Ecological risk assessment of heavy metals in water and sediment of the Pearl River Estuary, China

Zepeng Jiao¹, Huanyong Li¹, * and Meiying Song² and Lin Wang¹

¹Analytical and Testing Center, Jinan University; Guangzhou, China
²Guangdong Provincial Institute of Food Inspection (Guangdong provincial Liquor Testing Center); Guangzhou, China

*Corresponding author e-mail: tlihuanyong@jnu.edu.cn

Abstract. The concentration of heavy metals (Cr, Cd, Pb, Cu, Zn, Co, Ni and Tl) in water and surface sediment were investigated in the Pearl River Estuary, China. The concentrations of heavy metals in sediment were 1000-100,000 times higher than those in water. Correlation analysis and principal component analysis found that heavy metals (Zn, Cr, Pb and Co) in water may originate from anthropogenic activities, but the heavy metals in sediment indicate that Pb was dominated by nature and Zn, Cr, Co, Cd, Cu, Tl and Ni were mostly influenced by anthropogenic pollution. Enrichment factor and accumulation index of sediment heavy metal concentrations showed that S5, S6 and S7 presented a relatively serious pollution.

1. Introduction
The rapid development of industry and agriculture has resulted in increasing pollution by heavy metals, which are a significant environmental hazard for invertebrates, fish, and humans [1]. Significant quantities of heavy metals are discharged into rivers, which can be strongly accumulated and biomagnified along water, sediment, and aquatic food chain, resulting in sublethal effects or death in local fish populations [2-3]. Metals can heavily accumulate in sediments, as a sink, or be released from sediments, acting as a source back to overlying water via natural or anthropogenic disturbance. The effects of metal pollution on local environments and organisms can be substantial and long lasting in spite of years of restoration efforts. More importantly, toxic metals can be taken up by organisms entering the food chain and be potentially transferred to the upper trophic levels, which can eventually lead to adverse effects on humans due to the consumption of contaminated seafood [4]. Suspended sediments absorb pollutants from the water, thus lowering their concentration in the water column, heavy metals are inert in the sediment environment and are often considered to be conservative pollutants [5] although they may be released into the water column in response to certain disturbances [6], causing potential threat to ecosystems [7]. Bottom sediments also provide habitats and a food source for benthic fauna. Thus, pollutants may be directly or indirectly toxic to the aquatic flora and fauna. The effects of pollutants may also be detected on land as a result of their bio-accumulation and bio-concentration in the food web [8]. Consequently, an analysis of the distribution of heavy metals in water and sediments adjacent to populated areas could be used to investigate anthropogenic impacts on ecosystems and would assist in the assessment of risks posed by human waste discharges [9].
Coastal and estuarine areas are among the most important places for human inhabitants, yet they are often the ultimate receptacles of anthropogenic pollutants. Toxic contaminants such as metals have placed increasing pressures on coastal and estuarine ecosystems over the past decades because of enhanced human activities in coastal areas. The input of toxic metals into coastal areas from estuary can result in deleterious effects on wildlife habitats, degradation of the ecosystem, and possible poisoning of humans [10-11].

In recent years, China has experienced rapid economic expansion, but environmental deterioration has become a serious problem. Contamination of heavy metals in estuarine water and sediments have become inevitable and observed in several estuaries in China, such as Haihe Estuary [12], Yellow River Estuary [13-14]. However, Pearl River Estuary consists of eight freshwater discharge outlets which is very different from the other estuaries. Chromium, Ni, Cu, Zn, Cd, Pb, Co and Tl are the most important heavy metals in environment, which have negative effects on agriculture and ecology [15]. The pollution of the heavy metals is serious in china and widely investigated. So, the pollution status of Cr, Ni, Cu, Zn, Cd, Pb, Co and Tl were studied in water and sediment of the PRE.

The Pearl River is the largest river system in South China. It consists of the Xijiang River, Dongjiang River, Beijiang River and Liuxi River, of which the Xijiang River is the largest. It was found that the main branches of the Pearl River all suffered from metal pollution [16-18]. The Pearl River runs into the South China Sea via eight outlets, including Humen, Jiaomen, Hongqimen, Hengmen, Modoamen, Jitimen, Hutiaomen and Yamen. The former four outlets run into Lingdingyang, and the latter four estuaries, called the west-four PRE regions, directly flow into the South China Sea [19]. Lingdingyang and the west-four PRE regions constitute the PRE which is the most important region for water-borne commerce in south China. The freshwater discharge outlets of the PRE include Jiaomen (S1), Hongqimen (S2), Modoamen (S5), Yamen (S6), Jitimen (S7) and two sites of Humen (S3, S4), which are selected as the sites in this study(Figure.1).

