Evaluation of Nutrient and Heavy Metal Pollution in Maozhou River in Shenzhen City

Daiwen Zhu1,2,*, Shizhang Wu3 and Nan Lu1,2

1Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi’an 710075, China
2Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi’an 710075, China
3PowerChina Northwest Engineering Corporation Limited. Xi’an city, Shaanxi province, China

*Corresponding author e-mail: zhudaiwen@163.com

Abstract. The sediment of Shenzhen Mazhou River was collected and sieved with different particle sizes to determine the physicochemical properties, nutrient contents and heavy metal contents of sediment, interstitial water and oversize mud. At the same time, the single factor evaluation and potential ecological risk assessment of heavy metals were carried out on the sediment of Mazhou River. The experimental results show that the screening of different particle size has little influence on the physicochemical properties and nutrient content of sediment. Mazhou River nitrogen and phosphorus nutrients pose little ecological risk effect on the environment. The ecological risk ranking of heavy metals is Hg> Cd> Cu> Ni> As> Zn = Cr> Pb. Mazhou river sediment comprehensive potential risk index RI values are greater than 1200, indicating that Maozhou river was in extremely high risk. Among them, Hg contributes the most, which is the most important factor controlling the risk of heavy metal pollution in sediment.

1. Introduction
River sediments are a variety of sources of nutrients deposited in the river bottom, which form nutrient-rich black sediment through physical, chemical and biological effects. Pollutants enter the body of water through various means and gradually accumulated into the sediment, finally resulting in sediment pollution in the river. Polluted sediments have high water content, complex composition, high content of heavy metals, with obvious odor and other characteristics [1]. Sediment, as an important part of the water environment, can absorb the pollutants in the water body to reduce water pollution. However, when the external conditions change, the form of pollutants in the sediment changed and the pollutants could re-dissolve into the water, resulting in secondary pollution of water [2]. In particular, part of the heavy metals in the sediment phase can return to the water phase. Therefore, the heavy metal pollution in river sediments is potential and long-term [3].

If the sediment pollution of the river could not be effectively disposed, it will inevitably cause secondary pollution. The best treatment and disposal methods for these polluted sediments are that the sediment meeting the resource utilization standard is directly recycled after being dehydrated, and the
sediments that do not meet the standard for resource utilization are treated and disposed finally. Among them, heavy metal is an important factor restricting the utilization of sediment [4]. The main factors affecting the content of heavy metals in particulate matter are the surface structure, specific surface area, particle size, organic matter and surface active adsorption potential, among which the particle size is the main factor [5]. Therefore, in this study, typical sediment from Maozhou River in Shenzhen was used as a research object to investigate particle size distribution and heavy metal accumulation in polluted sediments.

At the same time, the riverbed sediment will also have the release of nitrogen and phosphorus and the eutrophication problem. After the external conditions change, the deposited nutrients will enter the upper water body with the mixing of the surface layer and the bottom layer water, thus providing the necessary nutrition for the survival of the phytoplankton. This may aggravate the eutrophication of water body [6]. Therefore, the single factor evaluation of nitrogen and phosphorus nutrients was performed in this study. In order to deal with the heavy metal pollution in river sediments, the potential ecological risk index method proposed by Hakanson was used to evaluate the potential ecological risk of heavy metals in river sediment. This evaluation method takes into account the toxicity and migration rules of pollutants and eliminates the regional differences and the impact of heterogeneous pollution. Therefore, it is widely used in ecological risk assessment of heavy metals [7]. This study could provide scientific basis for the ecological environment protection, heavy metal pollution prevention and ecological risk management of Shenzhen river ecosystem and water source.

2. Material and methods

In September 2016, in a relatively gentle and abundant water area, sediment samples were selected along the river and a trunk sampler was used to take the tributaries of the Maozhou River, a typical polluted river in Shenzhen.

Typical samples were taken at two sites and three sediment samples were taken at each site. For the sampling point 1, the sediment was sieved with a size of 38 μm screen. The sediment at the sampling point 2 was sieved on with a size of 75 μm screen. Then the physicochemical properties of primary sediment, sediment above the screen and sieved interstitial water were analyzed. The levels of nitrogen and phosphorus nutrients and the contents of cadmium, chromium, mercury, arsenic, lead, copper, zinc, nickel was determined. The effects of different size of sediment on the levels of nitrogen and phosphorus nutrients and heavy metal in sediment were studied.

