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Multivariate Analyses and Evaluation of Heavy Metals by Chemometric BCR Sequential Extraction Method in Surface Sediments from Lingdingyang Bay, South China

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Abstract: Sediments in estuary areas are recognized as the ultimate reservoirs for numerous contaminants, e.g., toxic metals. Multivariate analyses by chemometric evaluation were performed to classify metal ions (Cu, Zn, As, Cr, Pb, Ni and Cd) in superficial sediments from Lingdingyang Bay and to determine whether or not there were potential contamination risks based on the BCR sequential extraction scheme. The results revealed that Cd was mainly in acid-soluble form with an average of 75.99% of its total contents and thus of high potential availability, indicating significant anthropogenic sources, while Cr, As, Ni were enriched in the residual fraction which could be considered as the safest ingredients to the environment. According to the proportion of secondary to primary phases (K_{RSP}), Cd had the highest bioavailable fraction and represented high or very high risk, followed by Pb and Cu with medium risks in most of samples. The combined evaluation of the Pollution Load Index (PLI) and the mean Effect Range Median Quotient (mERM-Q) highlighted that the greatest

potential environmental risk area was in the northwest of Lingdingyang Bay. Almost all of the sediments had a 21% probability of toxicity. Additionally, Principal Component Analysis (PCA) revealed that the survey region was significantly affected by two main sources of anthropogenic contributions: PC1 showed increased loadings of variables in acid-soluble and reducible fractions that were consistent with the input from industrial wastes (such as manufacturing, metallurgy, chemical industry) and domestic sewages; PC2 was characterized by increased loadings of variables in residual fraction that could be attributed to leaching and weathering of parent rocks. The results obtained demonstrated the need for appropriate remediation measures to alleviate soil pollution problem due to the more aggregation of potentially risky metals. Therefore, it is of crucial significance to implement the targeted strategies to tackle the contaminated sediments in Lingdingyang Bay.

1. Introduction

Rapid industrialization and urbanization have resulted in a large growth in consumption of sources of energy and severe environmental contamination. Among the different types of pollutions, heavy metal contamination in soils has become an increasing environmental problem throughout in China. Researches concerning metals and non-metals in Lingdingyang Bay sediments have increased in recent years [1–3]. Marine sediment contains metal ions in several different types of physicochemical fractions that function as reservoirs of metals. High contents of heavy metals in coastal sediments may result from several anthropogenic activities, such as industrial and urban effluents [4]. In addition, natural processes, such as rocks weathering and physical migration and transportation also play a noticeable role in the abundance of metals in environments. Therefore, it is reasonable that the measurement of metal fractionation has become increasingly significant since both the bioavailability and mobility of metal ions rely heavily on their specific chemical speciation and ways of tying to each of the diverse soil stages [3]. As a result, there has been considerable interest in understanding the associations between particulate metals and solid phase.

The Pearl River Delta (PRD) is the low-lying area around the Lingdingyang Bay where the Pearl River flows into the South China Sea through four major tributaries. It is one of the most densely urbanized areas all over China and one of the major hubs of China's economic development. The bell-shaped estuary carries and receives most of the outflow from the Pearl River, which is the largest estuary in Southern China. The relative intensity and movement of freshwater and seawater as well as the interactions between them are important factors controlling the sedimentation in the estuary. Over the past 20 years, pollution issues, especially heavy metal contamination, have led to local ecological and environmental degradation that threatens local fishing and aquaculture [5]. Although heavy metal pollution has been investigated in the bay, only sparse systematic researches on the spatial distribution of metals have been performed. Sequential fractionation of toxic metals and the related bioavailability in this area have thus far been rarely studied, even though they can be useful tools to establish adequate

strategies for pollution. Therefore, not enough data are available to evaluate the capacity of mobilization and bioavailability of these selected metals [1,2]. Hence, multivariate analysis and evaluation of heavy metals by chemometric BCR sequential extraction method are meaningful and timely. It is important to study Lingdingyang Bay since there are many activities in the area: socio-economic (commerce, mining, and tourism) and production (food) that put pressure on the water resources.

The objectives of this study were to: (1) determine and compare the chemical speciation of metals and to assess the migration and bioavailability of metals with a chemometric approach; (2) define the contributing origin of these metals using multivariate statistical techniques; and (3) propose a few corresponding countermeasures for prevention of metal pollution. The results from this paper will provide a better understanding of the environmental risks of metals in the sediments of the Lingdingyang Bay.

