Calculation and study on pollutant degradation coefficients of Qiantang River estuary

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Abstract. Qiantang River Estuary is a typical macro-tidal estuary in China, with features of strong tidal and high sediment concentration. In order to figure out degradation characterization of the major pollutants of Qiantang River estuary, water samples were taken in Xinsha Island, Changansha Island and Wenyan. CODMn, TN and NH3-N were chosen as the main pollutants of the three cross sections. Pollutants concentration were measured in the laboratory for 20 consecutive days. And the pollutant degradation coefficients (hereinafter referred to as PDCs) were calculated. Considering excluding the nonbiodegradable component in the shore run, pollutant concentration decreased rapidly, which was in keeping with the first-order kinetics equation. The PDC of CODMn is 0.376 d⁻¹, which was above average when comparing with other rivers in China. The PDCs of NH₃-N and TN were below average, which were 0.395 d⁻¹, 0.066 d⁻¹. Meanwhile, NH₃-N and TN are main pollutants exceeding the standard in Qiantang River.

Keywords: Qiantang River estuary; Pollutant; Degradation coefficient; CODMn; NH3-N.

1. Introduction
PDCs are important parameters to revealing descent rate of pollutants concentration in rivers, which are determined by river basin features and water pollution status. In natural water, pollutants are mainly degraded during physical dilution, chemical decomposition and biochemical degradation. PDCs are mathematics representation of the complex mechanisms. Figuring out PDCs is significant for accurately calculating environmental capacity, scientific distributing the pollution load and delicacy management of water environment [1]-[2].

Ways to obtain PDCs are various. For example, empirical formula estimation method, analogy method, field simulation method, Synchronous monitoring of dynamic water method, and laboratory static simulation method [3]. In this paper, laboratory static simulation method was chosen, for natural water is an unmanageable open system which was influenced by illumination intensity, temperature, pH value, microorganism and so on. Another reason is that results by laboratory method are well generalized and summarized, and reveal the peculiarity of water pollutant. This method is widely adopted in scientific research.

Qiantang River is the mother river of Zhejiang province, which is famous for the strong tide. As the pollutants destination of Hangzhou and Jiaxing, papers and research report about PDCs of Qiantang
River are rare to see. Aiming to provide technical support for urban development coastwise of Qiantang River, calculating the PDCs become significant for our research group.

2. Experimental contents and methods

2.1. Experimental principle
Researches show that the degradation of water pollutants is in keeping with the the first-order kinetics equation in natural rivers whose concentration is not very high [4]-[6]. This can be expressed as

\[ C_t = C_0 e^{-kt} \] (1)

Where \( t \) is reacting time(d), \( k \) is PDC, \( C_t \) is pollutant concentration at \( t \) moment, \( C_0 \) is the initial concentration. After manipulation, the formula can be described as

\[ k = \ln \left( \frac{C_0}{C_t} \right) / t \] (2)

Where \( k \) is the slope coefficient of \( \ln \left( \frac{C_0}{C_t} \right) \) and \( t \).

2.2. Experimental Scheme
Xinsha Island, Changansha Island and Wenyan are typical cross sections in Qiantang River, 15 litres of water were taken at each cross section as samples, then shift into open glass jars with capacity of 15 litres in the lab. Water samples should be put into 20 degrees thermostatic incubator and suspending culture for at least 20 days. On the intraday, 1st, 2nd, 3rd, 4th, 5th, 7th, 10th, 15th, 20th days, concentration of the samples must be estimated after shaking up and taking 2 parallel samples and took the average.

Rules should be followed everytime taking samples. Firstly, samples for estimating COD Mn should be taken immediately. Secondly, samples for estimating NH3-N should be filtered. Thirdly, samples for estimating TN should stand for 30 minutes.

3. Estimating results
For the first 5 days, pollutants concentration rapidly descended, then degradation slowed down. Pollutants concentration were almost unchanged for the last 5 days.

