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Research on Heavy Metals Release Pattern of Waterfront Tidal River Sediment

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The waterfront tidal river, Neijiang in Zhenjiang city, was studied by monitoring the heavy metals content distribution in sediment. In this study, the relationship between sedimentary heavy metals release rates and dynamic disturbance was established for different pollution situation in Neijiang. Based on the synchronous hydrological and water quality monitoring, the spatio-temporal changing laws of heavy metals release rates of different hydrological characteristics, such as in flood and dry seasons, was induced systematically. Experiment results show that As, Pb, Cd are the major heavy metals which pollute the water quality of Neijiang river. The heavy metals concentration in the south area is generally higher than that in the north area. The release rates of As, Pb, Cd increase with the growth of disturbance intensity and content in sediment and can reach 121.2 $mg/m^2.d$, 140.8 $mg/m^2.d$ and 4.4$mg/m^2.d$ respectively in flood seasons. The average release rates of As, Pb, and Cd in flood season increase by 210%, 121%, 198% than that in dry season respectively.

1. Introduction

Waterfront body is an important resource in urban ecology and is of great value in improving the quality of urban environment. However, with the increasing population and the rapid progress in industrialization, the waterfront body is also facing water quality deterioration, sediment deposition and other environmental problems. Now pollution has become a growing concern among people (Pang et al., 2008). The release of heavy metals in sediments is one of the important factors that directly affect the heavy metal environmental characteristics of water body. Therefore, it is necessary to study the release patterns of heavy metals in the sediment of waterfront bodies to help reasonable dredging schemes for waterfront bodies and effectively control the pollution of heavy metals. At present, there has been great progress in the researches on the release of heavy metals in sediments caused by changes in environmental chemical conditions (acidity, temperature, salinity and potential, etc.) in the water body, while only a few researches have been conducted on the kinetic aspects of heavy metal release (Huang, 1995). Huang (1995), Hong and Wang (1987), Fan et al., (2007), Song et al., (2008) studied the release kinetics and release flux of heavy metals in sediments, respectively. These research results have, to a certain extent, revealed the basic release patterns of heavy metals in sediments, but so far, these researches are mostly analysis based on laboratory experiments, and few has applied the laboratory test results in the field. In this paper, we study the release patterns of heavy metals in the sediment of the tide-influenced waterfront body - the Neijiang River in Zhenjiang affected by disturbance and substrate changes. The results are of great significance to the water environment management of tide-influenced waterfront bodies, especially the sediment dredging work.

2. Research area and background

The Neijiang River in Zhenjiang is a typical tide-influenced waterfront body in the middle and lower reaches of the Yangtze River. The upper and lower reaches of the Neijiang River are connected to the Yangtze River through the approach channel and Jiaonan Gate. Under the joint action of two dynamic factors – runoff and tide, the tide type of the Neijiang River is irregular mixed semi-diurnal tide, with obvious daily tidal fluctuations[6,7], and two high and low tides per day; within every year, there are also variations in the flood

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and dry seasons. The surface area and the storage capacity of the Neijiang River change greatly with the tide. The surface area is about 8.1km2 and the storage capacity is about 16 million m^3.

Currently, the sediment has been seriously deposited in the Neijiang River, with an annual sedimentation amount of about 650,000m^3 (Wang et al., 2009). In recent years, with the rapid economic development, large amount of agricultural and industrial water containing heavy metals is discharged into water bodies and carried back and forth by water flow under the tidal effects. When the load of the water exceeds its carrying capacity, these heavy metals will become part of the water sediments and gradually accumulate (Dexter and Ward, 2004).

3. Monitoring and data analysis

3.1 Materials and methods

3.1.1 Sample collection and preparation

From June 28th, 2007 to December 13th, 2007, we measured the content distribution of heavy metals in the sediment of the Neijiang River. We set up 35 sampling sites in total, as shown in Figure 1. We used a Petersen sampler to collect sediment in the depth of 0~10cm below the surface and placed the sample in a shaded and well ventilated area for air drying. Then we laid all the dried sample on a hardboard, crushed it with a glass rod, removed gravels and animal and plant residues, and then grinded it with an agate mortar until all sample went through the 100-mesh sieve. After that, we placed it in an amber wide-mouth bottle, stuck a label on it and cryopreserved it for testing.