2. Materials and Methods

2.1. Sampling and Pretreatment

Surface sediments (0–5 cm) were collected using Peterson grab in May 2011 from 31 sampling stations located in Lingdingyang Bay (Figure 1). These sampling sites located in the area were considered to be less affected by the continuously dumped materials and dredging activity. Sediment was freeze-dried, homogenized, ground, and sieved with a 200 μm-mesh nylon screen. The physic-chemical properties of sediment, including TOC (Total Organic Carbon), pH value, and particle size distribution were measured with the procedures reported in our early study [3].
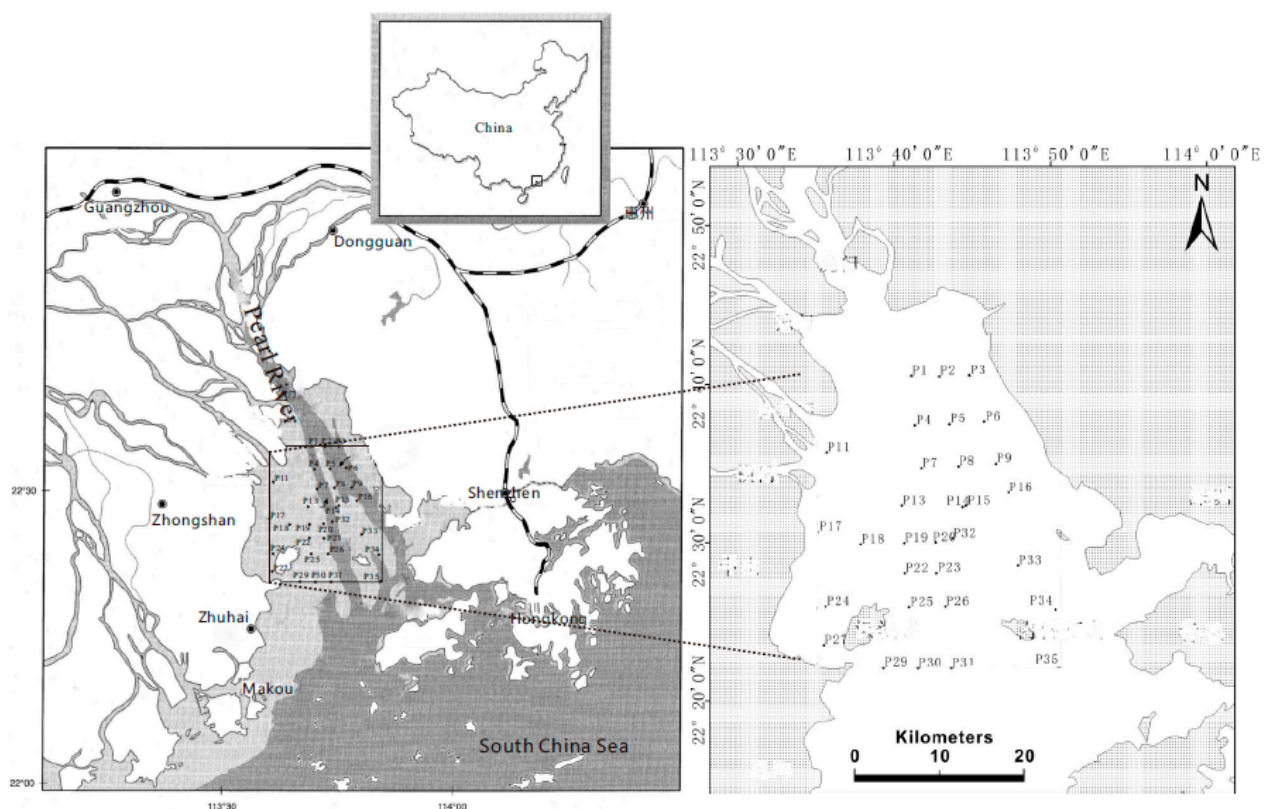

Figure 1. Map of sampling stations of the surface sediments.

2.2. Data and Methods

2.2.1. Analytical Methods

The concentrations of Cd, Cr, Pb, Cu, Zn, Ni and As were determined by inductively coupled plasma mass spectrometry (ICP-MS, Elan 9000, Waltham, MA, USA) directly when the solution was limpid.

Four well defined geochemical fractions of metals in sediments, *i.e.*, acid-soluble fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4) were determined with the method. The fractionation procedures were as follows [6–8]:

Step 1: Fraction 1 (F1, acid soluble fraction)

For each given sample, 30 mL of acetic acid were added to 500 mg of dry sediment in a 50 mL Pyrex tube. Tubes were shaken for 20 h at room temperature (22 ± 2 °C) and the extracts were separated from the residues by centrifugation at 3500 rpm. The supernatants were removed carefully and put into polyethylene containers. The residues were washed with 10 mL distilled water, shaken again for 10 min, and centrifuged for 20 min at 3500 rpm. The supernatants were decanted and removed completely and carefully without any loss of residues.

Step 2: Fraction 2 (F2, reducible fraction)

Exactly 20 mL of 0.1 M NH_2OHHCl (pH 2.0) were added to the residues obtained from *Step 1* and the extraction of the residues was performed exactly as described in *Step 1*.

