Study on Static and Dynamic Release Characteristics of River Sediment Pollutants

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Abstract. As the main accumulation reservoir of various pollutants, the sediment plays a very important carrier role in the process of migration and transformation of pollutants. In this paper, based on the test device such as the annular water tank developed, the pollutant release characteristics of the river sediment under still water and moving water conditions were studied. The experimental results show that the content of pollutants nitrogen and phosphorus in river sediments in Nanjing is higher and the content of heavy metals is lower. The static release of pollutants in the sediment reached an equilibrium state in about 60 hours, and the release was faster in the early stage, and the release rate in the later stage gradually slowed down and tended to the equilibrium state. The velocity of river water flow directly affects the release characteristics of sediments. As the water flow velocity increases continuously, the sediments have three states: “not started”, “small amount of movement” and “general movement”. The ratio of pollutants (total nitrogen, total phosphorus, heavy metals) release to total pollutants in the sediment of the river under still water conditions is 0.96%, 0.09%, 0.01-0.06%, about 18.46%, 15.43%, and 0.05-4.55% under hydrodynamic conditions, which are much higher than the amount of pollutants released under hydrostatic conditions, and the release amount of heavy metals Zn and total phosphorus is more affected by hydrodynamic conditions than other pollutants.

1. Introduction
In recent years, with the improvement of living standards and environmental quality, the voices and aspirations of urban residents for the management of urban river water have been increasing. With the comprehensive treatment of rivers, external source pollution has been effectively controlled, and river water quality has improved. However, the experience of Taihu, Qinghe and Suzhou rivers shows that pollutants in sediments have a higher risk of water pollution. The impact of pollution on river water quality is increasingly apparent[1-3]. The types of pollutants in the sediment are complex, mainly including nutrients, heavy metals and organic pollutants. As the main accumulation reservoir of various pollutants, the sediment plays a very important carrier role in the process of migration and transformation of pollutants[4], more and more scholars focus on the release characteristics of sediment pollutants under different hydraulic conditions[5].

Under the conditions of still water, some scholars have studied the nutrient salts in the sediment and concluded that the release of nitrogen and phosphorus is favorable under high temperature and anaerobic environment[6]. The release of phosphorus is stronger than the neutral condition under acidic (alkaline)
conditions, Nitrogen Release increases with decreasing pH[7]; some other scholars have focused on the study of heavy metal release characteristics, and concluded that high flow rates and low pH values can promote the release of heavy metals. The stability of Cd in heavy metal elements is the worst, and higher Hg and As are not conducive to release[8-9]. Because natural water bodies are in a certain state of movement, the shearing effect of the water flow will cause the sediment to resuspend, thus causing a large amount of pollutants to be released into the water, affecting the water quality[10]. In recent years, a large number of indoor studies have been conducted on the dynamic release of sediment pollutants. Ye Qingqing et al, used long straight water tanks to study the characteristics of pollutants under hydrodynamic conditions[11]; Wang Daozeng and others used a circular flume to study the layered release characteristics of sediment pollutants in water[12]. The research shows that the resuspension of the sediment is mainly affected by the hydraulic conditions of the upper water and the particle characteristics of the sediment, with the increase of the flow velocity, the sediment has undergone three states of "not started", "small movement" and "general movement", The particle size of the sediment determines the magnitude of the starting flow velocity [11].

The above scholars tend to study the release characteristics of single pollutants and water states, and lack systematic research on the total pollutants and hydraulic states of water bodies. This paper firstly conducts a static release test of river sediments, and grasps the major pollutants in urban river sediments and their release laws of overlying water. Subsequently, the developed annular water tank test was used to carry out the dynamic release test of the river sediment to study the influence of hydrodynamic conditions on the release characteristics of sediment pollutants, finally, systematically compare the release characteristics of river sediment pollutants under still water and moving water conditions, and provide theoretical basis and technical support for urban river governance in China.