3. Results

3.1. The physical and chemical properties of Mazhou River sediment

The moisture content of sediment at sampling point 1 and sampling point 2 were 3.87 and 2.77%, respectively, and the total phosphorus contents were 0.50 and 0.53 mg/kg respectively, and the total nitrogen contents were 9.12 and 9.63 mg/kg, respectively. The sampling point 1 sieved 38μm screen and sampling point 2 sieved 75μm. The change of interstitial water after screen for the water content, total phosphorus, total nitrogen content, is small. After screen, the sediment moisture content, total phosphorus, total nitrogen content, on the sieve were lower than those in the original sediment. The pH of the sediment and interstitial water was 7.44 and 7.54, respectively, which were neutral. Therefore, the screening of different particle size has little effect on the physical and chemical properties of sediment and the content of nitrogen and phosphorus nutrients.
Table 1. Physical and chemical index of sediment, interstitial water and the screen sediment in MaoZhou River

| index       | Sampling 1 |                      | Sampling 2 |                      |
|-------------|------------|----------------------|------------|----------------------|
|             | sediment   | interstitial water   | sediment   | interstitial water   |
| pH          | 7.54       | 7.5                  | 7.46       | 7.44                 |
| Moisture    | 3.87       | 3.1                  | 2.77       | 3.46                 |
| content (%) |            | 3.41                 | 3.46       | 3.51                 |
| TP(mg/kg)   | 0.5        | 0.45                 | 0.53       | 0.68                 |
| TN(mg/kg)   | 9.12       | 9.18                 | 9.63       | 9.71                 |
|             | 7.71       | 9.71                 | 6.13       |                      |

3.2. The heavy metal pollution status of Maozhou River sediment

The Cd concentrations in the sediment of sampling sites 1 and 2 were 0.762 and 0.780 mg/kg, respectively. After screening 38μm and 75μm sieve respectively, the Cd levels for interstitial water remained almost unchanged, also, the content of sediment above the sieve did not change much. Cr concentrations in the sediments of sampling points 1 and 2 were 289.8 and 306.6 mg/kg, respectively. After screening the 38μm and 75μm sieves respectively, the Cr level for remained almost same for interstitial water, however their levels above the sieve decreased. The contents of Hg in sediments 1 and 2 were 0.992 and 1.116 mg/kg, respectively. The content of Hg in the interstitial water after screening increased, and the content of Hg in the sediment above the sieve became smaller. The Pb contents in sediments 1 and 2 were 54.36 and 61.10 mg/kg, respectively, and the Pb concentrations in the interstitial water after filtration increased. The as concentrations of sediments 1 and 2 were 10.98 and 13.94 mg/kg respectively, and the contents of Cu were 740 and 931 mg/kg, respectively. Content of Zn in sediment were 605 and 627 mg/kg and Ni were 466 mg/kg, respectively. The contents of Cu, Zn, as and Ni for interstitial water after screen were all increased, and the contents of As, Cu, Zn and Ni in the sediment above the sieve all decreased. Furthermore, Ag and Se content were not detected. Consequently, the study found that the effect of different particle size of the sediment on the heavy metal content is little.

3.3. The nitrogen and phosphorus nutrients pollution assessment of Maozhou River sediment

The release of sediment nutrients is an important factor affecting the eutrophication status of the lake. Analysis of the changes of organic matter and nitrogen and phosphorus content in sediments is conducive to understanding the migration and transformation of nutrients and the sources and distribution of heavy metals. The single factor standard index method for total phosphorus, total nitrogen
was used in this study for evaluation of the Mazhou River sediments. The equation of the general standard index for a single pollution factor $i$ is: $S_i = \frac{C_i}{C_S}$ [8].