Step 3: Fraction 3 (F3, oxidizable fraction)

Exactly 20 mL of 8.8 M H_2O_2 (pH 2.0–3.0) were added drop-by-drop with stirring to the residues from *Step 2*. The tubes were sealed with caps and digestions were carried out at room temperature for 2 h and at 85 °C in a water bath for 1 h, respectively. Digestion mixtures were concentrated and final volumes of 2–3 mL were achieved by evaporation. *Step 3* was repeated twice and 25 mL of 1 M $NH_4C_2H3O_2$ (pH 2.0) were added to the cool residues. The residues were rinsed and separated as described above.

Step 4: Fraction 4 (F4, residual fraction)

The final residues remaining at the end of the BCR procedure were further digested in 20 mL aqua regia. The metals concentrations in the extracts obtained at each step were determined using an atomic absorption spectrophotometer (AAS, Hitachi Z2000, Tokyo, Japan). The AAS detection limits were calculated as $3\delta/S$ (δ was standard deviation of blank signal, and S was the sensitivity). The detection limits (mg/kg) were 0.03 (Cd), 0.1 (Pb), 0.5 (As), 0.2 (Cr), 0.1 (Ni), 0.05 (Cu) and 0.6 (Zn), respectively.

pH was measured *in situ*. The sample granulometry was determined using a Malven Laser Mastersizer 2000 Particle Size Analyzer-MS 2000 (Malve Instruments Ltd, Manchester, UK) (0.02–2000 μm). The total organic carbon (TOC) content of the sediment samples was determined by the loss on ignition method using a CHENS Elemental Analyzer-Varia EL (Elementar, Frankfurt, Germany).

2.2.2. Quality Assurance and Quality Control

All chemicals used in the experiment were guaranteed reagent grade. Blank determinations were performed for each set of analysis using the same reagents. Quality assurance was achieved in the same way as documented through the analysis of a marine sediment reference material (Offshore Marine Sediment, GBW 07314, Shanghai, China) with both duplicate samples and parallel samples. The results of the reference material analyses showed that the method was accurate, giving concentrations of better than 92% of the certified values for each of the metals. The duplicates showed a difference of <10%, while the spiked additions (blanks and samples) gave between 90 and 105 recovery percentage. These results indicated that the accuracy and reproducibility of the sequential extraction procedure used in this study were good.

3. Results and Discussion

3.1. Distribution of Metals in Sediments

To have a better understanding of potential bioavailability, mobility and chemometric toxicity of metals in sediments which largely depend on the physicochemical form [9,10], the BCR sequential extraction technique was applied to the sediments collected from the studied area. The percentages of metals from each extraction step are presented in Figure 2.
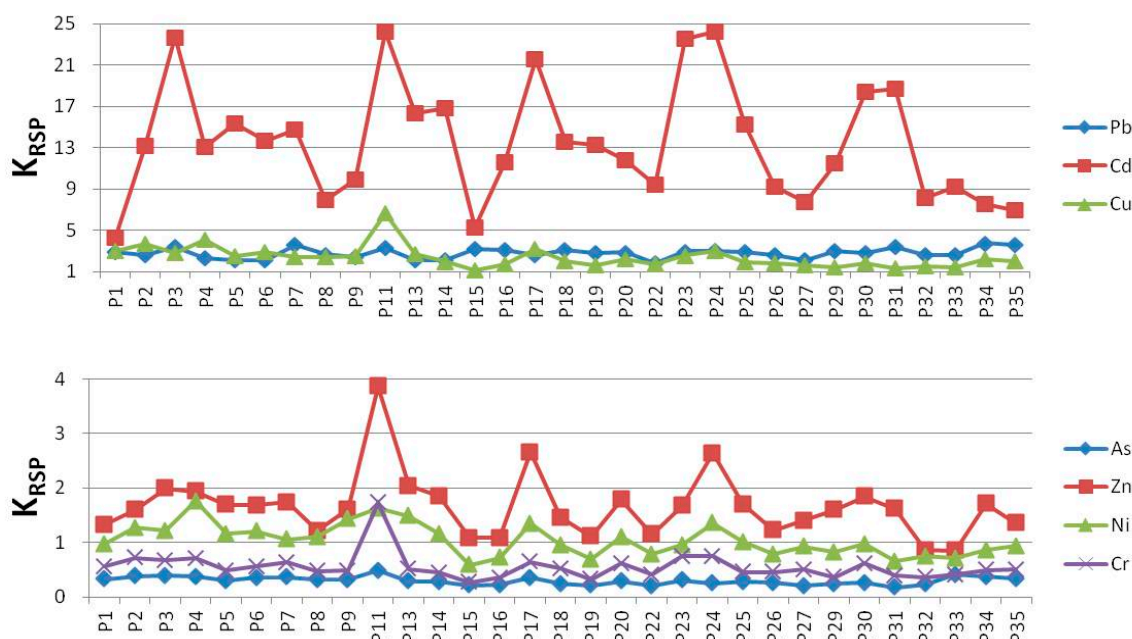

Figure 2. The variation characteristics of K_{RSP} in surface sediments.