2. Study on pollutant release characteristics of river sediments under still water conditions
Conduct in-situ static release tests of pollutants from river sediments to study the release characteristics of nutrients, heavy metals, and chemical oxygen demand (COD) in river sediments under still water conditions and their influence on overlying water.

2.1. Experiment material
Based on the field survey and preliminary sampling test results, the Yutang River in Nanjing was selected as the sampling site for polluted sediment (as shown in Figure 1). The Peterson-type mud grab was used to collect the polluted sediment at a distance of 5 cm from the river surface as the experimental sediment, after the sediment was collected, it was stored in a PVC bucket and sealed for transportation to the laboratory for future use.

![Figure 1. The collection of sediment.](image)

2.2. Experiment scheme and method
Sieve the river sediment to remove impurities such as stones, leaves, snails, etc., and then flatten the treated sediment in a plexiglass barrel and leave it to rest for 12 hours to restore the layered structure. Slowly add distilled water with a siphon device, and take overlying water samples at the time of 0.5h,
1h, 2h, 4h, 6h, 9h, 12h, 24h, 36h, 48h, 60h, 72h, and 96h, and load the corresponding numbers in the test tube. For the experiment, a siphon with a diameter of 2 mm was used, and 30 ml of water sample at a 15 cm scale of the model cylinder was taken. Before sampling, take a 10 ml water sample to eliminate impurities remaining in the siphon and make the water sample more uniform, take 2 water samples each time to test the content of pollutants.

The total nitrogen and total phosphorus in water samples were determined by spectrophotometry, the heavy metal content was measured by inductively coupled plasma mass spectrometry (ICP-MS), and the COD was measured by dichromate method.

2.3. Experiment results and analysis

2.3.1. Nitrogen and phosphorus release characteristics in sediment.

![Graphs](image)

Figure 2. Curves of nitrogen and phosphorus pollutant concentrations versus time.

As shown in Figure 2: The concentration of total nitrogen and total phosphorus in the water increased rapidly with the release process, and reached a state of release equilibrium at 60 hours. At equilibrium, the total nitrogen concentration in the water was 7.8 mg/L and the total phosphorus concentration was 0.5 mg/L, the total nitrogen concentration in the overlying water was close to 15 times the total phosphorus concentration. Combined with the "Quality Standard for Surface Water Environment" (GB3838-2015), the content of nitrogen and phosphorus pollutants in the water is higher than that of Class V water, and the water is seriously polluted (TN>2mg/L, TP>0.4mg/L). Nitrogen and phosphorus pollutants in the overlying water were quickly released within 4 hours before the test, and the release rate was rapidly reduced after 60 hours, indicating that the pollutants in the overlying water and sediment had gradually reached a state of release equilibrium.

2.3.2. Release characteristics of heavy metals in sediment

Three heavy metal pollutants (Cu, Zn, Hg) with relatively high content were selected as research objects, the deviation of the results of the parallel test in the test data is less than 10% except for the individual data, and the results are reliable, therefore, the experimental data uses the average of two parallel tests. The release test results of three heavy metal pollutants over time are shown in Figure 3, the content of heavy metal pollutants in the overlying water increased rapidly with time, and showed a slow decline after reaching the peak. The time for the pollutants in the overlying water to reach the release equilibrium is Zn>Cu>Hg, the shorter the initial content, the shorter the time to reach the release equilibrium, which is the same as that of the previous release of nitrogen and phosphorus. At the same time, when the heavy metals in the overlying water reach equilibrium, the concentration of pollutants Cu<0.01mg/L, Zn<0.05mg/L, Hg<0.00005mg/L, the content of the three heavy metals is far lower than the Class I water standard in the "Quality Standard for Surface Water Environment".
The heavy metals in the overlying water showed a downward trend at the later stage of the test, and the heavy metals in the overlying water were adsorbed or precipitated. In industry, soluble phosphates are mostly used to remove heavy metal elements in wastewater, because phosphorus-containing materials are an effective heavy metal deactivator, heavy metals can form phosphate precipitates with PO_4^{3-}, effectively reducing heavy metal content. At the same time, phosphate has been used as a heavy metal passivating agent for more than ten years at home and abroad, and phosphorus-based materials can repair heavy metal contaminated soil and effectively reduce the content of heavy metals[13-15]. Combined with the above research results, the combination of phosphate and heavy metal ions in the water to form a precipitate is the main reason for the decline of heavy metal content in the later stage. With the release of pollutants from the sediment, the content of each pollutant in the overlying water increased continuously, the precipitation in the early stage with the release of heavy metals was much smaller than the release, after the dynamic equilibrium is reached, the phosphorus in the polluted water is still increasing, and the precipitation is greater than the release, which causes the heavy metal content in the water to decrease.

