primary phase and the weathering products, such as R. Secondary metabolites, such as F1, F2 and F3, were called the secondary phase. The non-residual rateof 7 studied metals decreased in the sequence of Cd(87.02%)>Pb(84.46%)>Zn(59.09%)>Cu(53.65%)>Ni(53.16%)>As(46.93%)>Cr(41.31%), the same as the order of heavy metal migration in IPRE.

Correlations

The correlation analysis was performed to determine therelationships between the sediment characteristics (TOC,Mn-F2,Fe-F2,clay,Mz and depth) and the extracted heavymetals of each fraction by IBM SPSS 19.0. As shown in TABLE 1(**p < 0.01 and *p < 0.05), the analysis results were followed.

(1)ForCr,strong linear relationshipswere observed betweenthe Fe-F2, Mn-F2 and F2 fraction. The F2 were significant correlated with TOC,clay,Mz and depth, and R withMz(r=0.528, p<0.05) and depth(r=0.871, p<0.01). The similaranalysisisappear in Nithat R were significant correlated withMz(r=0.581, p<0.01) and depth(r=-0.803, p<0.01). Therefore, themain factors influencingCr and Ni in IPRE wereMz and depth because Cr was mainly composed of the R fraction.

(2) The four different fraction of Cu have significant negative correlationwithdepth, indicating variation of depth in study area may play important role in distribution of Cu. The R of Cu and As were all poses significance correlations toclay,Mz and depth. Therefore, themain factors influencing Cu and As in this area wereclay, Mz and depth because they all were mainly composed of the R fraction.

(3)For Pb, the F2 fraction were mainly significantly correlated withMn-F2, Fe-F2 clay, Mz and depth, but for the other three fractions,only F1 and R correlated with depth at the p < 0.01 level. Therefore, themain factors influencing Pb in IPRE were Mn-F2, Fe-F2clay, Mz and depth because Pb was mainly composed of the F2 fraction.

TABLE 1 : Correlation between different fractions and other environmental factors

F1	Cr	Ni	Cu	Pb	Zn	Cd	As
TOC	ns	ns	-0.521*	ns	ns	ns	ns
Depth	ns	ns	-0.657**	-0.481*	-0.633**	ns	ns
F2	**Cr**	**Ni**	**Cu**	**Pb**	**Zn**	**Cd**	**As**
TOC	ns	ns	ns	ns	ns	ns	ns
Mn-F2	0.766**	ns	0.556**	0.847**	0.445*	ns	0.807**
Fe-F2	0.856**	ns	0.632**	0.828**	0.544*	ns	0.828**
Clay	ns	ns	ns	0.576**	ns	ns	0.488*
Mz	ns	ns	ns	0.510*	ns	ns	ns
Depth	ns	ns	-0.450	-0.861**	ns	ns	-0.652**
F3	**Cr**	**Ni**	**Cu**	**Pb**	**Zn**	**Cd**	**As**
TOC	0.567**	0.514*	ns	ns	ns	ns	ns
Clay	0.532*	ns	0.676**	ns	0.584**	ns	ns
Mz	0.795**	0.467	0.725**	-0.589**	0.546*	-0.483*	ns
Depth	-0.512*	ns	-0.812**	ns	-0.677**	ns	ns
R	Cr	Ni	Cu	Pb	Zn	Cd	As
Clay	ns	ns	0.546**	ns	ns	ns	0.614**
Mz	0.528*	0.581**	0.728**	ns	ns	ns	0.515*
Depth	-0.871**	-0.803**	-0.867**	-0.328	ns	ns	-0.934**

ns correlation is not significant

(4) For Zn, F3showed significantly correlations to clay with the correlation coefficients of 0.584(p<0.01), Mz with the correlation coefficients of 0.546 (p<0.05) and depth with the negative correlation coefficients of -0.677 (p<0.01) respectively. The F2 was correlated with Mn-F2 (r=0.445, p<0.05), and Fe-F2 (r=0.544, p<0.05). Therefore,Mn-F2 and Fe-F2 mainly affected the distribution of Zn becausethe main fraction of Zn was F2 in this area.
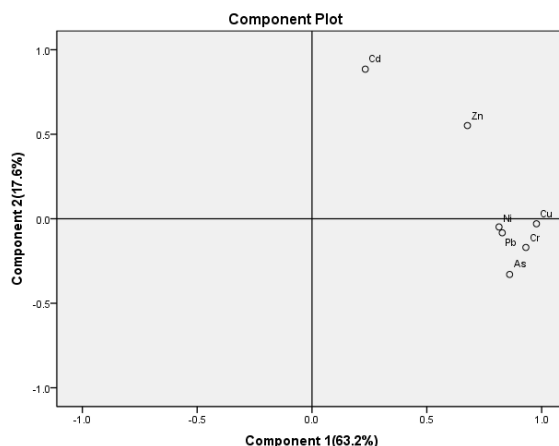

Figure 4 : The principal component analysis loading plot of metallic elements.

