Nutrient Variation Characteristics of Luanhekou - Beidaihe Ecological Monitoring Marine Area in summer

Zeng Zhaoshuang*

Qinhuangdao Marine Environment Monitoring Central Station, State Oceanic Administration, Hebei, China
e-mail: zhaoshuangzeng@yeah.net

Abstract. Based on the observation data and materials of Luanhekou - Beidaihe ecological monitoring marine area obtained during 1999 and 2014 in summer, the nutrient and its structure change were studied. The results showed that: with social and economic development in the coastal regional, compounds with three nitrogen atoms increased, but phosphate and silicate decreased in the past 16 years. Average N: P ratio increased from 4.951 in 1999 to 47.188 in 2014, while Si: N ratio decreased. Nutrient structure changed obviously. Phosphate was relative surplus but inorganic nitrogen was relative lack before 2004. However, the water quality characteristics turn into high nitrogen and low phosphorus after 2004.

1. Introduction
Luanhekou - Beidaihe ecological monitoring marine area (39°26′30″~39°47′00″N, 119°17′00″~119°32′51″E), locates in the northwest of the Bohai, and belongs to the typical estuarine ecosystem, which is one of the largest scallop culture area in China, and one of the important habitat of amphioxus animals. Monitoring area has built three tourism development zones, such as Beidaihe, Nandaihe and gold coast along the coast from north to south. The tributaries of Bohai mainly include the Luanhe, DapuHe, Yanghe and DaiHe. In recent years, with the vigorous development of the coastal aquaculture industry, agriculture and industry, environmental pollutants that are rich in nitrogen and phosphorus keeps increasing, which significantly affects the water quality of the nearshore and bring local waters eutrophication problems. Based on the nutrient monitoring data on August from 1999 to 2014, Ecological monitoring in Luanhe river mouth - Beidaihe district as the foundation, the long-term changes of nutrient and its structure characteristics in coastal waters were comprehensively analyzed to identify the water variation over the years, providing a scientific basis for improving the water quality and protection of the marine environment.
2. Materials and Methods

Figure 1 the layout of Luanhekou - Beidaihe ecological monitoring marine area monitoring stations

Luanhekou - Beidaihe ecological monitoring marine area has 24 monitoring stations (sampling station distribution is shown in Figure 1), mainly on-site sampling on the surface (0.5 m) seawater. The sampling and analysis methods for water quality monitoring follow "marine monitoring" (GB17378-2007) execution [3]. The main monitoring indicators include temperature (thermometer method), salinity (salinity meter method), pH (pH meter method), dissolved oxygen (DO, iodometry), chemical oxygen demand (COD, alkaline permanganate law), nitrite nitrogen (NO$_2$-N, hydrochloric acid naphthylethylenediamine spectrophotometry), nitrate (NO$_3$-N, zinc cadmium reduction method), ammonium nitrogen (NH$_4$-N, indigo spectrophotometric method), active phosphate (PO$_4$-P, phosphorus molybdenum blue spectrophotometric method), active silicate (SiO$_3$-Si, silicon molybdenum yellow method), chlorophyll a (Chl-a, acetone extraction spectrophotometry). Inorganic nitrogen (DIN) is the sum of the content of NO$_2$-N, NO$_3$-N and NH$_4$-N.

In order to identify the nutrient structure variation in summer in Luanhekou - Beidaihe ecological monitoring marine area, the content of phosphates, ammonia, nitrate, nitrite, silicate and inorganic nitrogen are selected as indicators in this study. According to monitoring data, the mean of each indicator is calculated from 1999 to 2014 to identify the summer water quality trends using Excel 2003 and SigamaPlot 1.2.0.

3. Results and Analysis

3.1 Variation of Nitrogenous Nutrients

As shown in Figure 2 (a), the average concentration of the quaternary ammonium salt of Luanhekou - Beidaihe water area increased from 1.013μmol / L in 1999 to 3.466μmol / L in 2014 with an increase rate of 0.153μmol / (a · L). The average concentration of nitrate increased from 2.013μmol / L in 1999 to 8.764μmol / L in 2014 with an increase rate of 0.422μmol / (a · L), as shown in Figure 2 (b). The average concentration of nitrite in 1999 was 0.136μmol / L, increased to 0.891μmol / L in 2014 with an increase rate of 0.047μmol / (a · L), as shown in Figure 2 (c). The concentration of quaternary ammonium salt, nitrate and nitrite have a tendency to increase, the maximum rate of increase in the
concentration of nitrate, followed by ammonium, nitrite minimum. The percentage of inorganic nitrogen salts form varied between 25% to 40% according to the year, the proportion of nitrate fluctuated between 50% to 70%, while the content of nitrite was less than 10%, shown in Figure 2 (d).