Figure 3. Curves of heavy metals versus time.
2.3.3. COD and pH in overlying water

It can be seen from Figure 4 that the concentration of COD in the overlying water increased rapidly in the initial period, and gradually reached the release equilibrium state, the COD concentration in the water in the later period showed a downward trend, which can be attributed to the self-purification effect of the water. The American scholar Streeter-Phelps did related research on the self-purification effect of water as early as 1925, thinking that time is the only parameter that affects pollutants in the water, and a one-dimensional water quality model was obtained. The COD release curve modified according to the water quality model is shown in the figure above, the COD change law of the riverbed sediment is consistent with the nitrogen and phosphorus release characteristics.

On the third day of the static release test, each pollutant in the sediment reached an equilibrium state, and the pH value of the overlying water also became stable. As shown in Figure 5: With the release of pollutants, the pH value in the overlying water gradually decreases and stabilizes, and finally stabilizes at about 7.5. This change law also indicates that the water is in a state of dynamic equilibrium at this time.

3. Study on release characteristics of pollutants from river sediment under moving water

Carry out a dynamic release test of pollutants in river sediments, and study the release characteristics of nutrients, heavy metals, and chemical oxygen demand (COD) in river sediments under dynamic water conditions and their influence on overlying water; Corresponding comparative studies have also been made in the aspects of degree and starting flow rate.

3.1. Experiment device

In this paper, develop a set of annular water tank test device to simulate natural river flow, and to study the release characteristics of pollutants in sediment under moving water conditions. The annular water tank does not need to be provided with a water storage tank and a return device, and has no influence of the inlet and outlet, and each section is relatively uniform. When the water flows stably in the annular water tank, the annular water tank is equivalent to an infinitely long straight water tank with the same cross-section water flow state, so the annular water tank device simulates the natural water flow characteristics close to the actual situation [16-17].

The developed annular water tank test device mainly consists of a plexiglass cylinder, a driving device, a shear ring, a test system, etc., and its schematic diagram is shown in Figure 6. The inner and outer cylinders of the water tank use 1.5 cm thick plexiglass cylinders, and the diameters of the inner and outer cylinders are 0.6 m and 1.0 m, respectively. The base is bonded to the inner and outer walls of the glass with hard rubber. The transverse shear force of the water flow in the model device is provided by four shear rings with a 90° distribution, the shear ring rotates at a constant speed to provide continuous tangential force to the water. The lever shaft is driven and rotated by a high-precision AC
servo motor, and the external encoder can control the speed of the servo motor to adjust the water flow speed in the device, the water line speed is controlled to 0-120cm/s and the control accuracy is 0.1cm/s. The actual water velocity was measured using a propeller-type flow meter fixed on a steel support. The test results of the test device show that the water flow speeds at different depths are close, and the flow speed is stable during the test.

![Schematic diagram of annular water tank](image)

1-outer glass tank, 2-inner glass tank, 3-shear ring, 4-motor and speed control device, 5-base, 6-steel member, 7-valve drain port, 8-rod shaft, 9-flow meter, 10-steel stand, 11-movable connection, 12-motor support.