Previous studies have been conducted on the distribution and the risk assessment of heavy metals in the PRE sediment [20-23]. However, none of the previous studies cover the whole freshwater discharge outlets of the PRE, which was important to reflect the pollution status of heavy metals comprehensively and crucial to evaluate the ecological risk of the heavy metals for estuary management. The objectives of this study were to determine concentrations of heavy metals in water and sediments of the PRE; to assess potential sources of the metals using principal component analysis (PCA) and correlation analysis (CA) among heavy metals; to assess environmental risks of these metals in the study area using Enrichment factor (EF) and geoaccumulation index (Igeo).

2. Materials and Methods

2.1. Water and Sediment Sampling
Water (21 samples) and surface sediment samples (21 samples) were collected from seven different areas of freshwater discharge outlets of Pearl River Estuary in July, 2017. Water samples were collected in an acid washed polyethylene bottles and immediately preserved by the addition of a few drops of concentrated nitric acid. Sediment samples were collected by a grab sampler and placed in pre-cleaned polyethylene bags. The samples were transferred to the laboratory in an icebox and were processed within 18-24 h. Before analysis, sediment samples were dried, ground, sieved with 60-mesh (0.3mm), and stored in plastic containers that were cleaned by 1:1 HNO₃.
2.2. Chemical and Physical Analyses of Water and Sediments

Physical and some chemical analysis of water samples were conducted following the river and estuary water standard procedures of Chinese Environmental Protection Agency. Field parameters included temperature (T), dissolved oxygen (DO), pH which were measured by a water quality analyzer professional series YSI (Assembled in USA). The water samples were filtered through 0.45μm

Filters and acidified to pH<2 using concentrated nitric acid and then stored in the dark at 4°C. The concentrations of heavy metals were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo Fisher scientific X series 2).
Heavy metals in sediment samples were determined according to Yang et al [24], the sediment samples were digested in concentrated nitric acid, Hydrofluoric acid and Hydrogen peroxide of 30% to dissolve heavy metals in solution. About 0.10 g of ground sediment samples were weighted and placed into acid-washed Teflon crucible. About 5.0 ml of nitric acid, 2.0 ml of Hydrogen peroxide and 1.0 ml Hydrofluoric acid were added to each crucible. Each crucible was placed in a heating block which can control its temperature. The crucibles were heated at about 80°C to keep boiling slightly, and stop heating the crucibles until closing to dry. 4 ml saturated boric acid solution was used to permit the complexation of fluoride to protect the quartz plasma torch. The solution was cooled, transferred quantitatively to a glass tube and diluted to 25 ml with nitric acid (1:99), then transferred to a plastic vial. The heavy metals (Pb, Cr, Co, Cu, Zn and Ni) concentrations of the solutions were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima, 2000DV), and Cd and Tl were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo Fisher scientific X series 2).

For quality control, reagent blanks, standard reference materials (GBW07333) from the State Oceanic Administration of China, and sample replicates were inserted in the analysis. All reagents were ultrapure and glassware/plastic ware/filters cleaned according to the method of Harrison and Laxen [25]. The result showed that there was no sign of contamination in the analysis and all of the relative standard deviations of the replicate samples were <10%. The recovery rates for the heavy metals in GBW07333 were higher than 82%. Mean recoveries were as follows: Pb, 89.0%; Cr, 84.0%; Cd, 82.1%; Co, 119%; Cu, 105%; Ni, 88.1%; Zn, 89.4% and Tl, 83.0%.

2.3. Statistical Analysis

Statistical analysis was performed using SPSS 19.0 statistical software. Pearson correlation analysis was implemented to determine the relationship among the heavy metals. To determine the common pollution sources, factor analysis was performed by PCA and eigenvectors analysis. The rotation of principal components was carried out according to the varimax method.

