Heavy metal pollution and potential ecological risk in urban river sediment of Huai'an City, China

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Abstract: Sediment heavy metal pollutant monitoring was carried out at 16 monitoring points of three rivers and one lake in Huai'an city. The contamination degree of heavy metals was evaluated by geoaccumulation index. The potential ecological risk of heavy metals was assessed. The results showed that Hg and Cu geoaccumulation index class exceeded moderately polluted level, especially Hg, and two monitoring points reached highly polluted level. Hg pollution is at a high/ extremely high potential ecological risk. Most of the other single-factor heavy metal indexes are at a low ecological risk level. The comprehensive ecological risk index of 6 monitoring points showed a high potential ecological risk. The Hg in urban rivers sediment of Huai'an may come from the deposition of long-term domestic sewage discharge or domestic refuse dump.

1. Introduction
Development of urbanization in China is rapid, but the construction of urban infrastructure and urban ecological environment protection lag behind. Urban infrastructure and environment can’t meet the requirements of urban dwellers. The neglect of urban environmental protection may lead to prominent ecological environment problems[1]. Especially in some small and medium-sized cities in China, rivers are occupied by urban constructions and polluted by domestic sewage. Under the influence of long-term sewage pollution, sediments in some urban rivers accumulate continuously and collect organic matter, nutrients and heavy metals, which have become one of the important sources of river pollution. Monitoring the sediment of urban rivers and analyzing its pollution, distribution, source and risk can provide basic support for developing appropriate river regulation and restoration plans.

The methods of cumulative index, potential ecological risk, Nemerow comprehensive index and sediment enrichment coefficient are widely used to evaluate the river sediment pollution[2-4]. Huai’an City has serious river pollution problems. The government has been carrying out river remediation actions, and plans to eliminate the black and odorous water in the city by 2019. This study monitored the heavy metal contents of some urban river sediments in Huai’an City, evaluated the pollution degree, spatial distribution and potential ecological risks of heavy metals, and analyzed the possible causes of pollution. It is a part work of the identification and evaluation of black and odorous water, and it provides reference for the river ecological restoration.
2. Study area and monitoring
Huai'an City, which belongs to Jiangsu Province, is located in the lower reaches of the Huai River. Huai'an District is an urban area with a total area of 1458.78 square kilometers. There are 39 first-and second-class rivers and 226 ditches in the area, including the Beijing-Hangzhou Grand Canal, the Northern Jiangsu Irrigation Canal and the Huaihe River Inlet Channel. In 2015, the population of Huai'an District was 987,400 with urbanization rate of 49.9%. The GDP of Huai'an District was 6.47 billion dollars (The average exchange rate in 2015 was 6.2284.). Most of the current drainage in the city is combined sewer system. The coverage rate of sewage system is 62%. Some industrial enterprises discharge sewage directly into the rivers or channels. In recent years, the government has carried out the ecological restoration of some rivers. In the investigation of the black and odorous water bodies in the city, 18 rivers in Huai'an District have been identified as black and odorous water bodies. Bantiao River, Luoliu River, Xiaohu Lake and Xinyi Canal are included in the pollution river list, which is also in the ecological restoration lists.

Sediment monitoring was conducted at 3 monitoring points of Bantiao River (0.45 km), 3 points of Luoliu River (0.95 km) and 3 points of Xiaohu Lake (0.22 km²). Seven monitoring points of Xinyi Canal (3.9 km) were sampled. Sediment monitoring indicators included 8 heavy metals including Cd, Hg, Ni, Pb, As, Cu, Zn, Cr. Sampling date is April 10-11, 2018. Sediment sampling was based on "Technical Guidelines for Water Quality Sampling" (HJ494-2009). Sediment sampler was used for sampling, and sealed polyethylene was used to keep it away from light. The samples were sent to laboratory for testing as soon as possible. Heavy metals Cd and Pb were determined by graphite furnace atomic absorption spectrophotometer iCE3300. Heavy metals Ni, Cu, Zn and Cr were determined by flame atomic absorption spectrophotometer iCE3400. Heavy metals Hg and As were determined by SA-20 atomic fluorescence speciation analyzer. Blank, standard sample and parallel sample were used for monitoring quality control. The relative errors of parallel samples all met the requirements.

