Evolution of nutrient structure and phytoplankton composition in the Jiaozhou Bay ecosystem

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Abstract: The inventories of nutrients in the surface water and large phytoplankton(> 69 μm) were analyzed from the data set of JERS ecological database about a typical coastal waters, the Jiaozhou Bay, China, from 1960s for N, P and from 1980s for Si. By examining long-term changes of nutrient concentration, calculating stoichiometric balance, and comparing diatom composition, Si limitation of diatom production was found to be more possible. The possibility of Si limitation was from 37% in 1980s to 50% in 1990s. Jiaozhou Bay ecosystem is becoming serious eutrophication, with notable increase of NO_2-N, NO_3-N and NH_4-N from 0.1417 μmol/L, 0.5414 μmol/L, 1.7222 μmol/L in 1960s to 0.9551 μmol/L, 3.001 μmol/L, 8.0359 μmol/L in late 1990s respectively and prominent decrease of Si from 4.2614 μmol/L in 1980s to 1.5861 μmol/L in late 1990s; the nutrient structure is controlled by nitrogen; the main limiting nutrient is probably silicon; because of the Si limitation the phytoplankton community structure has changed drastically.

Keywords: nutrients; Si-limitation; stoichiometric ratios; species composition; Jiaozhou Bay

Introduction

The health of coastal environment has been drawing the people's attentions all over the world. The budgets of nutrients in this area are one of the main focuses. Although nitrogen is the primary limiting nutrient for marine phytoplankton on a global basis, exceptions are often seen and particular kinds of nutrient limitation seem to be situation-specific in most cases. In recent years, phosphorus has been frequently reported to be the limiting nutrient for phytoplankton productivity in coastal waters with high input from land runoff(Bonin, 1989; Mahoney, 1989; Heiskanen, 1996). Trace nutrients such as iron (Martin, 1991; Behrenfeld, 1996) have been considered to be limiting to phytoplankton growth in vast areas of the world's oceans.

However, silicon, a primary nutrient for marine primary production, has been largely overlooked and thus less studied until recent research revealed its importance in marine ecosystems (Blain, 1997; Brzezinski, 1998). In the so-called "high nitrate-low silicate-low chlorophyll" (HNLSLC) regions, and in some other special regions, phytoplankton biomass remains low throughout the year despite the high concentrations of nitrate and phosphate (Dugdale, 1995). Dugdale's researches showed that in the HNLC region the magnitude of new production is a function of the input of dissolved silica by upwelling of deeper water (Dugdale, 1998). Si limitation often occurs where new production is monopolized by diatoms, whose growth rates are limited by the supply of silicate(Smetacek, 1998). So Si, through its link to diatom structure and metabolism, may control phytoplankton production in some important regions of the ocean, e.g. in coastal upwelling(Dugdale, 1985), Antarctic seas(Sakshaug, 1991) and sometimes in some semi-enclosed bays(Glibert, 1995).

Si, unlike N and P, occurs predominantly as orthosilicic acid, and its regeneration is not by organic degradation but by dissolution of opaline SiO_2 (Brzezinski, 1989). Once $Si(OH)_4$ is incorporated into the diatoms, it is primarily exported to deep water through sinking of phytoplankton particulate silicon(biogenic silicon, BSi) or $Si(OH)_4$-riched fecal pellets(Staresinic, 1983). So the distribution of silicic acid differs sharply from the distributions of nitrate and phosphate in Antarctic, subantarctic surface waters, and in some diatom-dominant waters, in which Si availability is potentially limiting to diatom growth and productivity but N and P availability are not(Nelson, 2001). Diatoms are the main agents of autotrophic new production in most of the Southern Ocean (Nelson, 1995) and globally important primary producers. It was estimated that diatoms account for ~ 40% of global oceanic primary production (Tréguer, 1995). The percentage of diatom in the primary production was much higher in coastal seas than in the ocean. The removal of Si in the ocean was mainly through the flux from water to the bottom(Sigmon, 2002), but the removal of Si in the coastal seas, beside the removal above, was also through the filtering by organisms (grazing pressure from phytoplankton and mollusk, etc.). Si limitation of diatom production has been hypothesized to be a major regulator of new production and organic matter export in these regions (Dugdale, 1995).

The coastal seas, such as bays, are one of the most valuable, and even moreover, the most vulnerable of Earth's

habitats to where abundant inputs of nutrients arrive through rivers, groundwater. Nutrient fluxes through these routes have been strongly influenced by human activity, such as agricultural activities, sewage from industry and civil life. Moreover, heavy exploitation such as aquaculture of mollusks often existed in these regions, which removed much diatoms from the water. So the N : P : Si ratios of these inputs have severely been disturbed(Jickells, 1998).