The fractions from the first step of sequential extraction bound to acid-soluble fractions (F1) included water soluble, ion exchange and carbonate binding states, which were absorbed in clay and soil humus and were vulnerable to environmental changes and easier to be transformed and migrated under acidic conditions. The high bioavailability, mobility and potential toxicity of acid-soluble metals in aquatic organisms are of great concern and changes in salinity and increase in pH value have been reported to

increase metal mobility in aquatic ecosystems [11]. The results in Figure 3 revealed that Cd was dominantly associated with the mobile fraction with an average of 75.99% and a maximum of 82.71% of its total contents. This raised concerns about the potential ecological constraints mainly related to Cd due to its well-known noxious effects on aquatic organisms. On the other hand, a low % of association with the acid-soluble fractions (F1) was observed for most of the remaining metals: Zn (32.44%) > Ni (27.06%) > Cu (24.37%) > Pb (6.29%) > As (3.90%) > Cr (2.74%). These results were in accord with previous studies that highlight that the potential risks caused by Cd were extremely associated with F1 [12]. However, the potential ecological risks still exist and cannot be ignored even with the low % of association with the mobile fraction since environmental conditions could modify this scenario [13].
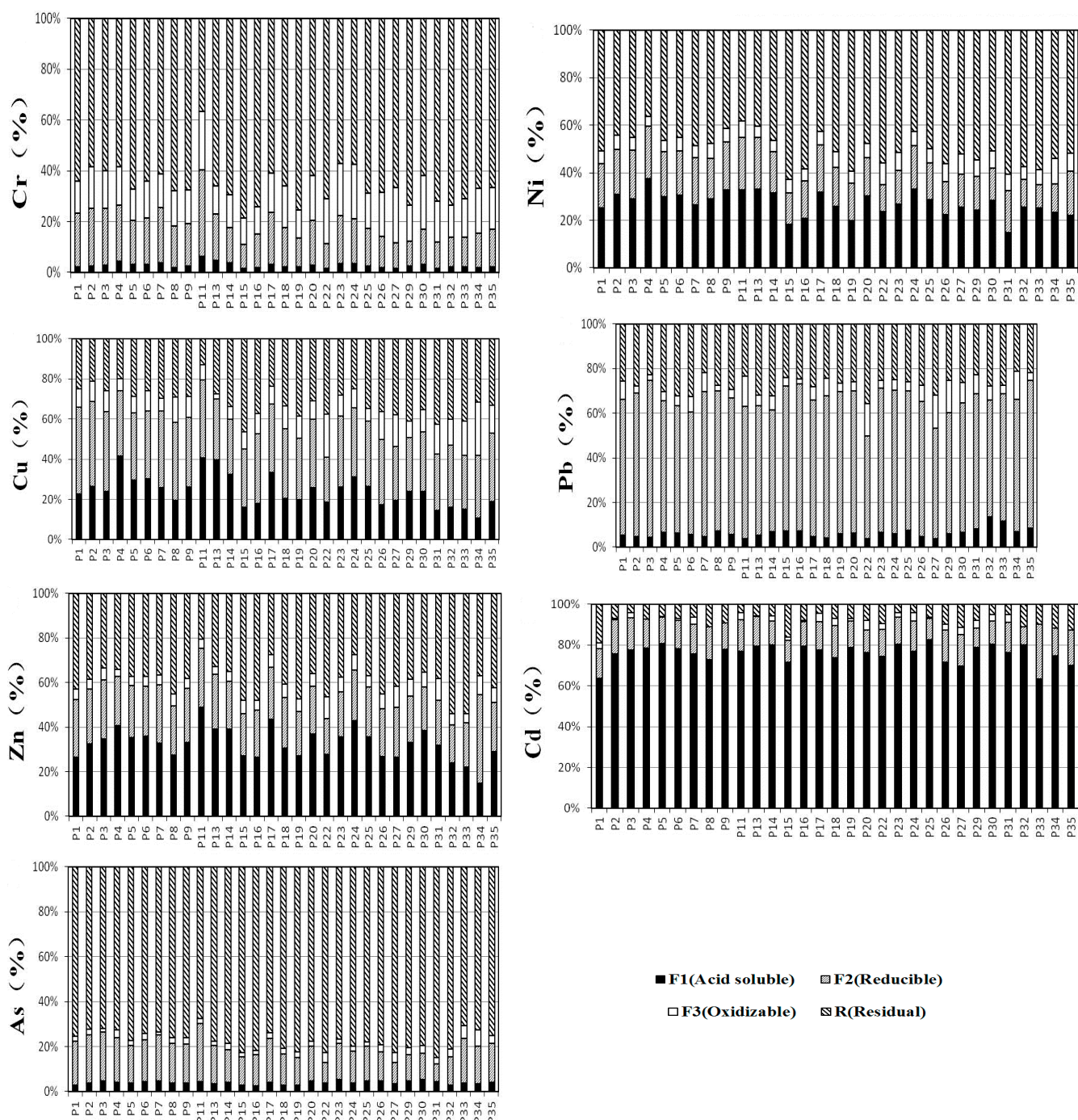

Figure 3. The distribution in different geochemical fractions of surface sediments.