Figure 6. Schematic diagram of annular water tank.

3.2. Experiment scheme and method
The in-situ sediment sample was laid flat on the bottom of the circular water tank with a thickness of 5 cm. After standing for a while, the overlying water was sucked out, then, 20 cm of overlying water was slowly added with a siphon device, and left to stand for about 90 hours to restore the layered structure to the bottom sediment. Considering the lower starting flow velocity of the in-situ sediment, the hydrodynamic test was performed at four different flow rates of 5 cm / s, 10 cm / s, 15 cm / s, and 20 cm / s, the duration of each flow rate state was 2 hours. Take parallel water samples at 6cm, 15cm, and 25cm, and enter the next flow state after sampling. Before sampling, measure the pH value at the flow rate. After the sampling is finished, shake the sample evenly, and immediately analyze the turbidity of the water samples at different water depths with a turbidimeter.

3.3. Experiment results and analysis

3.3.1. Nitrogen and phosphorus release characteristics in sediment
The curves of nitrogen and phosphorus pollutants with flow rate is shown in Figure 7. With the continuous increase of the water flow velocity, the sediment has three states of "not started", "small movement" and "general movement". When the flow rate is lower than the starting flow rate, the sediment is not started, and the amount of pollutants released and the turbidity in the overlying water are close to the conditions of the still water, when the flow velocity is higher than the starting flow velocity, the sediment is greatly activated, and the amount of pollutants released from the overlying water is greatly increased. With the increase of flow velocity, the concentration of nitrogen and phosphorus pollutants in the overlying water increased, and the change trend was not obvious. When $V=20\text{cm/s}$, the sediment started in a large area. At this time, the nitrogen and phosphorus in the overlying water increased sharply, reaching about 100 times of the previous flow rate stage ($V=15\text{cm/s}$). At this time, the pollutant content in the overlying water was far exceeding surface water standards.
It can be known from Figure 8 that the increase of the velocity of the overlying water causes the pollutants in the water to stratify significantly. When $V=10\text{cm/s}$, a small amount of sediment is started, and the layering phenomenon is not obvious; when $V=15\text{cm/s}$, more fine particles on the surface of the sediment are driven by the water flow to diffuse into the upper and middle water, showing that the concentration of pollutants at the bottom is lower than the upper. At $V=20\text{cm/s}$, the sediment was lifted up by a large area, and the larger sediment particles in the middle and lower parts could not be distributed to the upper water, so that the concentration of pollutants in the lower and middle water was higher than the upper part.

3.3.2. Heavy metal release characteristics

Under hydrodynamic conditions, the change curve of heavy metals with velocity in the overlying water is shown in Figure 9. At lower flow rates, the sediment did not start to suspend. At this time, heavy metals were more stable in the sediment and had less impact on water quality. The flow velocity exceeded the limit. After the sediment was started, heavy metals were quickly released into the water, and the heavy metals in the water increased sharply. After the sediment started to suspend, the concentrations of Cr, Ni, Zn, and Pb reached one hundred times the previous flow state, which seriously exceeded the standard.
3.3. Turbidity and pH in overlying water

Figure 10 shows the variation of pH and turbidity in the water overlying the sediment under the condition of moving water. With the increase of the flow velocity, the pH value of the overlying water has no obvious change; the pH value of the water has a tendency to decrease after the large area of the sediment is lifted. The curve of turbidity and pollutant concentration in the overlying water is basically consistent.

