Research on the Nutrient and Heavy Metal Pollution Characteristics of Sediment in Zaoxia River in Shenzhen City

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Abstract. This paper mainly investigated the black-smelly Zaoxia River in Shenzhen city and analyzed the moisture content, nutrients and heavy metal levels in river sediments. The results showed that total phosphorus, total nitrogen and heavy metals in the sediment of Zaoxia River Shenzhen City exceeded the standard, and the pollution levels ranged from moderate to serious. Meantime, water content, total phosphorus, total nitrogen, heavy metals were closely related. The order of potential ecological risk of a single heavy metal was Cd> Cu> Ni> Pb> Cr> Zn. Finally, based on the spatial distribution of pollutants, the proposed range of environmental dredging was given in this study.

1. Introduction
Black and smelly river was the ubiquitous environmental pollution problems in cities in our country, seriously affecting the image of the city and the life of residents [1]. Sediment deposited with a large number of organic matter, nitrogen and phosphorus nutrients and heavy metals, was an important sources and sinks for black smelly river [2]. Also it played a crucial role in the biogeochemical cycle of pollutants in inland river ecosystems [3]. Therefore, the study of the sediment pollution status was of great significance to solve the problem of black-smelly river [4]. The poor water quality, serious black-water body in Shenzhen City River was not conducive to the normal operation of the city and sustained economic and social development [5]. Consequently, the purpose of this study was to evaluate the pollution status and characteristics of river sediment by analyzing the content and spatial distribution of total nitrogen (TN), total phosphorus (TP) and heavy metals in the sediment of the Zaoxia River. It provides a theoretical basis and a scientific basis for the comprehensive improvement of urban black-smelly rivers.

2. Materials and methods

2.1. Sample collection
The experimental samples were collected in May 2017 from Zaoxia River in Shenzhen City. According to the pollution status of Zaoxia River, a total of three cross-section settings was set and one sampling point was set for each section. Furthermore, the sediment sampling depth was less than 2.5m and was...
separated according to the pollution status. The collected sediment samples were stored in a sealed bag, transported back to the laboratory for air drying and grinding and sieving.

2.2. Sample determination

Soil moisture content was calculated by soil dry weight. Total nitrogen in the sediment was digested by potassium dichromate-sulfuric acid method and determined by the Nessler's reagent colorimetric method [6]. Total phosphorus was analyzed using molybdenum antimony after melting sodium antiphosphomethylation, and the determination method was complied with the relevant provisions in CJ/T221. Elements of copper, chromium, cadmium, lead, zinc, arsenic and nickel was digested using microwave digestion for ICP-MS determination [7].

3. Results and Discussions

3.1. The spatial distribution characteristics of parameters in river sediment

The moisture content of 0-20cm in different sections of sediment was between 35.87 and 58.69%. The depth of 30cm-50cm sediment moisture content was in the range of 40.01% -58.07%. The moisture content of sediment in the depth of 80-100cm was 35.59% -44.01%. The moisture content of the depth of 130cm-150cm sediment was 34.46% -57.39%. The moisture content of sediment in the depth of 230cm-250cm was 14.85% -53.33%.

The total phosphorus in 0-20cm depth of sediment at different sections in Zaoxia River was in the range of 568-1104mg/kg with an average value of 839mg/kg and the total nitrogen was 733mg/kg-1610mg/kg with an average value of 1138mg/kg (Table 1). Total phosphorus at 30-50cm depth sediment was between 92.3mg/kg and 362mg/kg with an average of 255mg/kg and total nitrogen ranged from 855mg/kg to 1599mg/kg with an average value of 1327mg/kg. Total phosphorus in the depth of 80-100cm sediment was 45.8mg/kg-1105mg/kg with an average of 706mg/kg and total nitrogen was 740mg/kg-1293mg/kg with an average value of 995mg/kg. The average total phosphorus and nitrogen at 130-150cm depth sediment was 1406mg/kg and 1443mg/kg, respectively. At 230-250cm depth, the value for total phosphorus was 434mg/kg-1180mg/kg, with an average of 683mg/kg and was in the range of 325mg/kg-1392mg/kg, with an average of 909mg/kg for total nitrogen.