Typically we can research the Si limitation according to Liebig's "law of the minimum" with a stoichiometric approach that compares environmental nutrient ratios with the composition ratio of biomass to determine which nutrient will be exhausted first(Hecky, 1988). In evaluating Si limitation the Si:N:P ratio of 16:16:1 is often used(Redfield, 1963; Brzezinski, 1985). So diatom cultures can be carried out to examine the diatom metabolism and growth under the conditions of Si limitation (Olsen, 1986). In other approaches, Si uptake rates have been measured as a function of extracellular $Si(OH)_4$-Si under the condition of unialgal diatom culture(Paasche, 1973) and in natural mixed diatom assemblages, in which the specific rate of Si uptake has been found to depend on the extracellular $Si(OH)_4$-Si in a manner that can be described by the Michaelis-Menten situation function(Nelson, 1996). Recently, tracer (^{30}Si, ^{32}Si or ^{68}Ge) kinetic studies of Si uptake have widely been used in assessing Si limitation in the ocean(Nelson, 1992; 1996; Brzezinski, 1996; Leynaert, 2000) in which the research results showed that Si limitation is likely in the low Si, high N and high P surface water(Nelson, 2001).

We demonstrated here a case of Si-limitation, by examining long-term changes of nutrients, calculating stoichiometric balance, and comparing diatom composition in a typical coastal waters, the Jiaozhou Bay, China.

1 Overview of the Jiaozhou Bay and the JERS data set

The sampling stations are in the Jiaozhou Bay which is a semi-closed small bay with an area of 390 km^2, average depth of 7 m, and the bay mouth of 2.5 km, located in the southeast of the Shandong Peninsula adjacent to the Yellow Sea on the west coast of the Northwest Pacific(Fig.1). There are about ten rivers meeting the sea in the bay, among which the main rivers are Dagu, Moshui, Licun, Haibo. Surrounded by the Qingdao and its precinct (Jiaozhou and Jiaonan), Jiaozhou Bay receives great impact from human activities.

Since 1960s the Jiaozhou Bay Ecosystem Research Station(JERS) of the Chinese Ecosystem Research Network (CERN) has been committed ecological investigation, and has accumulated diverse ecological data including biological, chemical, hydrological, geological, meteorological data, based upon which an ecological database of Jiaozhou Bay ecosystem was constructed. In the ecological investigations of
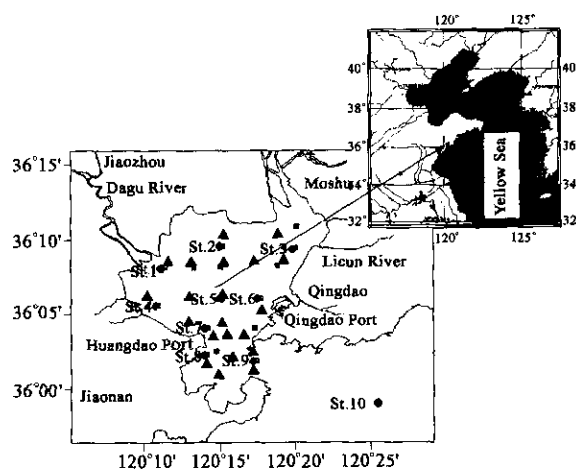

Fig.1   Map of Jiaozhou Bay, showing the 10 main investigating stations and the nearby stations

Jiaozhou Bay ecosystem in the past decades, over 367 investigating stations were used, among them only 10 stations were often used since 1990s. All the nutrient data(including NO_2-N, NO_3-N, NH_4-N, PO_4-P and $Si(OH)_4$-Si), Chl-*a* data and phytoplankton taxonomic data used in this study were selected from this database. The nutrients concentrations are based upon the samples of surface water.

2 Analysis methods

All the surface water nutrient data in the bay since 1960s are included to compare the long-term change trend according to time series. The means of nutrients were obtained by comparing means with statistical software SPSS. The variances was tested by using t-test (independent-samples t-test) with SPSS. The stoichiometric limitation criteria set by Justic *et al*. (Justic, 1995) in accordance with the Redfield ratio Si : N : P = 16 : 16 : 1 (Redfield, 1963; Brzezinski, 1985) and results from previous studies (Levasseur, 1987; Dortch, 1992; Elser, 1994), was adopted in the present study: Si:P > 22 and N:P > 22 for P-limitation; N:P < 10 and Si:N > 1 for N-limitation, and Si:P < 10 and Si:N < 1 for Si-limitation. The phytoplankton is net-sized(> 69 μm).

