Distribution characteristics and ecological risk assessment of nutrients in sediment particles in Hangzhou Bay, China

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Abstract. In April 2011, the contents of TC, TP, TN, NH\textsubscript{4}-N and the particle size and pH of surface sediment and suspended particulate matter at 18 stations in Hangzhou Bay were detected and analyzed. The content of nutrients in the bay features high values in the middle and mouth of the bay while low values at the top of the bay, and low values on the north side while high values on the south side of the bay. The contents of TC, TN and NH\textsubscript{4}-N in suspended particulate matter were significantly higher than those in surface sediments. To a certain extent, this feature reflected the effect of water and sediment transportation. Hydrodynamics in the studied area were active. The sediment differentiation caused by the repeated suspension-transport and sedimentation of the tidal current was one of the important reasons for the difference of the contents and dispersion of nutrients in suspended sediments and surface sediments. The contents of TP in the Hangzhou Bay were high and the contents of most of the sediment samples collected exceeded the class I, which indicated that the sediments in Hangzhou Bay had been contaminated. However, most areas were still within the range of benthic organisms. In terms of the distribution of pollution, the TP had the most obvious toxicity in front of the south shore of Hangzhou Bay.

1. Instruction

The nutrients are the most basic components of the marine food chain, their contents and variations control the succession and variation of the marine food chain, and then affect the changes in the ecosystem \cite{1-3}. On one hand, the nutrients in seawater are the material basis for the growth and reproduction of marine phytoplankton. The content and structure of nitrogen, phosphorus, silicon and carbon in seawater have great influence on the primary production level of phytoplankton and the structure of ecosystem. The lack of a nutrient can also limit phytoplankton growth and can be a limiting factor in the growth of plankton in water \cite{4,5}, on the other hand, with the rapid economic and social development, the increase of imbalance of biogenic elements makes the eutrophication of water bodies in estuaries and coastal waters much more serious.

Hangzhou Bay is one of the most famous strong tidal estuaries in both China and the world. The upper boundary of the bay is around Ganpu which is adjacent to the Qiantang River, the northern side is adjacent to the Yangtze River estuary with abundant water and sediment, and outside the bay in the east is the East China Sea and Zhoushan Islands. In general, Hangzhou Bay is characterized by large tidal range, high sediment concentration, strong dynamic conditions, frequent exchange of sediment and other substances, and large changes in physical and chemical factors. In the meantime, the
environmental problems in the area are more prominent. For example, since 2010, China's State of the Environment Bulletin released by China's Ministry of Environmental Protection had showed that the proportion of inferior grade IV seawater in the Hangzhou Bay was close to 100%. It also pointed out that the main pollution indicators were biogenic nitrogen and reactive phosphate.

Given the fact that the contents of biogenic elements in Hangzhou Bay had exceeded the standards of Sea water quality Standard China and the ecological environment had been deteriorating and based on investigation data of suspended particulates and surface sediments in Hangzhou Bay in April 2011, this paper studied and discussed the contents, distribution, origin, geochemical characteristics and influential factors of nutrients in Hangzhou Bay.

2. Sampling and determination

18 sampling stations were set up. According to the width and sedimentary characteristics of sections, 2 stations were employed in each of section 1 to 4 from Ganpu to Zhapu, 3 stations in section 5 and 6 from Jinshan to Fengxian. Section 7 near Luchaogang was arranged with 4 stations (figure 1).

![Figure 1. Study area and sampling stations.](image)

Sampling work carried out in May 2011. Navigation and positioning used DGPS global differential positioning system. Grab sampler was used to collect surface sediment samples which were not less than 500 g. The samples were enclosed in polyethylene bags treated with 5% HNO₃ solution and placed in refrigeration equipment. After landing, the samples were placed in a freezer and refrigerated at 4°C for laboratory determination. The entire operation of sampling and pre-treatment was carried out in strict accordance with the standards of the Specifications for oceanographic survey and the specification for marine monitoring.

The samples were measured for particle size (Mz), Total carbon (TC), Total phosphorus (TP), Total nitrogen (TN) and Ammonia nitrogen (NH₄-N).