3. Results and Discussion

3.1. The Heavy Metal Contamination in Water and Sediment

Concentrations of metals in water of the freshwater discharge outlets are given in Fig.2A. The concentration (μg/L) of metals in water showed slight variations with Co, 0.075-0.319; Cr, 0.355-1.10; Cu, 3.00-5.00; Ni, 1.42-4.53; Pb, 0.057-1.09; Zn, 16.5-60.7; Cd, 0.050-0.752 and Tl, 0.026-0.047. The maximum and the minimum level of heavy metal was at S6 and S4 for Co; S1 and S7 for Cr; S2 and S5 for Cu; S3 and S7 for Ni; S2 and S7 for Pb; S6 and S2 for Zn; S7 and S1 for Cd; and S4 and S1 for Tl, respectively (Fig.2A). Sampling site, i.e. S5 was the least polluted site of the PRE in respect to metal contaminations. However, Cu, Cd and Zn was relatively higher than the report in the water of the PRE[26], but all the metals in the water except for Zn did not exceed the water quality standard[27].

Overall difference for metal level in sediment varied significantly among sampling stations (Fig.2B). The range of metals in sediments were: 17.3-28.5 mg/kg for Co, 64.2-94.3 mg/kg for Cr, 61.2-98.4 mg/kg for Cu, 35.1-41.8 mg/kg for Ni, 45.5-61.4 mg/kg for Pb, 140.4-508.6 mg/kg for Zn, 0.22-1.03 mg/kg for Cd and 0.55-0.87 mg/kg for Tl. The maximum level of Zn in sediment was at S5 (508.6 mg/kg), followed by S7 (499.8 mg/kg), S6 (396.2 mg/kg), S4 (338.0 mg/kg), S3 (168.0 mg/kg) and S1=S2 (140.4 mg/kg). The average level of individual heavy metal showed significant variations in freshly deposited sediments. Overall concentration of heavy metal in sediment was in the order: Zn > Cr > Cu > Pb > Ni > Co > Cd > Tl. The highest mean concentration of Co, Cu and Cd was at S7 sampling station, while Cr and Zn showed the maximum level at S5 site. Similarly, Ni and Tl showed the maximum concentration at S6. The sediments collected from S3 showed the maximum level of Pb (Fig.2B). Li et al [20] studied the heavy metal contamination in sediments of the PRE, they reported metals (mg/kg) in range of 7.1-63.0 for Cu, 7.5-48.5 for Ni, 27-72 for Pb and 32.2-210 for Zn. Liu et al [28] reported the range of Co was 5.8-18.8 mg/kg, Huang et al [29] reported the range of Cd was 0.04-
0.7 mg/kg. The higher ranges of metals in sediments in present study clearly indicate the increasing metal pollution level of the PRE in recent years.

Figure 2. Heavy metal concentration in water (A) and sediment (B) from different sampling sites of the PRE.
The concentrations of heavy metals in the sediment were 1000-100,000 times higher than those in the water (Fig.2A and Fig.2B). A number of studies have reported a similar phenomenon [30-31]. Heavy metals entering the water body would be absorbed in sediments, and subsequently might migrate as a result of exchanges between water, sediment, and biota, through biological and chemical processes. Heavy metals do not degrade in water but are generally not found in high concentrations, primarily due to deposition in sediments but also because of uptake by plant and animals [32]. And heavy metals in the sediment enter the food chain via the feeding of benthic animals.

3.2. Heavy Metal Pollution Source Analysis

| Sampling site | $I_{\text{geo}}$ (Co) | $I_{\text{geo}}$ (Cr) | $I_{\text{geo}}$ (Cu) | $I_{\text{geo}}$ (Ni) | $I_{\text{geo}}$ (Pb) | $I_{\text{geo}}$ (Zn) | $I_{\text{geo}}$ (Cd) | $I_{\text{geo}}$ (Tl) |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| S1            | 0.77            | 0.64            | 0.93            | 0.35            | 0.91            | 0.40            | 0.82            | -0.98           |
| S2            | 0.84            | 0.54            | 0.79            | 0.26            | 0.86            | 0.40            | 0.58            | -1.03           |
| S3            | 0.27            | 0.40            | 0.96            | 0.23            | 1.03            | 0.66            | 0.77            | -0.81           |
| S4            | 0.21            | 0.29            | 0.71            | 0.26            | 0.71            | 1.67            | 0.88            | -1.01           |
| S5            | 0.67            | 0.84            | 1.10            | 0.42            | 0.97            | 2.26            | 2.41            | -0.71           |
| S6            | 0.87            | 0.77            | 1.00            | 0.48            | 0.60            | 1.90            | 1.44            | -0.37           |
| S7            | 0.93            | 0.71            | 1.39            | 0.43            | 0.64            | 2.23            | 2.81            | -0.55           |
| Minimum       | 0.21            | 0.29            | 0.71            | 0.23            | 0.60            | 0.40            | 0.58            | -1.03           |
| Maximum       | 0.93            | 0.84            | 1.39            | 0.48            | 1.03            | 2.26            | 2.81            | -0.37           |
| Mean          | 0.65            | 0.60            | 0.98            | 0.35            | 0.82            | 1.36            | 1.39            | -0.78           |
| SD\textsuperscript{a} | 0.29            | 0.20            | 0.22            | 0.099           | 0.17            | 0.84            | 0.88            | 0.25            |

