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Temporal and spatial distributions of nutrients under the influence of human activities in Sishili Bay, northern Yellow Sea of China

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ABSTRACT

The temporal and spatial distributions of dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), soluble reactive phosphorus (SRP) and dissolved reactive silica (DRSi) together with chlorophyll-*a*, temperature and salinity were analyzed monthly from December 2008 to March 2010 at four zones in Sishili Bay located in the northern Yellow Sea. The nutrient distribution was impacted by seasonal factors (biotic factors, temperature and wet deposition), physical factors (water exchange) and anthropogenic loadings. The seasonal variations of nutrients were mainly determined by the seasonal factors and the spatial distribution of nutrients was mainly related to water exchange. Anthropogenic loadings for DIN, SRP and DRSi were mainly from point sources, but for DON, non-point sources were also important. Nutrient limitation has changed from DIN in 1997 to SRP and DRSi in 2010, and this has resulted in changes in the dominant red tide species from diatom to dinoflagellates.

1. Introduction

It is well-established that eutrophication, due to nutrient over-enrichment, is a major environmental problem in many coastal ecosystems around the world (Cloern, 2001; Seitzinger et al., 2005). Nutrient sources driving coastal eutrophication are primarily associated with increasing human population, energy production, agriculture and coastal aquaculture (Howarth et al., 1996, 2002; Alles, 2008). Human activity has an enormous influence on the global cycling of nutrients, especially on the movement of nutrients to estuarine and coastal waters. The influences of various human activities on the coastal environment differ in terms of measures and results. For example, in the USA, N from animal wastes that leaks directly to surface waters or is volatilized to the atmosphere as ammonia may be the single largest source of N that moves from agricultural operations into coastal waters. Sewage, however, contributed only 12% of the flux of N from the North American landscape to the North Atlantic Ocean (Howarth et al., 1996, 2002). In addition to the effects of agriculture, industry and sewage discharge, the aquaculture industry also has created major environmental damage in coastal areas around the world. The quality and quantity of waste from aquaculture depends mainly on the culture system characteristics and the choice of species, but also on feed quality and management (Troell et al., 1999; Wang et al., 2005; Cao et al., 2007). Industrial pollution, however, is mainly reflected through chemical pollution with nitrogen, phosphorus, mercury and sediment (Alles, 2008).

The content and composition of nutrients not only causes serious environmental problems but also affects the biomass and composition of phytoplankton. Nutrient overload can cause the rapid growth of primary producers and lead to algal blooms. For example, a fivefold decline of the phytoplankton biomass as well as a fundamental change in the community structure from cyanobacteria to diatom dominance occurred after the culture of bivalves in the Danish lagoon Ringkøbing Fjord (Petersen et al., 2008). In the Gulf of California, nitrogen-rich agricultural runoff exerts a strong and consistent influence on biological processes, with 80% of phytoplankton blooms occurring within days of fertilization and irrigation of agricultural fields (Beman et al., 2005). Both Chesapeake Bay and the Albemarle-Pamlico Sounds suffered from massive nutrient runoff from industrial farming in North Carolina, which not only caused the outbreak of phytoplankton blooms, but also a dramatic crash in 2003 with another small decline in 2004 of the nurseries for Maryland's famous blue crabs (Alles, 2008).

Sishili Bay (Fig. 1), semi-enclosed by Yantai, one of the fastest developing coastal areas in China, is affected by various human activities including: (1) marine aquaculture. As one of the most intensive culture areas in China, suspension aquaculture became the main contamination source after the 1990s (Zhao and Wang, 2004). Scallop culture, with an estimated standing stock of 30000 t, has carried out along the coast and the islands, accounting for ca. 70% of the bay area; (2) wastewater discharge from domestic, industrial and agriculture activities. There are three sewage out-

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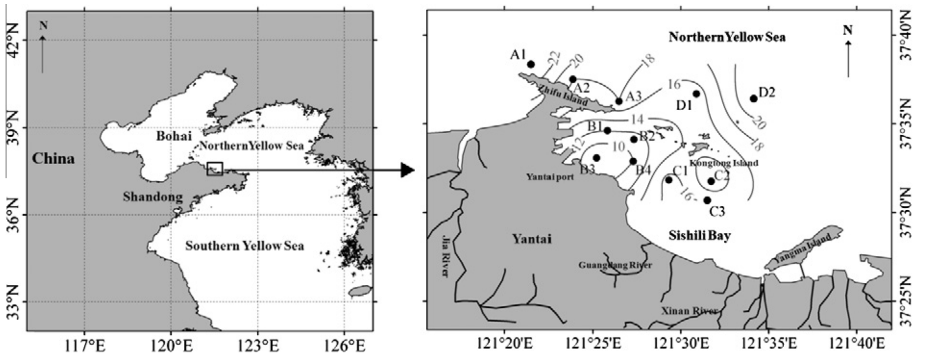

Fig. 1. Sampling stations in the study area. Stations are represented by black circles and lines are isobaths and depth is given in meters.

falls and one dumping site in this area. All these activities brought a large amount of pollutants to the bay. For example, it was estimated that 25 × 10^4 tonnes of waste water were discharged into the bay per day from the Taozi Bay sewage treatment plant (Wang and Li, 1997; Ji et al., 2003); (3) harbor pollution. Yantai harbor is an important coastal harbor in the north of China and cargo transport in 2009 reached 169.26 million tonnes, fourfold increase comparing with that in 2001 (Yantai Statistical Yearbook, 2009). The shipping activities brought pollutants, such as waste waters, oil and heavy metals to the harbor (Wang et al., 1994). The frequent occurrences of red tides since the 1990s as a result of nutrient inputs have attracted major attention to the Sishili Bay environment (Hao et al., 2011).

Today, much remains to be learned about the relative eutrophication susceptibility of different coastal ecosystems and the most effective nutrient control strategies. There is also a great need to better translate scientific knowledge into effective policy and management strategies, which require an understanding of the sources, distribution and variation of nutrients in coastal areas and the effect of nutrient content and composition under different human activities in the classic coastal areas. For example, although studies on the environment of Sishili Bay looking at water column and sediment have been carried out since 1980s, the studies mainly focused on the water quality or environmental pollutions related to aquaculture (Zhao et al., 2000a, 2000b; Zhou et al., 2002; Zhao and Wang, 2004), analysis only for part of the bay in particular months or some special events (e.g., harmful algal bloom, jellyfish bloom) (Ji et al., 2003; Ye et al., 2006; Dong et al., 2010; Hao et al., 2011). However, none of these previous studies looked at the whole system, comparing the spatial differences inside and outside the bay. There is also a lack of continuous monthly research and this makes it difficult to make temporal comparison between different studies. Thus, the lack of spatial wholeness and temporal continuity resulted in limitations in the evaluation of the Sishili Bay environment and prevented the development of effective strategies to reduce and control the nutrient pollution, eutrophication, and associated impacts.

In this study, dissolved nutrients were investigated monthly at 12 sampling stations in Sishili Bay from December 2008 to March 2010 to gain a better understanding of the nutrient status and distribution in Sishili Bay, and further have a clear view of the relationship between temporal and spatial variations of nutrients and different human activities.

2. Methods

2.1. Study area

Sishili Bay (37.42-37.63°N, 120.35-120.63°E), located on the coast of northern Yellow Sea, China, covers an area of 130 km^2 with a 20 km long coastline (Fig. 1). Average water depth in the bay is about 8–10 m (max. 20 m), with a tidal range of 1.66 m and water exchange time ca. 7.6 days (Zhou et al., 2006). Average water temperature is 2.5–3 °C in winter and ca. 20 °C in summer (Wu et al., 2001).

2.2. Sampling and analysis

Twelve stations distributed in four zones were selected for this study (Fig. 1). The four zones were influenced by different human activities: (1) Zone A (3 sites), in the northwest of Sishili Bay, close to sewage outfalls; (2) Zone B (4 sites), in the center of Sishili Bay, close to the harbor and residential areas; (3) Zone C (3 sites), in the southeast of Sishili Bay with aquaculture activities and (4) Zone D (2 sites), in the northeast of Sishili Bay, close to a marine dumping site. Among these, two Zones (B and C) were considered inside Sishili Bay and two zones (A and D) were outside the bay.