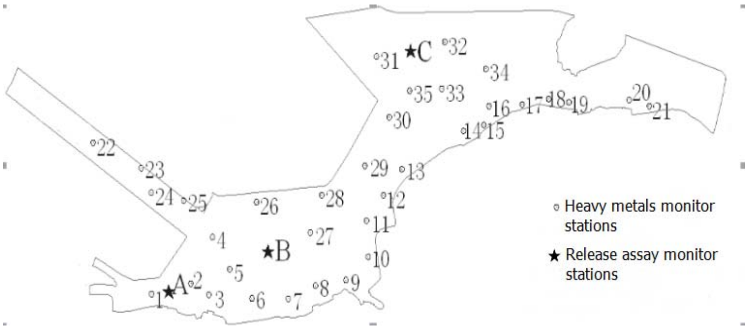

Figure 1: Monitoring site map for heavy metals in the sediment of the Neijiang River

3.1.2 Sample analysis and determination

After digesting the sediment with HCl-HNO_3-$HClO_4$, we determined the concentrations of As, Pb, Cd, Zn, Cu, Cr, Hg and Ni. For Pb and CD, we adopted the graphite furnace atomic absorption spectrometry (GB/T17141-1997); for As, we adopted the atomic fluorescence spectrometry (*Monitoring and Analysis Methods for Water and Wastewater* (Edition 4)), for Cr, Cu, Zn and Ni, we adopted the flame atomic absorption spectrometry (GB/T17137, 38, 39-1997) and for Hg, we adopted the cold atomic absorption spectrometry (GB/T17136-1997).

3.2 Results and analysis

Monitoring results of the spatial distribution of heavy metals in the sediment of the Neijiang River are shown in Figure 2. From the analysis and monitoring results, we can see that:

(1) The average monitoring values of As, Pb, Cd and Hg in the sediment exceed the soil environmental background values in the Neijiang River (Wu Chundu et al. conducted a detailed analysis on the environmental background values of the sediment in the Neijiang River in Zhenjiang[10-11]). The comparison between the sediment monitoring values and the soil environmental background values of the Neijiang River is shown in Tab.1; by analyzing the water quality monitoring data on heavy metals in the Neijiang River, we find that that the concentrations of As, Pb and Cd exceed the minimum detection limits and those of other elements do not. Therefore, in this paper, we select As, Pb and Cd as the factors to study the release patterns of the heavy metal pollutants in the sediment of the Neijiang River.

(2) The contents of heavy metals in the sediment of the south beachland are all higher than those in the north beachland - specifically, the average contents of As, Pb and Cd are higher than those in the north beachland by 16.55%, 33.4% and 223.67%, respectively, mainly because the south beachland is close to the urban area of Zhenjiang and there are pollution channels and chemical plants there like the Yunniang River and Hongqiao Harbor that connect to the Neijiang River, making this area greatly affected by industrial pollution and human activities.

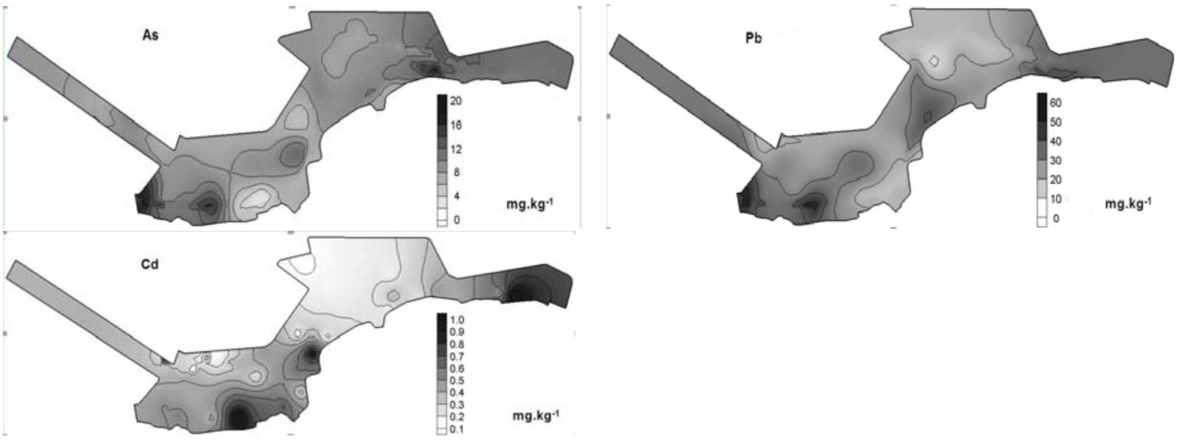

Figure 2: Content distribution of As, Pb and Cd in the sediment of the Neijiang River

Table 1: Neijiang sediment monitoring values vs. soil environmental background values (mg/kg)

Types of heavy metals monitored	Cd	As	Pb	Hg	Zn	Cu	Ni	Cr
Average sediment monitoring value	0.42	9.49	31.97	0.74	144	51.78	28.59	40.46
Neijiang soil environment background value	0.31	3.94	26.03	0.21	252	54.08	33	83.17