4. Comparison of static and dynamic release characteristics of river sediment

Table 1 shows the release amount and release ratio of pollutants from river sediments under still water and moving water conditions. The main pollutants in the sediment are nutrients (nitrogen, phosphorus), and the content of heavy metal pollutants is low. The release amount of nitrogen and phosphorus in the sediment under hydrostatic conditions was significantly lower than that under hydrodynamic conditions. The ratio of the amount of pollutants (total nitrogen and total phosphorus) released from the river sediment to the total amount of pollutants under still water conditions is about 0.96% and 0.09%; the pollutants (total nitrogen and total phosphorus) from the river sediments under flowing water conditions was approximately 18.46% and 15.43%. The release amount of heavy metals in the sediment under hydrostatic conditions was significantly lower than that under hydrodynamic conditions. The ratio of the release amount of heavy metal pollutants to the total amount of pollutants in the sediment under the condition of still water is about 0.01-0.06%, and the ratio of the release amount of heavy metal pollutants to the total amount of pollutants in the sediment...
is about 0.05-4.55% under the condition of moving water. Hydrodynamic conditions can promote the rapid release of heavy metal Zn in the sediment, the release ratio is higher than other pollutants; Cu and As are less affected by hydrodynamic conditions. Therefore, when the river flow speed is large, it is necessary to carry out key prevention and control of Zn, TP and other pollutants that are greatly affected by hydraulic conditions.

Table 1. Comparison of pollutant releases in different states.

| Pollutant content /mg | Cr  | Ni  | Cu  | Zn  | As  | TN  | TP  |
|-----------------------|-----|-----|-----|-----|-----|-----|-----|
| Total pollutants in   | 2538| 1027| 3482| 15274| 713 | 136263| 75454|
| sediment              |     |     |     |      |     |     |     |
| Still water           | 0.18| 0.33| 0.34| 0.53 | 0.42| 1311.58| 69.33|
| Release Percentage (%)| 0.01| 0.03| 0.01| 0.00 | 0.06| 0.96  | 0.09 |
| Moving water          | 41.06| 37.51| 1.57| 695  | 4.48| 25150 | 11641|
| Release Percentage (%)| 1.62| 3.65| 0.05| 4.55 | 0.63| 18.46 | 15.43|
| Still/ Moving water   | 227.16| 113.75| 4.56| 1321.36| 10.80| 19.18 | 167.91|

5. Conclusions
This paper first conducts a static release test of river sediment to study the release characteristics of different types of pollutants overlying water bodies. On this basis, the effect of hydrodynamic conditions on the release characteristics of sediments in river channels was studied. Finally, compared the static and dynamic release characteristics of river sediments, the main conclusions are as follows:

1) The content of pollutants nitrogen and phosphorus in river sediments in Nanjing is higher, and the content of heavy metals is lower. The static release of pollutants in the sediment reached an equilibrium state in about 60 hours, and the release was faster in the early stage. The release rate in the later stage gradually slowed down and tended to be in equilibrium. After static release, the pH value of the in-situ sediment overlying water continued to decrease; the COD content increased in the initial period, and decreased in the later period due to the self-purification of the water.

2) After static release, the content of nitrogen and phosphorus pollutants in the overlying water are all higher than the Class V water standard in the Surface Water Environmental Quality Standards; the content of heavy metals is far lower than that of Class I water standard, and the distribution pattern of heavy metal pollutants is Zn > Cu > Hg.

3) The river flow velocity directly affects the release characteristics of sediment pollutants. With the continuous increase of the water flow velocity, the sediment has three states of "not started", "small movement" and "general movement". When the flow rate is lower than the starting flow rate, the sediment is not started, the amount of pollutants released from the overlying water and the turbidity are close to the conditions of the still water. When the flow rate is higher than the starting flow rate, the sediment is activated greatly, and the amount of pollutants released from the overlying water is about a hundred times that of the "non-startup". The nitrogen, phosphorus, heavy metals, and COD in the water are far beyond the standard values.

4) The ratio of the release amount of pollutants (total nitrogen, total phosphorus, heavy metals) to the total pollutants in the sediment of the river under the condition of still water are 0.96%, 0.09%, 0.01-0.06%. The ratio of the moving water are about 18.46%, 15.43%, and 0.05-4.55%, which are much higher than those in the still water release amount. The release of heavy metals Zn and Tp is more affected by hydrodynamic conditions than other pollutants.

