Experimental and simulation studies on the attenuation coefficients of organic pollutants in “Han River and Three Tributaries” basin, China

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Abstract: In order to study the attenuation mechanism and spatial and temporal evolution of organic pollutants in “Han River and Three Tributaries” basin, laboratory experiments were conducted, and a novel COD attenuation coefficient model was proposed. The main environmental factors affecting COD attenuation were identified. On this basis, the attenuation term of the one-dimensional water quality model is modified, and the spatial and temporal distribution characteristics of COD in Hanbei River are simulated and analyzed using the modified water quality model. The results show that: (1) the attenuation process of COD in Hanbei River is basically in accordance with the first-order reaction kinetics, and biodegradation accounts for a large proportion of the whole attenuation process. Within a certain range, the increase of flow velocity, water temperature and sand content promoted COD attenuation, and the effect of sediment particle size on COD attenuation in Hanbei River was not obvious; (2) based on the experimental results, a model for calculating the attenuation coefficient of pollutants is derived. A time varying attenuation coefficient can be calculated, which can realistically reflect the attenuation process and the distribution pattern along the river under the changing environment; (3) Model simulations determined that the COD attenuation coefficient of Hanbei River ranged from 0.03 to 0.19. The research results of this paper provide a scientific and theoretical method to accurately determine the attenuation coefficient of pollutants. It also provides scientific support for determining the ecological water demand of typical rivers and lakes similar to “Han River and Three Tributaries” and the scale of water diversion for Interconnected River System Network.

1. Introduction
The “Han River and Three Tributaries” basin refers to the mainstream Han River and its tributaries Hanbei River, Tianmen River and Fuhuan River. They are located in the hinterland of the Jianghan Plain, with a well-developed water system and a dense network of rivers. The flat and complex distribution of the river network and the large inflow of pollutant load make the water quality of the rivers in the network deteriorate. Most of water quality in the region meets the water quality threshold of Grade I of the Chinese Surface Water Environmental Quality Standard and organic pollution becoming one of the most prominent problems in the “Han River and Three Tributaries” basin[1]. Therefore, Hubei Province launched Interconnected River System Network to improve water quality in the basin.

The management department carried out a study on the ecological water demand of key rivers and lakes in the basin, and used numerical models to conduct coupled simulation analysis of water quality and water ecology in order to scientifically determine the scale of water diversion for the
Interconnected River System Network. As pollutants are affected by hydrological, hydraulic, chemical, physical, biological and meteorological factors in the process of attenuation\textsuperscript{[4]}, attenuation coefficient is commonly used in water quality models. However, existing studies have not yet revealed the factors and mechanisms influencing the attenuation of pollutants in the basin under the effect of Interconnected River System Network, and there are not yet enough research results to support the determination of attenuation coefficient in the region of “Han River and Three Tributaries”.

The main methods for determining the combined attenuation coefficients are borrowing methods, empirical formulas, simulation trial-and-error, and in-house laboratory experiments\textsuperscript{[2]}. The borrowing method and empirical formulae method are easy and fast methods, but often not very accurate. The simulation trial-and-error method repeatedly adjusts the parameters through numerical simulation techniques to compare the simulated values with the actual measured values, but it relies on the accuracy of the monitoring data and has a certain subjectivity. The attenuation coefficient is usually a fixed constant in the model, and this simplification does not match with the actual. The in-house laboratory method is easy to operate, has higher credibility, and can objectively reveal the attenuation process of pollutants under different environmental conditions. Zhou Guosheng\textsuperscript{[3]} studied the degradation pattern of organic pollutants COD in the Laofu River in Hubei through static experiments and determined the COD attenuation coefficient to be $0.0268\text{--}0.0717\ \text{d}^{-1}$. Du Yuhong et al.\textsuperscript{[4]} analyzed the degradation coefficient of NH$_3$-N at different temperatures in the Baotou section of the Yellow River through stirring experiments, and the results showed that the higher the temperature, the greater the NH$_3$-N attenuation coefficient, and the range was $0.04\text{--}0.70\ \text{d}^{-1}$. However, the previous experiments often used static or intermittent mixing methods, which could not adequately simulate the hydrodynamic conditions of the river in the field, and most of the experiments did not fully consider the main factors affecting the attenuation of pollutants.