4. Tests on release patterns of heavy metals in the sediment of the Neijiang River

4.1 Materials and methods

4.1.1 Sample collection and preparation

According to the distribution of heavy metals in the sediment of the Neijiang River, we used GPS to select three representative sampling sites, which are located at A (32°13′16″N, 119°25′34″), B (32°13′13″N, 119°26′31″E) and C (32°14′6″N, 119°29′1″E) (see Fig.2), respectively, and conducted study on the release patterns of heavy metals in the sediment. On November 18th, 2007, we collected about 3,000g of overlying sediment at the sampling site with a Petersen sampler, took a piece of columnar overlying layer with a length of 10cm with a plastic knife, removed gravels and large impurities, homogenized it and placed it in a clean polyethylene storage bag for later use. We also collected 25L of overlying water at each sampling site with an organic class sampler, placed it into a clean polyethylene storage bag and removed all the bubbles. After getting back to the laboratory, we immediately filtered the sample with a glass fiber filter membrane with an aperture of 0.45μm (WhatmanGF/C). Then we placed the filtered overlying water sample into the refrigerator for storage at 4°C.

Through test analysis, we find that the contents of As in the sediment at Site A, B and C are 18.2mg/kg, 9.74mg/kg and 6.5mg/kg, those of Pb 53mg/kg, 32mg/kg and 9mg/kg and those of Cd 1.03mg/kg, 0.39mg/kg and 0.11mg/kg. This shows that the contents of As, Pb and Cd at Site A are the highest, followed by those at Site B and then Site C. In order to make sure the heavy metals in the sediment of Site A, B and C are representative of the situation in the Neijiang River, we compare the experimental content values of heavy metals in the sediment at these three sites with the monitoring values obtained at 35 sites in the Neijiang River. According to the results: the probabilities of the monitoring values being greater than those at Site A, closer to those at Site B and smaller than those at Site C are less than 7%, 6% and 9%, indicating that Site A, B and C can represent the areas in the Neijiang River with high, medium and low concentration of heavy metals in the sediment.

4.1.2 Testing apparatuses

Constant shaking incubator (ZHWY-2102, accuracy±1rpm), pipette, conical flasks, Milli-Q water purifier, drying oven and electronic balance (accuracy±0.0001g).

4.1.3 Testing methods

We conducted the test at the molecular biology laboratory of Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences from November 13th, 2007 to January 10th, 2008.

We took sediment samples with a weight of 50g (wet weight) each, laid each sample flat at the bottom of a conical flask, slowly injected 250ml of raw water from the Neijiang River along with the flask wall, and put them into the shaking incubator. We adjusted the shaker's speed to 90 $r{\cdot}min^{-1}$, 120 $r{\cdot}min^{-1}$, 180 $r{\bullet}min^{-1}$ and 220 r•min^{-1} to exert disturbance to the conical flasks at different intensities. We kept the shaking incubator running for 30min to balance the disturbance effects. Each time after disturbance, we took out 5mL of overlying liquid from each conical flask with a pipette, and determine the concentrations of As, Pb and Cd. In each group, there are three duplicate samples.

4.2 Calculation of release rates of heavy metals in the sediment

The calculation formula for the release rate of a heavy metal in the sediment is as follows (Fan et al., 1998 and 2000):

$$R = \left[\overline{V}(C_n - C_0) + \sum_{j=1}^{n} V_i (C_{j-1} - C_a) \right] / (A \bullet t) \tag{1}$$

Where, R is the release rate [mg/(m^2.d)]; V is the volume of the overlying water above the sediment (L); C_n is the pollutant concentration in water in the *n-th* sampling; C_0 is the initial pollutant concentration; C_{j-1} is the pollutant concentration in water in the j-1-th sampling (mg.L^{-1}); C_a is the pollutant concentration in water after raw water is added (mg.L^{-1}); V_i is the volume of sample collected each time (L); A is the water-sediment contact area (m^2); t is the release duration (d).

4.3 Result discussion

Figure 3 shows the test results of how the release rates of As, Pb and Cd in the sediment of the Neijiang River change with the disturbance intensity. As can be seen from this figure: (1) the release rates of pollutants in the sediment at all monitoring sites are increased with the increase of the disturbance intensity, which is consistent with the research results obtained by Huang (1995) and Song et al., (2008); (2) at the same disturbance intensity, the release rates of sediment pollutants are increased with the increase of the pollution level.