The determination of total carbon content was measured by infrared carbon and sulfur analyzer (HCS878C2). The TP samples were dissolved in hydrochloric acid, nitric acid, hydrofluoric acid, perchloric acid before being measured by ICP-AES. The content of TN was determined by KDN Kjeldahl apparatus; The pH value of the water was measured by a portable acidometer; the suspended
sediment content (SS) was measured by the dry weight method. In the process of sample analysis, the test results of national first-class standard substances were used for comparison; the parallel sample analysis was carried out, and the relative standard deviation was less than 5%. The test results were accurate and reliable.

Sediment particle size was measured by using a Malvern-Masters 2000 laser particle size analyzer. The grain-size units adopted the Udon-Wendt Fahrenheit Φ particle size standard, and Fokker and Ward grain size formulas were applied to calculate the grain size parameters.

The chemical analysis of the samples was completed by Key Laboratory of Clay Minerals, Ministry of Land and Resources of Ministry of Land and Resources Hangzhou Mineral Resources Supervision and Testing Center (Zhejiang Institute of Geology and Mineral Resources). The particle size analysis of samples was completed by Zhejiang Surveying institute of Estuary and coast.

3. Results and discussion

3.1. content and distribution

The content of TC in suspended sediment was 11800~15500 mg·kg\(^{-1}\) and the mean value was 13743 mg·kg\(^{-1}\). The highest value was located at the front of the An-Dong shore outside the south bank of Hangzhou Bay and the second highest value was in the 13 station near the middle of the bay mouth. The content of TP was 530-790 mg·kg\(^{-1}\), with the highest value distributed in the northern coast of Hangzhou Bay near Zhaupu port and the lowest value in the bay top and middle area of bay mouth (figure 2).

![Figure 2](image-url)

**Figure 2.** The Spatial variation of the contents of TC, TN, TP, HN\(_4\)-N in surface sediments and suspended particulate matter (—: surface sediment; —: suspended sediment unit: mg·kg\(^{-1}\)).
TN content was 495-853 mg·kg\(^{-1}\) and the average value was 486 mg·kg\(^{-1}\). The content in station 13 was the highest in the middle of the bay mouth while the content in the north and top of the bay was lower. The content of NH\(_4\)-N was 9.8-31.2 mg·kg\(^{-1}\), with an average value of 21.4 mg·kg\(^{-1}\). The highest content was found near the north shore of Zhapu, followed by the station 13 near the middle of the bay mouth. The area in the northeast of Gupu had the lowest content.

Regarding the surface sediments, the TC content was 5700-15700 mg·kg\(^{-1}\) with an average of 11555 mg·kg\(^{-1}\). The highest value (station 17, 15700 mg·kg\(^{-1}\)) was distributed in the middle of the baymouth and a significant decrease was observed toward the bay top. The content of TP was 280-1280 mg·kg\(^{-1}\), with an average of 697 mg·kg\(^{-1}\). The maximum value was found outside the Andong shore, and the content was significantly reduced to the top and the baymouth. The TN content was 225-840 mg·kg\(^{-1}\) with an average of 486 mg·kg\(^{-1}\). Among all the stations, the content in station 14 in the northern part of the bay mouth was the highest, and it was significantly reduced to the top of the bay. The lowest content was in the sea area between Gupu and Zhapu, which slightly increased towards the upstream. The content of NH\(_4\)-N was 7.2-24.8 mg·kg\(^{-1}\), with an average of 15.6 mg·kg\(^{-1}\). The highest value was distributed in the central part of Bayou station 13 and it noticeably decreased towards the upstream direction. The content near Gupu was the smallest.
towards Luchaogang.

The coefficient of variation (CV) can quantitatively reflect the degree of spatial fluctuation of each chemical component in the studied area. The CV of all the biogenic elements in surface sediment and suspended particulate matter were between 0.30-0.43 and 0.11-0.23 respectively. The differences of CV between suspended sediments and surface sediments indicated that the spatial distribution of the content of each chemical component in suspended particulate matter was more uniform and the variation was smaller (table 1).