In this paper, the COD attenuation process of Hanbei River under different environmental conditions is studied by optimizing the method of laboratory experiments and considering various attenuation influencing factors under the flowing water conditions. Then a novel COD attenuation coefficient model is proposed. This model is coupled with a one-dimensional water quality model, and the attenuation term of the one-dimensional water quality model is modified, and the modified water quality model is used to simulate and analyze the spatial and temporal distribution characteristics of COD in the Hanbei River, to determine the range of COD attenuation coefficients in the Hanbei River in combination with historical hydro-meteorological observations of the Hanbei River, and to provide technical support for the accurate determination of the comprehensive attenuation coefficients of pollutants for the “Han River and Three Tributaries”. It provides a scientific basis for the coupled model of water quantity, water quality and water ecology of typical rivers and lakes, the ecological water demand of rivers and lakes, and the determination of the scale of water diversion for Interconnected River System Network.

2. study area

The study area is Hanbei River (Tianmen City section), which is one of the most important area of “Han River and Three Tributaries” basin, including Hanbei River, Tianmen River and four tributaries (Longxi River, Nansancha River, Fengshou Ditch, Tuanjie Ditch) (Fig.1). Hanbei River relies mainly on upstream water recharge. It splits into two branches near Tianmen City, with one part flowing north to the lower Hanbei River and the remaining part flowing east to Tianmen River.
3. Pollutant attenuation experiment

3.1. Test conditions and methods

We investigate the COD attenuation process in Hanbei River under different flow velocity, water temperature, sand content and sediment particle size conditions by conducting multiple groups of attenuation experiments, and establish quantitative relationships between pollutant attenuation coefficients and major influencing factors. All the water and sand collected in the field of Hanbei River (Tianmen section) were used in this study for the experiments.

All experiments were conducted in the temperature and light control test platform (covering an area of 5.6 m²) developed by Yangtze River Scientific Research Institute (Fig. 2). The experimental equipment in this platform mainly consists of a circulating water tank and an electric stirrer. The circulating water tank is composed of two straight sections with rectangular cross section and two circular arc sections, the length of the straight section is 2.0m, the width is 0.1m, the depth is 0.12m, the inner radius of the circular arc bend section is 0.4m, the outer radius is 0.5m, the depth is 0.12m. The flow rate of the water body in the circulating water tank is regulated by a variable frequency circulation pump. The electric stirrer consists of 6 independent electronic stirrers with a speed of 0~3000r/min. The experimental equipment is placed in a closed temperature and light control room, which includes a set of light control device and temperature control device. The light control device regulates the experimental light conditions through fluorescent lamps, and the temperature control device consists of high-power air conditioners and heat pipes to ensure that the room temperature is in a constant state. A data acquisition monitor is installed outside the room to collect and display experimental data such as flow rate, flow rate and temperature.

Two batches of experiments were conducted to investigate the effects of different rotational speeds, temperatures, sand content, sediment particle size, and sterilized and unsterilized raw water on COD concentration attenuation. The first batch of experiments was conducted to investigate the effect of water flow rate on COD attenuation. Because of the large number of experimental setup groups and the limited experimental field, the first batch experiments were considered to explore the conversion
of agitator disturbance speed into water flow velocity in the tank environment at the same time. It has been shown that the agitator perturbation speed causing the same decay rate and the water flow rate of the water tank whose dynamic effect is comparable[5]. Based on the above idea, the experiments were carried out using a combination of stirrer experiments and water tank experiments. Several sets of stirrer experiments with different rotational speeds (0, 150, 200, 300, 450, 600, 800 r/min) and water tank experiments with different flow velocities (0.1, 0.4, 0.7 m/s) were carried out to analyze the attenuation rate of pollutants under different water flow disturbances and to investigate the equivariant transformation relationship between the disturbance rotational speed and the water flow velocity. The second batch of experiments was conducted on the basis of the equivalent relationship of rotational speed ~ flow velocity obtained from the first batch of experiments. All groups used stirrers. By changing the rotational speed of the stirrer instead of the water flow in the tank, the experiments of pollutant attenuation at different temperatures (18 and 28°C), sand contents (20 and 40 mg/L) and sediment particle sizes (<0.058 mm and 0.058-0.125 mm) were carried out at a typical rotational speed of 450 r/min (the corresponding equivalent flow velocity of the tank was initially inferred to be 0.4 m/s). In order to analyze the effect of biodegradation on COD attenuation, two sets of experiments were set up, sterilized and unsterilized. A set of blank control group (original water samples filtered out all sediment) was also set up, and the details of the second batch of experimental working conditions are shown in Table 1.

