Acta Oceanol. Sin., 2012, Vol. 31, No. 4, P. 101-112 DOI: 10.1007/s13131-012-0224-x http://www.hyxb.org.cn E-mail: hyxbe@263.net

Changes of nutrient concentrations and N:P:Si ratios and their possible impacts on the Huanghai Sea ecosystem

FU Mingzhu1*,*2, WANG Zongling1*,*2∗, PU Xinming1*,*2, XU Zongjun1*,*2, ZHU Mingyuan1*,*²

¹ Key Laboratory of Science and Engineering for Marine Ecological Environment, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China

² Marine Ecology Research Centre, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China

Received 28 August 2011; accepted 21 April 2012

©The Chinese Society of Oceanography and Springer-Verlag Berlin Heidelberg 2012

Abstract

To investigate the impacts of nutrient concentrations and N:P:Si ratios on the ecosystem of the Huanghai Sea (Yellow Sea), the current status and long-term variation of nutrients concentrations and ratios as well as phytoplankton community structure in the Huanghai Sea were collected and analyzed. The results reveal great annual and seasonal fluctuations in the nutrient concentrations and N:P:Si ratios during 1998–2008 with no clear pattern observed in the whole region. Yet on a seasonal scale of spring and in the coastal regions such as the Jiaozhou Bay and Sanggou Bay, the increase of DIN concentration and N:P ratio as well as the decrease of phosphate and silicate concentrations and Si:N ratios were relatively significant. Many pelagic ecosystem changes have occurred concurrent with these changes of the nutrient regime, such as the recent increase of primary production, changes of phytoplankton chlorophyll a biomass and abundance, an increase of eutrophication, and occurrence of HABs. In addition, new trends in the variation of nutrients seem to be developing in some particular transect such as $36°N$, which suggests that long-term and systematic ecosystem monitoring in the Huanghai Sea is necessary.

Key words: nutrient concentration and ratio, long-term variation, Huanghai Sea, ecosystem response

1 Introduction

The classical Redfield ratio of C_{106} : N_{16} : P_1 is a cornerstone of aquatic biogeochemistry (Sterner et al., 2008; Geider and La Roche, 2002). This concept refers to the relationship between the chemical composition of organisms and of the water in which they grow and decay. The Redfield ratio was later extended to incorporate also silica, i.e., C_{106} : N_{16} : P_1 : Si_{16} (Harrison et al., 1977). Deviations in nutrient concentrations from these proportions have been used as indicators of the limitation of primary production in pelagic systems. The marine environment is often assumed nitrogen limited (Nixon et al., 1996), while freshwaters are mainly thought as phosphorus limited (Correll, 1998; Schindler, 1974).

Fertilizer and detergent usage, sewage discharge and damming have significantly changed the nutrient concentrations and their stoichiometric ratios in

the coastal areas through riverine input. The anthropogenic input of N to riverine systems, and hence to coastal waters from agricultural and domestic sources have increased over recent decades possibly by a factor of two to three globally (Jickells, 1998). The damming of river systems for power generation, domestic consumption or irrigation can lead to a net decrease in the amount of silicate reaching the coast waters and recent evidences suggests that silica has become a potential limiting factor in some coastal waters (e.g., Conley et al., 2000), including the Changjiang River Estuary (Yangtze River Estuary) (Chai et al., 2009). This limitation will affect the plankton composition, which in a longer perspective may change the entire food web (Humborg et al., 1997).

It was reported that changes in the proportions of dissolved Si, N and P in riverine nutrient loads may be important for coastal phytoplankton communities (Justić et al., 1995). Officer and Ryther (1980) hypo-

Foundation item: The China-Korea Cooperative Research on the Yellow Sea Cold Water Mass; the National Key Basic Research Project of China under contract No. 2010CB428703.

[∗]Corresponding author, E-mail: wangzl@fio.org.cn

thesized that decreasing Si:N ratio may exacerbate the effects of eutrophication by reducing the potential for diatom growth, in favour of noxious flagellates. Smayda (1990) discussed the effect of change in Si:P ratios on planktonic assemblages, in terms of a possible shift from diatom to flagellate dominance and also with respect to changes in the species composition of the diatom assemblage itself, and suggested that longterm decline in Si:P ratios was associated with significant blooms of non-siliceous algae in coastal waters worldwide. Turner et al. (1998) have proposed that changes in the N:Si ratio of the Mississippi delta, potentially shifting the diatom population from a state of N to Si limitation, has markedly influenced the species composition of the meso-zooplankton assemblage.