\textsuperscript{a}Standard deviation.

Because heavy metals in water and sediments have now been shown to threaten the health of aquatic animals and humans, it is important to analyse and to control the sources of pollution. Heavy metals in sediments often exhibit complex interrelationships. Numerous factors control their relative abundance; e.g., the original heavy metal contents of rocks and parent materials, processes of soil formation, contamination by human activities, and other anthropogenic factors [33]. Using SPSS software, Pearson correlation (PC) analysis was implemented to determine the relationship between the heavy metals and their pollution sources, and Principal components analysis (PCA) was performed to determine the most common pollution sources.

Table 1 depicts the correlation coefficient matrix, listing the Pearson product moment correlation coefficients. In water, very significant correlations were found between Co and Cu ($r=0.656$), Co and Zn ($r=0.740$), Cr and Pb ($r=0.578$), Ni and Tl ($r=0.661$) at the $p<0.05$ level. And in sediment, very significant correlations were found between Cr and Ni ($r=0.893$), Cu and Cd ($r=0.914$) at the $p<0.01$ level, very significant correlations were found between Tl and Ni ($r=0.828$), Tl and Zn ($r=0.848$) at the $p<0.05$ level. High correlations between specific heavy metals in the water and sediments may reflect similar levels of contamination or release from the same sources of pollution [34-35]. There were relative strong positive correlations between Co, Cu and Zn in water, but Cd and Tl did not show significant correlations with these metals (Table2). And in sediments, there are relative strong positive correlations between Co, Cr, Cu, Ni, Zn, Cd and Tl (Table2). The elements, Co, Cr, Cu, Ni, Zn, Cd and Tl, are grouped together, indicating that the anthropogenic sources of these heavy metals are closely related in the sediments of the study area. Pb is a proven human carcinogen, and it also has the potential to damage ecological communities [36]. The negative correlations between Pb and other heavy metals in sediments suggesting that the pollution sources of Pb differed from those of other metals.
Table 2. Pearson correlation matrix of heavy metals in the freshwater discharge outlets of the PRE.

|        | Co   | Cr   | Cu   | Ni   | Pb   | Zn   | Cd   | Tl   |
|--------|------|------|------|------|------|------|------|------|
| Water  |      |      |      |      |      |      |      |      |
| Co     | 1    |      |      |      |      |      |      |      |
| Cr     | 0.351| 1    |      |      |      |      |      |      |
| Cu     | 0.656| 0.303| 1    |      |      |      |      |      |
| Ni     | 0.348| -0.084| 0.390| 1    |      |      |      |      |
| Pb     | 0.488| 0.578| -0.064| 0.089| 1    |      |      |      |
| Zn     | 0.740| 0.043| 0.137| -0.089| 0.443| 1    |      |      |
| Cd     | -0.129| -0.571| -0.009| -0.392| -0.591| 0.000| 1    |      |
| Tl     | -0.256| -0.599| 0.012| 0.661| -0.344| -0.301| -0.195| 1    |
| Sediment |    |      |      |      |      |      |      |      |
| Co     | 1    |      |      |      |      |      |      |      |
| Cr     | 0.746| 1    |      |      |      |      |      |      |
| Cu     | 0.536| 0.612| 1    |      |      |      |      |      |
| Ni     | 0.699| 0.893**| 0.634| 1    |      |      |      |      |
| Pb     | -0.417| -0.131| -0.244| -0.500| 1    |      |      |      |
| Zn     | 0.238| 0.576| 0.650| 0.713| -0.467| 1    |      |      |
| Cd     | 0.448| 0.633| 0.914**| 0.643| -0.284| 0.848*| 1    |      |
| Tl     | 0.481| 0.643| 0.641| 0.828*| -0.523| 0.663| 0.552| 1    |

Bold values represent correlation with significance.
** Correlation with significance at the 0.01 probability level (2-tailed).
* Correlation with significance at the 0.05 probability level (2-tailed).