3 Results

3.1 Long-term variation of nutrients concentrations

Since 1960s last century the nutrient concentrations had greatly changed in the surface water in Jiaozhou Bay and the integrated inventories of the nutrients had displayed significant variability and several consistent long-term trends. The concentrations of NO_2-N, NO_3-N, NH_4-N had significantly increased, and the concentration of PO_4-P fluctuated since 1960s last century, and yet the concentration of $Si(HO)_4$-Si had decreased significantly since 1980s last century.

The mean concentration of NO_2-N in 1960s(1962 and

1963) last century was 0.1417 μmol/L. From then on the concentration of NO_2-N had been consistently rising to the level of 0.9551 μmol/L in late 1990s(1997—1999)(0.367 μmol/L in 1980s(1981—1986, not 1982) and 0.5367 μmol/ L in early 1990s(1991—1994) last century), resulting in a 5.74 times net increase in NO_2-N inventory(Fig.2). The t-test showed that the mean concentration of NO_2-N of 1960s population(1962 and 1963) was significantly different from that of 1981—1986 population(except 1982; $p = 0.000 <$ 0.05), and from that of early 1990s population (1991— 1994; $p = 0.000 < 0.05$), and from that of late 1990s population(1997—1999; $p = 0.000 < 0.05$); and the mean concentration of NO_2-N of 1981—1986 population (except 1982) was significantly different from that of early 1990s population(1991—1994; $p = 0.000 < 0.05$), and from that of late 1990s population(1997—1999; $p = 0.000 < 0.05$); and also the concentration of NO_2-N of early 1990s population (1991—1994) was significantly different from that of late 1990s(1997—1999; $p = 0.000 < 0.05$).
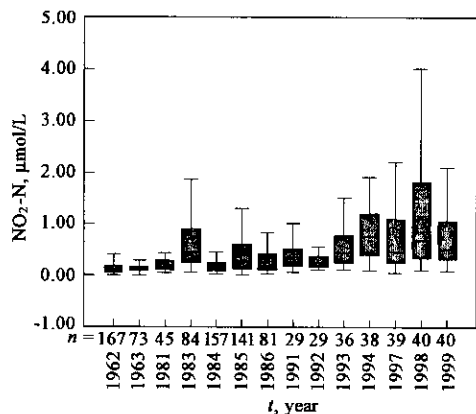
Fig.2　Mean interannual changes of NO_2-N concentration in Jiaozhou Bay based on full data sets. Boxes represent annual divisions of NO_2-N stocks in the bay. The line inside the box indicates the annual mean, and the upper and lower boundaries of each box are the 75th and 25th percentiles, respectively. The capped bars show the 10th and 90th percentiles of the data

The mean concentration of NO_3-N in 1960s last century was 0.5414 μmol/L. Henceforth the concentration of NO_3-N had been fluctuantly increasing to the level of 3.001 μmol/L in late 1990s(0.893 μmol/L in 1980s and 1.804 μmol/L in early 1990s), resulting in a 4.54 times net increase in NO_3-N inventory (Fig. 3). The t-test showed that the mean concentration of NO_3-N of 1960s population was significantly different from that of 1980s population($p = 0.000 < 0.05$), and from that of early 1990s population($p = 0.000 < 0.05$), and from that of late 1990s population($p = 0.000 < 0.05$); and the mean concentration of NO_3-N of 1980s population was not significantly different from that of early 1990s population($p = 0.680 > 0.05$), but significantly different from that of late 1990s population($p = 0.001 < 0.05$); and also the concentration of NO_3-N of early 1990s population was significantly different from that of late 1990s($p = 0.001 <$

0.05). The study periods were the same as NO_2-N.
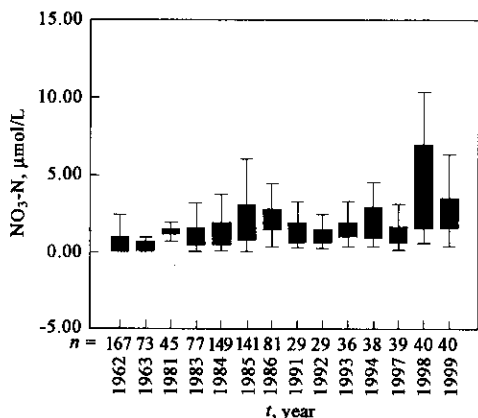
Fig.3　Mean interannual changes of NO_3-N concentration in Jiaozhou Bay based on full data sets. Boxes represent annual divisions of NO_3-N stocks in the bay. The box and the capped bars in the plot have the same meaning as in Fig.2