| Sampling place | Moisture Content(%) | TP (mg/kg) | TN | Moisture content(%) | TP (mg/kg) | TN | Moisture content(%) | TP (mg/kg) | TN |
|----------------|---------------------|------------|----|---------------------|------------|----|---------------------|------------|----|
| 0-20           | 58.69               | 1104       | 1610 | 41.82               | 845        | 1071 | 35.87               | 568        | 733 |
| 30-50          | 58.07               | 362        | 1529 | 48.03               | 312        | 1599 | 48.03               | 92.3       | 855 |
| 80-100         | 40.59               | 967        | 952  | 44.01               | 1105       | 1293 | 35.59               | 45.8       | 740 |
| 130-150        | 51.96               | 1453       | 1457 | 57.39               | 2196       | 2160 | 34.46               | 568        | 712 |
| 230-250        | 37.76               | 434        | 1011 | 53.33               | 1180       | 1392 | 14.85               | 437        | 325 |
According to monitoring sediment data (Table 1), the spatial distribution of moisture content as well as the nitrogen and phosphorus contents of Zaoxia River sediment was simulated. It can be seen (Figure 2) that the high value zone of moisture content as well as the nitrogen and phosphorus contents was all mainly in the upstream 600m. Specifically, the high value in the upper 400m range of moisture content as well as the nitrogen and phosphorus contents mainly distributed in the depth of 100cm-300cm, 100cm-200cm and 100cm-200cm, respectively. Meanwhile, their high value in the 400m-600m range mainly distributed in the depth of 0-50cm, 0-50cm and 100-150cm, respectively. Their greatest value could be up to 58%, 2100mg/kg and 2200mg/kg, respectively.

3.2. The evaluation of the nitrogen and phosphorus nutrients in Zaoxia River sediment

The single factor pollution index method was used in this study for the evaluation of the total phosphorus, total nitrogen in sediment of Zaoxia River sediments. The general standard index for a single pollution factor has the following relationship [8]:

$$PI = \frac{C_i}{C_s}$$

Where: PI is a single pollution index, Ci is the actual value of the element, and Cs is the evaluation standard value of the element. The lowest ecological effect for total nitrogen content of sediments was 550mg/kg, and the total nitrogen content with serious ecological effects was 4800mg/kg. The total phosphorus content of the sediments with the lowest ecological effect was 600 mg/kg, and the total phosphorus content with the serious ecological effects was 2000 mg/kg [9]. Therefore, in this study, the standard values of total nitrogen and total phosphorus were 800mg/kg and 600mg/kg, respectively. Based on the calculation, the pollution index of sediment of nitrogen and phosphorus nutrients at different depths at three sampling points could be obtained (Table 2).

| Sampling place | ZX-1 | ZX-2 | ZX-2 |
|----------------|------|------|------|
|                 | PITP | PITN | PITP | PITN | PITP | PITN |
| 0-20(cm)        | 1.8  | 2.0  | 1.4  | 1.3  | 0.9  | 0.9  |
| 30-50(cm)       | 0.6  | 1.9  | 0.5  | 2.0  | 0.2  | 1.1  |
| 80-100(cm)      | 1.6  | 1.2  | 1.8  | 1.6  | 0.1  | 0.9  |
| 130-150(cm)     | 2.4  | 1.8  | 3.7  | 2.7  | 0.9  | 0.9  |
| 230-250(cm)     | 0.7  | 1.3  | 2.0  | 1.7  | 0.7  | 0.4  |
| Average         | 1.4  | 1.6  | 1.9  | 1.9  | 0.6  | 0.8  |
The pollution index for phosphorus nutrition of ZX-1 in Zaoxia River was 1.4 and 1.6 for nitrogen index. The pollution index for phosphorus and nitrogen nutrient at ZX-2 in Zaoxia River was both 1.9. The pollution index at ZX-3 in Zaoxia River was 0.6 for phosphorus nutrition, and 0.8 for nitrogen index. According to sediment total nitrogen and total phosphorus pollution levels grade (Table 3), it could be inferred that the ZX-1 was in medium pollution of phosphorus and nitrogen. Also, the ZX-2 sediment was heavily polluted by phosphorus and moderate polluted by nitrogen. The ZX-3 sediment was unpolluted by nitrogen and was in minor pollution of phosphorus.