Another statistical analyses of the surface sediments and the water in the PRE were performed to further evaluate the relationship between the heavy metal concentrations. The loading plot of the first two principal components (PCs) of the samples are depicted in Fig.3 and Fig.4. Principal component analysis (PCA) is one of the analytical tools used to assess metal behaviour in the aquatic system [28, 37]. Fig.3 shows the results of factor analysis for heavy metals concentrations in water from the freshwater discharge outlets of the PRE. The first component with a variance of 36.93%, was highly correlated with Zn, Cr, Pb and Co. This component was called the anthropogenic factor. This suggests that the water of the PRE may have been subjected to a high input of waste water containing heavy metals from industries and residential areas surrounded the Pearl River. The second component explained 25.30% of the total variance with positive loadings on Tl and Ni. This component was called natural factor, which indicated that Tl and Ni were derived from nature. Cu was divided almost equally between the two components, revealing an equal correlation with two groups and suggesting that their sources could be both natural and anthropogenic. Cd formed a distinct group away from other elements, but it was still dominated by the second component. Fig.4 shows the results of factor analysis for heavy metals concentrations in sediments of the PRE. The first component accounted for 64.21% of the total variance, was highly correlated with Zn, Cr, Co, Cd, Cu, Tl and Ni, which indicated that these heavy metals were mostly derived from anthropogenic pollution. The second component explained 12.57% of the total variance with positive loading on Pb, which indicated that Pb was derived from the weathering of parent materials and subsequent paedogenesis. The results of the PCA [21] also showed a strong association among Zn, Cr, Cu and Co in sediments. The results of PC and PCA showed good agreement with each other.
The results of statistical analyses, both of the PC and PCA, may indicate that these heavy metals in water and sediments had distinct geochemical behaviours, and possibly originated from major anthropogenic sources through inputs of water and air. According to a study of heavy metal pollution of the Pearl River Estuary [26], the source of heavy metals in this area comes mainly from metal processing, electroplating industries, industrial wastewater, and domestic sewage.

### 3.3. Environmental Assessment of the Sediment

The enrichment factor (EF) and geoaccumulation index (Igeo) for different metals was calculated for the PRE. EF (%) is used to estimate the sediment chemistry in relation to natural and anthropogenic pollution sources. EF was calculated using following equation [38-39]:

\[
EF(\%) = \frac{C - C_{\text{min}}}{C_{\text{max}} - C_{\text{min}}} \times 100
\]

where \( C \) is the mean metal concentration in sediment (mg/kg), \( C_{\text{max}} \), \( C_{\text{min}} \) is the maximum and minimum concentration in (mg/kg) determined during the study.
Chen et al [23] concluded that metal pollution load in the PRE is increased due to mixing of anthropogenic discharge and industrial effluents, and diverse sources of different metals in Pearl River. We calculated the enrichment factors (EF) (%) for different metals in all study sites of the freshwater discharge outlets (Table3). Results of analysis shows enrichment factors, EF(Co), ranges from 8.16-84.4, EF (Cr) from 5.30 to 99.1, EF(Cu) from 5.91 to 93.9, EF(Ni) from 23.8 to 78.7, EF (Pb) from 19.1 to 91.4, EF (Zn) from 0.59 to 99.7, EF (Cd) from 1.19 to 97.6 and EF(Tl) from 9.30 to 83.7. As described in Table3, the maximum EF (%) value was at S5, S6 and S7 sampling sites where were affected by the metal pollution from the upstream rivers.

### Table 3. Enrichment factor (EF) (%) of different metals in sediments.

| Sampling site | EF (Co) | EF (Cr) | EF (Cu) | EF (Ni) | EF (Pb) | EF (Zn) | EF (Cd) | EF (Tl) |
|---------------|---------|---------|---------|---------|---------|---------|---------|---------|
| S1            | 63.9    | 59.8    | 30.0    | 50.0    | 69.1    | 0.59    | 5.95    | 13.9    |
| S2            | 72.8    | 43.3    | 14.2    | 31.1    | 59.1    | 0.59    | 1.19    | 9.30    |
| S3            | 13.6    | 20.9    | 33.3    | 23.8    | 91.4    | 8.02    | 4.76    | 30.2    |
| S4            | 8.16    | 5.30    | 5.91    | 30.3    | 35.5    | 53.8    | 7.14    | 11.6    |
| S5            | 53.1    | 99.1    | 50.8    | 65.6    | 79.1    | 99.7    | 67.9    | 41.9    |
| S6            | 77.6    | 83.5    | 39.0    | 78.7    | 19.1    | 69.4    | 22.6    | 83.7    |
| S7            | 84.4    | 72.6    | 93.9    | 66.4    | 24.5    | 97.3    | 97.6    | 60.5    |