3.2 Variation of Active Phosphate

In the last 16 years, the concentration of phosphate in Luanhekou - Beidaihe summer water area waters decreased from 0.639μmol / L in 1999 to 0.278μmol / L in 2014, with a decrease rate of 0.023μmol / (a · L ), as shown in Figure 3. Phytoplankton and zooplankton breed in spring, consuming a lot of nutrients in water, but land runoff does not bring adequate nutrient supplement with less rainfall. Therefore, phosphate decreased in spring. During the rainy season in the summer, terrestrial runoff brings a wealth of nutrients, and then phosphate concentration gradually increased. Temperature drops in winter, phytoplankton and zooplankton recession and death, which cause part of the phosphate decompose and reconstitute in the water and the other part of the phosphate form organic phosphorus and deposite in the bottom of the sea [4].
3.3 Variation of Silicates

The relative content of silicates in Luanhekou - Beidaihe summer sea water area varies between 13.505–13.679μmol / L in 1999–2014 years, showing a slight downward trend with the annual decreasing rate of 0.011μmol / (a · L), as shown in Figure 4. Silicate is an important source of nutrients necessary for the growth of phytoplankton. Silicate is absorbed by phytoplankton in growing season and reproductive period of phytoplankton, and the silicon content in seawater decreased. When phytoplankton growth was inhibited by such as water temperature, the silicate content in water has a certain recovery. But the change and distribution of seawater silicate content is not only subject to biological effects, but also affected by the continent drainage and water movement [5]. Although there is no big river importing Luanhekou - Beidaihe ecological monitoring marine area, but there are Ruanhe, Daihe Dapuhe and the other small rivers importing to supplement silicate. Coupled with the water vertical circulation effect, the underlying silicon continue to add salt to the top.

3.4 Nutrient Structure Characteristics

Si: N: P is an important Marine chemistry and Marine biology parameter in seawater, becoming the key indicators of phytoplankton limiting factors. According to Redfield proposal, the ratio of Si: N: P by photosynthesis of phytoplankton assimilation is 16:16:1, and the deviation of the ratio portend the phytoplankton is limited by N \ P or Si [6, 7]. Some studies show that if the N: P < 10 or Si: N > 1, N limits. If Si: N < 1 and Si: P < 3, showing that Si restrictions. When Si: P > 20 ~ 30, suggesting that P
Nutrient limiting factor of phytoplankton in summer is evaluated with years of monitoring data using the Redfield standard (Si: N: P = 16:16:1) in Luanhekou - Beidaihe ecological monitoring marine area. According to the monitoring results of Si: N: P in 16 years (table 1), the overall silicate displayed the relative surplus, while N and P showed obvious phases. N: P in Luanhekou - Beidaihe ecological monitoring marine area varied between 4.951-47.188, and the average N: P was 23.493. N: P were below 16.0. Before 2003, N: P showed relative excess phosphate, and relative lack of inorganic nitrogen. After 2004, N: P changes in 16.661-47.188, showing relative excess of inorganic nitrogen but relative lack of phosphate. As shown in Figure 5, Si: N has a downward trend in the last 16 years, it is speculated that the three concentration of nitrogen compounds showed growth trend, but silicate decreased. N: P showed increasing trend, for three compounds concentration increased on one hand, while on the other hand, active phosphate concentration decreased. So N was the limit factor for the Luanhekou - Beidaihe ecological monitoring marine area from 1999 to 2003, but P became the limit factor after 2004, which indicating social economic activity has obviously affected the nutrient structure of Luanhekou - Beidaihe ecological monitoring marine area.

| Time  | 1999  | 2000  | 2001  | 2002  |
|-------|-------|-------|-------|-------|
| Si:N:P| 21.322:4.951:1 | 30.288:10.170:1 | 34.913:13.410:1 | 40.601:13.903:1 |

| Time  | 2003  | 2004  | 2005  | 2006  |
|-------|-------|-------|-------|-------|
| Si:N:P| 35.366:14.377:1 | 38.166:16.661:1 | 41.226:18.431:1 | 45.641:21.471:1 |

| Time  | 2007  | 2008  | 2009  | 2010  |
|-------|-------|-------|-------|-------|
| Si:N:P| 46.532:23.720:1 | 39.402:18.906:1 | 42.612:23.342:1 | 47.200:24.118:1 |

| Time  | 2011  | 2012  | 2013  | 2014  |
|-------|-------|-------|-------|-------|
| Si:N:P| 40.180:34.817:1 | 45.650:44.815:1 | 46.107:45.654:1 | 48.667:47.188:1 |

