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Investigation on Heavy Metal Pollution Risk of Sediment in a Human-disturbed River, China

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Abstract. Analysis of heavy metal pollution in sediment is of importance to water treatment. In the present study, borehole columnar sediment samples with 3~4 m thickness from 86 points along Maozhou River were collected to determine the concentrations of six main metal elements (Cu, Cr, Cd, Pb, Zn, Ni) using plasma direct reading spectroscopy. Then, the vertical distribution of heavy metal among sediment is revealed. What's more, the pollution risk levels at different depths are determined by potential ecological risk index. The heavy metal source is also discussed through correlation analysis between different heavy metal elements. The result of this study provide valuable reference for dredging depth determination as well as treatment of malodorous black water body.

1. Introduction

Sediment is one of the most important component of an aquatic ecosystem which can provide a production environment for microorganisms and food for fish. It is also the main sink of various extraneous chemicals. As a result, the sediment will be polluted if chemical concentration exceeds a threshold, called contaminated sediment, thus causing permanent hazards to water bodies [1, 2]. Contaminated sediment also causes threat to benthic habitants directly [3]. What's worse, accumulated contaminants in sediment could result in secondary pollution because they can be released back to the water body under disturbance of hydrodynamic force or human activities by effect of molecular diffusion, particle resuspension, and bioturbation [4]. Therefore, contaminated sediment is often regarded as the secondary pollution source in deteriorating water quality and becomes the focus in water treatment [5]. In brief, sediment quality is a key indicator of water deterioration and aquatic ecological environment.

Among many chemicals in sediment, Heavy metal elements (HME) should be given enough attention. HME are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. HME are accumulated in sediment under effect of adsorption, complexation and precipitation. They are associated with human activities, such as industrial, metalliferous mining, agricultural, atmospheric deposition, sewage and waste disposal [6]. These sources can be divided into two types of sources of pollutants: point sources (industrial), and nonpoint sources (metalliferous mining, agricultural, atmospheric deposition, sewage and waste disposal). Heavy metals are the most dangerous pollutant of anthropogenic environmental pollutants due to their toxicity and persistence in the environment [7, 8]. Past studies have also revealed that human exposure to high concentrations of



heavy metals will lead to their accumulation in the human body [9]. They not only influence aquatic ecosystem but also threaten human health. Thus, researchers and river managers attach increasing attention on the heavy metal pollution [10-12].

Maozhou River, located in Bao'an District of Shenzhen, Guangdong Province, Southwestern China, which has been experiencing rapid urbanization and industrialization. More and more HME are released to river body and then accumulated in the sediment. As a result, the sediment is characterized as to be malodorous and black, which is threatening the living environment. A few of studies have been conducted to investigate the HME content in the surface with depth about 30~60 cm of riverbed based on a little data from year 1996 to 2016 [13-15]. It can be seen that heavy metals content of Pb, Cd, Cr, Zn, Cu and Ni are relatively high with great geo-accumulation index. Sediment has been faced with significant ecological risk. However, existing studies are not enough to reveal the vertical distribution of heavy metals.

Therefore, the objectives of the present study are: (1) to reveal the vertical distribution of heavy metal among sediment; (2) to evaluate the pollution levels of the selected heavy metal elements.

2. Materials and methods

2.1. Study area

Maozhou River springs from the Yangtai Mountain, running through Dongguan and Shenzhen and into the Pearl River Estuary, as shown in Figure 1. There are about forty one rivers in the basin area, including 1 trunk stream, 23 second-order tributaries and 17 third-order tributaries. Due to the urbanization and industrialization in recent decades, Maozhou River has been disturbed by human activities significantly. Increasing domestic, municipal and industrial wastewater discharge into rivers which have damaged the balance between sewage and self-purification capacity in the natural system and have further resulted in water quality deterioration. Thus heavy metals have also been accumulated in sediment. Then, water body becomes malodorous and black under combination effect of sewage and sediment. Therefore, investigation on heavy metals is necessary to understand the elemental distribution and pollution levels.



Figure 1. Maozhou River Basin

2.2. Sample collection

In the present study, the trunk reach downstream Yangchong Sluice and tributary reach downstream intersection of Tantou Canal and Tantou River were chosen to collect sediment samples. Sample collection was conducted by boring method during the summer months of July and August in 2016. For easy analysis, studied reach were marked as reach A (from Yangchong Sluice to intersection of

Maozhou River and Shajing River), reach B (from intersection of Tantou Canal and Tantou River to intersection of Maozhou River and Shajing River) and reach C (from intersection of Maozhou River and Shajing River to the Pearl River Estuary). Observed sections were set along river with spacing between 3~4 m. For each section, observed points were set with spacing between 1~2 m. Therefore, there were 46 sections along with 86 points, as shown in Figure 2.

Borehole columnar samples with depth between 3~4 m were collected at each observed point. These points were located by GPS precisely. In order to investigate the vertical distribution of HME in sediment, each borehole columnar sample was divided into four layers, marked as I (0~1 m), II (1~2 m), III (2~3 m), IV (>3 m) and layer I represents the surface. The collected sediment samples were stored in polytetrafluoroethylene bags and numbered, and brought back to the laboratory. The sediment samples were naturally air-dried in the laboratory, of which the impurities such as stones, animal and plant residues were removed. Then they would be grinded with a mortar for test.