Surface seawater samples at the twelve stations were collected using a Go-Flo bottle (5 L). Nutrients including dissolved inorganic nitrogen (DIN: NO_3–N + NO_2–N + NH_4–N), dissolved organic nitrogen (DON), soluble reactive phosphorus (SRP) and dissolved reactive silica (DRSi) were analyzed using Flow Injection Analysis (AA3, Bran + Luebbe, Germany) after filtration through cellulose acetate membranes (Whatman, 0.45 μm). Nutrient analyses were executed according to the WOCE (World Ocean Circulation Experiment) Methods Manual WHPO 91-1 (Gordon et al., 1993; JGOFS Protocols, June 1994).

The detection limits were analyzed with 10 standard blank solutions according to the method of US Environmental Protection Agency (EPA). The limits of detection were 0.015 μM for NO_3–N, 0.003 μM for NO_2–N, 0.04 μM for NH_4–N, 0.02 μM for SRP and 0.03 μM for DRSi. The recovery tests ($n = 6$) were tried with the recovery (%) (RSD (%)) being 93.7 (2.3)–102.2 (1.6) for NO_3–N, 94.0 (1.5)–104.0 (1.0) for NO_2–N, 98.8 (2.4)–106.0 (2.3) for NH_4–N, 93.6 (1.6)–102.4 (2.0) for SRP and 97.0 (0.7)–102.0 (1.2) for DRSi. Chl-*a* was determined by filtering one liter water samples using GF/F filters under low vacuum. The Chl-*a* concentration was detected using spectrophotometry (TU-1800, Persee, China) after being extracted with 15 mL of 90% acetone in the dark for 24 h in refrigerator (Lorenzen, 1967). Temperature, depth and salinity were recorded in situ using a YSI (Yellow Spring Ohio, USA).

2.3. Data analysis

Temporal variations of temperature and salinity in the study area are expressed as the mean value and standard deviation. According to the nutrient status, resemblance clusters were created for the four zones using Primer 6; Figures of isoline distributions of nutrient species and ratios were prepared using Surfer 8.0, and temporal variations of the four nutrient species and ratios of the four zones were conducted with Origin 8.0.

3. Results

3.1. Seawater temperature and salinity

Seawater temperatures showed little difference among sites in the Sishili Bay during the sampling period (Fig. 2A). They were characterized by the expected seasonal changes with higher temperatures in summer (Maximum in August: 24.4 ± 0.82 °C) and lower in winter (Minimum in January: −0.08 ± 0.19 °C), reflecting the temperate climatic regime of the region.

In comparison, salinity displayed a typical pattern responding to wet and dry seasons in the region (Fig. 2B), with a range of 29.6 ± 0.55–33.0 ± 0.02. From spring to summer (March–August), salinity among sites was characterized by variable and lower values due to increased rainfall, but a high and stable salinity pattern occurred in autumn and winter (September–February).

3.2. Temporal and spatial variations of nutrient species in Sishili Bay

Temporal and spatial variations of nutrient species including DIN, DON, SRP and DRSi are shown in Figs. 3–7. Although the temporal variation of different nutrient species in the whole study area indicated different seasonal patterns, a common variation trend of accumulation in winter and fall and consumption in spring and summer was found for most nutrient species.

3.2.1. DIN

Temporal variation of DIN showed a trend of accumulation between December 2008 and February 2009, followed by consumption in the spring and exhaustion in June 2009, then accumulation again in winter 2009 followed by another period of consumption (Fig. 3A). The monthly mean concentration of DIN for the whole study area climbed to peak values in February 2009 (18.46 ± 5.64 μM), September 2009 (19.84 ± 7.87 μM) and March 2010 (18.61 ± 14.21 μM), respectively; and the lowest value was found in June 2009 (0.56 ± 0.64 μM). Contrary to its regular seasonal pattern of accumulation in winter and consumption in spring in 2009, DIN concentration showed low values in January and February and a sharp increase in March 2010, which was most obvious in Zone A. In 8 of 14 months, DIN concentrations were higher in Zone A than in the other three zones, especially in winter of 2010 when the DIN concentration was 31.61 μM in Zone A but only 10.83–18.08 μM in the other three zones (Fig. 3A).

Spatial distribution of DIN over the 16 months showed that the loadings of DIN are largely from Zones A and B (Fig. 4). It is likely that DIN mainly spread from west (Zone A) to east (Zones C and D) during most of the study period (January, February, April, May, June, September, October 2009 and the 3 months of 2010). Loadings in Zone B spread from inside to outside Sishili Bay, especially visible in December 2008, February, March, July, September, December 2009 and March 2010. DIN Input in Zone A (and Zone B) in the 3 months of 2010, especially the heavy loadings in Stn. A1 (50.14 μM) and Stn. B3 (41.69 μM) in March 2010 resulted in the higher DIN concentration in Zone A and Zone B, and even an increase of DIN in the whole study area. High concentrations of DIN to Zone C (especially Stn. C3) were also found in April, September and December 2009 (Fig. 4).

3.2.2. DON

DON concentrations in the study area were much higher than DIN and comprised the main component of TDN (97% of DON/TDN ratios were higher than 50%, including 82% of them higher than 70%). DON concentrations showed slight variations during most of the study period with two exceptions: one is the obvious decrease from about 50–70 μM to about 20–40 μM in June and July 2009; the other is a sharp decline in the winter of 2010, when the concentration decreased to 15–20 μM. Variations of DON concentration among different zones were not as distinct as DIN, with only slightly higher values in Zone C during March and May 2009 and lower values in Zone B in July and September of 2009 (Fig. 3B).

Results showed that the spatial distributions of DON were irregular (Fig. 5). Loadings of DON from Zone A, especially Stn. A1 were found to play an important role. DON had the same sources and probably spread along similar directions as DIN in Zone A in the 3 months of 2010 and in Zone C in April 2009. However, in February, July, November, and December 2009 when DIN concentrations were low, DON concentrations were high. The high background of DON concentration during most of the study period (from December 2008 to December 2009) indicated that nonpoint impact factors play a dominant role in the DON concentration in the study area (Fig. 5).

3.2.3. SRP

SRP concentrations in the four zones all were relatively high in December 2008 and January 2009 (>0.40 μM) (Fig. 3C). After a slight decline in February 2009, SRP concentrations decreased sharply from about 0.40 μM to about 0.11 μM during March and April 2009. Accumulation was again found between August 2009 and January 2010 with SRP concentrations increasing from less than 0.1 μM to more than 0.4 μM. Similar to the pattern in 2009, SRP was almost exhausted in March 2010 in the whole study area except for Zone C. Different from the sharp increase and decline in

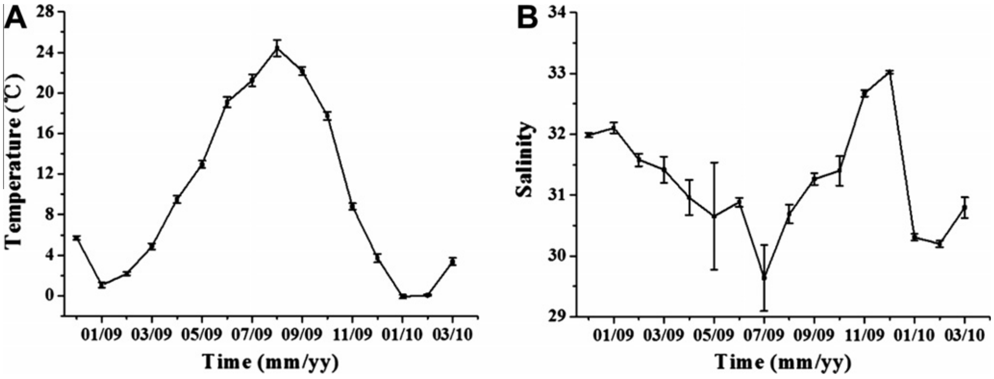

Fig. 2. Temporal variations of temperature (A) and salinity (B) in the study area from December 2008 to March 2010. Variables are expressed as the mean value of 12 stations ($n = 12$), and error bars (±SE) are given.