Geoaccumulation index($I_{geo}$) introduced by Müller[40] in order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels, the geoaccumulation index($I_{geo}$) is defined by the following equation:

$$I_{geo} = \log_{2}(\frac{C_n}{1.5B_n})$$

Where $C_n$ is the measured concentration of the examined metal (n) in the sediment and $B_n$ is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lactogenic effects. We referred geochemical background values (as mg/kg) as described by Taylor and McLennan[41] 0.098 for Cd, 35.0 for Cr, 20.0 for Pb, 20.0 for Ni, 25.0 for Cu, 71.0 for Zn, 10.0 for Co and 0.75 for Tl.

Similar to enrichment factor, geoaccumulation index can be used as a reference to estimate the extent of heavy metal pollution in aquatic system. We calculated the geoaccumulation index ($I_{geo}$) of different metals for study sites of the PRE Table1. $I_{geo}$ values from this study are 0.21-0.93 for Co, 0.29-0.84 for Cr, 0.71-1.39 for Cu, 0.23-0.48 for Ni, 0.60-1.03 for Pb, 0.40-2.26 for Zn, 0.58-2.81 for Cd and (-0.03)-(-0.37) for Tl. A seven level classification of $I_{geo}$ is defined as: unpolluted (<0), unpolluted to moderately polluted (0-1), moderately polluted (1-2), moderately to strongly pollute (2-3), strongly polluted (>3), strongly to extremely pollute (3-4), and extremely polluted (>4) [40]. Results thus suggested “unpolluted” pollution of Tl, “unpolluted to moderately polluted” of Cr, Co and Ni, “moderately polluted” of Cu and Pb, and “moderately polluted to strongly polluted” of Zn and Cd in the freshwater discharge outlets of PRE. The average geoaccumulation index was 0.65 for Co, 0.60 for Cr, 0.98 for Cu, 0.35 for Ni, 0.82 for Pb, 1.36 for Zn, 1.39 for Cd and -0.78 for Tl. It was suggested that S2, S6 and S7 were severely polluted by Co, S1, S3 and S5 by Pb, and S5, S6 and S7 by Cr, Cu, Ni, Zn and Cd, all sites were not polluted by Tl. The results revealed that S5, S6 and S7 were the most polluted sites by the metals. The source of heavy metals to the PRE should include anthropogenic land-based point and non-point inputs. Some earlier reports suggested that industrial and urban wastewater discharges are the main sources of heavy metals in the PRE [21, 23]. But the most polluted sites as S5, S6 and S7 may polluted due to the thermal power plant and mine waste water discharge in the upstream river.
4. Conclusion

Heavy metal pollution is an important problem for the Pearl River Estuary. On the basis of investigations at 7 stations of the freshwater discharge outlets, heavy metal concentrations in the water, surface sediments were measured, enrichment factor and geoaccumulation index were calculated, and the possible sources of pollution were analyzed.

The heavy metal concentrations in the sediment were higher than those in the water. Correlation analysis and PCA illustrated that heavy metals (Zn, Cr, Pb and Co) in water may originate from metal processing, electroplating industries, industrial wastewater, and domestic sewage. Tl and Ni may be derived from nature, and Cu derived from nature and anthropogenic activities. But Cd did not show significant correlation with other heavy metals. PCA and correlation analysis for heavy metals in sediment indicate that Pb was dominated by nature and Zn, Cr, Co, Cd, Cu, Tl and Ni were mostly influenced by anthropogenic pollution. Analysis of the enrichment factor of sediment heavy metal concentrations showed that S5, S6 and S7 presented a relatively high enrichment factor. According to the geaccumulation index, Tl posed “unpolluted”; Cr, Co and Ni presented “unpolluted to moderately pollute”; Cu and Pb presented “moderately polluted”, and Zn and Cd presented “moderately polluted to strongly polluted”.