3. Evaluation method

3.1. Pollution evaluation method
(1) Benchmark method
According to the lower limit (TEL) and upper limit (PEL) of sediment benchmark values proposed by Wang[5], when the content of heavy metals is lower than TEL, there will be no toxic effects on organisms, but when the content of heavy metals is higher than PEL, adverse biological toxic reactions will occur frequently.

(2) Geoaccumulation index
The method of geoaccumulation index was proposed by Professor Müller. The pollution degree was classified according to the calculated geoaccumulation index. The method has been widely used to evaluate the pollution degree of heavy metals in sediments.

\[ I_{geo} = \log_2\left(\frac{C_n}{(kB_n)}\right) \]  

\( C_n \) is the content of heavy metal n in the sample. K is a correction factor, which is usually used to represent sedimentary characteristics, rock geology and other effects. In general, K is taken as 1.5. \( B_n \) is the geochemical background value of heavy metal n in sedimentary rocks. The background values of heavy metals in this study refer to the values of neighboring areas. The background data of Hongze Lake and Chaohu Lake in reference[6] and reference[7] were used. Hg 0.2mg·kg⁻¹, Cd 1mg·kg⁻¹, As 15mg·kg⁻¹, Pb 26mg·kg⁻¹, Cu 20.2mg·kg⁻¹, Ni 31.6mg·kg⁻¹, Cr 67mg·kg⁻¹, Zn 56.3mg·kg⁻¹. Classification standard of geoaccumulation index is shown in Tab 1.

| Class | Sediment quality | \( I_{geo} \) | 0~1 | 1~2 | 2~3 |
|-------|-----------------|-------------|-----|-----|-----|
| 0     | Unpolluted      | 3~4         | Unpollotted to moderately polluted | Moderately polluted | Moderately to highly polluted |
| 1     |                 | 4~5         |     |     |     |

Tab.1 Classification standard of geoaccumulation index
3.2. Potential Ecological Risk evaluation method

Potential ecological risk assessment method was proposed by Swedish scientist Hakanson in 1980 and has been widely used in heavy metal risk assessment of sediments. The method includes a single potential risk index $E_{r,i}$ of heavy metals and a comprehensive potential ecological risk index $R_i$. The expressions are as follows:

$$
E_{r,i} = T_{r,i}C_{r,i}, \quad C_{r,i} = \frac{C_{si}}{C_{ri}}
$$

(2)

$$
R_i = \sum_{i=1}^{n} E_{r,i} = \sum_{i=1}^{n} T_{r,i}C_{r,i} = \sum_{i=1}^{n} T_{r,i} \frac{C_{si}}{C_{ri}}
$$

(3)

$C_{r,i}$ is the content of heavy metal $i$ in sediments, mg kg$^{-1}$. $C_{ri}$ is the reference value of heavy metal $i$, mg kg$^{-1}$. It is the same as the background value in the evaluation of accumulation index. $T_{r,i}$ is the toxicity coefficient of heavy metal $i$, which reflects the impact of heavy metals on organisms and toxicity level. The greater the toxicity coefficient, the greater the impact and harmfulness of heavy metals on organisms. According to the current research, the toxicity coefficient is as follows: Hg, 40, Cd, 30, As, 10, Pb, Cu, Ni is 5, Cr is 2, Zn is 1. The classification criteria for potential ecological risks are shown in Tab 2.

| Single potential risk index | Comprehensive potential risk index | Risk degree |
|-----------------------------|------------------------------------|-------------|
| 1  <40                       | 150-300                            | Low risk    |
| 2  40-80                     | 300-600                            | Moderate risk|
| 3  80-160                    | 600                                | Moderate to high risk|
| 4  160-320                   | ≥600                               | High risk   |
| 5  ≥320                      |                                    | Extremely high risk|

Tab.2 Classification of potential ecological risk of heavy metals

4. Results and discussion

4.1. Heavy metal pollution

The content of heavy metals in river sediment in Huai’an city are shown in Table 3. Compared with the benchmark value, the contents of Cd, As and Cu in the sediment did not exceed the upper limit (PEL). The highest values of Ni, Pb and Zn slightly exceeded the upper limit (PEL). The highest values of Hg and Cr were higher than the upper limit. Especially, the highest value of Hg were nearly 10 times as much as the upper limit (PEL).