Concentration of pollutant COD Mn on cross section Xinsha Island descended from 2.42mg/L to 1.08mg/L, On Changansha Island section it descended from 2.08mg/L to 1.00mg/L, and from 2.02mg/L to 0.96mg/L on Wenyan section. COD Mn in Xinsha Island was higher than the other. Other pollutants, TN and NH3-N, demonstrated the same regularity as well. TN and NH3-N in Changansha Island seemed to be higher than the other.

Figure 1. Variation tendency of pollutants concentration in the lab in 20 days.
Figure 2. Variation tendency of pollutants concentration in the lab in 20days.

Figure 3. Variation tendency of pollutants concentration in the lab in 20days.

Figure 4. COD$_{Mn}$ linear fitting on 3 cross section.
4. Calculating PDCs

COD\textsubscript{Mn} is an index that represents how much reproducibility material in water. In general, pollutant comes in two parts in natural waters, biodegradable and non-biodegradable. The process of biochemical degradation of pollutants approximately obeys the first-order kinetics equation, that is to say, only when substance in COD\textsubscript{Mn} are all biodegradable, PDC of COD\textsubscript{Mn} obeys the first-order kinetics equation. More often than not, some percentage of non-biodegradable material exist in natural water. The biodegradable part degraded quickly, thus, it seems that the first-order kinetics equation is true to the biodegradable material in the first 5 days \cite{7}. And the equation can be recast as

\[ C_t - C_n = (C_0 - C_n) e^{-kt} \]

Where \( C_n \) stands for the non-biodegradable part in water.

In this paper \( C_n \) is the concentration that residual concentration after 20 days. PDCs k can be simulated and calculated with linear regression method.

As shows in table 1 and figure 4, PDCs of COD\textsubscript{Mn} on cross section of Xinsha Island, Changansha Island and Wenyan are 0.377 d\(^{-1}\), 0.3403 d\(^{-1}\), 0.411 d\(^{-1}\). The average PDC of COD\textsubscript{Mn} in Qiantang River estuary is 0.3760 d\(^{-1}\). Comparing with other rivers in China, whose PDC of COD\textsubscript{Mn} range from 0.009 d\(^{-1}\) to 0.417 d\(^{-1}\), PDC of Qiantang River estuary is above the average level\cite{8}. Which is to say, under natural conditions, Qiantang River have a preferable self cleaning capacity of COD\textsubscript{Mn}. Maybe this is the reason why COD pollution in Qiantang River remain in low level.

| COD\textsubscript{Mn} | fitting formula y\(=a \times x^b\) | linear fitting formula | \(K_{COD\textsubscript{Mn}}\) (d\(^{-1}\)) |
|----------------------|-----------------|-----------------------|-------------------|
| Xinsha Island        | y=1.693*x\(^{-0.150}\) R\(^2=0.98\) | y=0.3766x R\(^2=0.7746\) | 0.3766 |
| Changansha Island    | y=1.544*x\(^{-0.142}\) R\(^2=0.98\) | y=0.3403x R\(^2=0.7757\) | 0.3403 |
| Wenyan              | y=1.486*x\(^{-0.146}\) R\(^2=0.99\) | y=0.4110x R\(^2=0.895\) | 0.411 |

As shows in table 2 and figure 5, PDCs of TN on cross section of Xinsha Island, Changansha Island and Wenyan are 0.4057 d\(^{-1}\), 0.3744 d\(^{-1}\), 0.3834 d\(^{-1}\). The average PDC of TN in Qiantang River estuary is 0.3878 d\(^{-1}\).

| TN | fitting formula y\(=a \times x^b\) | linear fitting formula | \(K_{TN}\) (d\(^{-1}\)) |
|----|-----------------|-----------------------|-------------------|
| Xinsha Island | y=0.894*x\(^{-0.212}\) R\(^2=0.92\) | y=0.4057x R\(^2=0.9147\) | 0.4057 |
| Changansha Island | y=1.262*x\(^{-0.299}\) R\(^2=0.96\) | y=0.3944x R\(^2=0.8383\) | 0.3744 |
| Wenyan | y=0.984*x\(^{-0.215}\) R\(^2=0.87\) | y=0.3834x R\(^2=0.8016\) | 0.3834 |