**Figure 5** The variation of Si:N:P

4. Discussion
The studies show that as the increase of the intensity of human activities in the Luanhekou - Beidaihe ecological monitoring marine area, the concentration and structure of nutrient are changed obviously. One is the total dissolved inorganic nitrogen content continue to rise especially after 2004, phosphate and silicate content decreased. The other is the change of the nutrient structure, phosphate was relative surplus and inorganic nitrogen was relative lack before 2003. However, inorganic nitrogen became relative excess and phosphate changed to relative lack after 2004.

According to the ways of nutrient input, the nutrient sources in Luanhekou - Beidaihe ecological
monitoring marine area mainly includes terrigenous emissions and mariculture[1]. According to statistical yearbook data of Qinhuangdao in 1999-2012 (Figure 6), it displayed that the amount of ammonia nitrogen from terrestrial to seawater in Luanhekou - Beidaihe ecological monitoring marine area increased from 348.66 t in 1999 to 881.81 t in 2012, increased more than 1.5 times [11, 12], but the amount of total phosphate reduced from 193.10 t in 1999 to 40.45 t in 2012 [11, 12], decreased nearly 80%. With the ariculture mode transformation from extensive farming to ecological farming model since 2004, the implementation of seawater reconstruction project, prohibition of the use of phosphorus-containing chemicals, the pollution in phosphate gradually reduce Luanhekou - Beidaihe ecological monitoring marine area, causing the decrease in the phosphate content in the water.

![Figure 6 The nutrients from terrestrial to seawater in Luanhekou - Beidaihe ecological monitoring marine area](image)

There is no relevant studies on the change of nutrient proportion in Luanhekou - Beidaihe water area. The results of this study indicate that the nutrientsin structural loss balance in Luanhekou - Beidaihe ecological monitoring marine area, gradually changing from nitrogen limitation into a phosphorus limit, primarily due to the increase of three nitrogen compound concentration but the negative growth of silicates, phosphates within the period. Therefore, the nutrient control focus remains on reducing the increase speed of total dissolved inorganic nitrogen in Luanhekou - Beidaihe water area.

The nutrient structural in Luanhekou - Beidaihe water area changes similarly with that in Bohai seawater area. The concentration and structure of nutrients in the central Bohai have undergone significant changes in the past 20 years, showing as nitrate, nitrite, total inorganic nitrogen continues to increase, the activity of phosphorus and silicon significantly reduce, inducing N / P value increase but Si / N value decrease [13]. Zheng Bing-hui et al (2007) found that Nutrients structure in Tianjin Bohai coastal waters undergone great changes between 1985 to 2003, the nitrogen limit in 1985 transited to phosphorus limit state [14].

The average N / P ratio in Daya Bay rised 1 / 1.5 in 1980s to over 50 in recent years, the nutrient limiting factor change from nitrogen limitation to the current phosphorus restriction [15]. Affected by the increasing flux of land-based pollution, regional development and other factors, the nutrient concentrations and structure in Luanhekou - Beidaihe monitoring area need to attract high attention. Due to the changes of nutrient structure will directly affect the changes in ocean phytoplankton community structure, and thus cause changes in ecosystem structure and function of the whole system. Therefore, the control of nutrient content, especially the increase in inorganic nitrogen, is essential for the maintenance of the regional ecosystem in Luanhekou - Beidaihe water area.

5. Conclusion

Through the analysis of the nutrition concentration and structural in Luanhekou - Beidaihe ecological
monitoring marine area for 16 years, it can be drown the following conclusions:

1) The summer nutrient content shows a different variation in Luanhekou - Beidaihe ecological monitoring area, the content of inorganic nitrogen continues to rise especially after 2004, while the PO₄-P and SiO₃-Si are showing decreasing trend;

2) The summer nutrient structure changes, Si: N shows a downward trend, while N: P shows upward trend, indicating relative excess phosphate and relative lack of inorganic nitrogen before 2004, while relative surplus of inorganic nitrogen and relative lack of phosphoric acid after 2004;

3) The water quality characteristics changed from low nitrogen and high phosphorus (before 2004) to high nitrogen and low phosphorus under the influence of human activities. The nutrient concentration and structural variation trends need to attract high attention, especially on the emphasis control of the growth of inorganic nitrogen in Luanhekou - Beidaihe ecological monitoring area.

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