The mean concentration of NH_4-N in 1960s was 1.7222 μmol/L. Henceforward the concentration of NH_4-N had been fluctuantly increasing to the level of 8.0359 μmol/L in late 1990s(6.1950 μmol/L in 1980s and 8.1831 μmol/L in early 1990s), resulting in a 3.67 times net increase in NH_4-N inventory (Fig. 4). The t-test showed that the mean concentration NH_4-N of 1960s population was significantly different from that of 1980s population($p = 0.000 < 0.05$), and from that of early 1990s population ($p = 0.000 < 0.05$), and from that of late 1990s population($p = 0.000 < 0.05$); and the mean concentration of NH_4-N of 1980s population was significantly different from that of early 1990s population ($p = 0.000 < 0.05$), and from that of late 1990s population ($p = 0.001 < 0.05$); but the concentration of NH_4-N of early 1990s population was not significantly different from that of late 1990s($p = 0.808 > 0.05$). The study periods were the same as NO_2-N.
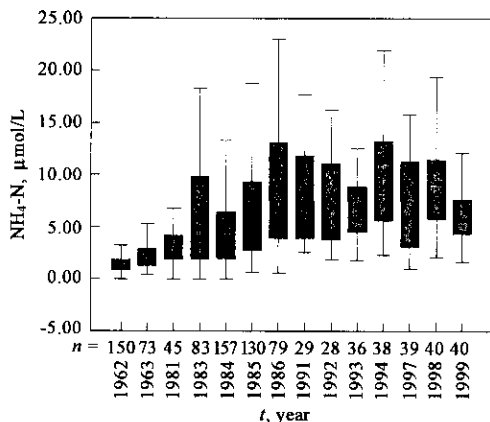
Fig.4　Mean interannual changes of NH_4-N concentration in Jiaozhou Bay based on full data sets. Boxes represent annual divisions of NH_4-N stocks in the bay. The box and the capped bars in the plot have the same meaning as in Fig.2

The mean concentration of PO_4-P in 1960s was 0.1854

μmol/L. It reached the peak in 1980s (0.5554 μmol/L). Then the concentration of PO_4-P kept a decreasing trend in PO_4-P inventory(Fig.5), 0.3353 μmol/L in early 1990s and 0.3308 μmol/L in late 1990s. The t-test showed that the mean concentration PO_4-P of 1960s population was significantly different from that of 1980s population (p = 0.000 < 0.05), and from that of early 1990s population(p = 0.000 < 0.05), and from that of late 1990s population(p = 0.000 < 0.05); and the mean concentration of PO_4-P of 1980s population was significantly different from that of early 1990s population(p = 0.000 < 0.05), and from that of late 1990s population(p = 0.000 < 0.05); but the concentration of PO_4-P of early 1990s population was not significantly different from that of late 1990s (p = 0.808 > 0.05). The study periods were the same as NO_2-N.
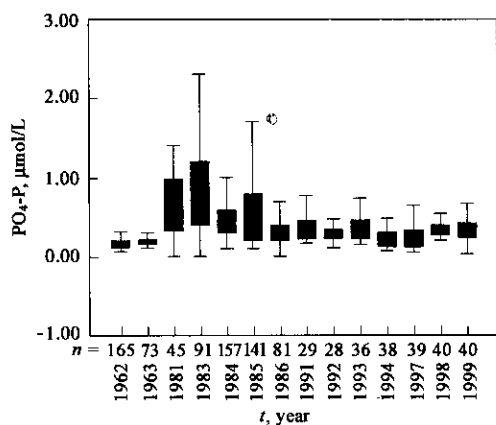

Fig.5   Mean interannual changes of PO_4-P concentration in Jiaozhou Bay based on full data sets. Boxes represent annual divisions of PO_4-P stocks in the bay. The box and the capped bars in the plot have the same meaning as in Fig. 2

The mean concentration of Si(OH)$_4$-Si in 1980s (1985 and 1986) last century was 4.2614 μmol/L. Henceforward it showed a fluctuantly decreasing trend. The concentration of Si(OH)$_4$-Si was 3.3757 μmol/L in early 1990s (1991—1994) and 1.5861 μmol/L in late 1990s(1997—1999)(Fig. 6). The t-test showed that the mean concentration SiO$_3$-Si of 1980s population was not significantly different from that of early 1990s population (p = 0.8856 > 0.05), but was significantly different from that of late 1990s population(p = 0.000 < 0.05); but the concentration of Si(OH)$_4$-Si of early 1990s population was significantly different from that of late 1990s(p = 0.000 < 0.05).