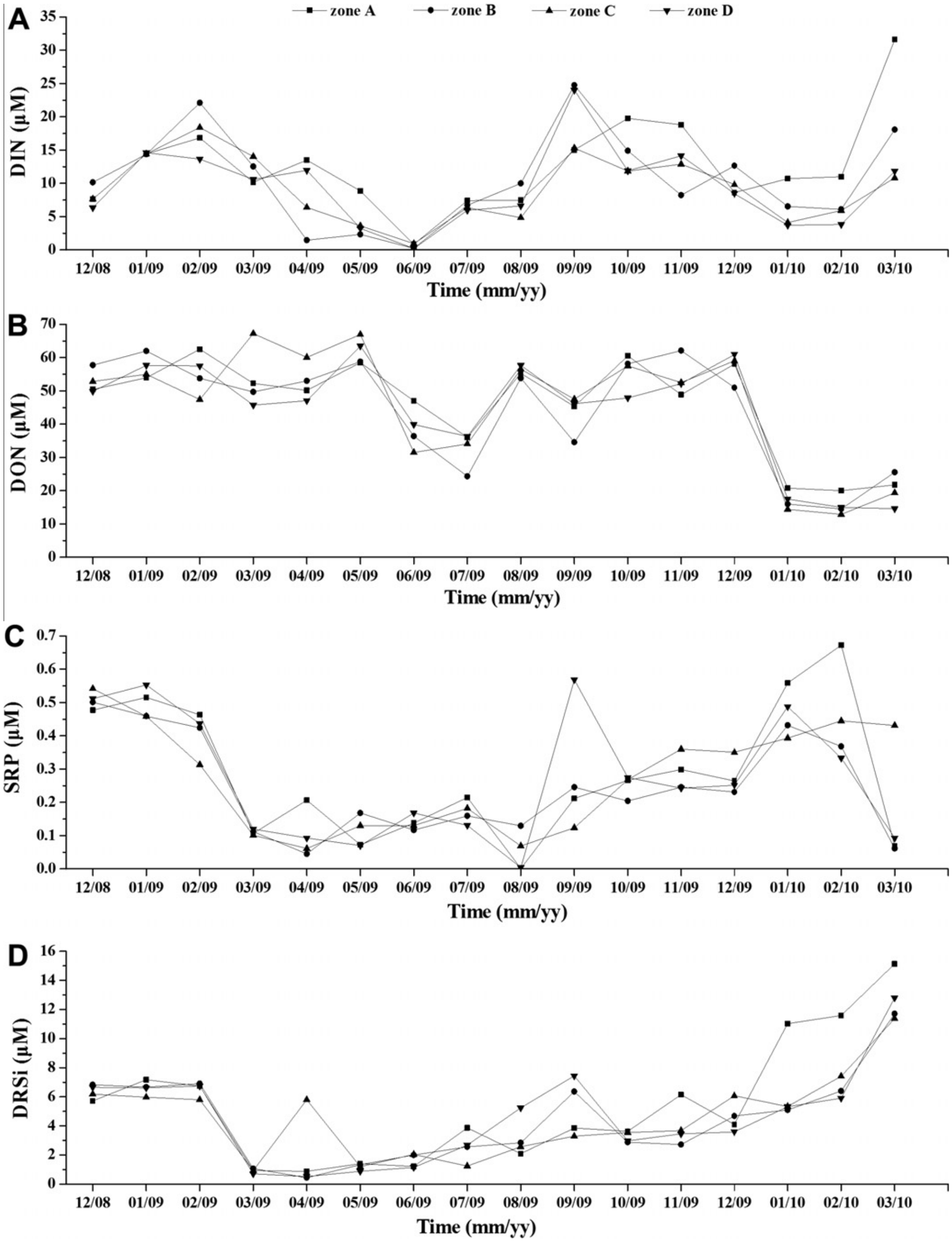

Fig. 3. Temporal variations of DIN (A), DON (B), SRP (C) and DRSi (D) of the four zones in the study area.

the other three zones, during the period between August 2009 and March 2010, SRP in Zone C kept accumulating steadily. Contrary to the decline of DIN and DON in January 2010, SRP increased to 0.40–0.56 μM in January and remained at this high value in February until being exhausted in March 2010 (Fig. 3C).

The spatial distribution indicated the importance of Zone A in SRP loadings (Fig. 6). High SRP concentrations were found in the southeast corner of the Zhifu Island during most of the study period (13 of the 16 months) with loadings of SRP from Zone A (mainly Stn. A3), Stn. B1 and Stn. B2. Loadings from Zone D, outside the bay, were also shown to be important for SRP (D2 in December 2008, September 2009 and D1 in January 2009, June 2009 and January 2010). The loadings of SRP in Zone D together with the effect of Zone A (February, April 2009 and January 2010) resulted in high SRP concentrations in Zone D during most of the study period. Compared to the two zones inside the bay (Zones B and C), low SRP concentrations in Zone A and D were only found in May and August 2009 and in March 2010. The SRP concentrations in Zone C were relatively lower compared to the other three zones with occasional increase in December 2008, 2009 and November 2009.

3.2.4. DRSi

The temporal variations DRSi were similar to those of SRP. Values kept stable in the four zones with a mean of 3.25 ± 0.35 μM from December 2008 to February 2009, followed by a decrease from 3.28 ± 0.38 μM in February to 0.47 ± 0.13 μM in March 2009 and its lowest value of 0.28 ± 0.14 μM in April 2009. DRSi then kept increasing during the period from May 2009 to March 2010. Different to the consumption in March 2009, DRSi in March 2010 maintained an upward trend and increased to 6.40 ± 0.83 μM. Similar to the variation of DIN in the first 3 months of 2010, higher DRSi con-

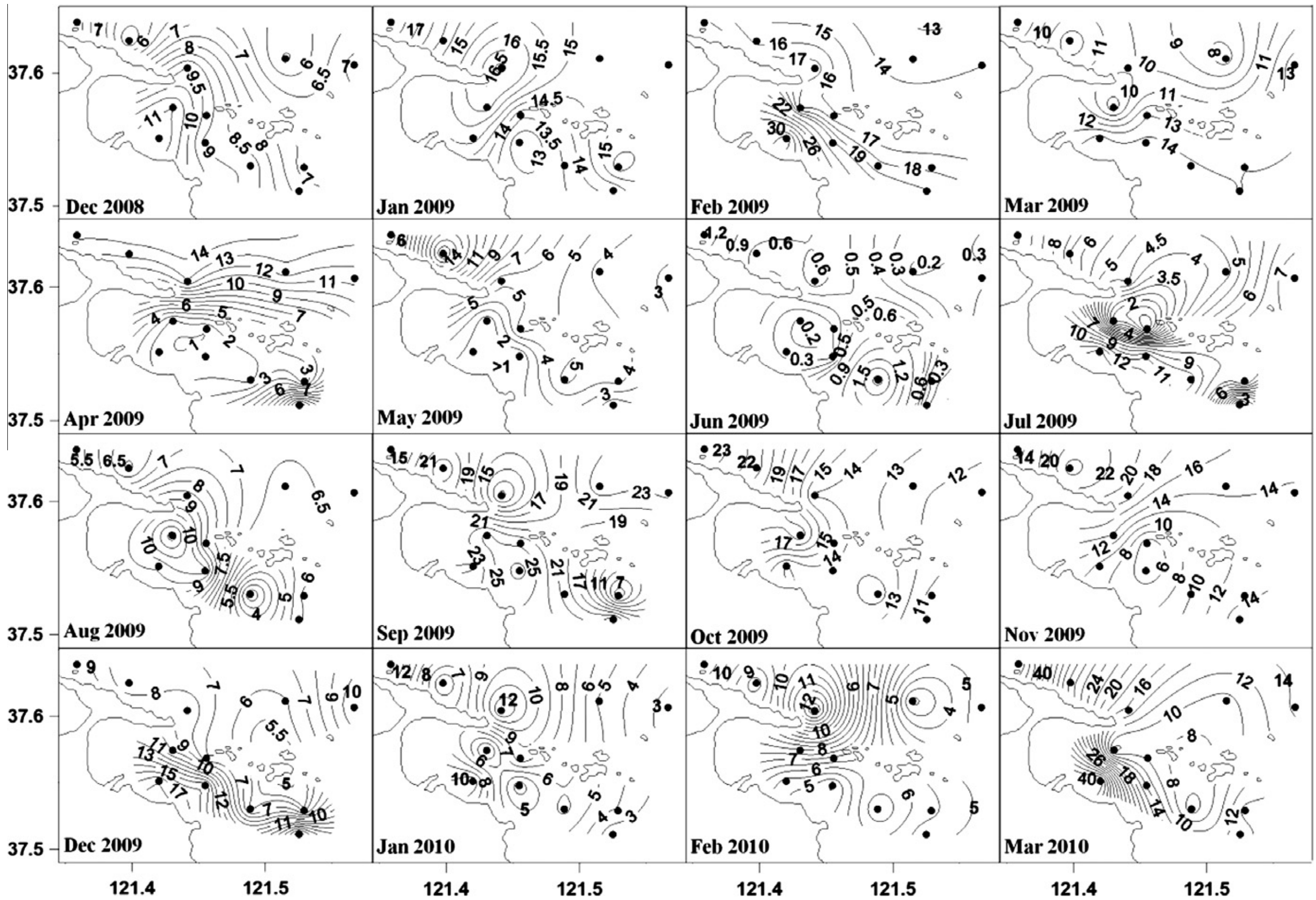

Fig. 4. Horizontal distribution of DIN in the study area from December 2008 to March 2010. Lines are isolines and concentration is given in μM.

centrations were found in the same period in Zone A compared to the other three zones (Fig. 3D).