The second fraction of the extracted metals, the reducible fraction (F2), is the part of the trace metals in the binding state of Fe/Mn oxide or hydroxide precipitation, which is difficult to release due to strong ionic wrapping. It was observed that Pb was highly correlated with the reducible fraction with an average of 60.24% of its total contents. The rank order of metals associated with the reducible fractions was: Pb (60.24%) > Cu (32.93%) > Zn (22.65%) > Ni (16.73%) > Cr (16.14%) > As (15.93%) > Cd (13.99%). High % of association of Pb to the reducible fraction (F2) in the sediments of estuaries and bays has been reported [3,14]. A fact is revealed that industrial effluents related to high associations of Pb to the reducible phase cannot be ruled out in Lingdingyang Bay. The fraction from the third step of the sequential fractionation (oxidizable fraction) was extracted. Under oxidizing conditions, organic matter degradation can lead to a release of metals bound to this fraction (F3). The organic fraction released during the extraction was not bioavailable due to its association with stable humic substances that discharged from small amounts of metals slowly. The results revealed that the association with F3 was as low as 5.63%, 6.87%, 6.92%, 10.19%, 10.74% and 14.03% for As, Cd, Zn, Cr, Pb, Cu, Cr and Ni, respectively. The low contents of metals in the oxidizable fraction were associated with the low contents of organic matter of 12.5% in the studied areas.

The results of the fourth fraction of extracted metals, the residual fraction (R), indicated that the metal fraction was associated with the alumino-silicate minerals. Metals in the residual fraction (R) are the most stable, mainly boundto the crystal lattices of silicate, can only be released during the weathering process. Therefore, it is basically not bioavailable because the weathering process is much longer than the life period. The common characteristics were that the most substantial quantities of As, Cr and Ni were associated with the residual fraction, with the average values of 77.31%, 65.55% and 51.01%, respectively. The relative metal concentration in residual fraction can be used as a measure of the contribution of natural sources, and a higher percentage in this fraction indicates a lower level of pollution and the mineralogical origin of the metal in sediments of the sampling regions. Therefore, the high percentage of As, Ni and Cr in the residual fraction indicated that they were relatively stable and had a low potential bioavailability and chemometric toxicity.

It is well known that, to some extent, the non-residual proportion reflects the reactivity of metals. The higher the proportion of heavy metal is, the stronger the activation is, and the easier the remobilization becomes. Based on the concentrations of fractions in each step of extraction, the descending sequence order in the proportion of non-residual form was as follows: Cd (91.92%) > Pb (73.09%) > Cu (68.31%) > Zn (60.86%) > Ni (50.10%) > Cr (34.45%) > As (22.69%).

In conclusion, the residual fraction (R) was the main speciation for Cr, As, Ni, which could be considered as the most environmentally safe component. In contrast, Pb was found to be mainly in the reducible fraction (F2), indicating that Pb was more or less available to aquatic biota and might correlate with its concentrations in microorganisms. Cd was mainly in the acid-soluble form (F1) and thus of high potential mobility and availability. Cu and Zn, on the other hand, were distributed dispersedly in different fractions.

The risk assessment integrating the geochemical fractionation and total content of metals is vital for the understanding of the pollution level of heavy metals for the better management practices of coastal sediments [1]. The correlation matrix between the geochemical phases and total content of metals in the studied areas are shown in Table 1. The results also showed that with the exception of Pb (F1) and As (F3), the concentrations of all metals in both areas were positively and highly correlated with their

metal speciation, indicating that it was reliable to some extent to determine the level of pollution by the total content.

Table1. Correlation matrix between total concentration and geochemical phases of selected metals.

	Variables	Cr	Ni	Cu	Pb	Zn	Cd	As
Lingdingyang Bay	F1	0.866 **	0.879 **	0.963 **	0.361	0.956 **	0.998 **	0.851 **
	F2	0.894 **	0.896 **	0.982 **	0.937 **	0.946 **	0.979 **	0.644 **
	F3	0.946 **	0.836 **	0.779 **	0.687 **	0.756 **	0.937 **	0.197
	R	0.813 **	0.857 **	0.710 **	0.828 **	0.780 **	0.662 **	0.967 **

* Correlation is significant at the 0.05 level (2-tailed) ** Correlation is significant at *P* the 0.01 level (2-tailed).

3.2. Chemometric Assessment

It is generally accepted that the higher the percentage of non-residual fraction (F1 + F2 + F3) is, the easier the release of metals is, and the higher the bioavailability of metals is. In general, the primary mineral in soil is called the primary phase or the weathering products, such as residual fraction. Secondary metabolites, such as F1, F2 and F3, are called the secondary phase. The anthropogenic contamination of metals is in the secondary phase, and the ratio of secondary to primary phases (K_{RSP}) can be used to represent the degree of metal contamination in sediments: the higher the value of K_{RSP} is, the greater the potential risk is. According to previous studies, $K_{RSP} < 1$, $1 < K_{RSP} < 2$, $2 < K_{RSP} < 3$, and $K_{RSP} > 3$ indicate no pollution, light pollution, moderate pollution, and heavy pollution, respectively [9].