3.2   Long-term variation of nutrient atomic ratios

Long-term variations of nutrients including nitrate and ammonium(N), phosphate(PO_4-P), and silicate(Si(OH)$_4$-Si) concentrations in Jiaozhou Bay were followed periodically in 1961—1963 (except for Si), 1981—1986 (Si except 1985), 1991—1994 and 1997—1998. The period-averaged concentrations of nitrate, and P were 0.45, 1.40, and 0.21 μmol/L for the 1960s, 1.40, 5.04 and 0.49 μmol/L for the
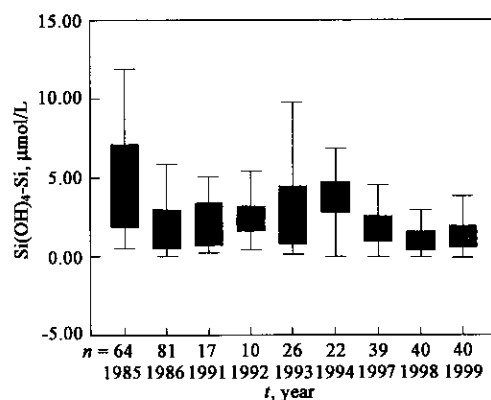

Fig.6   Mean interannual changes of Si(OH)$_4$-Si concentration in Jiaozhou Bay based on the data sets of 1980s and 1990s last century. Boxes represent annual divisions of NO_3-N stocks in the bay. The box and the capped bars in the plot have the same meaning as in Fig.2

1980s, and 1.98, 8.01 and 1.38 μmol/L for the 1990s respectively. Those of Si were 3.07 μmol/L for 1985—1986, 2.51 μmol/L for 1991—1994 and 1.54 μmol/L for 1997—1998. Concentrations of the principal inorganic nitrogen species, nitrate and ammonium increased 2.4-fold from the 1960s to the 1980s and another 0.6-fold in the following decade. P increased about 1.4-fold from the 1960s to the 1980s and 2.7-fold in the early 1990s, then decreased in more recent years to a level slightly higher than that in the 1960s. Concentrations of Si continuously decreased from the middle 1980s through the late 1990s, resulting in a two-fold decrease over this period. Among the nutrient species, the overall variability was the highest for P followed by nitrate; relatively, the most stable nutrient was Si. In terms of variability in different periods, N fluctuated most in the 1980s, but P and Si had the highest variation in the early 1990s. Along with variation in concentration, the nutrient structure changed greatly in the past few decades. The ratios of nitrate plus ammonium to phosphate(N/P) increased about 2.1-fold over the past 40 years with mean values of 9.21, 20.05, and 33.92 in the 1960s, 1980s and 1990s, respectively. The ratios of Si to nitrate plus ammonium(Si/N) and to phosphate (Si/P) were 0.35 and 8.97 in the 1980s and 0.21 and 5.03 in 1990s, respectively; both decreased sharply. The Si/N and the Si/P ratios were almost always below 1 and 16 respectively.

3.3   Stoichiometric nutrient balance

The stoichiometric ratios among N, P and Si were calculated for the 1980s and 1990s and for different seasons (spring, summer, fall and winter) for all the nutrient data. Here, we disregarded other considerations (such as the absolute nutrient concentration as discussed below) and only view the stoichiometric limitations. Clearly the probability for Si to be a limiting factor was much higher than for N and P over the long term and seasonally. There has been almost no possibility for N to be a widespread limiting factor since the 1980s: N-limitation could have taken place occasionally in

summer and spring with a probability of only 2%—3%. However the probability of P-limitation increased slightly from 8% in the 1980s to 12% in the 1990s due to the rapid increase of N. And notably the probability of Si-limitation dramatically increased from 37% in the 1980s to 50% in the 1990s. Seasonally, Si-limitation would have almost certainly occurred in spring(78% of all the observations) and winter (60%) but seldom in summer and fall(about 5%) in the past decade. P-limitation could have occasionally happened in fall(23%) and summer(11%) and less likely in spring (8%) and winter(6%).