Acknowledgments

This study was financially supported by the unite fund project of National Natural Science Foundation of China-Guangdong: Research of ecological chemical behavior and toxicology effect of the environmental hormonal compounds in the Pearl River estuary (No. U1133003), National Natural Science Foundation of China project: Algicidal mechanisms to Phaeocystis globosa by algicidal bacteria and their extracellular active compounds (No. 41076068), and National Natural Science Foundation of China project: Roles of CYP450 in metabolism and detoxification of DSP toxins in bivalve species (No. 41176088).

References

[1] Uluturhan E, Kucuksezgin F. Heavy metal contaminants in Red Pandora (Pagellus erythrinus) tissues from the eastern Aegean Sea, Turkey [J]. Water research, 2007, 41 (6): 1185 - 1192.
[2] Almeida J A, Diniz Y S, Marques S F G, et al. The use of the oxidative stress responses as biomarkers in Nile tilapia (Oreochromis niloticus) exposed to in vivo cadmium contamination [J]. Environment International, 2002, 27 (8): 673 - 679.
[3] Xu Y, Liu X, Ma A. Current research on toxicity effect and molecular mechanism of heavy metals on fish [J]. MARINE SCIENCES-QINGDAO-CHINESE EDITION-, 2004, 28(10): 67 - 70.
[4] Wang W X. Interactions of trace metals and different marine food chains [J]. Marine Ecology Progress Series, 2002, 243: 295 - 309.
[5] Olivares-Rieumont S, De la Rosa D, Lima L, et al. Assessment of heavy metal levels in Almendares River sediments-Havana City, Cuba[J]. Water Research, 2005, 39 (16): 3945-3953.
[6] Agarwal A, Singh R D, Mishra S K, et al. ANN-based sediment yield models for Vamsadhara river basin (India) [J]. Water Sa, 2005, 31 (1): 85 - 100.
[7] Hope B K. An examination of ecological risk assessment and management practices [J]. Environment International, 2006, 32 (8): 985 - 995.
[8] Wu J, Meng X X, Li K. Phytoremediation of soils contaminated by lead [J]. Soils, 2005, 37 (3): 258 - 264.
[9] Zheng N A, Wang Q, Liang Z, et al. Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China [J]. Environmental pollution, 2008, 154 (1): 135 - 142.
[10] Fung C N, Lam J C W, Zheng G J, et al. Mussel-based monitoring of trace metal and organic contaminants along the east coast of China using Perna viridis and Mytilus edulis[J]. Environmental Pollution, 2004, 127 (2): 203 - 216.
[11] Ip C C M, Li X D, Zhang G, et al. Over one hundred years of trace metal fluxes in the sediments of the Pearl River Estuary, South China [J]. Environmental Pollution, 2004, 132 (1): 157 - 172.
[12] Liu L, Xiong D Q, Gao X H, et al. Characteristics of heavy metals contamination and distribution in surficial sediment of Haihe River and the adjacent sea area[J]. Marine Environmental Science, 2006, 25 (2): 40D44.
[13] Wu X Y, Liu R H, Qin J, et al. Study on the variance character of heavy metals contents in sediments in Yellow River Estuary [J]. Trans Oceanol Limnol, 2007, 1: 69 - 74.
[14] An Q, Wu Y, Wang J, et al. Assessment of dissolved heavy metal in the Yangtze River estuary and its adjacent sea, China [J]. Environmental monitoring and assessment, 2010, 164 (1-4): 173 - 187.
[15] Alloway, B.J (2013). Heavy metals in soils-trace metals and metalloids in soils and their bioavailability. Springer, Dordrecht.
[16] Ouyang T P, Zhu Z Y, Kuang Y Q, et al. Dissolved trace elements in river water: spatial distribution and the influencing factor, a study for the Pearl River Delta Economic Zone, China [J]. Environmental geology, 2006, 49 (5): 733 - 742.
[17] Xu Z C, Yang X Y, Wen Y, et al. Evaluation of the heavy metals contamination and its potential ecological risk of the sediments in Beijiang River's upper and middle reaches [J]. Huan jing ke xue= Huanjing kexue, 2009, 30 (11): 3262 - 3268.
[18] Xie W P, Wang S B, Zhu X P, et al. Residues and potential ecological risk assessment of metal in sediments from lower reaches and estuary of Pearl River[J]. Huan jing ke xue= Huanjing kexue, 2012, 33 (6): 1808 - 1815.
[19] Wang S, Cao Z, Lan D, et al. Concentration distribution and assessment of several heavy metals in sediments of west-four Pearl River Estuary [J]. Environmental Geology, 2008, 55 (5): 963 - 975.
[20] Li X, Wai O W H, Li Y S, et al. Heavy metal distribution in sediment profiles of the Pearl River estuary, South China [J]. Applied Geochemistry, 2000, 15 (5): 567 - 581.
[21] Ip C C M, Li X D, Zhang G, et al. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China [J]. Environmental Pollution, 2007, 147 (2): 311 - 323.
[22] Yu X, Yan Y, Wang W X. The distribution and speciation of trace metals in surface sediments from the Pearl River Estuary and the Daya Bay, Southern China [J]. Marine Pollution Bulletin, 2010, 60 (8): 1364 - 1371.
[23] Chen B, Liang X, Xu W, et al. The changes in trace metal contamination over the last decade in surface sediments of the Pearl River Estuary, South China [J]. Science of the total environment, 2012, 439: 141 - 149.
[24] Yang Y, Chen F, Zhang L, et al. Comprehensive assessment of heavy metal contamination in sediment of the Pearl River Estuary and adjacent shelf [J]. Marine Pollution Bulletin, 2012, 64 (9): 1947 - 1955.
[25] Harrison R M, Laxen D P H. Physicochemical speciation of lead in drinking water [J]. Nature, 1980, 286 (5775): 791.
[26] Zhang D, Zhang X, Tian L, et al. Seasonal and spatial dynamics of trace elements in water and sediment from Pearl River Estuary, South China [J]. Environmental earth sciences, 2013, 68 (4): 1053 - 1063.
[27] State Environmental Protection Administration of China (SEPA) .Sea Water Quality Standard (GB3097-1997). Standards Press of China, Beijing.1997.
[28] Liu W X, Li X D, Shen Z G, et al. Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary[J]. Environmental Pollution, 2003, 121 (3): 377 - 388.
[29] Xiangqing H. The distribution and assessment of heavy metals in surficial sediments in the Pearl River Estuary [J]. Transactions of Oceanology and Limnology, 2006, 3(109): 27.
[30] Anderson R V, Vinikour W S, Brower J E. The distribution of Cd, Cu, Pb and Zn in the biota of two freshwater sites with different trace metal inputs [J]. Ecography, 1978, 1 (4): 377 - 384.
[31] Barak N A E, Mason C F. Heavy metals in water, sediment and invertebrates from rivers in eastern England [J]. Chemosphere, 1989, 19 (10-11): 1709 - 1714.