The spatial distribution of DRSi showed that point loadings from different zones were irregular (Fig. 7). Data indicated Zone A to be an important DRSi source and the high DRSi loadings in Zone A spreading to the east and southeast might affect its distribution in Zones B and D (January, May and November, 2009 and the first 3 months in 2010). Similarly, DRSi input in Zone B spreading to the north and northwest also have an effect on its distribution in Zones A and D (February, June and July 2009). Similar to the spatial distributions of DIN and DON, a high DRSi concentration in Stn. C3 in April 2009 was found as a one-off event. DRSi differences between Zone A and the other three zones in the first 3 months of 2010 were probably caused by the continuous loadings from Stn. A1. The loading from Stn. A1 spreading from west to east caused an increase of DRSi concentration for the whole area with the mean value of 6.40 μM in March 2010.

3.3. Temporal and spatial variation of nutrient structure in Sishili Bay

The ratios of SRP to DIN, DRSi to DIN and SRP to DRSi were calculated in this study (Fig. 8).

The SRP/DIN ratios of the 12 stations during the study period ranged from 0 to 1.16 (Fig. 8A). Its temporal variation was not distinct except in May, June, July 2009 and January 2010. Except for 9 stations in June 2009 and two stations (Stn. B2 and Stn. C3) in July 2009, SRP/DIN ratios were all lower than 1:5. 89% of the values were lower than 1:10, and even more than 70% of the values were much lower than 1:22 (nutrient limitation ratio suggested by Justić et al. (1995). The ratios (>22) were mainly occurred in December 2008, May and June 2009, and January and February 2010 (Fig. 8A).

DRSi/DIN ratios mainly ranged from 0.04 to 2.0 for most of the study period except for the wide range of 1.0 to 11.95 in June 2009 (Fig. 8B). 79% were less than one and the low ratios were mainly found between December 2008 and December 2009 except for June 2009 when high values and a wide range of SRP/DIN and DRSi/DIN were both found. Temporal variations indicated exhaustion of DIN in June and accumulation of SRP and DRSi from April to June were major causes of this similarity (Fig. 3).

Ratios of SRP/DRSi ranged from 0 to 0.50 with more than 82.8% being lower than 0.1 (Fig. 8C). The high ratios were mainly found from March to June 2009. Different from the wide variation of DRSi/DIN and SRP/DIN in June 2009, the wide variations of SRP/DRSi were found in April and May 2009.

The temporal variation of nutrient ratios showed that a wide variation was mainly found from April to July 2009; as a result, the spatial distributions of three nutrient ratios in these 4 months are presented in Figs. 9–11. Spatial distribution of SRP/DIN indicated that in April, May and June 2009 when the ratios were lower than 0.1, the values were higher inside Sishili Bay (Zone B and Zone C) and lower outside Sishili Bay (Zone A and Zone D). However, for June, when SRP/DIN ratios were higher than 0.1, the relatively high ratios were found in Zone D (Fig. 9). The spatial distributions of DRSi/DIN ratios for the 4 months were similar to SRP/DIN with much higher values in June compared to the other 3 months. The distribution of SRP/DIN in April, May and July showed high values inside Sishili Bay and low values outside Sishili Bay (Fig. 10). Combining the spatial distribution patterns of DIN, SRP, and DRSi, the spatial distribution patterns of SRP/DIN and DRSi/DIN ratios in June

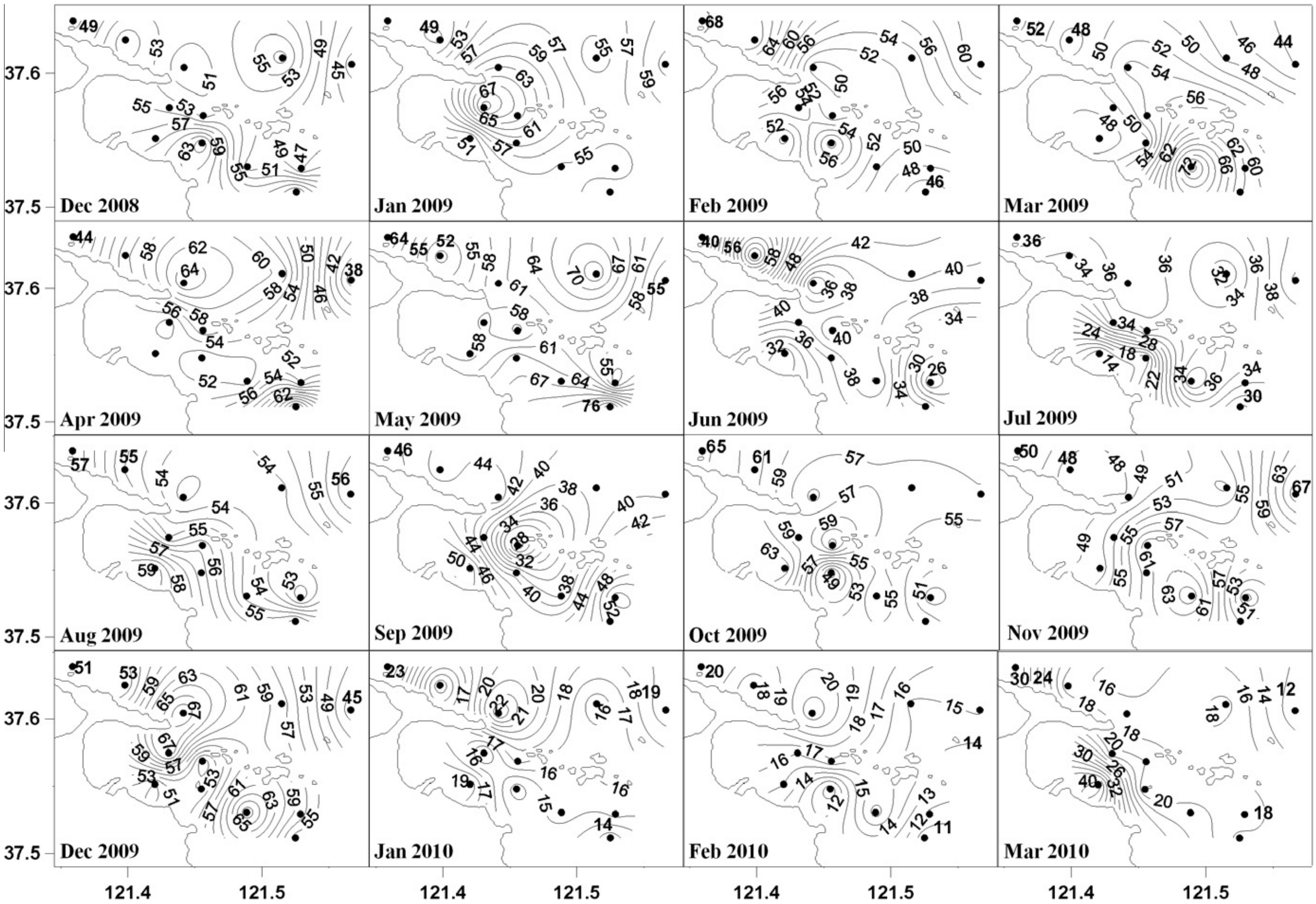

Fig. 5. Horizontal distribution of DON in the study area from December 2008 to March 2010. Lines are isolines and concentration is given in μM.