The grinded sediment were sieved using a 100-mesh nylon sieve. Afterwards, the powdered sediment about 0.5 g was digested in a stainless digestion tank coupled with HNO₃ (1 ml) and HF (1 ml). The tank was put in a constant temperature oven with temperature of 270 °C for 48 hours. Then, the tank was put on the graphite electrothermal plate with temperature of 110 °C coupled with nitrite nitric acid (1 ml) until the mixed solution was dry. Afterwards, the dry sediment mixed with ultra pure water (1 ml), nitrite nitric acid (1 ml) and HNO₃ (1 ml) was put in a constant temperature oven with temperature of 190 °C for 24 hours until the mixed solution is clear. The HME content in the clear solution could be tested by ICP-AES.

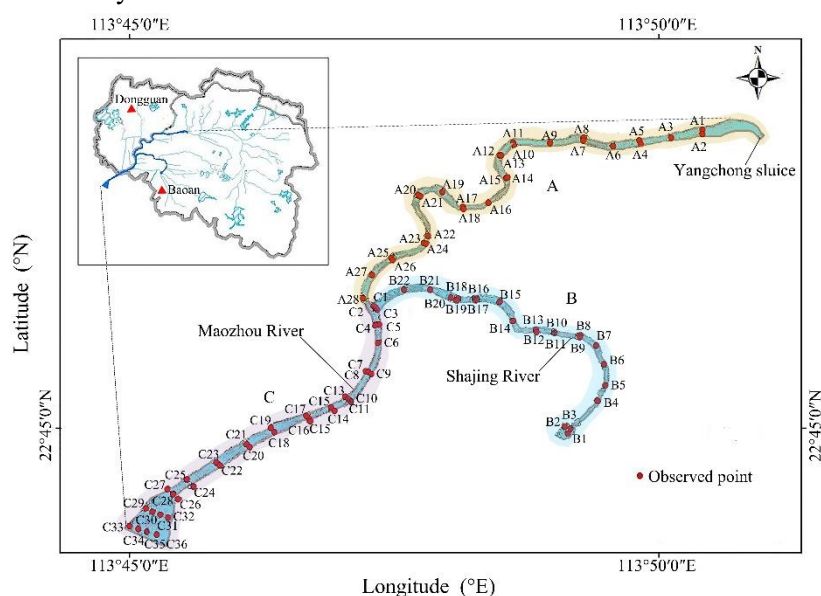


Figure 2. Distribution of observed sections and points

2.3. Analysis method

The potential ecological risk index (*RI*) is applied to evaluate pollution risk level of HME. It was proposed by Hakanson in 1980, which takes into account the effects of pollutant concentration and toxicity on the environment, and can comprehensively reflect the impact of heavy metals on the ecological environment [16, 17]. *RI* can be calculated as follows:

$$RI = \sum_{i=1}^n E_{r,i} \quad (1)$$

$$E_{r,i} = T_{r,i} \times P_i \quad (2)$$

$$P_i = \frac{C_i}{C_0} \quad (3)$$

Where RI is the potential ecological risk index; $E_{r,i}$ is the potential ecological risk coefficient of a certain heavy metal element; P_i is pollution index of a certain heavy metal element; $T_{r,i}$ is biotoxicity weighting coefficient of a certain heavy metal element, according to Table 1; C_i is the measured concentration of pollutants of a certain heavy metal element; C_0 is the soil background values of Shenzhen City, according to Table 2.

Table 1. Biotoxicity of heavy metals.

Element species	Cu	Zn	Cr	Ni	Pb	Cd
Biotoxicity	5	1	2	5	5	30

Once the RI is calculated, pollution risk level can be determined according to Table 3.

Table 2. Background values of heavy metals

Element species	Cu	Zn	Cr	Ni	Pb	Cd
Background values (mg/kg)	11.10	78.70	30.97	17.80	40.90	0.09

Table 3. Potential ecological risk coefficient and comprehensive potential ecological risk index

$E_{r,i}$	RI	Pollution risk level
<40	<150	Light ecological risk
40~80	150~300	Medium ecological risk
80~160	300~600	Strong ecological risk
160~320	≥ 600	Very strong ecological risk
≥ 320	≥ 600	Extremely strong ecological risk

3. Results and discussion

3.1. Distribution of HME in sediment

According to the analysis of ICP-AES, HME content of each observed point in different layers can be achieved. Then the average HME content of each reach (reach A, B and C) is calculated, as shown in Figure 3.

Generally, along with the increase of depth from riverbed surface, the HME content decreases gradually for all reaches. That is, the surface layer (layer I) is the most polluted. It can also be implied that human activities give rise to more effect on river in recent decades, which can be reflected vividly by Figure 4. The green area in Maozhou River basin has been decreasing significantly from 1987 to 2017.