Each group of experiments lasted for 3 days, and the sampling time of each group was 0, 0.2, 0.5, 1, 2 and 3 days. The pollutant concentration was detected by sampling 20 ml each time, and the COD integrated attenuation coefficient was calculated based on the experimental results with the following equation:

$$K = \ln \left( \frac{c_0}{c} \right) / t$$

(1)

Where: $K$ is the first-order kinetic reaction rate of pollutant, which is the integrated decay coefficient of pollutant, 1/d; $c$ is the concentration value of pollutant at moment t, mg/L; $c_0$ is the initial concentration value of pollutant, mg/L.

Tab.1 Experimental working conditions table

| Working conditions | Water samples                      | Temperature (°C) | Sand content (mg/L) | Particle size (mm) |
|--------------------|------------------------------------|------------------|---------------------|-------------------|
| 1                  | Initial water sample               | 28               | Initial water sample| Initial water sample |
| 2                  | Sterilized water samples           | 28               | Initial water sample| Initial water sample |
| 3                  | Filtered water with added sediment| 18               | 40                  | D1 (<0.058)       |
| 4                  | Filtered water with added sediment| 28               | 40                  | D1 (<0.058)       |
| 5                  | Filtered water with added sediment| 28               | 20                  | D1 (<0.058)       |
| 6                  | Filtered water with added sediment| 28               | 40                  | D1 (<0.058)       |
| 7                  | Filtered water with added sediment| 28               | 20                  | D2 (0.058-0.125)  |
| 8                  | Filtered water with added sediment| 28               | 40                  | D2 (0.058-0.125)  |
| 9                  | Filtered water                     | 28               | 0                   | 0                 |

3.2. Analysis of test results

According to the experimental results, the process of COD concentration change under different speed, temperature, sand content, sediment particle size and sterilization condition are plotted in Fig. 3 and
Fig. 4. The following conclusions can be drawn: (1) The attenuation process of COD in Hanbei River is basically consistent with the primary reaction kinetics. (2) The water velocity is closely related to the attenuation rate of COD. In a certain speed range (150-600r/min), the faster the speed of the stirrer, the more fully the water exchange, the stronger the reoxygenation capacity, and thus the attenuation rate of COD increases. (3) When the speed is too fast (more than 600r/min), the water turbulence is too strong, resulting in great interference with microbial life activities. This seriously stalls all kinds of physical and chemical reaction processes in the water body, resulting in a sharp decrease in the attenuation rate of COD. (4) With the increase of sand content, the suspended sand played a biofilm-like role, which enhanced the microbial degradation effect and therefore accelerated the decay process of COD. (5) In the selected particle size range, the attenuation coefficients of different sediment particle size groups did not differ significantly. (6) The COD attenuation rate of unsterilized water samples was significantly faster than that of sterilization. This indicates that biodegradation accounts for a large proportion of the overall attenuation process.