2009 were mainly related to the distribution patterns of SRP and DRSi concentration, and patterns in the other 3 months were mainly related the DIN distribution pattern (Figs. 4–6). No obvious patterns of SRP/DRSi ratios were found in April, May and July and the distribution in June showed an increase tendency from inside Sishili Bay to outside Sishili Bay (Fig. 11).

4. Discussion

4.1. Nutrient variations as a function of natural and anthropogenic factors

In our study area, the factors which can affect the distribution of nutrients include seasonal effects such as temperature, wet deposition and biotic factors, physical factors such as water flow and exchange, and anthropogenic activities including aquaculture, domestic sewage effluent discharge and harbor pollution.

4.1.1. Seasonal effects on the nutrients variation

During the annual survey, the temporal variations showed the common accumulation in winter and fall and consumption in summer for most nutrient species, which were mainly related to the wet deposition and phytoplankton annual pattern. In Yantai, increased summer rainfall (July–September) and winter snow (January and February) play important role on nutrient supply in coastal waters. The low salinity in July 2009 and January–February 2010 in Sishili Bay displayed the impacts from rainfall and snow dilution, respectively (Fig. 2B). The nutrients from atmospheric and terrestrial loading can significantly increase the nutrient concentrations in coastal waters by wet deposition, riverine input or sewage outfalls. In our study, winter nutrient maxima were clear in January or February (Fig. 3) and these sufficient nutrients supported the phytoplankton spring bloom in March 2009 (Fig. 12). The growth of phytoplankton in March 2010 might mainly be inhibited by the low temperature. Temperature in winter 2010 was about two degrees lower than in 2009, which resulted in the difference of the growth of phytoplankton between 2009 and 2010 (Figs. 2A and 12). As a result, nutrients consumption in March 2010 was not obvious except SRP. The growth of phytoplankton from spring to early summer mainly consumed the dissolved inorganic nutrients accumulated in winter. SRP was consumed quickly after phytoplankton spring bloom in March, but DIN reached the lowest value in June and increased in autumn and winter, indicating a shift from summer consumption to winter accumulation. Phytoplankton summer peak from July to September (Fig. 12) played an important role on the consumption of DIN and SRP. Moreover, DON consumption was observed in July after DIN was exhausted by phytoplankton (Fig. 3). Thus, DON and DIN could jointly support the growth of phytoplankton in summer (Fig. 12).

In comparison, DRSi concentrations showed a slow recovery after they were consumed by phytoplankton spring bloom (Fig. 3). The process of DRSi increase includes the release of DRSi from diatom dissolution, sediment re-suspension and river input. Depending on the season and composition of phytoplankton spring bloom, it would take in the order of 30 to 80 days to increase the DRSi concentration in the above 40 m water column by 1 μM (Olli et al., 2008). In our study, DRSi concentrations increased by 3.0 μM from March to August and 2.2 μM from August to September. Water depth in Sishili Bay is less than 20 m and according to Olli

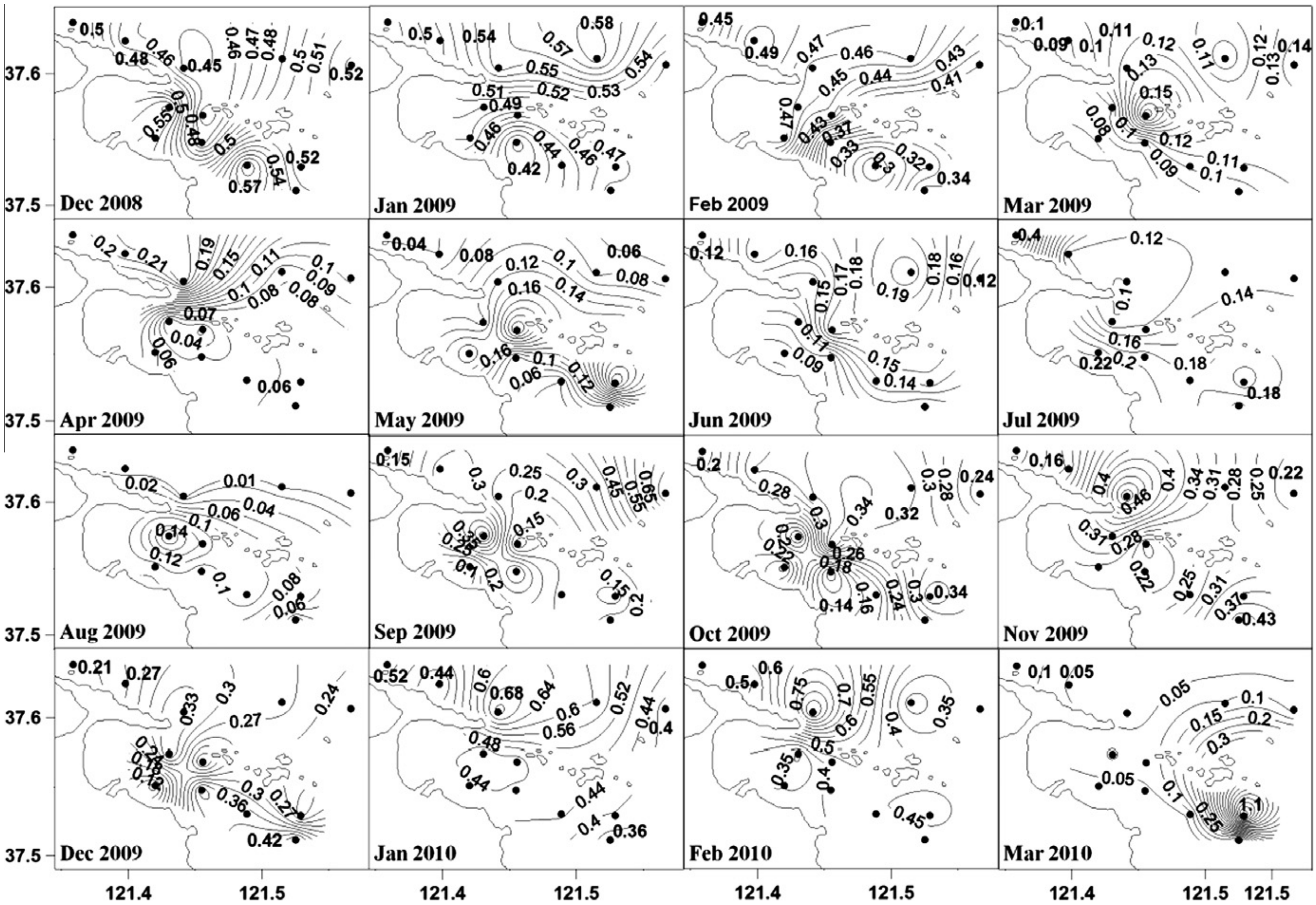

Fig. 6. Horizontal distribution of SRP in the study area from December 2008 to March 2010. Lines are isolines and concentration is given in μM.

et al. (2008), it would need 90–240 days to increase DRSi by 3 μM. In this study, it took 5 months for DRSi increase by 3 μM, indicating the release of diatom dissolution might be one of the DRSi sources.

4.1.2. The effect of physical factor on the nutrient variations

The main physical factor affecting nutrient distributions in our study is the water exchange. The water exchange is stronger in the two zones outside the bay (Zones A and D) and weaker in the two zones inside the bay (Zones B and C) (Zhou, 2000). The residual current which runs parallel to the coast could bring nutrients from Zone A and Zone D to the east and southeast (Zhang and Dong, 1990). The loadings of nutrients from Zone A could spread to other zones (especially Zone D) and cause nutrient variation over the whole study area, such as the high concentrations of DIN and DRSi in March 2010.

Bivalve aquaculture is the main aquaculture activity in the two zones inside Sishili Bay and the lantern nets used in the aquaculture block the water flow and exchange there. The connecting dikes of east and west Yangma Island also affect the water exchange of the two zones inside the bay (Liu et al., 2009). Thus nutrient loadings from Zone B and Zone C would have problems reaching the two zones outside the bay which was indicated by the high concentrations of DIN, DON, SRP and DRSi found in Stn. C3 in April 2009. The water exchange caused distribution differences in nutrient species between inside and outside Sishili Bay, and this is also shown in the results of the cluster analysis (Fig. 13).