3.4   Changes of netplankton species composition in Jiaozhou Bay

Comparison of samples in the 1980s and 1990s showed that great changes in composition of the common netplankton species had taken place in the bay. The numbers of species of the dominant and ubiquitous large diatoms(> 69 μm) in winter and autumn, the seasons with the highest diversity of diatoms, decreased from about 18 species in the 1980s to less than 5 species in the 1990s. Some year-round dominant species in the 1980s had disappeared in the 1990s and were replaced by others(Table 1).

Table 1   Decadal changes in ubiquitous species(recorded at all investigation stations) between 1980s and 1990s

	Recorded at all stations in 1981 but not in 1990s	Recorded at all stations in 1990—1994 but not in 1981	Recorded at all stations in 1998 but not in 1981	Recorded at all stations in 1998 but not in 1981 and 1991—1994
Spring	Biddulphia sinensis	Chaetoceros compressus	Pseudo-nitzschia spp.	Asterionella Kariana
	Rhizosolenia delicatula	Pseudo-nitzschia spp.	Asterionella Kariana	
Summer	Chaetoceros densus	Guinardia flaccida		
	Biddulphia sinensis			
Autumn	Skeletonema costatum	Biddulphia sinensis		
	Rhizosolenia delicatula			
	Rhizosolenia setigera			
	Hemiaulus sinensis			
Winter	Leptocylindrus danicus	Pseudo-nitzschia spp.	Pseudo-nitzschia spp.	
	Chaetoceros debilis			
	Biddulphia sinensis			
	Hemiaulus sinensis			

Overall, however, the diversity of ubiquitous species was substantially reduced. Their absolute abundance was also reduced remarkably. Especially in winter and spring, the difference in concentration of dominant species between the 1980s and the 1990s was more than an order of magnitude.

4   Discussion

4.1   Nutrient budgets in Jiaozhou Bay

Human activities have increased the input of nitrogen and phosphorus nutrients to the Jiaozhou Bay. And due to the persistently increasing concentration of NO_2-N, NO_3-N, NH_4-N, the fluctuatingly rising of PO_4-P, despite the rapidly sinking of $Si(OH)_4$-Si, the nitrogen-controlled eutrophication was becoming more and more severe.

In Mississippi River plume uptake by diatoms over Louisiana shelf resulted in the non-conservative removal of at least 80% of the $Si(OH)_4$-Si delivered by the Mississippi River in July 1992 and 99% of that delivered in April 1993 (Nelson, 1996). In Jiaozhou Bay, though the uptake of Si by diatoms has not been examined, the phytoplankton assemblages are monopolized by diatoms, the removal of Si by diatom uptake might be great too. There are several mollusk culture farms in the bay, which heavily increases the removal of plankton, intensifying the removal of Si. Jiaozhou Bay is a semi-closed and the bay mouth is only 22.5 km, and only 7% waters are exchanged during one tide period. Much of the nutrients required by plankton are delivered by the runoff

and the drainage of civil and industrial sewages. The higher and higher nitrogen concentration in the surface water of Jiaozhou Bay is mainly transferred over by the runoff and by the drainage. While the silicon concentration does not brought over as much with the same way due to the decrease of farmlands and precipitation in the nearby area(Fig.7 and Fig.8). The increased anthropogenic inputs of nitrogen and phosphorus had led to a decline of dissolved Si : N and Si : P ratios in the bay, which trended towards the increase of Si limitation. About 77% of annual precipitation drops in summer and fall in Jiaozhou Bay area, which delivers much Si to the bay, and very little precipitation in other seasons (Fig.9). That is why the possibility of Si limitation was mainly in winter and spring and little in summer and fall.
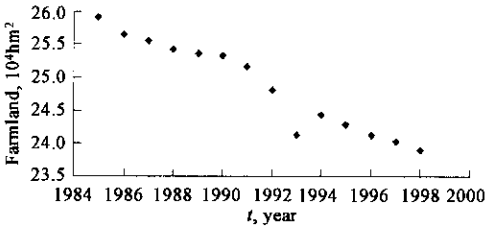