[32] Yujun Y, Zhaoyin W, Zhang K, et al. Sediment pollution and its effect on fish through food chain in the Yangtze River [J]. International Journal of Sediment Research, 2008, 23 (4): 338 - 347.

[33] Li C, Lu F Y, Zhang Y, et al. Spatial distribution characteristics of heavy metals in street dust in Shenyang city [J]. Ecol Environ, 2008, 17 (2): 560 - 564.

[34] Håkanson, L., Jansson, M. Principles of Lake Sedimentology. Springer Verlag, Berlin.1983.

[35] Li F, Fan Z, Xiao P, et al. Contamination, chemical speciation and vertical distribution of heavy metals in soils of an old and large industrial zone in Northeast China [J]. Environmental Geology, 2009, 57 (8): 1815 - 1823.

[36] Sadiq R, Husain T, Bose N, et al. Distribution of heavy metals in sediment pore water due to offshore discharges: an ecological risk assessment [J]. Environmental Modelling & Software, 2003, 18 (5): 451 - 461.

[37] Shine J P, Ika R V, Ford T E. Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbor marine sediments [J]. Environmental Science & Technology, 1995, 29 (7): 1781 - 1788.

[38] Loska K, Wiechula D. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir [J]. Chemosphere, 2003, 51 (8): 723 - 733.

[39] Zonta R, Zaggia L, Argese E. Heavy metal and grain-size distributions in estuarine shallow water sediments of the Cona Marsh (Venice Lagoon, Italy) [J]. Science of the total environment, 1994, 151 (1): 19 - 28.

[40] Müller, G (1981). Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chemical Zeitung. 105 (2), 157 - 164.

[41] Taylor S R, McLennan S M. The geochemical evolution of the continental crust [J]. Reviews of Geophysics, 1995, 33 (2): 241 - 265.