The K_{RSP} of seven selected metals decreased in the sequence order of Cd > Pb > Cu > Zn > Ni > Cr > As in Lingdingyang Bay. The average K_{RSP} value of Cd was 13.54, and it was the highest in the studied metals, indicating that the pollution degree of Cd was the greatest. The average value of K_{RSP} of Pb and Cu was between 2 and 3, implying a moderate anthropogenic pollution. The mean K_{RSP} value of Zn and Ni was between 1 and 2, indicating a light pollution for both of them. The K_{RSP} value of Cr and As was less than 1, indicating that there was basically no pollution in this area.

The Pollution Load Index (PLI) is introduced to evaluate the level of metal contamination and thus applied to determine the integrated pollution status of combined toxicant groups at sampling stations by calculating the *n*th root of the *n* contamination factors (CF_n) multiplied together and calculated using the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_4 \times \ldots.. CF_n)^{1/n} \tag{1}$$

The *CF* for each metal is the ratio of the measured concentration in the sediment to the background value, which is classified into four grades for monitoring the pollution of one single metal over a certain period of time [15].

The PLI value >1 indicates a polluted condition, while PLI < 1 signifies no metal pollution [16].

The spatial map of PLI in Figure 2 shows that except for station P29 in Lingdingyang Bay with a PLI value of 0.75, the PLI results for all the other stations ranged from 1.07 to 3.81, with the highest PLI value of 3.81 at station P10, the most contaminated site of all, followed by P21, P27, P3, P26 and P24 in sequence, the PLI values of which were 3.04, 2.85, 2.71, 2.58 and 2.62, respectively. The results

revealed that the contamination distribution pattern was in accord with that of concentration as a whole, and the contamination risk decreased gradually from the northwest to the southeast.

The individual metals were taken into account when all the indices applied above were calculated. Based on the fact that metals always occur in sediments as complex mixtures, the mean Effects Range-Median (ERM) quotient method was used to determine the possible biological effects of the combined toxicant groups, by computing the mean quotients for a large range of pollution [17]. The mean ERM quotient is calculated using the following formula:

$$\text{mean-ERM quotient} = \sum(C_x/\text{ERM}_x)/n \tag{2}$$

where C_x is the concentration, and $\text{ERM}x$ is the ERM value for metal x, n is the number of metals. The mean-ERM quotient (mERM-Q) is classified into four levels: low priority site (≤ 1), medium-low priority site (0.1–0.5), high-medium priority site (0.5–1.5), and high priority site (>1.5), having a probability of 9%, 21%, 49% and 76% of being toxic, respectively [18].

Based on the mERM-Q data, a contour map of ecological risk potential is presented in Figure 4. In the surface sediments of the selected region, all the investigated stations had mERM-Q < 0.5, ranging from 0.06 to 0.37. In general, all sites except P29 in Lingdingyang Bay were medium-low priority sites, indicating that the combination of the seven selected metals had a 21% probability of being toxic. Both PLI and mERM-Q revealed that the highest potential ecological and toxicity risk zone was found in the northwest of Lingdingyang Bay.
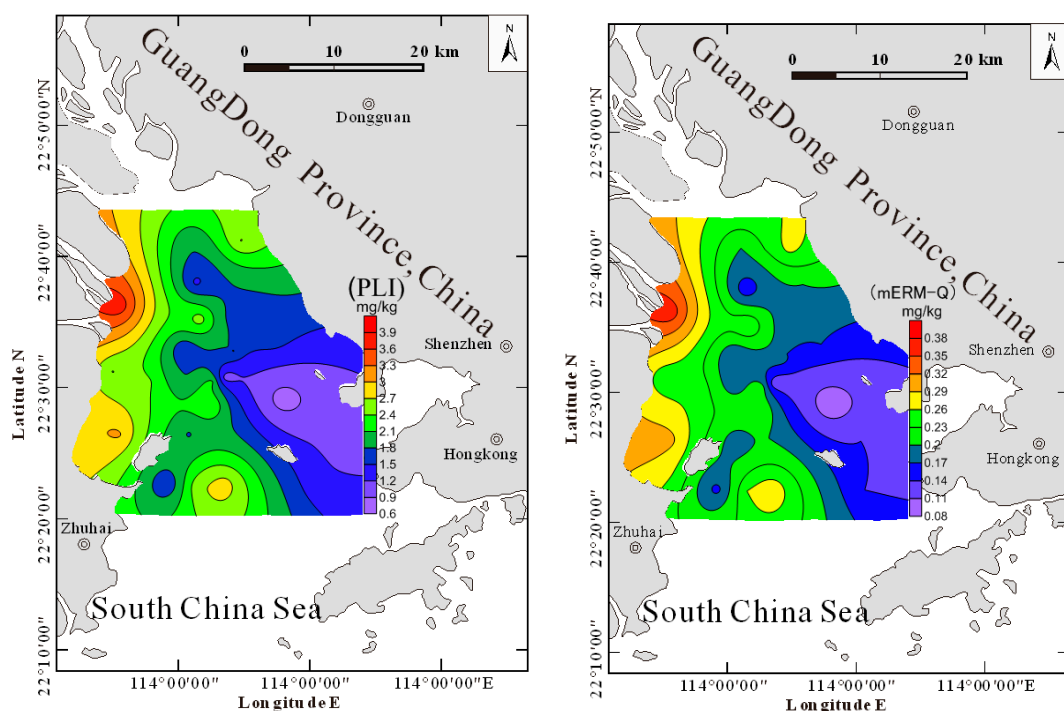

