Aquatic Ecological Risk Assessment of Surface Sediment PAHs in Beijiang River Basin

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Abstract. Beijiang River Basin is one of the main water sources of the Pearl River Delta city group, but in recent years the aquatic ecological environment changed. Ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in sediments is an important issue to protect the ecosystem. In the paper, 16 priority control polycyclic aromatic hydrocarbons (PAHs) in the surface sediment from Beijiang River in China were quantitatively determined by GC/MS. Monte Carlo simulation method was used to analyze the ecological risk probabilities of PAHs in the sediments. Results showed that the risks of 3 PAH species were in the order of pyrene > phenanthrene > benzo[a]anthracene, the concentration of 16 PAHs are medium both at home and abroad.

Keywords: Ecological Risk, Polycyclic Aromatic Hydrocarbons, Monte Carlo Method.

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are a class of thick ring compounds widely distributed in the environment, which are arranged in linear, angular or cluster form by two or more benzene rings [1]. They have potential teratological, carcinogenic and mutagenic effects, and are typical EDCs pollutants in beijiang River Basin. The US Environmental Protection Agency has selected 16 PAHs to be on the priority list of toxic organic pollution control, and these 16 PAHs are also the main research objects [2]. As a carcinogen, PAHs is a serious threat to human health and ecological environment, and has attracted much attention from the international community [3]. At the same time, as sediment is an important source and sink of PAHs, ecological risk assessment of PAHs is particularly important and has important practical significance.

Beijiang River is one of the main drinking water sources in the urban agglomeration of The Pearl River Delta and the second largest water system in the Pearl River Basin [4]. But in recent years, the aquatic ecological environment of Beijiang River has changed greatly, and the water quality protection is under great pressure. In this study, the potential risk of polycyclic aromatic hydrocarbons was tested...
in sediments, and probability distribution model is established, which quantitatively obtained probability of Beijiang River basin ecological risk of PAHs in sediment.

2. Materials and Methods

2.1. Data Sources
The data are from published literature, especially articles related to environmental monitoring and analysis of the Beijiang River basin.

2.2. Hazard quotients
Hazard Quotients (HQ) is a simple and conservative method of representing risk, also known as "exposure quotients" (HQ). Quotient method was used to screen potential risk PAHs pollutant types in sediments, and extrapolation method was used to predict the safety threshold of pollutants to biological communities for selected ecological receptors. To calculate the risk quotient for each PAH monomer by comparing exposure concentration and toxicity reference values, compounds of HQ > 1 are generally considered to have potential ecological risks [5]. HQ is calculated as follows:

\[
HQ = \frac{EXP}{TRV}
\]  

Where, EXP is the exposure concentration (NG·g⁻¹), TRV is the toxicity reference value (NG·g⁻¹), TRV generally adopts the sediment ecological reference value. The ecological reference value of a pollutant refers to the safety threshold of no potential ecological risk for the ecological receptor of the pollutant in the biological environmental media, and NOAEL or LOAEL is usually selected instead [6]. Usually, a Consensus based threshold effect Concentration (TEC) of PAHs is selected.

2.3. Quotient-Probability Distribution
Monte Carlo algorithm is generally used to simulate the ECD (Exposure Concentration Distribution), and the probability distribution model is established based on the eigenvalues of all the SSD variables for random sampling. The quotient distribution of ECD and SSD is calculated under the set confidence level, so as to quantitatively obtain the risk of aquatic ecology of pollutants. The Monte Carlo method is used to analyze environmental risks, the requirements of the random number sequence should accord with certain probability distribution of uncertainty factors, resulting in a specific, non-uniform probability distribution of random number sequence. Monte Carlo method is mainly used to simulate the probability distribution of input variables in the risk assessment of aquatic ecology, so as to analyze the reliability of risk assessment.