Table 3. Classification of sediment pollution index

| TN  | TP  | Classification |
|-----|-----|----------------|
| PI<1.0 | PI<0.5 | non-pollution |
| 1.0<PI≤1.5 | 0.5<PI≤1.0 | minor pollution |
| 1.5<PI≤2.0 | 1.0<PI≤1.5 | medium pollution |
| PI>2.0 | PI>1.5 | heavy pollution |

3.3. Spatial distribution and evaluation of heavy metals in the sediment of the Zaoxia River

Three sampling points at different depths of sediment in heavy metal content in Zaoxia River was given in Table 4. The heavy metal contents of Cd, Pb, Cr, Cu, Ni and Zn at ZX-1 was 0.481mg/kg, 38.71mg/kg, 110mg/kg, 374mg/kg, 46.11mg/kg and 146 mg/kg, respectively. Meantime, the heavy metal contents of Cd, Pb, Cr, Cu, Ni and Zn at ZX-2 was 0.578mg/kg, 40.54mg/kg, 120mg/kg, 442mg/kg, 51.73mg/kg and 170 mg/kg, respectively. The heavy metal contents of Cd, Pb, Cr, Cu, Ni and Zn at ZX-3 was 0.229mg/kg, 30.68mg/kg, 29mg/kg, 35mg/kg, 15.02mg/kg and 59 mg/kg, respectively. It is evident that sediment the heavy metal contents of ZX-3 was far less than the other. Furthermore, it is obvious that the heavy metal content of sediments in different sections decreased with the increase of depth.

Table 4. The heavy metal contents of sediment at different depths in Zaoxia River

| Sampling place | Depth (cm) | Cd (mg/kg) | Pb (mg/kg) | Cr (mg/kg) | Cu (mg/kg) | Ni (mg/kg) | Zn (mg/kg) |
|----------------|------------|------------|------------|------------|------------|------------|------------|
| ZX-1           | 0-20       | 0.749      | 46.58      | 164        | 674        | 74.01      | 227        |
|                | 30-50      | 0.627      | 41.53      | 150        | 491        | 56.87      | 178        |
|                | 80-100     | 0.263      | 35.16      | 64         | 157        | 25.42      | 85         |
|                | 130-150    | 0.585      | 38.89      | 133        | 471        | 55.50      | 168        |
|                | 230-250    | 0.181      | 31.40      | 40         | 75         | 18.74      | 70         |
|                | Average    | 0.481      | 38.71      | 110        | 374        | 46.11      | 146        |
| ZX-2           | 0-20       | 0.462      | 35.57      | 81         | 258        | 35.26      | 118        |
|                | 30-50      | 0.604      | 40.77      | 134        | 494        | 56.73      | 179        |
|                | 80-100     | 0.443      | 37.78      | 95         | 341        | 41.51      | 160        |
|                | 130-150    | 0.837      | 49.58      | 184        | 739        | 78.28      | 241        |
|                | 230-250    | 0.542      | 39.00      | 105        | 377        | 46.89      | 151        |
|                | Average    | 0.578      | 40.54      | 120        | 442        | 51.73      | 170        |
| ZX-3           | 0-20       | 0.210      | 32.19      | 27         | 33         | 14.63      | 57         |
|                | 30-50      | 0.299      | 39.40      | 35         | 54         | 19.15      | 78         |
|                | 80-100     | 0.258      | 32.63      | 29         | 33         | 15.38      | 63         |
|                | 130-150    | 0.202      | 30.79      | 30         | 34         | 15.59      | 62         |
|                | 230-250    | 0.175      | 18.39      | 24         | 24         | 10.35      | 38         |
|                | Average    | 0.229      | 30.68      | 29         | 35         | 15.02      | 59         |

Based on the potential ecological risk factors of single species of metals, the potential ecological risk index of various heavy metals in sediments was cumulatively determined. It not only reflected the impact
of various pollutants in a specific environment, but also indicated the combined effects of multiple pollutants. Accordingly, the potential ecological risk was and quantified. The formula is as follows [10]:

\[ C^i = \frac{C_D^i}{C_R^i} \]
\[ E^i = T^i C^i \]
\[ RI = \sum_{i=1}^{n} E^i \]