The Huanghai Sea is one of several regional seas which are heavily influenced by human activities. According to previous studies, the Huanghai Sea ecosystem has been experienced many unexpected changes over the past several decades, including the changes of nutrient concentrations and ratios in western coastal waters and along particular transects (Lin et al., 2005; Gao and Li, 2009); increased eutrophication and more frequent occurrence of HABs, mainly on the Chinese side (She, 1999); and changes in the composition of both phytoplankton and zooplankton communities (GEF/UNDP, 2007). In addition, two widespread and ecologically notable abnormalities have been observed in the Huanghai Sea–the significant increase in the jellyfish blooms (Dong et al., 2010) and the recurrence of massive blooms of macroalgal green tides since 2007 (Sun et al., 2008b).

Although some of the ecological changes are strongly suggested to be linked with nutrient concentrations and stoichiometric ratios, relevant studies of ecological relationships on large spatial and temporal scale are fairly limited. The aims of the present study were: (1) to study the variation of nutrient concentrations and ratios in the Huanghai Sea, especially during the last decade; (2) to study the changes in the ecosystem, e.g., chlorophyll a, primary production, phytoplankton abundance, relative proportions of diatom and dinoflagellates and the occurrence of HABs; and (3) attempt to determine the impacts of changes in nutrient levels and ratios on the phytoplankton community. The results are expected to serve well for management policies in the Huanghai Sea based on an improved understanding of how nutrients may have influenced the observed ecosystem changes.

2 Material and methods

2.1 *Study area*

The Huanghai Sea is a semi-enclosed marginal sea in northwestern Pacific that has an area of about $400\ 000\ \mathrm{km}^2$ with an average depth of 44 m and maximum depth about 100 m (Fig. 1). Being bounded by China Mainland to the west and the Korean Peninsula to the east, the Huanghai Sea is at the confluence of warm and cold waters. Several tidal mixing fronts exist in the Huanghai Sea, including the front observed around Shandong Peninsula, off Jiangsu Shoal, and off two major bays west of the Korean Peninsula (Belkin et al., 2009). A monsoon climate regime prevails in this region. During the winter, a strong northerly monsoon prevails over the area from late November to early April. In the summer, a much weaker southerly winds prevails. The Huanghe River, the Han River, the Yalujiang River and the Changjiang River are the main rivers discharge directly into the Huanghai Sea. In addition to river runoff, other major potential sources of nutrient inputs into the Huanghai Sea are atmospheric deposition and intrusion of oceanic water from the Kuroshio Current (Zhang et al., 1995). It has also been widely recognized that the nutrient concentrations of Huanghai Sea waters are very high, and that the Yellow Sea Large Marine Ecosystem (YSLME) is a Class I, highly productive ecosystem (primary productivity greater than 300 $g/(m^2 \cdot a)$) (Heileman and Jiang, 2009).

2.2 *Data source*

To achieve the aims of our study, the historic monitoring data involving inorganic nutrient (DIN, PO_4^{3-} , $SiO₃²$), phytoplankton biomass and community structure, etc. were collected from sources including the scientific literature, YSLME national reports, published atlases, related PhD and MS theses, and some primary data measured in the southern Huanghai Sea, especially during four cruises conducted in 2006–2007.

The data were obtained from various important projects conducted in the Huanghai Sea, including: the China National Marine Integrated Investigation (1959–1960); Marine Atlas (1984–1985); China-Korea Joint Research on the Seawater Circulation Dynamics in the Yellow Sea (1996–1998); China Coastal Investigation (1998–2000); Ecosystem Dynamics and Sustainable Utilization of Marine Living Resources in the

Fig.1. Topography of the Huanghai Sea and the location of transect 36◦N.

East China Sea and Yellow Sea (EYSEC, China GLOBEC II) (1999–2004); China SOLAS (survey conducted in the Huanghai Sea during 2005–2006); China's National Comprehensive Marine Investigation Project (908 project, 2006–2007); and the UNDP/GEF YSLME winter and summer cruises (2008).