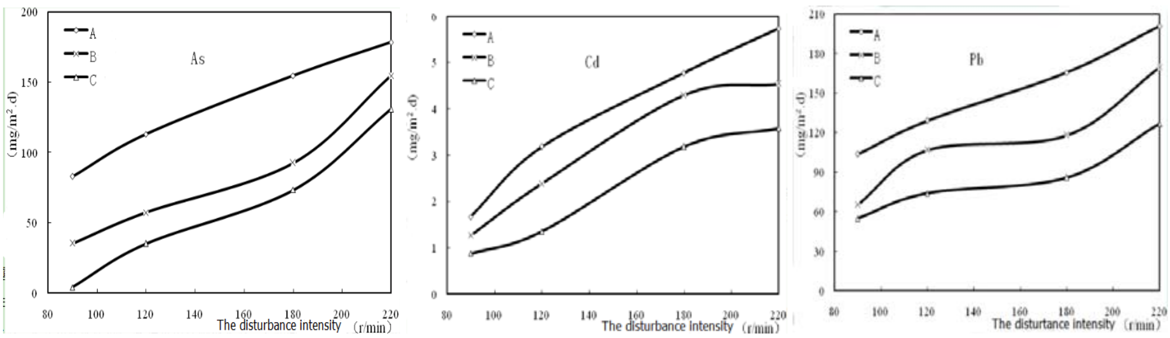

Figure 3: Correlations of release rates of As, Pb and Cd with disturbance intensity

5. Analysis on the temporal and spatial distribution features of heavy metal release

5.1 Relationships study

In April and August 2004 - the flood season and the dry season with typical diurnal tides, we conducted monitoring on the flow velocity and suspended sediment in the Neijiang River. We set up 7 verticals in total for hydrological survey to monitor water flow, hydrology and sediment pollution simultaneously. Through the field water flow and suspended sediment measurement and sediment suspension test in the Neijiang River, with the suspended sediment concentration as the intermediate factor, we establish a transforming relationship between disturbance intensity and flow velocity in the Neijiang River, as shown below:

$$u = \sqrt{0.01\exp(0.0211\omega)} - 0.1215 \quad (\omega>0) \tag{2}$$

Where, ω is the disturbance rotating speed, r.min^{-1}; u is the water flow velocity, m.s^{-1}.
According to the test results regarding the relationship between the release intensity of As, Pb and Cd in the sediment of the Neijiang River and the disturbance intensity, and by using Formula (2), we can obtain the relationships between the release rates of heavy metals in the sediment and flow velocity under different flow velocities and pollution levels, as shown in Tab. 2. The high, medium and low pollution levels listed in Tab. 2 correspond to the three sampling sites A, B and C, respectively in Fig. 2. The four velocities (0.14 m/s, 0.23 m/s, 0.55 m/s, 0.7m/s) are consistent with the four velocity values corresponding to the disturbance intensities in the test.

Table 2: Relationships between the release rates of heavy metals in the sediment and the water flow velocity of the Neijiang River (unit: mg/m^2.d)

Factor	Pollution level	0.14m/s	0.23m/s	0.55m/s	0.7m/s
As	High	82.84	112.92	154.46	178.33
	Medium	35.09	57.22	93.39	154.46
	Low	4.05	35.09	73.29	130.59
Pb	High	103.45	128.92	165.51	200.53
	Medium	65.25	106.63	117.77	169.50
	Low	54.91	74.01	85.94	126.52
Cd	High	1.67	3.18	4.77	5.73
	Medium	1.27	2.39	4.29	4.54
	Low	0.87	1.35	3.18	3.58

5.2 Temporal and spatial distribution features

According to the monitoring results of spatial distribution of heavy metals in the sediment of the Neijiang River and based on the laboratory test on the release patterns of heavy metals and the simultaneous field hydrologic monitoring, we obtain the temporal and spatial distribution characteristics of the heavy metal release in the sediment of the Neijiang River, as shown in Figure 4. From this figure, we can see that: (1) the release rates of heavy metals in the sediment of the south beachland are all higher than those in the north beachland, mainly because the sediment of the south beachland is more seriously polluted, especially in those areas with great accumulation of heavy metals, like the intersection between the Yunliang River and the Neijiang River, the area near the old coking plant and Wharf No.3. The maximum release rates of As, Pb and Cd in the flood season can be up to 121.18 mg/m^2.d, 140.80 mg/m^2.d and 4.42mg/m^2.d; (2) the release rates of heavy metals in the sediment in the flood season are higher than those in the dry season. On average, the release rates of As, Pb and Cd in the flood season are higher than those in the dry season by 210%, 121% and 198%. This is mainly because the flow velocity in the flood season is much higher than in the dry season. (3) The release rates of heavy metals are still fairly high in the sediment in the midstream area where the pollution of heavy metals is not so serious, because the flow velocity is relatively high in the midstream, facilitating the release of pollution from the sediment.