Principal component analysis(PCA)

To further analyze the general characteristic of the sediments inthe studied region, multivariate PrincipalComponent Analysis (PCA) were conducted. PCA analysis incorporates the seven metal concentration data of all sampling stations and exploresthe possible similar distribution behavior of metals. In our studythe two principal components (PCs) extracted together explained80.8% (PC1: 63.2%；PC2:17.6%) of the metal variance. The principalcomponent analysis loading plot (Figure 4)

showed that these metalswere classified into Group 1 (Cr, Ni,Cu, Pb and As) and Group 2 (Cd and Zn)according to the similarities in behavior and the distribution ofthose metals in sediments. Firstly, all the five metals were strongly associated with PC1 (positive loading), especially Cu,Cr,As and Niwere mainly present in R fraction reflecting the lithogenic origin, soPC1 is supposed to reflect the contribution of natural geologicalsources of metals into the coastal sediments. Then, the PCA resultsshow that Cdand Zn diverged far from Group 2, and were mainly present in F1 and F2 fraction respectively. It is reported that input of Cd and Zn to the oceans is dominated byriverine sources[6]. So these metals wouldbe due to anthropogenic inputs from riverine sources containingboth some natural component in the water and sediment and asubstantial proportion of anthropogenic waste ended up into estuaries and continental margins of the oceans.

CONCLUSION

The purpose of this study was to assess the pollution status ofsome selected metals (Cr, Ni, Cu, Pb, Zn, Cd and As) using a combination of multivariate statistical analyses, sequential extraction dataand the ecological risk indexesin surface sediments collected fromIPRE. Geochemical fractional results of the sediment samplesrevealed that the Cd,Pb and Zn with high acid-solublefraction created higher environmental risks and exertedvarious negative impacts on the aquatic biota. Metals (Cr, Ni, Cu and As), onthe other hand, most often existed inresidual form thus of low bioavailability. Such a scenario indicates thatthe partly metals were highly mobile and potentially available foraquatic organisms in the river and consequently poseserious risks to the environment. The high mobility of themetals most often results from the natural sourcesand anthropogenic impacts. Withregard to environmental pollution, the BCR sequentialextraction method, which provides crucial informationregarding metal mobility and bioavailability, warrantsfurther implementation in different, terrestrial and aquaticareas.

ACKNOWLEDGEMENTS

REFERENCES

[1] L.L.Cao, P.Wang, H.T.Tian; Distribution and ecological evaluation of heavy metalsin multi-medium of DongzhaiHarbor. Marine Science Bulletin, **32(4)**, 403-407 **(2013)**.
[2] T.El-Hasan, A.Jiries; Heavy metal distribution in valley sediments in Wadi Al-Karak catchment area, South Jordan. Environmental Geochemistry and Health, **23(2)**, 105–116 **(2001)**.
[3] Y.Liang, J.He, C.W.Lv; Concentration and spatial distribution of bio-available fraction of heavy metals in the sediments from the Nanhailake. Journal of Agro-Environment Science (in Chinese), **28(6)**, 1208–1213 **(2001)**.
[4] L.L.Cao, J.H.Wang, S.G.Huang, Z.X.Ni; Speciation,source analysis and risk assessment of Trace Metals in Superficial Sediment of Daya Bay. J. Jilin Univer.(Ear.Sci.Edi.), **3**, 145-152 **(2014)**.
[5] Y.T.Kwon, C.W.Lee; Ecological risk assessment of sediment in wastewater discharging area by means of metal speciation.Microchemical Journal, **70(3)**, 255–264 **(2001)**.
[6] H.R.Ma, H.Li, J.F.Ji; Speciation and phytoavailability of heavy metals in sediments in Nanjing section of Changjiang River. Environmental Earth Sciences, **64(1)**, 185–192 **(2011)**.
[7] M.Pueyo, J.Sastre, E.Hernandez, M.Vidal, J.Lopez-Sanchez, G.Rauret; Prediction of trace element mobility in contaminated soilsby sequential extraction. J.Environ.Qual., **32(6)**, 2054–2066 **(2003)**.
[8] USEPA; 600/R-94-111 reference methodology method 200.2: sample preparation. Procedure for Spectrochemical Analyses of Total Recoverable Elements, **(1994)**.
[9] G.Rauret, J.F.Lopez-Sanchez, A.Sahuquillo, R.Rubio, C.Davidson, A.Ure, P.Quevauviller; Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J.Environ.Monit., **1**, 57-61 **(1999)**.
[10] L.L.Huang, X.M.Pu, J.F.Pan, B.Wang, Heavy metal pollution status in surface sediments of Swan Lake lagoon and Rongcheng Bay in the northern Yellow Sea.Chemosphere, **93**, 1957-1964 **(2013)**.