Figure 4. Spatial distribution of pollution load index (PLI) and the mean Effects Range-Median (ERM) quotient (mERM-Q) in surface sediments from the studied regions.

3.3. Potential Factors Influencing Chemical Fraction

Previous studies [3,6,12] regarding chemical fractionation were usually carried out using univariate procedures; however, multivariate methods such as Pearson correlation and multivariate principal

component analysis (PCA) may provide further statistical interpretation of the results. To explore the correlations among the concerned variables, the Pearson correlation analysis was performed and the results are shown in Table 2. Significantly positive correlations were observed for selected metals, indicating that these metals were associated with each other and may had common natural or anthropogenic sources.

PCA was applied to the chemical fractionation data to determine the basic statistical parameters and to provide further identification of the potential sources between different metals and metalloids. PCA was applied to the matrix of seven metals of the PRE. Many previous researches have used PCA to probe into sources of metal contamination, which is believed that the original variables are mutually significantly correlated. PCA was performed with the metal fractionation data, and the scores in the rotated principal component space are presented in Table 3.

PCA in the Lingdingyang Bay data set involved two PCs (Principal components) with eigenvalues >1, explaining approximately 62.13% (PC1: 31.79% and PC2: 30.34%) of the information contained in the total variables, which was sufficient to provide information for the data structure. Based on the weight of the contribution of each variable, it was revealed that the acid-soluble fraction (Cr, Ni, Cu, Zn, Cd, As) and reducible fraction (Cr, Ni, Cu, Zn, Cd, As) were strongly and positively associated with the first component (PC1). Specifically, Cu-F1 and Cd-F1, had the weights of 0.85 and 0.77, respectively, and were mainly in the acid soluble fraction (65%). These results indicated that PC1 had different geochemical behaviors and was mainly sourced from mixed anthropogenic inputs, including industrial wastes (such as manufacturing, metallurgy, chemical industry) and sewages. Previous studies have reported that input of Cd and Cu to the oceans is dominated by riverine sources [19]. Therefore, these metals should be due to anthropogenic inputs from riverine sources containing both naturally occurring components in the water and sediment and a large proportion of anthropogenic wastes ended up into estuaries and oceans, which is in accord with the above-mentioned geochemical fractions analysis.

The second PC (PC2), which accounted for 30.34% of the total variance with high positive loading on the residual forms (Cr, Ni, Cu, Zn, Cd, As), especially Cr with the contribution of 0.80 was mainly present in the residual fraction (55%), reflecting the lithogenic origin. Therefore, it is reasonable to suppose that PC2 mainly originates from natural geological sources of metals into the coastal sediments.

The relationship between the metals fractions and sediment properties (e.g., TOC, pH and clay content) is shown in Figure 5. The pH value was significantly positively correlated with the percentages of residual fraction of the selected metals, indicating that decreased pH could promote the transformation ability of metal speciation into mobile phases. Yang *et al.* [19] found that this correlation may associate with the effect of urbanization and industrialization on local scale. Especially in a highly developed Pearl River Delta region, the low pH in surface runoff enhances dissolution of non-residual fractions of metals in catchment sediments with the increasing of acid rain, subsequently increases the transportation of metals into receiving rivers and induces the effect of neutralization with alkalinity.

The percentage of clay in soils was significantly positively correlated with the acid soluble fraction and reducible fractions of Cr, Ni, Cu, Zn, Cd and As, which was the main factor to influence the bioavailability of trace metals. Similarly, the content of TOC was significantly positively correlated with the levels of Pb in reducible and oxidizable fractions and Cu in oxidizable fractions, indicating that Pb and Cu could easily complex with organic matters.

Table 2. Pearson correlation coefficients between heavy metals, pH, total organic carbon (TOC) and clay in the studied regions.