Where: $S_i$ is the single standard index, $C_i$ is greater than 1, indicating that the content exceeds the evaluation standard value; $C_i$ is the measured value of evaluation factor $i$; $C_S$ is the evaluation standard value. The total nitrogen content of sediments with the lowest ecological effect is 550mg/kg, and the total nitrogen content with serious ecological effects is 4800mg/kg. The total phosphorus content of the sediments with the lowest ecological effect is 600 mg/kg, and the total phosphorus content with the serious ecological effects is 2000 mg/kg[9]. Therefore, in this study, the standard values of total nitrogen and total phosphorus were 550mg/kg and 600mg/kg, respectively. Accordingly, the calculated standard index of total nitrogen in sediment of sampling points 1 and 2 were 0.17 and 0.18 respectively, and total phosphorus standard index were 0.0008 and 0.0009, which were both far less than 1. Therefore, the nitrogen and phosphorous nutrients in Mazhou River do not have the ecological risk effect and have less harm to the environment.

3.4. The heavy metal pollution assessment of Maozhou River sediment

This study intends to use the potential ecological risk index proposed by Hakanson to evaluate the potential ecological risk of heavy metals in sediment. The formula is: [7]

$$C^R_i = \frac{C^D_i}{C^R_i}$$

$$E^R_i = T^R_i C^R_i$$

$$RI = \sum_{i=1}^{m} E^R_i$$

Where: $C^D_i$ represents the measured concentration of the sample; $C^R_i$ is the background value of the corresponding pollutants in the sediment; $RI$ is the potential ecological risk index of a variety of heavy metals in a certain sample: $E^R_i$ is the single heavy metal potential ecological risk index, $T^R_i$ is the toxicity coefficient of the heavy metal, which reflects the toxicity level of pollutants [10].

The required toxicity coefficient, background values, and evaluation classification was provided in Tables 2 and 3. The background value of heavy metal mainly refers to the background value of soil metal in Guangdong Province, because the background value of local heavy metal can relatively reflect the pollution degree of sediment in each sampling site [11].

| Table 2. Heavy metal background reference and toxicity factor |
|---------------------------------------------------------------|
| Element | Cd | Cr | Hg | As | Pb | Cu | Zn | Ni |
|---------|----|----|----|----|----|----|----|----|
| $C^R_1$ | 0.04 | 35.6 | 0.055 | 6.8 | 29.8 | 10.5 | 36.3 | 9.6 |
| $T^R_1$ | 30 | 2 | 40 | 10 | 5 | 5 | 1 | 5 |

| Table 3. Grade of potential ecological risk index of heavy metal pollution |
|---------------------------------------------------------------|
| $E^R_1$ | Ecological risk level | RI | Ecological risk level |
|---------|----------------------|----|----------------------|
| <40     | Low risk             | <150 | Low risk             |
| 40–80   | Moderate risk        | 150–300 | Moderate risk       |
| 80–160  | Considerable risk    | 300–600 | High risk          |
| 160–320 | High risk            | 600–1200 | Serious risk       |
| ≥320    | Serious risk         | ≥1200 | Extremely serious risk |
Table 4. Potential ecological risk assessment of heavy metals in river sediments

| Sample      | Cd   | Cr  | Hg  | As   | Pb   | Cu  | Zn  | Ni | RI  |
|-------------|------|-----|-----|------|------|-----|-----|----|-----|
| Sampling 1  | 585  | 17  | 812 | 16   | 9    | 443 | 17  | 243| 2142|
| Sampling 2  | 572  | 16  | 721 | 21   | 10   | 352 | 17  | 243| 1952|
| Average     | 579  | 17  | 767 | 19   | 10   | 398 | 17  | 243| 2047|