3. Result and Discussion

3.1. Preliminary screening of risk monomers
Exposure-effect analysis estimation refers to the analysis of the relationship between the dose or exposure level of a substance and the scope and degree of impact. For most pollutants, the half-lethal (effect) concentration (LC50 or EC50) derived from animal studies in short-term trials or the non-impact concentration in long-term trials can be converted to predict or assess the non-impact concentration in humans or the environment. According to the determination of this study on PAHs in surface sediments of the Beijiang River main stream, the exposure of PAHs in sediments is shown in Table. 1
Table 1. Descriptive statistical data of PAHs in sediment samples (ng/g).

| PAHs | Maximum | Minim | Median | Mean    | Standard deviation |
|------|---------|-------|--------|---------|-------------------|
| Nap  | 547     | 4.99  | 33.8   | 78.65   | 110.88            |
| Ace  | 46.3    | 0.365 | 3.99   | 8.06    | 11.10             |
| Acy  | 146     | 0.407 | 6.34   | 16.12   | 30.68             |
| Fl   | 282     | 2.34  | 22.4   | 39.18   | 59.40             |
| Phe  | 963     | 10.2  | 83.6   | 154.58  | 198.79            |
| Ant  | 154     | 0.729 | 11.2   | 20.44   | 30.82             |
| Flu  | 778     | 3.25  | 83.7   | 145.81  | 175.26            |
| Pyr  | 623     | 2.56  | 73.5   | 127.02  | 153.88            |
| BaA  | 324     | 1.1   | 34.2   | 59.45   | 75.91             |
| Chr  | 284     | 1.58  | 41.3   | 58.63   | 61.07             |
| BbF  | 1060    | 2.07  | 56.8   | 107.51  | 192.63            |
| BkF  | 1090    | 0.662 | 20.3   | 64.30   | 193.01            |
| Bap  | 272     | 0.877 | 36.2   | 51.57   | 54.73             |
| lcdP | 198     | 0.93  | 32.2   | 39.56   | 42.58             |
| DahA | 89.5    | 0.43  | 8.99   | 12.91   | 17.80             |
| BghiP| 316     | 1.26  | 40.2   | 50.69   | 62.98             |
| ∑PAH16| 7172.8 | 33.75 | 588.72 | 1034.49 | 1471.50          |

3.2. Predicted NO effect concentration
According to the Environmental Data Manual on Organic Pollutants (Verschueren, K. In 1983, the toxicity of PAHs to aquatic organisms showed that the concentration of lethal effect (LC50 or EC50) was one half, and the concentration of no effect concentration Predicted by 7 PAHs for different aquatic organisms was Predicted, as shown in Table2. Q-Q diagram test showed that the PAHs toxicity data to aquatic organisms was in line with the normal distribution, so Monte Carlo simulation could be used to construct the species sensitivity (SSD) distributions of 7 PAHs.

Table 2. Napierian Logarithm of predicted no effect concentrations (PNECs) for 7 PAHs.

| PAHs | Species | (LC50) Min | (LC50) Max | Mean | Standard Deviation |
|------|---------|------------|------------|------|-------------------|
| ANT  | 13      | 1.61       | 5.89       | --   | --                |
| PHE  | 27      | 6.23       | 10.37      | 8.23 | 3.03              |
| NAP  | 31      | 4.70       | 12.30      | --   | --                |
| FLU  | 8       | 4.14       | 11.51      | --   | --                |
| FLT  | 109     | 0.63       | 16.38      | 6.08 | 7.07              |
| PYR  | 13      | 2.19       | 11.46      | 5.89 | 3.87              |
| BaA  | 10      | 2.49       | 9.21       | 5.20 | 3.38              |
| CHR  | 7       | 1.95       | 11.51      | 7.26 | 5.22              |
| BaP  | 23      | 0.92       | 12.43      | 6.73 | 5.90              |
| DBA  | 4       | 8.29       | 15.42      | 11.03| 3.14              |