4.1.3. Spatial nutrient distribution linked to different human activities

Spatial distribution of different nutrient species indicated that anthropogenic inputs in Sishili Bay seemed to be mainly point sources with irregular inputs in time and quantity. The point sources input could result in a nutrient increase around the pollutant sources and, therefore, cause the spatial differences in the study area. As a result of the common function of nutrient loadings and water exchange, cluster analysis of the four nutrient species in the four zones indicated obvious differences between inside (Zones B and C) and outside (Zones A and D) areas of Sishili Bay with a D1 Euclidean distance of 60 (Fig. 13). The main anthropogenic impacts in our study area that caused the spatial differences included sewage discharge in Zone A, harbor and domestic pollution in Zone B, coastal loadings and aquaculture activities in Zone C.

Figs. 4–7 indicate that sewage discharge in Zone A mainly affected DIN, DON and DRSi distributions in the study area but had no obvious effects on SRP. The sewage discharge in Zone A caused the variations of all nutrient species to different degrees in our study area. Closing the sewage outfall near to Zone A or improving sewage treatment to reduce the nutrients concentrations discharged would appear to be effective paths for environment improvement in this study area.

The nutrient species in the harbor and domestic discharge area are mainly nitrogen (especially DIN) and SRP. Although the loadings from harbor and domestic discharge were not as obvious as the sewage discharge, the environmental effects could not be neglected because of the limited water exchange there. Zone C, located in the aquaculture area, is affected by the coastal loadings and aquaculture activities. Riverine inputs caused the infrequent and irregular loadings of nutrients in time and species (Fig. 1). Aquaculture activities that affect the nutrient composition have been investigated by Zhao et al. (2000b) and (2006). Nitrogenous compounds (ammonia, nitrite and nitrate) are considered as major

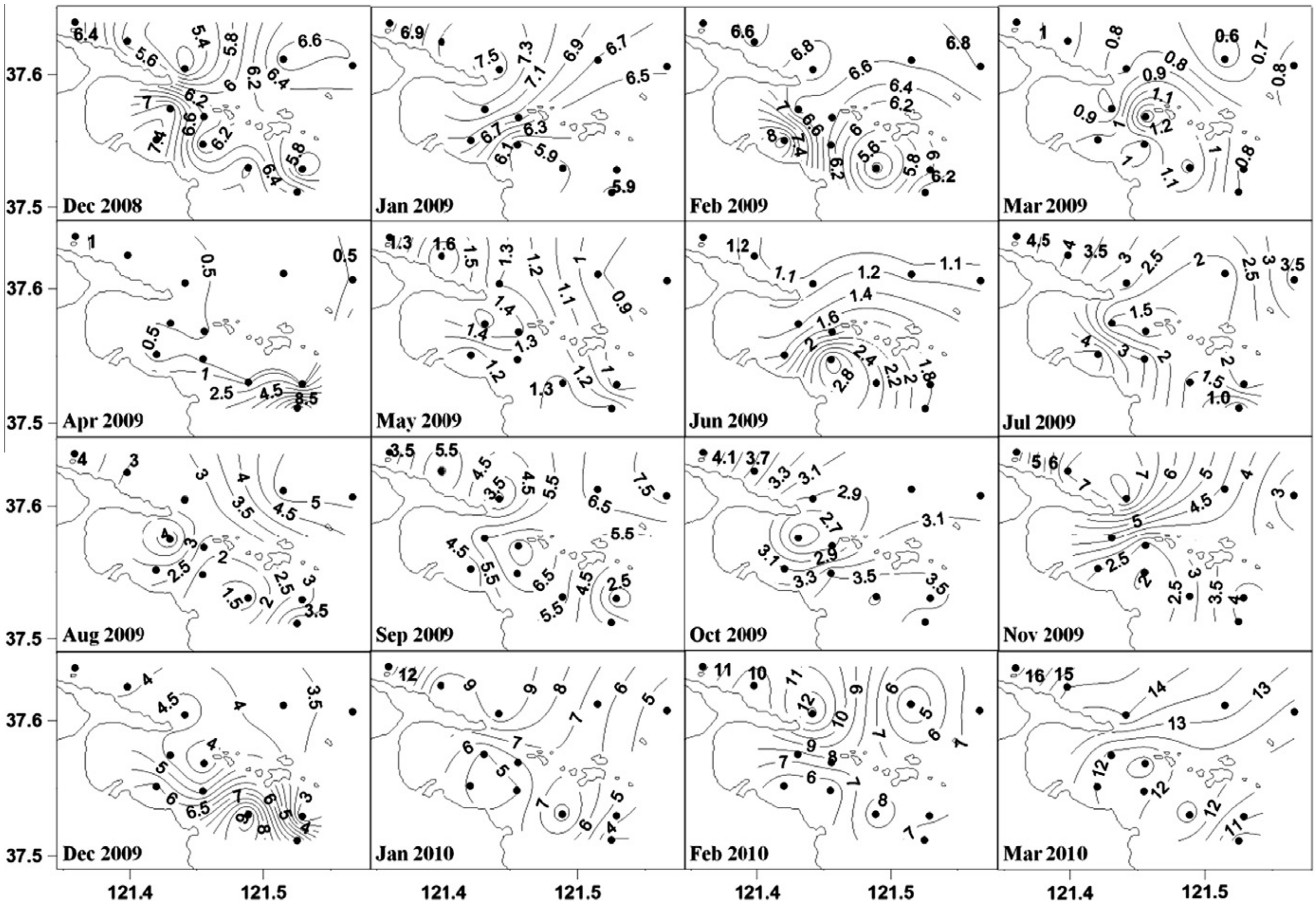

Fig. 7. Horizontal distribution of DRSi in the study area from December 2008 to March 2010. Lines are isolines and concentration is given in μM.

contaminants in aquaculture wastewater. Ammonia is the principal nitrogenous waste produced by aquatic animals, whereas particulate P is the main component of P leading mainly to increase of P in sediment (Olsen et al., 2008). The effect of aquaculture activities on nitrogen in Sishili Bay has been proved by Zhao et al. (2000a). In our study, the aquaculture activities had an obvious effect on the nutrients distribution, especially when nutrients were exhausted by phytoplankton. For the two zones inside the bay, DIN was only exhausted in Zone B during April to June 2009. The aquaculture activities in Zone C were probably the main factor resulting in the higher DIN concentrations compared with other zones. The cultured species in the bay, *M. edulis* filters phytoplankton and releases nutrients at the same time (Prins et al., 1995). Although nutrients were almost exhausted by phytoplankton during April to June 2009, the release of nutrients to the water column can help prevent the exhaustion in Zone C.

The impact of marine dumping activities in Zone D was not obvious in our study. This is not unexpected as the dumped material contains mostly metals and plastics with limited nutrients.

It has been reported that DIN and SRP in Sishili Bay are mainly from surface runoff and wet deposition, and DRSi comes from upwelling and sediment release (Liu et al., 2006). Our study has shown that biotic factors were important in controlling the seasonal and annual nutrient variations. Wet deposition might make contributions to the temporal variations of all nutrient species, especially to DON. Anthropogenic loadings play dominant roles in the composition and distribution of nutrient species. Different from the result in 2003 (Liu et al., 2006), anthropogenic loadings also play dominant roles in the distribution of DRSi in our study period. Our study indicated an increase of DIN loadings by anthropogenic actions from 2003 to 2010, which is in agreement with results found in 2009 (Sang and Sun, 2010).

4.2. Nutrient limitations in the study area

Nutrient limitations vary based on the different biogeochemistry within and between ecosystems and different seasons (Boesch et al., 2001). In our study, 79% of DRSi/DIN ratio values were less than 1. The low DRSi/DIN ratios were mainly found between December 2008 and December 2009 except June 2009, indicating relative DRSi limitation to DIN during this period. The DRSi limitation was much more serious in the area outside Sishili Bay. Although ratios of DRSi/DIN in June 2009 were higher than 1, DRSi concentrations were much lower than 2 μM, and during the period of March 2009 to June 2009, 94% of the values were less than 2 μM, indicating an absolute limitation of DRSi during this period. According to the assessment rules for nutrient limitation given by Justić et al. (1995), DRSi limitation was obvious in our study area from December 2008 to December 2009, especially from March to June 2009. The high DRSi concentrations in the first 3 months in 2010 reduced the DRSi limitation in the whole area.