As shows in table 2 and figure 5, PDCs of NH\(_3\)-N on cross section of Xinsha Island, Changansha Island and Wenyan are 0.0561 d\(^{-1}\), 0.0964 d\(^{-1}\) and 0.0460 d\(^{-1}\). The average PDC of NH\(_3\)-N in Qiantang
River estuary is 0.066 d⁻¹. Comparing with other rivers in China, whose PDC of NH₃-N range from 0.105 d⁻¹ to 0.350 d⁻¹, PDC of Qiantang River estuary is below the average level [8]. Which is to say, under natural conditions, Qiantang River have a inferior self cleaning capacity of NH₃-N. Therefore, NH₃-N is the main excessive pollutant. We suggest that sewage discharge along the Qiantang River should be strengthen supervision.

Table 3. PDC Fitting results of NH₃-N.

|          | NH₃-N fitting formula y=a*xᵇ | linear fitting formula | K NH₃-N (d⁻¹) |
|----------|------------------------------|------------------------|---------------|
| Xinsha Island | y=0.232*x⁻⁰.⁶²³ | R²=0.92 | y=0.0561x | R²=0.9969 | 0.0561 |
| Changansha Island | y=0.305*x⁻⁰.⁵⁴⁸ | R²=0.91 | y=0.0964x | R²=0.855 | 0.0964 |
| Wenyuan | y=0.309*x⁻⁰.⁷⁷⁷ | R²=0.94 | y=0.0460x | R²=0.9972 | 0.0460 |

5. Conclusion

Water simples were taken on cross section of Xinsha Island, Changansha Island and Wenyuan. Pollutants concentration were measured in laboratory for 20 consecutive days. And the pollutant degradation coefficients (hereinafter referred to as PDCs) were calculated. Considering excluding the nonbiodegradable component in the shore run, pollutant concentration decreased, which was in keeping with the the first-order kinetics equation. The PDC of CODₘₙ is 0.376 d⁻¹, which was above average when comparing with other rivers in China. The PDCs of NH₃-N and TN are below average, which were 0.395 d⁻¹, 0.066 d⁻¹. Meanwhile, NH₃-N and TN are main pollutants exceeding the standard in Qiantang River.

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References

[1] Guoquan Li, The research on pollutant degradation rule in the sewage outlet downstream of the three gorges reservoir area (in chinese), D. Chongqing Jiaotong University, 2013.
[2] Zhang Yali, Dynamic Change of the River Pollutions’ Composite Degradation Coefficient in Huaihe River’s Tributary [J], Environmental Monitoring in China, 2015(2) 64-67.
[3] Jinbo Mu, Indoor study on degradation coefficients of organic pollutants in a river [J]. SHANDONG SCIENCE, 1997(2): 50-55.
[4] Zu Bo, Degradation of pollutants in the downstream of a sewage outfall in chongqing section of three gorges reservoir [J], Resources and Environment in the Yangtze Basin, 1004-8227 (2017) 01–0134–08
[5] Chen Xiaoyan, The calculation and analysis of the eric lake's organic pollutants degradation coefficient during melt periodJournal of Xinjiang University (Natural Science Edition) (J), 2018 (1) 80-85
[6] Hwang Huey-Min, Hodson R.E., Lee R.F., Degradation of aniline and chloroanilines by sunlight and microbes in estuarine water [J]. Hwang Huey-Min, Hodson R.E.; Lee R.F., 1987, 21(3).
[7] Wu Jianlan, Determining pollutant degradation coefficients of nantong section Yangtze River by rating method in laboratory [J]. Sichuan environment, 2012, 31(05): 36-40.
[8] Liu yang, Calculation and comparative study on pollutant degradation coefficients of rivers in the Huaihe River branch [J], Anhui Agricultural Science, 2020, 48(03): 76-78.