Where: \( E^i \) is the potential ecological risk factor of a single metal; \( RI \) is the comprehensive potential ecological risk index; \( C_D^i \) represents the measured heavy metal concentration of the sample; \( C_R^i \) is the background value of the corresponding pollutants in the sediment; \( T^i \) is toxic response factor, which reflects response of the metal between the aqueous phase, the deposited solid phase and the biological phase[11]. The required toxic response factor and background values along with evaluation classification for the potential ecological risk index were presented in Table 4 and Table 5[12]. And the background value of soil metal in Guangdong Province background value was used in this study as \( C_R^i \) [13].

| Table 5. Background values and toxicity factor of heavy metals in the sediments |
|-----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Element  | Cd  | Cr  | Hg  | As  | Pb  | Cu  | Zn  | Ni  |
| C^i (mg/kg) | 0.04 | 35.6 | 0.055 | 6.8 | 29.8 | 10.5 | 36.3 | 9.6 |
| T^i       | 30  | 2   | 40  | 10  | 5   | 5   | 1   | 5   |

| Table 6. Grades of potential ecological risk index of heavy metal pollution |
|-----------------------------|-----|-----|-----|-----|-----|
| \( E^i \)                | 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 |

According to the measured sediment data, based on the above calculation method, the potential ecological risk index of single metals and the comprehensive potential ecological risk index were calculated (Table 7).

The average value of potential ecological risk index of Cd, Pb, Cr, Cu, Ni and Zn in ZX-1 was 360.8, 6.5, 6.2, 177.9, 9.8 and 4.0, respectively, and the value of RI is 579. The average value of potential ecological risk index of Cd, Pb, Cr, Cu, Ni and Zn in ZX-2 was 433.2, 6.8, 6.7, 210.4, 26.9 and 4.7, respectively, and the value of RI is 689. The average value of potential ecological risk index of Cd, Pb, Cr, Cu, Ni and Zn in ZX-3 was 171.6, 5.2, 1.7, 16.9, 7.8 and 1.6, and the value of RI is 205. The order of the potential ecological risk index was ZX-1 > ZX-2 > ZX-3.
Table 7. $E_i$ and RI values of sediment of different sampling sites in Zaoxia River

| Sampling place | Depth(cm)       | $E_i$ (Cd) | $E_i$ (Pb) | $E_i$ (Cr) | $E_i$ (Cu) | $E_i$ (Ni) | $E_i$ (Zn) | IR |
|----------------|----------------|------------|------------|------------|------------|------------|------------|----|
|                | 0-20           | 561.8      | 7.8        | 9.2        | 321.0      | 38.5       | 6.3        | 945|
|                | 30-50          | 470.3      | 7.0        | 8.4        | 238.8      | 29.6       | 4.9        | 754|
|                | 80-100         | 197.3      | 5.9        | 3.6        | 74.8       | 13.2       | 2.3        | 297|
|                | 130-150        | 438.8      | 6.5        | 7.5        | 224.3      | 28.9       | 4.6        | 711|
|                | 230-250        | 135.8      | 5.3        | 2.3        | 35.8       | 9.8        | 1.9        | 191|
|                | Average        | 360.8      | 6.5        | 6.2        | 177.9      | 24.0       | 4.0        | 579|
| ZX-2           | 0-20           | 346.5      | 6.0        | 4.5        | 122.9      | 18.4       | 3.3        | 502|
|                | 30-50          | 453.0      | 6.8        | 7.5        | 235.2      | 29.5       | 4.9        | 737|
|                | 80-100         | 332.3      | 6.3        | 5.3        | 162.4      | 21.6       | 4.4        | 532|
|                | 130-150        | 627.8      | 8.3        | 10.3       | 351.9      | 40.8       | 6.6        | 1046|
|                | 230-250        | 406.5      | 6.5        | 5.9        | 179.5      | 24.4       | 4.2        | 627|
|                | Average        | 433.2      | 6.8        | 6.7        | 210.4      | 26.9       | 4.7        | 689|
| ZX-3           | 0-20           | 157.5      | 5.4        | 1.5        | 15.8       | 7.6        | 1.6        | 189|
|                | 30-50          | 224.3      | 6.6        | 2.0        | 25.6       | 10.0       | 2.1        | 271|
|                | 80-100         | 193.5      | 5.5        | 1.7        | 15.9       | 8.0        | 1.7        | 226|
|                | 130-150        | 151.5      | 5.2        | 1.7        | 16.0       | 8.1        | 1.7        | 184|
|                | 230-250        | 131.3      | 3.1        | 1.4        | 11.3       | 5.4        | 1.0        | 153|
|                | Average        | 171.6      | 5.2        | 1.7        | 16.9       | 7.8        | 1.6        | 205|
|                | Average        | 321.9      | 6.2        | 4.9        | 135.1      | 19.6       | 3.4        | 491|