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References

[1] Itakura, T., Airey, D.W., Leo, C.J. (2003) The diffusion and sorption of volatile organic compounds through kaolinitic clayey soils. Journal of Contaminant Hydrology, 65(3-4): 219-243.

[2] Zhou, Y., Li H.F., Li, D.R. (2015) Water pollution analysis and treatment countermeasures of Jialu River in Zhengzhou. Henan Science, 33(10): 1820-1827(in chinese).

[3] Zhu, Q.L., Li, L., Li, Y.J. (2019) Analysis on comprehensive treatment of water environment of polluted lakes in cities. Journal of North China University of Water Resources and Electric Power(Natural Science Edition), 40(5): 41-47(in chinese).

[4] Chen, Y., Chen, W., Shi, M., etc. (2017) The distribution feature of the pollutants in sediment pore water and overlying water of Shaanxi segment in Weihe River. Journal of Water Resources and Water Engineering, 28(1): 50-55(in chinese).

[5] Zhang, Q., Cao, X.Q., Hu, M., etc. (2019) Research on effects of perturbation on release of pollutions from sediments. Environmental Engineering, 37(09): 40-44(in chinese).

[6] Gao, X., Li, Y., He, Y. (2015) Phosphorus release and phosphorus form change in lake sediments. Chinese Journal of Environmental Engineering, 9(7): 3350-3354(in chinese).

[7] Zhou, C. (2017) Experimental study on mechanism of nutrient release from lake polluted sediment and impact on water quality. Wuhan: Wuhan University(in chinese).

[8] Zhong, Y., Fu, G.Y., Xiang, R.J., etc. (2018) The ecological risk assessment and releasing flux estimation of heavy metal in the Xiangjiang River sediments. China Environmental Science, 38(10): 3933-3940(in chinese).

[9] Liu, Q.Q., Meng, F.P., Lin, Y.C. (2019) Study on bioavailability and ecological risk assessment of heavy metals in sediments of Jiaozhou Bay. Periodical of Ocean University of China, 49(5): 35-44(in chinese).

[10] Duan, Y.J., Liu, X.N., Chen, G.Y., etc. (2017) Influence of sediment re-suspension on black-and-malodorous status and water quality of overlying water. Ecology and Environment, 26(5): 837-842(in chinese).

[11] Ye, Q.Q., Guan, B.H., Li, J. (2009) Phosphorus pollution of the sediment from Hangzhou Urban River and hydraulic simulation of phosphorus release. Chinese Journal of Environmental Science, 30(5): 1351-1356(in chinese).

[12] Wang, D.Z., Zhou, X., Zhu H.W., etc. (2014) Stratified release characteristics of sediments contaminants during re-suspension in water column. Journal of Hydrodynamics, 29(5): 592-598(in chinese).

[13] Wang, D.F. (2019) Study on passivation of heavy metals in municipal sludge by composite phosphorus-bearing materials. Jinan: Qilu University of Technology(in chinese).

[14] Wang, M. (2014) Research on hydroxyapatite complex technology to immobilize heavy metals in contaminated sediment. Jinan: Shandong Jianzhu University(in chinese).

[15] Fang, Y.Y., Cao, X.D., Zhao, L. (2012) Effects of phosphorus amendments and plant growth on the mobility of Pb,Cu and Zn in a multi-metal contaminated soil. Environment Science Pollution Research, 19(5): 1659-1667.

[16] Huang, J.Z., Ge, X.P., Yang, X.F., etc. (2012) Remobilization of heavy metals during the resuspension of Liangshui River sediments using an annular flume. Science Bulletin, 57(21): 2015-2021(in chinese).

[17] Zhou, J.J., Zhang, C.K., Jin, Y. (2008) Experimental research on cohesive free sediment of the South Passage in the Yangtze estuary by two-way annular flume. Yangtze River, 39(16): 48-51(in chinese).