Among six HME, Cu content is obviously greater than other HME, of which the maximum value reaches 802 mg/kg; Cd content is less than other HME, of which the minimum value is 0.44 mg/kg. The relationship between six HME content in Maozhou River can be found that: Cu>Zn>Cr>Ni>Pb>Cd.

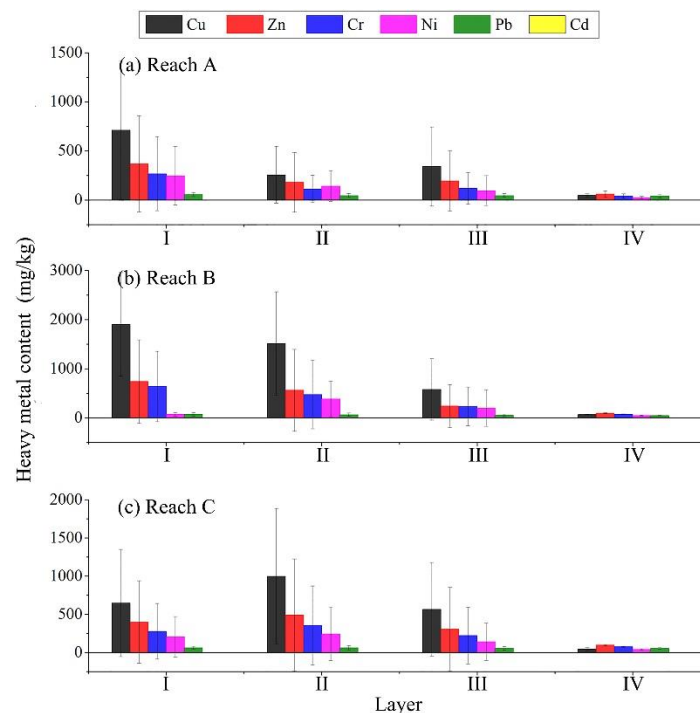


Figure 3. The average HME content at different layers for each reach



Figure 4. Changes in green area from 1987 to 2017

3.2. Pollution risk level analysis

Based on the HME content and potential ecological risk index as described above. The pollution risk level can also be obtained, as shown in Figure 5. The RI in layers I~III of reach B and C are greater than 300. That is, the pollution risk level has exceeded 'very strong'; it even reaches 'extremely strong' for reach B in layer I and II. For reach A, RI in layer I approaches to 300, thus the pollution risk level is 'medium'; RI in layers II and III are all less than 150, of which the pollution risk levels are 'light'. Lastly, for reach A, B and C, RI in layer IV are all less than 150, of which the pollution risk levels appear to be 'light'.

In a word, the surface layers (layer I and II) are polluted by heavy metal obviously, indicating that sediment dredging is urgent.

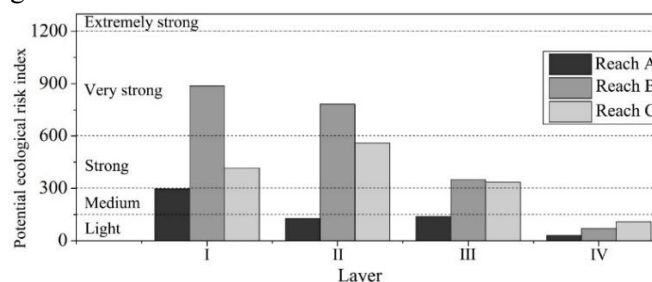


Figure 5. Potential ecological risk index at different layers for each reach

3.3. Analysis of Heavy Metal Sources

Correlation analysis is applied in the present study to explore the relationship between six heavy metal elements, as shown in Table 4. Correlation coefficients between any two HME are all greater than 0.88, indicating that a significant positive correlation exists between heavy metal elements. Therefore, these HME come from the same source.

According to statistical data, the pollutant industry in Maozhou River basin mainly consists of electroplating workshop. There are about 174 electroplating workshop, of which the sewage has been discharged into river without treatment. Consequently, a lot of HME have been drained into river and stored in sediment.

Table 4. Correlation coefficients between any two HME

	Cu	Zn	Cr	Ni	Pb	Cd
Cu	1.00	0.97	0.97	0.94	0.88	0.93
Zn		1.00	0.97	0.94	0.90	0.93
Cr			1.00	0.93	0.88	0.94
Ni				1.00	0.88	0.93
Pb					1.00	0.89
Cd						1.00

4. Conclusion

In the present study, the vertical distribution of six heavy metal elements among sediment and the pollution risk levels of selected heavy metal elements have been investigated. From the previous discussion, the following important conclusions can be drawn.

The HME content decreases for all river reaches along with the increase of depth from layer I to layer IV, which indicates that HME has been discharged into river obviously due to industrialization and urbanization in recent decades.

Sediment in the surface layer is suffering strong ecological risk even very strong ecological risk, which is necessarily to be treated. Sediment with depth greater than 3 m appears to be light ecological risk.

The relationship between six heavy metal elements is Cu>Zn>Cr>Ni>Pb>Cd. According to correlation analysis, the six heavy metal elements have the same source.

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