3.3. Result of the quotient probability distribution
The exposure concentration distribution and species sensitivity distribution were randomly sampled for 10,000 times by Monte Carlo simulation. The possible quotient distribution of three PAHs was calculated under the 95% confidence interval, and the quotient probability distribution curve was obtained by using Crystal Ball 11.1 (Figure. 1).
Understanding the 95% confidence level, the probabilities of phenanthrene, pyrene and benzo [A] anthracene value less than 1 are 84.99%, 92.84% and 97.25%, respectively. In general, the risk of PAHs aquatic ecology in sediments of Beijiang River basin is low, but some sampling sites have been able to affect a certain number of species. The influence of three PAH monomers is Phe > Pyr > BaA.

**Table 3.** The statistic table of PAHs.

| Statistic       | Forecast Values |
|-----------------|-----------------|
|                 | Phe  | Pyr  | BaA  |
| **Trials**      | 1,000 | 1,000 | 1,000 |
| **Mean**        | 0.44  | 0.2   | 0.12 |
| **Median**      | 0.41  | 0.18  | 0.06 |
| **Mode**        | ---   | ---   | ---  |
| **Standard Deviation** | 0.98 | 2.99  | 0.71 |
| **Variance**    | 0.96  | 8.96  | 0.5  |
| **Maximum**     | 6.6   | 32.36 | 11.75|
| **Mean Std. Error** | 0.03 | 0.09  | 0.02 |

**4. Conclusions**

Quantitative results of beijiang surface sediment samples showed that the detection rate of 16 kinds of optimized PAHs reached 100%, with the total amount ranging from 38.2 to 6470 ng/g, and the average value was 1071 ng/g. The content of 16 kinds of controlled POLY cyclic aromatic hydrocarbons in the study area was 1034.486±1471.504 ng/g, with the highest value being 7172.8 ng/g.

Quotient analysis shows that most PAHs risk providers are < 1, indicating that the potential ecological risk is small. However, serious PAHs pollution in some stations should be paid attention to.
by the environmental protection department, so as to identify the source of pollution, carry out risk assessment and block the input route.

Monte Carlo method was used to simulate the environmental risk of three PAHs pollutants on aquatic organisms in Beijiang River Basin. The results showed that the overall PAHs risk in sediments of Beijiang River Basin was relatively low, but the content of some sample points could affect a certain number of species. Phe, Pyr and BaA have a cumulative probability of 16%, 8% and 3%, and the quotient may be greater than L, that is, it may cause harm to aquatic organisms.

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References
[1] Fan-Sheng M, Jing C, Ye-Yao W. Review of Pretreatment and Analysis Methods of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment [J]. Environmental Monitoring and Forewarning, 2011.
[2] Hu Y, Yu W, Wibowo H, et al. Effect of catalysts on distribution of polycyclic-aromatic hydrocarbon (PAHs) in bio-oils from the pyrolysis of dewatered sewage sludge at high and low temperatures [J]. The Science of the Total Environment, 2019, 667(JUN.1):263-270.
[3] Moddassir Ahmed, Muhammad Rau, Zahid Mukhtar, et al. Excessive use of nitrogenous fertilizers: an unawareness causing serious threats to environment and human health [J]. Environmental Science and Pollution Research, 2017.
[4] An T, Qiao M, Li G, et al. Distribution, sources, and potential toxicological significance of PAHs in drinking water sources within the Pearl River Delta [J]. Journal of Environmental Monitoring Jem, 2011, 13(5):1457-1463.
[5] Hlihor R M, Apostol L C, Smaranda C, et al. Bioavailability processes for contaminants in soils and their use in risk assessment [J]. Environmental Engineering & Management Journal, 2009, 8(5): 1199-1206.
[6] Li Z, Wen-Wen W, Xia J, et al. [Determination of Background Value and Potential Ecological Risk Assessment of Heavy Metals in Sediments of the Danjiangkou Reservoir] [J]. Huan Jing Ke Xue, 2016:2113-2120.