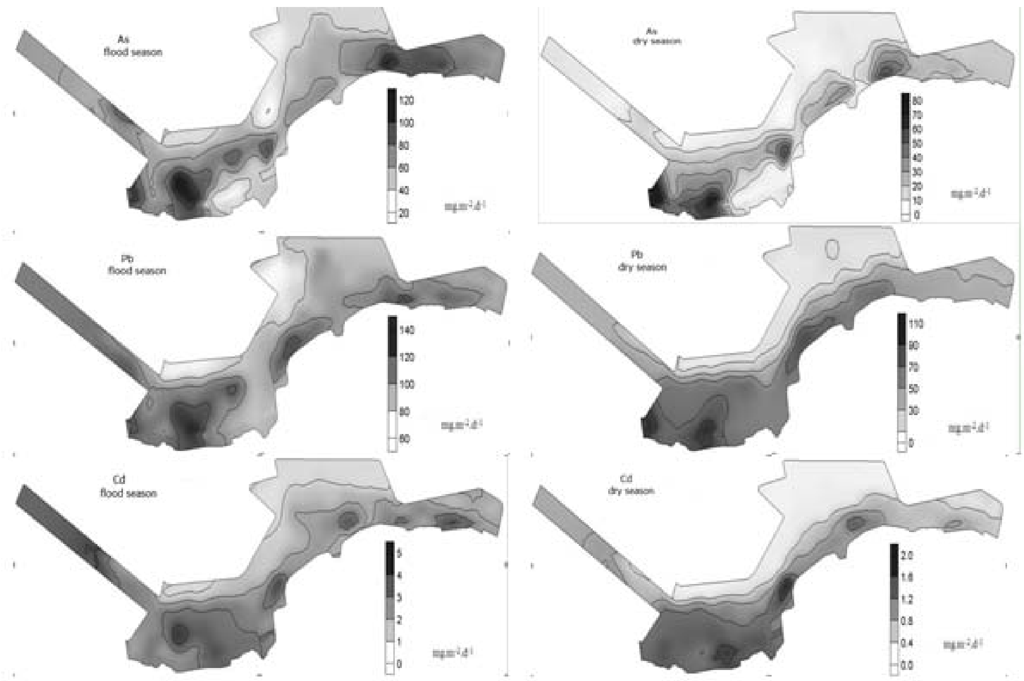

Figure 4: Spatial distribution of release rates of heavy metals in the sediment of the Neijiang River

6. Conclusions

1. By monitoring the contents of heavy metals in the sediment of the Neijiang River, we analyze the spatial distribution features and find that: As, Pb and Cd are the major heavy metals that affect the water quality of the Neijiang River; the contents of heavy metals in the sediment of the south beachland are all higher than those in the north beachland - specifically, the average contents of As, Pb and Cd are higher than those in the north beachland by 16.55%, 33.4% and 223.67%, respectively, mainly caused by the pollution previously accumulated in the industrial park in the south. 2. Based on the laboratory test on the release patterns of heavy metals in the sediment, we study the release patterns of heavy metals in the sediment under different dynamic conditions. And the results show that: the release rates of the heavy metals in the sediment are increased with the increase of the disturbance intensity, and at the same disturbance intensity, the release rates of sediment pollutants are increased with the increase of the pollution level. 3. Based on the laboratory disturbance test and simultaneous field hydrologic monitoring, we establish the relationships between heavy metals in the sediment and dynamic disturbance and flow rate under different pollution conditions; according to the monitoring results of the spatial distribution of heavy metals in the sediment of the Neijiang River, we obtain the temporal and spatial distribution features of heavy metal release in the sediment of the Neijiang River. The results show that: the release rates of heavy metals in the sediment of the south beachland are all higher than those in the north beachland; this is mainly because the sediment of the south beachland is more seriously polluted. In the flood season, the maximum release rates of As, Pb and Cd can be up to 121.18 $mg/m^2.d$, 140.80 $mg/m^2.d$ and 4.42$mg/m^2.d$; the release rates of heavy metals in the sediment in the flood season are higher than those in the dry season. On average, the release rates of As, Pb and Cd in the flood season are higher than those in the dry season by 210%, 121% and 198%. This is mainly because the flow velocity in the flood season is much higher than in the dry season. The release rates of heavy metals are still fairly high in the sediment in the midstream area where the pollution of heavy metals is not so serious, because the flow velocity is relatively high in the midstream, facilitating the release of pollution from the sediment.

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