According to the sediment data shown in Figure 1, the potential ecological risk index and comprehensive potential ecological risk index of each heavy metal in the sediment were calculated and the results were shown in Table 4. Based on the potential ecological risk analysis of single heavy metals, the potential ecological risk index of Cd, Hg and Cu in river sediments were more than 320, belonging to serious risk. The potential ecological risk index for heavy metals in Ni was between 160-320, which was high risk. The potential ecological risk index of heavy metals in Cr, Zn, As and Pb were all less than 40, which belonged to low risk. Some industrial and agricultural production activities include metal smelting, fossil fuel combustion, and industrial wastewater and urban domestic wastewater discharge, leading to the entry of heavy metals such as Cu, Hg, and Cd into the water environment of the Maozhou River in Shenzhen and their deposition and enrichment in sediments. Based on the comprehensive potential ecological risk analysis of various heavy metals, the comprehensive potential risk index (RI) values of the two sampling points were both greater than 1200, which is extremely high risk. The average contributions of Cd, Cr, Hg, As, Pb, Cu, Zn and Ni to RI were 28.3%, 0.8%, 37.4%, 0.9%, 0.5%, 19.4%, 0.8% and 11.9%, respectively. The order of the contribution rate of various heavy metals to RI was Hg > Cd > Cu > Ni > As > Zn = Cr > Pb. Among them, the contribution rate of Hg was the largest, which could be considered to be the most important factor controlling the risk of heavy metal pollution in sediments.

4. Discussions

Maozhou River is the largest river in Shenzhen and has a large river basin. However, due to the accumulation of backward industries in the Maozhou River Basin, heavily polluting enterprises are more concentrated, and the problems of waste-water treatment and undocumented sewage discharge are more serious. Accordingly, the discharge of domestic sewage caused serious black-odor phenomenon in Maozhou River. This study evaluated the potential ecological risk of nutrients and heavy metals in Mazhou River. However, the sampling number is too small. At the same time, only the surface sediment is collected, however the sediment of different depth is not collected, so that the depth of sediment dredging could not be calculated. In this paper, the collected sediment were sieved with different particle sizes in order to get the influence of particle size on the heavy metals in the sediment, so as to provide a method for river dredging to better realize the utilization of heavy metal contaminated sediments. However, it was found that the screening of different particle size has no significant effect on heavy metals contents in sediment in this study. On the contrary, it was found that the amount of heavy metals in sediment with different particle sizes increased with decreasing particle size [5].

There have been some researches on ecological risk assessment of river sediment. And there are many methods to evaluate river sediment pollutants. Commonly used method are single factor index evaluation method, the geo-accumulation index method, the Neolithic integrated pollution index method, the sediment enrichment factor method, the potential ecological risk index method [12]. In this paper, the single factor index method was used for assessment of nutrient contamination. The larger index indicates the higher the degree of eutrophication. Zhou et al found that u that the risk of phosphorus and nitrogen in Shanmei Reservoir sediment is low using single factor index [6]. The geo-accumulation index method can only reflect the pollution characteristics of a single pollution index in a specific pollution area, and could not comprehensively reflect the pollution degree of all the pollutants. Sediment enrichment factor method is by measuring the content of heavy metals in sediment to reflect the degree of pollution of sediment. The greater the enrichment factor of heavy metals in sediment suggested the higher the degree of heavy metal contamination. Kongtae using sediment enrichment factor method and
the geo-accumulation index method found that Cu, Zn, As, Cd, Pb and Hg sediments accumulated serious in Korea Ulsan port [13].

The evaluation method of heavy metals used in sediment of rivers in this paper is the potential ecological risk index method, and is also the most commonly used method to evaluate the heavy metal pollution of sediment. Although this method can comprehensively reflect the possible ecological hazards caused by all kinds of heavy metals, it has certain subjectivity in determining the toxicity coefficient and does not fully consider the various parameters in the water environment (such as pH, Eh, alkalinity, etc.). Also, the effect of the different forms of heavy metals on the biological hazards was not fully considered. Therefore, there is a certain error in this study when calculating the potential ecological risk index of heavy metals in Maozhou River sediment.

5. Conclusion
Different particle of sediment in Shenzhen city has less effect on the physicochemical properties as well as nutrient content and heavy metal of sediment. The nitrogen and phosphorus nutrients in Maozhou River do not have the ecological risk effect and have less harm to the environment. The order of ecological risk of heavy metal is Hg> Cd> Cu> Ni> As> Zn = Cr> Pb. The comprehensive potential risk index RI value in Mazhou River sediment were greater than 1200, which indicate extremely serious risk of the Mazhou River. The contribution rate of Hg was the largest, which could be considered to be the most important factor in the control of heavy metal pollution risk of sediment.

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