Tab.3 Heavy metal concentration of river sediment (mg·kg$^{-1}$)

| Heavy metal | Cd  | Hg  | Ni  | Pb  | As  | Cu  | Zn  | Cr  |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|
| TEL         | 0.6 | 0.17| 16.0| 35.0| 7.2 | 36.0| 123.0| 42.0|
| PEL         | 3.5 | 0.49| 43.0| 91.0| 42.0| 197.0| 315.0| 160.0|
| Monitoring range | 0.14-1.3 | 0.06-4.84 | 19.8-63.1 | 17.4-98.8 | 6.84-22.3 | 21.8-189 | 46.8-329 | 54.4-341 |
| Average     | 0.525 | 1.162 | 32.3 | 50.1 | 11.8 | 69.0 | 121.9 | 116.6 |

As shown in Table 4, Cd, As and Ni index class of almost all the monitoring points are 0 (unpolluted). Pb, Zn and Cr index class are between 0 to 2, with some monitoring points (T3, T7, T12, T13) show moderately polluted. Both Hg and Cu with some monitoring points exceed moderately polluted. Especially Hg, it has been highly polluted at T5 of Luoliu River and highly to very highly polluted at T8 of Xiaohu Lake.

Tab.4 Heavy metal geoaccumulation index class of river sediment

| River  | Point | Cd | Hg | Ni  | Pb  | As  | Cu  | Zn  | Cr  |
|--------|-------|----|----|-----|-----|-----|-----|-----|-----|
| Bantiao| T1    | 0  | 0  | 0   | 0   | 0   | 1   | 0   | 0   |
| River  | T2    | 0  | 2  | 0   | 0   | 0   | 1   | 0   | 1   |
4.2. Heavy metal potential Ecological Risk

The single potential ecological risk index of heavy metals in river sediment of Huai’an city shows that the mean values of Cd, Hg, Ni, Pb, As, Cu, Zn and Cr are 16, 232, 5, 10, 8, 17, 2 and 3, respectively, as shown in Table 5. The average value of the comprehensive potential ecological risk index of heavy metals is 293, the minimum value is T14 (53), and the maximum value is T8 (1055). The single ecological risk index of heavy metals showed that the risk degree was Hg>Cu>Cd>Pb>As>Ni>Cr>Zn. Only Hg risk index of some points was higher than 160, which reached high ecological risk level. Especially the monitoring points of T3, T5, T8, T12 and T13 reached extremely high ecological risk level. Most of the other single ecological risk index of heavy metals were lower than 40, with low ecological risk. The comprehensive ecological risk index of each monitoring point showed that Xiaohu T8 had high ecological risk, while T3, T5, T7, T12 and T13 were at moderate to high ecological risk level. The comprehensive ecological risk index is mainly affected by content of Hg.