	Cr	Ni	Cu	Pb	Zn	Cd	As	pH	TOC	Clay
Cr	1			–						
Ni	0.871 **	1								
Cu	0.924 **	0.869 **	1							
Pb	0.761 **	0.739 **	0.702 *	1						
Zn	0.966 **	0.920 **	0.944 **	0.809 **	1					
Cd	0.722 **	0.774 **	0.674 *	0.725 **	0.832 **	1				
As	0.764 **	0.840 **	0.661 *	0.862 **	0.764 **	0.748 **	1			
pH	−0.531 *	−0.203	−0.434	0.110	0.522 *	−0.145	−0.472 *	1		
TOC	−0.551 *	0.257	−0.559 *	−0.662 *	−0.389	0.068	−0.282	0.214	1	
Clay	0.544 *	0.840 **	0.310	0.592 *	0.428	0.726 **	0.440	0.121	0.211	1

* Coefficients at 0.05 significance level, $p < 0.05$. ** Coefficients at 0.01 significance level, $p < 0.01$.

Table 3. Loadings in fractions of metals on VARIMAX-rotated factors.

Factors	PC1	PC2
%F1	0.75	0.09
%F2	0.69	0.14
%F3	−0.08	0.23
%R	0.35	0.76
Percentage of total variance	31.792	30.339
Cumulative percentage variance	31.792	62.130
Components	acid-soluble fraction (Cr, Ni, Cu, Zn, Cd, As) and reducible fraction (Cr, Ni, Cu, Zn, Cd, As)	the residual forms (Cr, Ni, Cu, Zn, Cd, As)
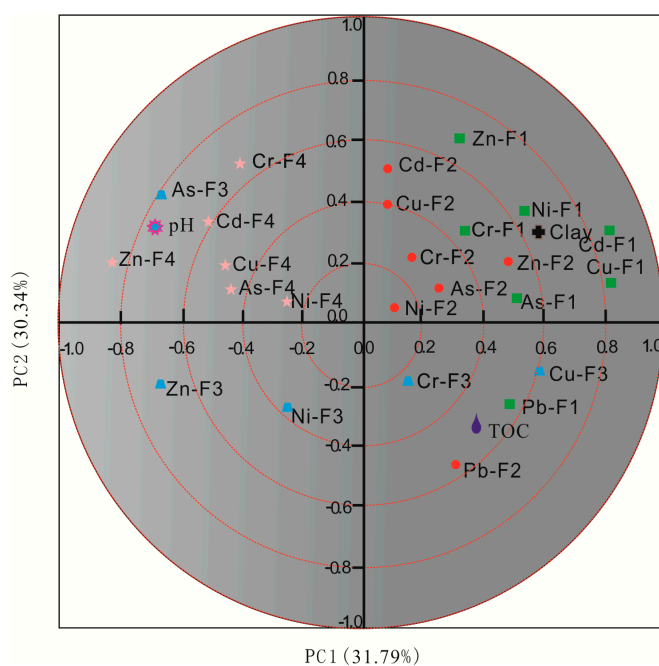
Figure 5. Principle component analysis of chemical speciation of selected metals and physical-chemical properties (total organic carbon (TOC), pH, and clay) of sediment from Lingdingyang Bay.

4. Conclusions

In the present study, chemical speciation analysis and comparative assessments of Cr, Ni, Cu, Pb, Zn, Cd and As in forms of acid-soluble (F1), reducible (F2), oxidizable (F3) and residual (R) fractions in contaminated sediments from the Lingdingyang Bay showed that rapid industrialization and urbanization contributed considerably to the enrichment of heavy metals.

Sequential extractions analysis suggested that the increasing levels of non-residual fractions of Cr, Ni, Cu, Pb, Zn, Cd and As from the studied areas could generally reflect the increasing anthropogenic inputs since most anthropogenic metals loosely bind to mineral or organic matters in sediment in the form of non-residual fractions. Furthermore, both Cd and Pb are of high potential availability and high risk. The sequence order of migration and transformation on the basis of the non-residual content of the elements was Cd > Pb > Cu > Zn > Ni > Cr > As. The source analysis showed that the pollutants were mainly mixed anthropogenic inputs, including industrial wastes (such as manufacturing, metallurgy, chemical industry) and sewages, and minimally originated from mineral weathering. This study also revealed that clay and pH of sediment had a good correlation with acid-soluble and residual fractions of selected metals respectively.

The results of this research provide a reference for future activities that may affect the sediments of the Lingdingyang Bay. The following suggestions are made based on the results and analyses of the present study: firstly, the sediment quality should be monitored for a long term for the sake of environmental protection and management in Lingdingyang Bay, especially considering the continuous contaminant inputs; secondly, it is important to perform further studies in order to have a better understanding of the feasibility of recovering different metals and developing more appealing technologies that can be applied in a cost-effective way; thirdly, it is crucial to coordinate the behavior of the government and market to put the discharges of heavy metals under surveillance.

Acknowledgments

Author Contributions

Linglong Cao, Ping Shi and Quansheng Lou designed this research; Linglong Cao and Haitao Tian collected and interpreted the data and wrote the paper with significant contributions from other authors. Jie Yang and Lali Waxi provided support in performing the data analysis. All authors have read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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