Fig.7   Change of farmland in Jiaozhou Bay area

Moreover, nitrogen and phosphorus are recycled more rapidly in the water than silicon, silicate pump (Dugdale, 1995) in diatom-dominated communities enhances the loss of silicate from the euphotic zone to deep water, resulting in low silicate.
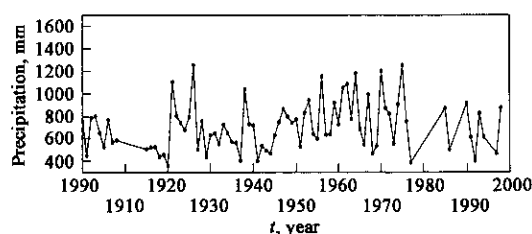
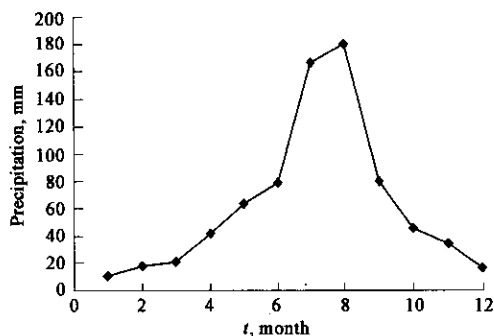Fig.8   Annual change of precipitation in Jiaozhou Bay area

Fig.9   Monthly change of precipitation in Jiaozhou Bay area(average from 1970—1998)

4.2   Mean annual Chl-*a* and the numbers of phytoplankton in Jiaozhou Bay

Historically, Chl-*a* do not change much, with the average concentration of about 3.55 mg/m³ on the yearly-averaged basis in Jiaozhou Bay, while the numerical abundance of large phytoplankton dropped substantially from 881 × 10⁴ cells/m³ in 1981 to 39 × 10⁴ cells/m³ in 1997, with a decrease of 96% (Zhao, 2001). And also net-sized diatom species and the dominant and ubiquitous species decreases sharply from 1980s to 1990s, that reasoned the great change of nutrient structure(Qian, 1983; Jiao, 2001). Due to the change of nutrient structure, the species succession of plankton assemblages took place, HAB haunted, and even some latent-toxic plankton bloomed, such as *Pseudonitzschia pungens* (Zhao, 2002). With the disappear of some large plankton in Jiaozhou Bay, the vacated niche might be filled by the nano-and pico-plankton in view of the importance of the later.

In   Jiaozhou   Bay,   diatoms   and   dinoflagellate overwhelmingly dominate the phytoplankton assemblages, especially the former, no matter species or cells(over 90% of total cells; Qian, 1983), whose growth rates are basically limited by the supply of silicate.

4.3   The relationship between the changes of nutrient structure and plankton composition

The main sources of nutrients in Jiaozhou Bay are the runoff from the land and the drainage of civil and industrial sewages. Since 1980s the local economy developed rapidly, which resulted in the large increase of drainage with much nutrients by way of the rivers, and the heavy eutrophication of waters in Jiaozhou Bay. But with the decrease of farmland

and precipitation in Jiaozhou Bay area, which are the source and delivered means of Si respectively, and lead to the decrease of inputs of Si, the nutrient structure changed greatly. That made Si limitation more likely than ever before. So our research answered Smayda's suggestion (Smayda, 1989; 1990). Besides, the grazing pressure from zooplankton leads much more regeneration of N than Si. So the supply of Si is becoming lesser, while the output to the bottom is large, eventually resulting in the Si limitation. Eutrophication resulting from the increased N and P runoff from the land may result in Si limitation of the diatoms and in blooms of other algae(Smayda, 1989).

To the change of nutrient structure, phytoplankton would respond in different ways, including the change of species growth characteristics and population structure. So Si limitation might result in considerable modification of the phytoplankton community structure at the species-composition level or at the size-structure level.

Similarly, in central North Sea and Elbe-influenced water masses, while nitrate and phosphorus had significant increases the silicate kept constant or decreasing; over the same period the biomass of flagellates had increased by a factor of 6 to 16 while the biomass of diatoms had been constant or decreasing(Smayda, 1990).

The change of nutrient structure must influences the phytoplankton composition, on the contrary the change of phytoplankton composition might modify the nutrient composition.