3.3. Empirical model of the integrated COD attenuation coefficient
The effect of individual factors such as flow rate and sediment on the attenuation is generally described by an exponential function and can usually be linearly cumulated. The influence of temperature on the overall chemical reaction process can be described by a power function with reference to the Arrhenius equation. Because there are some differences between the actual water environment of Hanbei River and the water environment of the indoor simulation experiment, the experimentally obtained integrated attenuation coefficients of pollutants need to be corrected in order to conform to the real river and lake. In summary, the quantitative relationship between the COD attenuation coefficient and flow velocity, sand content, particle size and temperature in the Hanbei River is given by
Where \( k \) is the integrated attenuation coefficient of pollutants; \( \alpha \) is the correction factor; \( U \) is the flow velocity; \( S \) is the sand content; \( T \) is the temperature; \( D \) is the sediment particle size; \( a, b, c, d, e, f, g, h, \) and \( \theta \) are the relevant coefficients. The values of each parameter of the model were obtained by data fitting analysis: \( a=0.8916, b=0.7331, c=0.2189, d=0.5838, e=-0.1530, f=0.5628, g=-1.8045, h=20, \) \( \theta=1.0011 \). The correction coefficient \( \alpha \) was taken as 0.25 by comparing the test results with the results obtained by the actual measurement method.

Equation (2) is the model for calculating COD attenuation coefficient of Hanbei River, which can calculate a time-varying attenuation coefficient. It can be coupled with the one-dimension water quality model, which can more truly reflect the attenuation process and the distribution pattern along the river pollutants under the changing environment. Based on the historical hydro-meteorological observations of the Hanbei River, nine sets of representative hydro-meteorological conditions (Table 2) were selected for different water periods of abundant, flat and dry. Using equation (2), the threshold values of COD integrated attenuation coefficient of Hanbei River were calculated to be about 0.03~0.19.

### Tab. 2 Representative hydrometeorological condition settings for the Hanbei River

| No. | Flow rate (m/s) | Sand content (mg/L) | Grain size (nm) | Temperature (°C) |
|-----|----------------|---------------------|----------------|-----------------|
| 1   | 0.22           | 32                  | 0.016          | 6               |
| 2   | 0.25           | 30                  | 0.015          | 15              |
| 3   | 0.32           | 34                  | 0.011          | 16              |
| 4   | 0.43           | 34                  | 0.013          | 20              |
| 5   | 0.62           | 33                  | 0.014          | 24              |
| 6   | 0.61           | 36                  | 0.012          | 30              |
| 7   | 0.82           | 36                  | 0.013          | 32              |
| 8   | 0.76           | 41                  | 0.012          | 33              |
| 9   | 0.73           | 37                  | 0.018          | 34              |

4. River water quality model

#### 4.1. Hydrodynamic model

For natural rivers and channels, the flow is continuous and satisfies conservation of momentum. It can be described by a system of one-dimensional Saint Venant equations.

\[
B \frac{\partial Z}{\partial t} + \frac{\partial Q}{\partial s} = q_i \quad (3)
\]

\[
\frac{\partial Q}{\partial t} + \frac{2}{A} \frac{Q \cdot \partial Q}{\partial s} + (gA - B \frac{Q^2}{A^2}) \frac{\partial Z}{\partial s} - \left( \frac{Q}{A} \right)^2 \frac{\partial A}{\partial s} + g \frac{Q|Q|AC^2}{AC^2} = 0 \quad (4)
\]

Where \( Z \) is the water level, \( Q \) is the flow rate, \( B \) is the water surface width, \( A \) is the overflow area, \( q_i \) is the side inlet or outlet flow per unit length, \( g \) is the acceleration of gravity, \( t \) is time, \( s \) is the distance along the course, \( R \) is the hydraulic radius and \( C \) is the Chézy coefficient. The system of equations is discretized using the Preissmann implicit form to obtain a linear system of equations after the discretization of the Saint Venant equation, and the linear system of equations is solved using the catch-up method.

#### 4.2. Water quality model

On the basis of the flow and water level calculated by the hydrodynamic model, considering the transport, diffusion and attenuation of pollutants in the water body, the proposed model for calculating the COD integrated attenuation coefficient is used to modify the attenuation term in the
one-dimensional convective diffusion equation and establish a one-dimensional water quality model describing the changes in the distribution of COD in Hanbei River.

\[
\frac{\partial AC}{\partial t} + U \frac{\partial QC}{\partial x} = \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \right) + KAC + S
\]

\[K = 0.25 \cdot (0.8916U^{0.7331} + 0.2189S^{0.5838} - 0.1530D^{0.5628} - 1.8045) \cdot 1.0011T^{-0.25}
\]

Where \(C\) is the cross-sectional average concentration of the pollutant, \(Q\) is the cross-sectional flow rate, \(E\) is the dispersion coefficient of the cross-section, \(S\) is the amount of pollutant in the side inlet stream and \(K\) is the combined attenuation coefficient of the pollutant, calculated using the COD combined attenuation coefficient model.