In contrast, the contents of TC, TN and NH$_4$-N in suspended particulates were obviously higher than those in surface sediments except for TP, which was slightly higher in surface sediments.

| Table 1. Statistics of chemical elements contents in surface sediments and suspended sediments in Hangzhou Bay. |
|---------------------------------------------------------------|
| sediment           | statistic project | Mz | pH  | TC (mg·kg$^{-1}$) | TP (mg·kg$^{-1}$) | TN (mg·kg$^{-1}$) | NH$_4$-N (mg·kg$^{-1}$) |
|--------------------|-------------------|----|-----|------------------|------------------|------------------|----------------------|
| surface sediment   | Average           | 5.08 | 8.43 | 11555            | 697              | 486              | 15.6                 |
|                    | Max               | 7.04 | 8.85 | 15700            | 1280             | 840              | 24.8                 |
|                    | Min               | 3.02 | 8.07 | 5700             | 280              | 225              | 7.2                  |
|                    | standard deviation | 1.48 | 0.28 | 3655             | 206              | 206              | 5.1                  |
|                    | CV***             | 0.29 | 0.03 | 0.32             | 0.30             | 0.42             | 0.33                 |
| suspended sediment | Average           | 6.85 | 7.99 | 13743            | 668              | 644              | 21.4                 |
|                    | Max               | 7.42 | 8.26 | 15500            | 790              | 853              | 31.2                 |
|                    | Min               | 5.87 | 7.79 | 11800            | 530              | 495              | 9.8                  |
|                    | standard deviation | 0.01 | 0.17 | 1587             | 74               | 127              | 5.0                  |
|                    | CV***             | 0.68 | 0.02 | 0.12             | 0.11             | 0.20             | 0.23                 |

**CV=s/Average, CV>0.5 Discreteness is more obvious**

3.2. **Toxicity evaluation**

TC, TN, and TP can poison benthic organisms when a certain concentration is reached in sediments [6,7]. Mollenhauer believed that the increasing TC content in sediments had led to continuous decrease of dissolved oxygen in the bottom layer and increase of H$_2$S and other gases in the bottom water, which results in a large number of benthic deaths [8].

At present, because there were very few standards to evaluate the ecotoxicological effects of TN and TP in sediments, the quality evaluation guideline formulated by the Department of Environment and Energy of Ontario (1992), Canada was adopted in most cases [6-12]. The Evaluation criteria divides the environment into three levels. level I: no toxic effects are found in aquatic organisms; level II: the sediment is contaminated but most benthic organisms are viable; level III: the benthic community has been damaged significantly (table 2).

| Table 2. Indices of Potential toxic ecological risk assessment. |
|---------------------------------------------------------------|
| Biogenic elements | level I | level II | level III |
|-------------------|---------|----------|-----------|
| TN (mg·kg$^{-1}$) | <550    | 550-4800 | ≥4800     |
| TP (mg·kg$^{-1}$) | <600    | 600-2000 | ≥2000     |

According to this criteria, the average value of TN was 486 mg·kg$^{-1}$, which belonged to level I. There were 11 stations with contents of TN smaller than 550 mg·kg$^{-1}$ and 7 stations larger than 550 mg·kg$^{-1}$. The average value of TP was 697 mg·kg$^{-1}$, which belonged to the level II. There were 3 stations with contents of TP smaller than 600 mg·kg$^{-1}$ and 15 stations larger than 600 mg·kg$^{-1}$.

Overall, the concentrations of TP in the Hangzhou Bay were high since most of the stations
exceeding level I, which indicates that the Hangzhou Bay’s sediments had been contaminated. However, most areas were still inhabitable by benthic organisms. In terms of the distribution of pollution (figure 4), the most obvious effect of TP toxicity was observed on the forefront of the beach on the south bank of Hangzhou Bay.

4. Conclusions
The nutrients in Hangzhou bay showed an obvious feature that the contents in the middle and mouth of bay was high while the contents in the top and the north side of the bay was low. The distribution of the chemical components in the suspended particles was more even and less changeable. The contents of TC, TN and NH$_4$-N in the suspended particulates were significantly higher than those in the surface sediments, which reflected the characteristics of the nutrients coming with water and sediment transportation. The sedimentary differentiation of tidal current was the important reason for the difference of nutrient content and dispersion in suspended sediments and surface sediments.

The contents of TP in Hangzhou bay were much higher than surrounding are so that most stations exceeded level I, which means the Hangzhou Bay sediment had been contaminated. However, most areas were still within the scope of benthic organisms. In terms of the distribution of pollution, the most obvious toxic effect TP was found in front of the south coast of Hangzhou Bay. However, due to the different latitudes and environments, the toxicity of nutrients also needs further toxicological analysis.

Acknowledgments
This paper was founded by the Science and Technology Plan for Zhejiang Province (2015F50064 2017F30008), The Natural Science Found of Zhejiang Province (LQ16E090004), The Science and technology project of Zhejiang Geological Survey Bureau (201713).

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