4.4   Si-limitation of diatom production in Jiaozhou Bay: possibility and stoichiometric ratios

Modern ecology knowledge argues that deviation of the ambient nutrient atomic ratio from the Redfield ratio Si:N:P = 16:16:1(Redfield, 1963; Brzezinski, 1985) could result in nutrient limitation of phytoplankton growth(Dortch, 1992; Justic, 1995). In this study, the Si/N and Si/16P ratios were almost always below 1, indicating persistent possible Si-limitation. Detailed stoichiometric calculations according to the limitation criteria of Justic *et al*. (Justic, 1995) confirm this conclusion(the probability of Si-limitation from 37% in the 1980s to 50% in the 1990s and the possibility of 78% in spring and 60% in winter). It is unusual Si limitation in such a bay but can be easily understood with respect to the high N input and even relatively high P input. Justic *et al*. (Justic, 1995) pointed out that on a worldwide basis, coastal ecosystems influenced by anthropogenic nutrient loads may experience a change from N or P-limitation to Si-limitation. Smayda (Smayda, 1989; 1990) proposed that coastal eutrophication resulting from increased N and P runoff from the lands might result in Si limitation of the diatoms and hence in blooms of other algae, including toxic species. The Mississippi River plume and nearby regions are instances of such situations(Dortch, 1992) and Jiaozhou Bay seems to be a typical one also.

Seasonal P-limitation in coastal waters has been frequently reported (Pennock, 1994). In Jiaozhou Bay, P-limitation, although not to the extent of Si-limitation, could occur seasonally except in winter, as seen from the stoichiometric calculations. In view of the high N-input and rapid N-regeneration in the bay (Jiao, 1993), it can be concluded that N is not a limiting factor in any way on large temporal or spatial scales. However, in summer, when small algae including *Synechococcus* thrive, demands for N reach their annual peak(Jiao, 1994); N could occasionally become limiting as shown by the stoichiometric calculations. Similar situations are reported in other coastal waters(Dortch, 1992; Pennock, 1994). On the other hand, ratios showed only the possibility of certain nutrients to be relatively deficient but do not necessarily indicate that such nutrients are likely to be limiting. Egge and Aksnes's study (Egge, 1992) also indicated that diatoms dominated as long as silicate concentration was held above 2 μmol/L over a wide range of environmental conditions. Taking the ambient concentrations of Si = 2 μmol/L, N = 1 μmol/L and P = 0.1 μmol/L as the thresholds(Justic, 1995), and combining the results of this study (the Si concentration was 1.5861 μmol/L in late 1990s, Si < 2 μmol/L) and the results from the *in situ* incubation bioassays(unpublished), we can conclude that Si is the major concern in terms of large-scale nutrient limitation in Jiaozhou Bay.

The silicate of phytoplankton is bound in mineral shells, and exports wholesale to the bottom of the sea (Smetacek, 1998). As the export of particulate carbon is predominantly mediated by large phytoplankton and by diatoms in particular (Sieracki, 1993; Dugdale, 1998), all these biological processes may have a profound impact on the carbon cycle.

Many evidences demonstrated that nitrate concentrations in Rhine, Seine, Mississippi and other major rivers in the world have increased by factors of 2 to 3 in the past century, while silicic acid remained constant or decreased (Meybeck, 1982; Turner, 1991; Justic, 1995). So it is speculated that the increased N supply from rivers, and the consequently decreased Si : N ratios from those rivers, might result in Si limitation and floristic shifts away from diatoms in the adjacent coastal waters(Smayda, 1990). In the northern Gulf of Mexico, the changes of nutrient concentrations and ratios in the plume of Mississippi might result in more likely Si limitation than either N or P limitation, especially in spring (Dortch, 1992; Smith, 1994) and development of Si limitation over historical time might be under way (Nelson, 1996).

Si limitation would only impede diatom growth, resulting in the floristic changes. And since the abundance of the netplankton has been consistently decreasing but the averaged total Chl-a concentration has remained roughly unchanged at around 3.55 μg/L on an annual basis for the past few decades, species successions must be taking place. It is

suspected that smaller species(pico-and nano-) are filling the niche vacated by the larger ones. Examination of picoplankton by flow cytometry showed their seasonal pattern to be the opposite of that of the big diatoms(data not shown). Although Si depletion may not cause a decrease in productivity, it could result in major changes in phytoplankton size and species composition(Dortch, 1992), and may ultimately lead to various functional and structural changes at the system level. Such as benthic-water hypoxia and shifts in the structure of planktonic and benthic communities, which would thus influence trophodynamics of the ecosystem and the fate of carbon there (Dortch, 1992; Justic, 1994). In this sort of sea area, if the possibility of Si limitation is high, the export of organic carbon from surface to deeper layers through biological pump(Doney, 1997) will be affected, which has implications for CO_2 exchange between ocean and atmosphere.

5 Conclusions

The Jiaozhou Bay ecosystem is becoming serious eutrophication; the nutrient structure is controlled by nitrogen; the main limiting nutrient is probably silicon; because of the Si limitation the phytoplankton community structure has changed drastically.

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