5. Simulation of spatial and temporal variation of organic pollutants in rivers

The COD spatial and temporal distribution of Hanbei River (Tianmen section) was numerically simulated using the modified river water quality model (RWQM). The river network generalization and the arrangement of boundary nodes are shown in Fig. 5. The generalized water system includes 2 main streams (Hanbei River and Tianmen River), 2 tributaries (Longxi River and Nansancha River), and 11 boundary nodes. Among the boundary nodes, three upstream boundaries are given to the incoming water pollution processes of Hanbei River, Longxi River, and South Sancha River, two downstream boundaries are given to the measured water level processes of Hanbei River and Tianmen River, and four side inlet boundaries are given to the inlet processes of two direct domestic sewage discharge outlets and agricultural surface pollution loads. The spatial step of the model is 100 m and the time step is 1 s. Simultaneous hydrological and water quality monitoring data from March to June 2017 are used for parameter rate determination. The value of the roughness \(n\) of Hanbei River is 0.025, and the COD diffusion coefficient is 13m\(^2\)/s.

Fig. 5 River network generalisation and boundary nodes

The month-by-month measured data from May to October 2018 were used for model validation. Based on simulation results, simulated values of three study sections, S2 (Hanbei River), S3 (Hanbei River), and S4 (Tianmen River), were plotted against the measured values, as shown in Figure 6. As can be seen from the figure, COD simulation results and monitoring results are in good accordance, which proves that water quality simulation effect is good and can reflect water quality change process of river section more accurately. Pollutant own attenuation and pollution load into the water body is main factor affecting change of pollutant concentration. How the pollutant concentration will change depends on which of the two influences plays a controlling role. COD concentrations at each study section were in line with the water quality management standard limits (Class III), but a sudden increase in COD concentrations occurred in September. Combining the results of the field survey and monitoring information, COD concentration in the upstream water from the Hanbei River had reached a high level on September 13. No significant scale rainfall had occurred
before that, and dissolved oxygen concentration (6.6-9.2 mg/L) was also at a normal level. Therefore, the cause of the sudden rise in COD in September is most likely upstream industrial discharge, rather than agricultural surface source pollution.

Fig.6 COD simulation results for S1, S2 and S3 cross-sections, May-October 2018

6. Summary
This paper combines physical experiment with numerical models, identifies the main environmental elements affecting COD attenuation in Hanbei River based on in-house pollutant attenuation experiments, proposes a model for calculating attenuation coefficient, and corrects the attenuation term of the one-dimensional water quality equation. Then we use the modified water quality model to simulate the spatial and temporal distribution characteristics of COD in Hanbei River water system, and obtains following conclusions.

(1) The attenuation process of Hanbei River COD is basically in line with the primary reaction kinetics, biodegradation accounts for a large proportion of whole attenuation process, flow velocity, temperature and sand content are main environmental factors affecting the attenuation of Hanbei River COD, and the influence of sediment particle size on attenuation process of Hanbei River COD is not obvious; (2) Based on the experimental results, the quantitative mathematical expressions of attenuation coefficient are derived, and a model for calculating attenuation coefficient of pollutants is established. (3) The COD concentration at each section of the Hanbei River shows uneven temporal distribution, with overall concentration during the flat water period (May-June and October) being lower than that during rich water period (July-September). At the same time, the difference in COD distribution along the river is not obvious, and the effect of pollutant attenuation on the overall water quality is relatively limited; (4) Based on the representative hydro-meteorological conditions of Hanbei River during the rich, flat and dry water periods, using attenuation coefficient model, the range of pollutant attenuation coefficient for COD was calculated as 0.03–0.19.

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