DRSi limitation in Sishili Bay had already been reported in early spring of 1997 (Zhao et al., 2000b). Our study indicated that the DRSi limitation in Sishili Bay has become more serious from 1997 to 2010. Serious DRSi limitations found in our study were probably related to the high consumption by diatoms in spring and the low inputs from outside. The regeneration from sediment and water column and wet deposition could not provide enough DRSi for diatom blooms. Nutrient limitations in coastal waters may seasonally and spatially switch between nitrogen and phos-

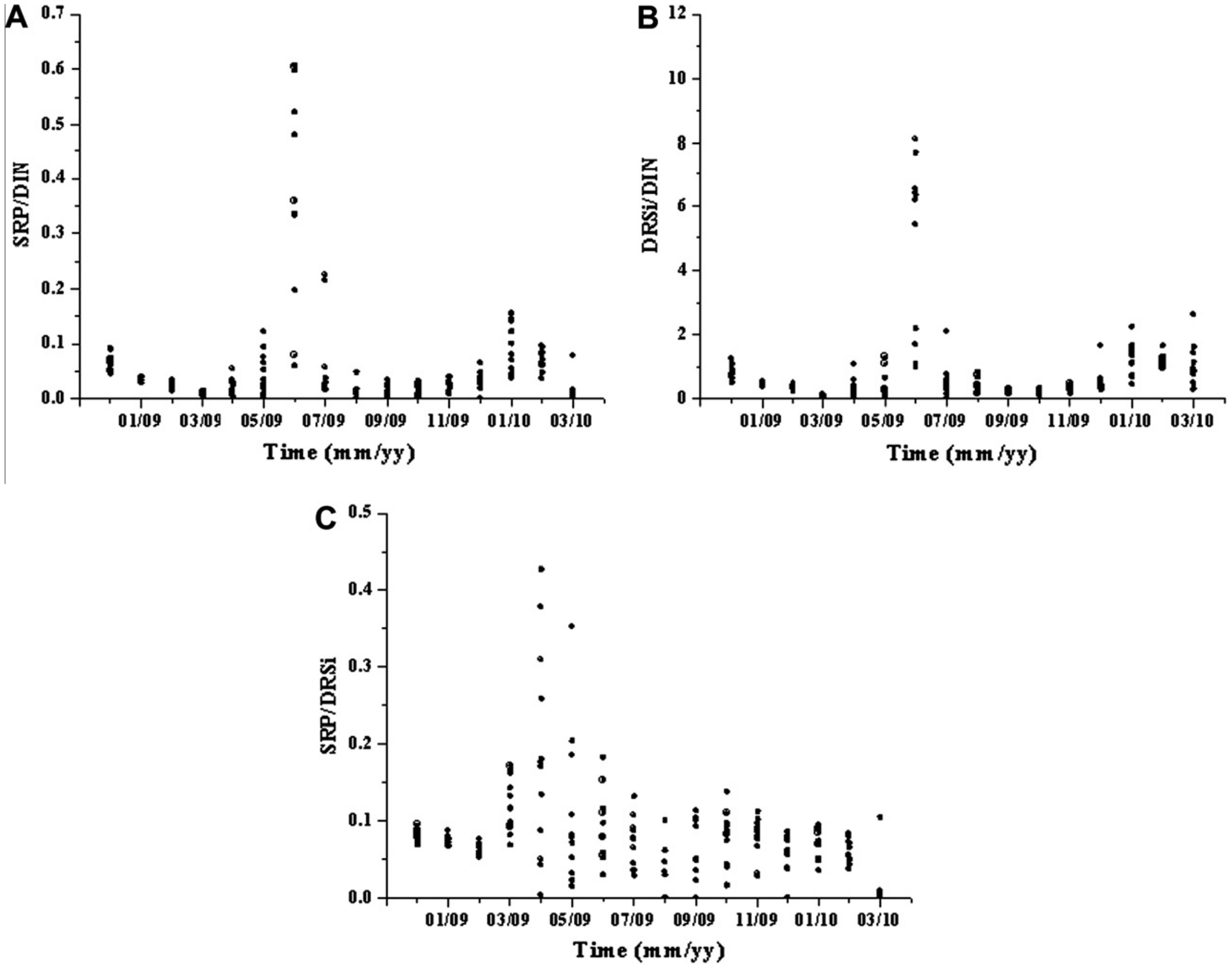

Fig. 8. Temporal variations of SRP to DIN (A), DRSi to DIN (B) and SRP to DRSi (C) in the study area.

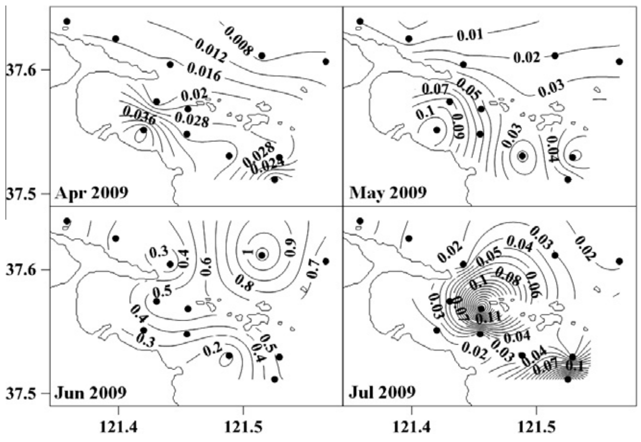

Fig. 9. Horizontal distribution of SRP to DIN in the study area from April to July, 2009.

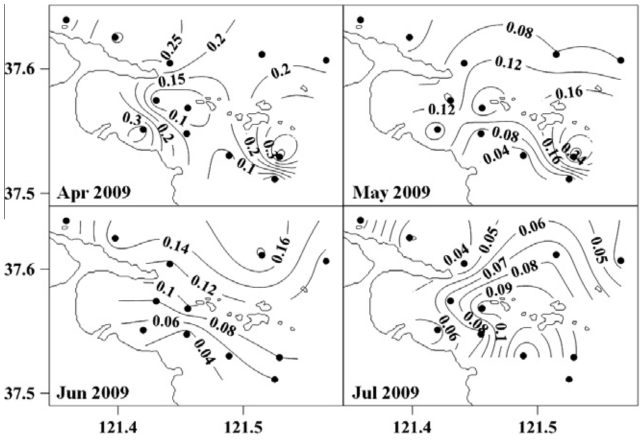

Fig. 10. Horizontal distribution of DRSi to DIN in the study area from April to July, 2009.

phorus limitation in response to variable nutrient inputs (Vuorio et al., 2005; Howarth and Marino, 2006; Jurgensone et al., 2011). In Sishili Bay, anthropogenic inputs also relieved DRSi limitations to a great extent, especially in the first 3 months of 2010. The increase of DRSi concentrations in fall of 2009 and winter 2010 might also be related to the wet deposition which reduced the DRSi limitation.

An absolute limitation of SRP was found in August 2009 with concentrations in most sites less than 0.1 μM. Relative limitations of SRP to DIN were also found in our study in early spring, late summer and fall with 70% of the SRP/DIN ratios much less than 1:22 (Justić et al., 1995). The relative limitation of SRP to DIN contrasts with finding in 1997 that DIN was a limiting factor in autumn (Zhao et al., 2000b), but coincides with results in 2003 that SRP was a limiting factor relative to DIN (Liu et al., 2006). Similar

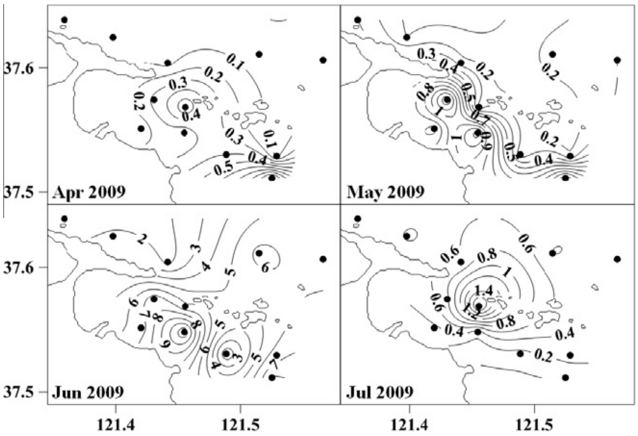

Fig. 11. Horizontal distribution of SRP to DRSi in the study area from April to July, 2009.