According to the calculation results, the average potential ecological risk index of Cd, Pb, Cr, Cu, Ni and Zn metal in Zaoxia River was 321.9, 6.2, 4.9, 135.1, 19.6 and 3.4, respectively. The order of potential ecological risk index for different heavy metals are Cd > Cu > Ni > Pb > Cr > Zn. Specifically, the average potential ecological risk index of Cd was extremely strong, and the average potential ecological risk index of Cu was considerable according to the risk level of Table 7. The average potential ecological risk index for the rest heavy metals was low. Because that the average RI value of sediment in Zaoxia River was 491, the degree of ecological risk was high risk.

![Figure 2. Spatial distribution of comprehensive potential ecological risk index (left) and environmental dredging depth (right) of sediment in Zaoxia River](image-url)

Furthermore, the spatial distribution of Cu, Zn, Pb, Cd, Cr and Ni were calculated, and the spatial distribution of RI value was obtained according to the above calculation method (Figure 1, left). It is evident that the high value zone mainly appears in the upstream 500m. The high value in the upper 400m...
range and 400-600m range was distributed in the depth of 100cm-200cm, and 0-50cm, respectively. The value of comprehensive potential risk index could be up to 1000. The heavy metal of Cd contributed most the potential risk, which could be considerable to be the most important element in the risk control of heavy metal pollution in sediments.

3.4. Contaminated sediment dredging depth

There are many methods for sediment pollution control. At present, the most common method was to dredge river sediments. One of the most important parameters of dredging was the depth. If the depth was too small, the pollutants could not be completely removed. However, the larger dredging depth will cause damage on river bottom ecosystem. As the potential ecological risk index of heavy metals decreased with the increase of depth in vertical direction, this paper proposed and constructed a critical risk control method based on the potential ecological risk assessment of heavy metals in river sediments. With a purpose of controlling the potential ecological risk of heavy metals through environmental dredging, the reasonable environmental dredging depth could be calculated through this method. The equation as follows [14]:

\[
\begin{align*}
    h_{\text{max}} &= h_0 \\
    \text{if} \quad & RI(h) > C_0 \quad h < h_0 \\
    \text{if} \quad & RI(h) = C_0 \quad h = h_0 \\
    \text{if} \quad & RI(h) < C_0 \quad h > h_0
\end{align*}
\]

Where \( h_{\text{max}} \) is the required environmental dredging depth. \( h_0 \) is the critical risk depth. And \( RI(h) \) is comprehensive potential ecological risk index at \( h_0 \) depth. \( C_0 \) is the comprehensive potential risk control level of heavy metals. \( C_0 \) was 300 in this study, indicating that potential risk level is controlled below the moderate level.

Based on the above analysis methods and calculation results, in order to achieve the pollution level for total nitrogen, total phosphorus and heavy metal was moderate degree, namely 1600 mg/kg, 900 mg/kg and 300, respectively, the range of dredging was shown in Figure 2, right. After superposition the dredging range of different pollutants, suggestions on the environmental protection dredging depth of the Shenzhen section was given. The dredging depth of river in the 0-500m and 500m-700m range, along with 700m-800m range and 800m-900m range was 3m, 2.5m, 2m and 1.5m, respectively.

4. Conclusion

In conclusion, the levels of total phosphorus, total nitrogen and heavy metal in the sediment in the Zaoxia River, Shenzhen City partly exceed the standard value. And the degree of pollution was from serious to moderate. Comparison of moisture content, total phosphorus, and total nitrogen, spatial distribution of heavy metals, the high value area and low-value area in spatial distribution is very close, which indicated their close relationship. The order of the potential ecological risk index for different heavy metal was Cd > Cu > Ni > Cr > Zn. The dredging depth of Zaoxia River in the 0-500m and 500m-700m range, along with 700m-800m range and 800m-900m range should be 3m, 2.5m, 2m and 1.5m, respectively.

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