| River          | Point | Cd  | Hg  | Ni  | Pb  | As  | Cu  | Zn  | Cr  | $R_I$ |
|----------------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-------|
| Bantiao River  | T1    | 14  | 12  | 4   | 7   | 6   | 8   | 1   | 2   | 54    |
|                | T2    | 15  | 179 | 4   | 3   | 8   | 11  | 1   | 5   | 226   |
|                | T3    | 27  | 372 | 7   | 17  | 12  | 29  | 5   | 3   | 470   |
|                | T4    | 6   | 164 | 4   | 4   | 7   | 10  | 1   | 3   | 200   |
| Luoliu River   | T5    | 9   | 496 | 4   | 5   | 15  | 47  | 2   | 6   | 583   |
|                | T6    | 10  | 236 | 4   | 11  | 6   | 13  | 2   | 3   | 284   |
|                | T7    | 39  | 262 | 8   | 10  | 9   | 29  | 4   | 10  | 372   |
|                | T8    | 33  | 968 | 6   | 15  | 8   | 20  | 2   | 3   | 1055  |
|                | T9    | 32  | 21  | 10  | 11  | 5   | 8   | 1   | 6   | 94    |
|                | T10   | 12  | 14  | 3   | 12  | 5   | 7   | 1   | 2   | 55    |
|                | T11   | 11  | 105 | 3   | 12  | 5   | 8   | 1   | 2   | 148   |
|                | T12   | 25  | 430 | 4   | 19  | 14  | 45  | 6   | 2   | 544   |
|                | T13   | 6   | 324 | 5   | 10  | 9   | 23  | 5   | 3   | 383   |
|                | T14   | 5   | 21  | 6   | 6   | 5   | 7   | 1   | 2   | 53    |
|                | T15   | 5   | 46  | 5   | 6   | 7   | 5   | 1   | 3   | 77    |
|                | T16   | 4   | 68  | 5   | 6   | 6   | 5   | 1   | 3   | 98    |
|                | Average| 16  | 232 | 5   | 10  | 8   | 17  | 2   | 3   | 293   |

Tab.5 Heavy metal potential ecological risk of river sediment
4.3. Analysis of pollution sources

Bantiao River, Luoliu River and Xiaohu Lake are located in the old town. There are mainly residential land and commercial land around the river. For most of the year, the flow of the rivers is small. According to the investigation of sewage discharge, there are 22 rain and sewage confluence outlets, 3 domestic sewage outlets in Bantiao River, 15 rain and sewage confluence outlets in Luoliu River, 25 rain and sewage confluence outlets and 50 domestic sewage outlets in Xiaohu Lake. There is no industrial sewage outlet around, and according to the river flow direction, it could not be affected by the pollution of other rivers. The possible sources of Hg include coal combustion, waste incineration, domestic sewage, industrial (such as chlor-alkali, plastics, electronics industry) sewage, etc. Studies have shown that the average mercury content in municipal sludge in China can reach \((2.19 + 3.16)\ mg\cdot kg^{-1}\) [8], indicating that municipal sewage may become an important source of mercury pollution. Hg pollution in sediments of Bantiao River, Luoliu River and Xiaohu River may mainly come from sediments formed by long-term domestic sewage discharge.

According to the investigation, the Xinyi Canal is mainly surrounded by farmland, living areas, business areas and schools, and the community is built later than the old town. There are 43 rain and sewage confluence outlets, no industrial sewage outlets and 2 garbage centralized storage points, which are located near T13 and downstream of T16 respectively. The Hg content of T12 and T13 monitoring points reached moderate pollution level. Pollution of the Xinyi Canal may be related to domestic waste dump. Heavy metals such as Hg and Cu in domestic waste mainly come from waste batteries and electrical appliances. However, to accurately determine the source of pollution, further sampling and monitoring of domestic sewage and garbage are needed. In Huai'nan City, it is suggested that sewage system should be improved to increase sewage collection and treatment rate, strengthen the garbage collection and harmless treatment. In addition, attention should be paid to avoid secondary pollution caused by heavy metals in river sediment cleaning and treatment.

5. Conclusions

(1) The heavy metal content in the urban rivers of Huai'an City was evaluated by geoaccumulation index. Hg and Cu index class exceeded moderately polluted level. Especially Hg, it reached highly polluted at the T5 of Luoliu River and highly to very highly polluted at T8 of Xiaohu Lake. (2) The potential ecological risk of heavy metals in urban rivers of Huai'an City was evaluated by the risk evaluation method. The single ecological risk index of heavy metals showed that Hg ecological risk index was high. T3, T5, T8, T12, T13 monitoring points reached extremely high ecological risk level, and other single ecological risk index of heavy metals was basically at a low level of ecological risk. In the comprehensive potential ecological risk index, T3, T5, T7, T8, T12, T13 reached moderate to high or high ecological risk level. (3) Hg pollution in Bantiao River, Luoliu River and Xiaohu Lake may be caused by long-term domestic sewage discharge and deposition, and the pollution in Xinyi Canal may be related to garbage dump near T13.

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