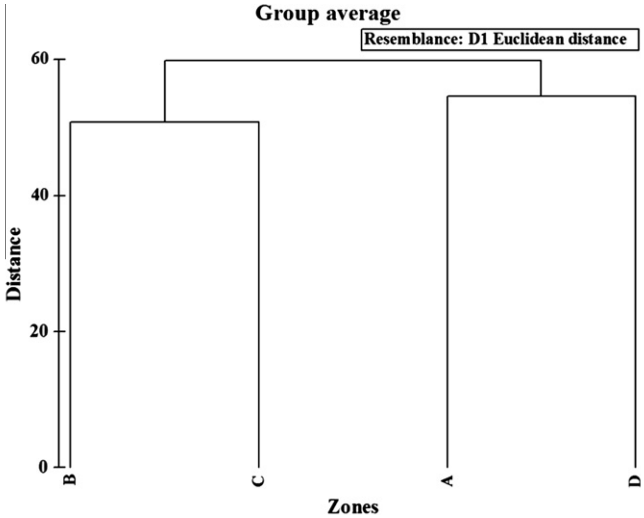

Fig. 13. Cluster analysis of nutrients of the four zones in the study area.

to DRSi, the relative limitation of SRP was more serious outside Sishili Bay (Figs. 9 and 11). According to DIN/DRSi ratio and DIN concentration, DIN was generally not a limiting factor. However, an absolute limitation of DIN (<1 μM in June 2009) and a relative nitrogen limitation with SRP/DIN higher than one in most of the study area were found (Fig. 9). In our study, a DIN limitation has almost disappeared except in June 2009. This implies that nutrient limitation variation in Sishili Bay changed from DIN limitation to SRP and DRSi limitation during the period between 1997 and 2010.

Changes in nutrient ratios and limitations caused by anthropogenic activities have become a normal situation in coastal areas in China and around the world. In the Bohai Bay, continuous increase of DIN has resulted in changes of the limiting nutrients from nitrogen in the early 1980s to nitrogen-phosphorus in the late 1980s, and then to phosphorus after the 1990s (Zheng et al., 2007; Xu et al., 2010). In Jiaozhou Bay, concentrations of both nitrogen and phosphorus showed increasing trends in the last four decades; however, the DRSi concentrations appeared an opposite trend during that period. DRSi has become the potential limiting factor (Liu et al., 2005; Yao et al., 2007). In Chesapeake Bay, high DIN concentration and DRSi/DIN less than one indicated that DRSi was more important in limiting the accumulation of diatom biomass during the spring biomass maximum (Conley and Malone, 1992). In our study, the increase of DIN in the Sishili Bay from anthropogenic loadings was one of the dominant reasons for changes of nutrient ratios. As discussed above, sewage discharge with heavy DIN loadings resulted in a high DIN concentration across the whole study area. In contrast, a decline of SRP loadings also reduced the SRP/DIN ratios. The use of phosphate-based detergents has caused increased eutrophication in coastal areas, and discontinuing the use of polyphosphate detergents resulted in significant reductions in phosphate loadings in Europe, North America, and Japan (Boesch, 2002). In Sishili Bay, it has also been shown that the use of phosphate-based detergents was the main reason for the increase of SRP in 1990s (Ji et al., 1998).

4.3. Response of phytoplankton to nutrients variations

The type of phytoplankton production is influenced by the composition of available nutrient species (Justić et al., 1995). In the southern North Sea and in the Black Sea, increasing the relative abundance of N and P compared to Si has resulted in displacement of diatoms by other phytoplankton species (Jickells, 1998). High DIN loadings to Jiaozhou Bay also resulted in variation of the dominant species and cell size (Shen, 2001; Liu et al., 2008). InSishili Bay, the causative species for harmful algal bloom shifted from diatoms (e.g., *Chaetoceros* sp.) to dinoflagellates (e.g., *Heterosigma akashiwo* and *Chattonella marina*) since 1990s (Hao et al., 2011). The change of nutrient limitation from DIN in 1997 to SRP and DRSi in 2009 might have played an important role for phytoplankton assemblage shift. This is also consistent with previous research which showed that silicate can regulate phytoplankton composition (Egge and Aksnes, 1992). Despite the long-term variations, seasonal changes of dominant species with variations of nutrient ratios were also found in Sishili Bay. Species analysis indicated that in August 2009 the dinoflagellate species *Chattonellamaia marina* accounted for more than 60% cell abundances in surface water while diatom species including *Paralia Sulcata*, *Chaetoceros* sp. and *Nitzschia closterium* became dominant in March 2010 (Jiang et al., 2011). This dominant species change is related to both DIN and DRSi. In March 2010, the wet deposition of DRSi and the anthropogenic loadings of DIN and DRSi supplied enough DIN

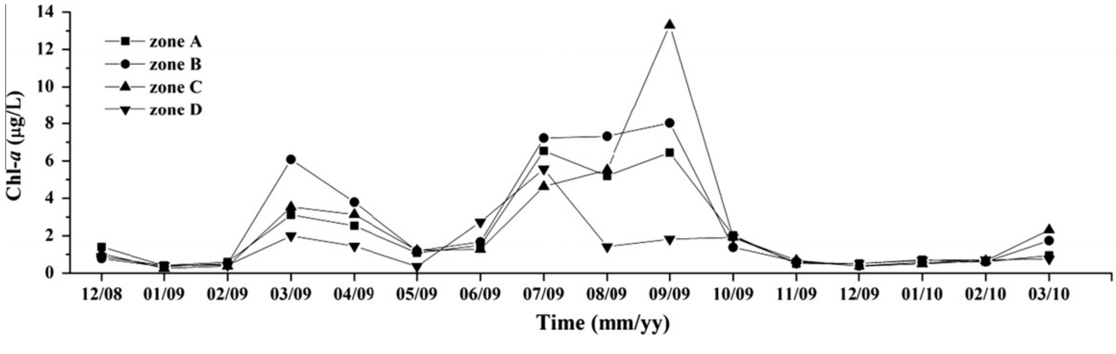

Fig. 12. Temporal variation of Chl-*a* of the four zones in the study area.

and DRSi for the growth diets. However, in August of 2009, DON became the dominant nitrogen source and was consumed by phytoplankton after DIN was exhausted in June. The DRSi from recycling and wet deposition was not enough to support the growth of diatoms; additionally, the SRP concentration was also low. All these factors prevented the rapid growth of diatoms. In contrast, the facultative heterotrophic character of dinoflagellates enables them to use organic nutrients and thus have a competitive advantage in an environment lacking inorganic nutrition at relatively high temperatures. Thus, in August 2009, dinoflagellate species were dominant while in March 2010 diatoms species again became dominant.

5. Conclusions

Spatial and temporal variations of nutrient species in Sishili Bay are mainly related to seasonal effects (biologic factors, temperature and wet deposition), water exchange, and anthropogenic effects. Biologic factors and wet deposition are more important for DON and SRP. Wet deposition plays a different role for the distributions of four nutrient species in our study: supplying SRP and DRSi but diluting DON. Aquaculture affected the distribution of DIN and SRP. Impacts from marine dumping were not obvious. Sewage discharge is the main factor that caused the increase of nitrogen (DIN and DON) and DRSi. Harbor and domestic pollution are also important nitrogen sources. It's imperative for the government to pay more attention to nitrogen loadings to Sishili Bay, especially nitrogen from the harbor and sewage discharge. Both absolute and relative limitation of DRSi was serious during the study period. Variations of nutrient limitation from DIN in 1997 to SRP and DRSi in 2009 were found, which caused the changes of dominant red tide species from diatoms to dinoflagellates. The seasonal variations of nutrient composition also caused the changes of phytoplankton composition in Sishili Bay. Obvious differences between the inside and outside of Sishili Bay were found in the distribution of nutrient species, ratios and limitations.

The Yantai government started to abolish lantern net culture of bivalves in Sishili Bay in 2010. This decision might improve the environment quality of Sishili Bay.

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