3 Results

3.1 *Long-term changes of nutrient concentrations and element ratios in the Huanghai Sea*

The nutrient concentrations and element ratios collected in the southern Huanghai Sea are summarized in Table 1. The nutrient concentrations showed great seasonal and annual variabilities. From 1998 to 2008, the average DIN concentrations in the southern Huanghai Sea varied between 1.12 and 10.2 *µ*mol/L. Except in 2000 and 2001, the DIN concentrations were all above 4 μ mol/L. The average phosphate concentration varied between 0.04 and 0.73 μ mol/L; in most

years the value was below 0.3 *µ*mol/L. Except in winter of 2008, measured phosphate concentrations were all lower than that in the spring of 1959. The average silicate concentration varied between 2.75 *µ*mol/L and 16.6 μ mol/L with significantly high values recorded in 1959 and 2001. The range and mean value of N:P ratios showed great annual and seasonal variations. Due to the differences in the purposes for studies, the sampling stations occupied were different among the cruises. So comparison between nutrient concentrations and element ratios should be made with caution. Generally, no clear variation trend can be identified on the basis of the data collected so far. However, the nutrient level in the southern Huanghai Sea showed significant seasonality. Therefore, we extracted the data recorded during spring and made a further comparison for this particular season (Figs 2 and 3).

In spring, the DIN concentration seemed to show a slight increasing trend in the past 10 a, while phosphate and silicate concentrations showed a decreasing trend compared with 50 a ago. Correspondingly, the N:P ratio showed an increasing trend and Si:N ratio

	Date	 DIN	PO_{4}^{3-}	SiO_3^{2-}	N:P	Si:N	Si : P	Reference
Spring	1959		(0.45)	(16.6)				Gao and Li
								(2009)
	1998	(5.1)	(0.28)	(4.5)	(18.2)			Gao and Li
								(2009)
	May 1998				$5.27 - 76.8$	$0.83 - 13.40$		Wang et al.
								(2003) Gao et al.
	$Mar.-Apr.$ 2001				(17.8)	(3.3)	(54.5)	(2004)
	May 2001	(1.16)	(0.08)	(13.1)	$4.3 - 557.6$			Gao et al.
					(17)			(2003)
	Mar. 2005	(8.68)	(0.75)	(6.74)	$1.30 - 50.8$	$0.06 - 3.13$	$0.77 - 65.0$	Xu (2007)
					(17.66)	(0.98)	(17.99)	
	May 2005	(6.18)	(0.25)	(2.75)	$2.22 - 80.2$	$0.07 - 3.81$	$1.76 - 58.3$	Xu(2007)
					(25.1)	(1.05)	(24.9)	
	Apr. 2006	(4.11)	(0.14)	(6.42)	8.32-149.29	$0.14 - 8.14$	8.08-181.52	Xu(2007)
					(39.41)	(1.90)	(55.81)	
	Apr. 2007	(6.36)	(0.28)	(4.5)	$1.4 - 117.3$	$0.1 - 12.6$	$2.1 - 74.4$	908 Project
Summer	Jul.-Aug.				(19.9) $3.66 - 19.5$	(1.7) $0.85 - 10.54$	(23.0)	Wang et al.
	1998							(2003)
	Jun. 2000	(1.12)	(0.04)		$4.8 - 812.5$			Gao et al.
					(237)			(2003)
	Jun. 2001	(1.82)	(0.05)	(14.1)	$7.2 - 423.1$	$0.2 - 75.33$		Gao et al.
					(66.6)	(16.8)		(2003)
	Jun. 2004	(9.75)		(3.9)	$18 - 88$	$\qquad \qquad -$		Sun et al.
								(2008a)
	Jul.-Aug.	$0.11 - 10.1$	$0 - 0.81$	$0 - 39.4$	$0.8 - 1832.6$	$0 - 21.7$	$0 - 579.1$	908 Project
	2006	(5.05)	(0.15)	(4.63)	(104.8)	(1.9)	(41.1)	
	Aug. 2008	$0.24 - 18.17$	$0.01 - 0.13$	$0.01 - 8.16$	$8.19 - 272.23$	$0 - 31.81$	$0.26 - 331.02$	YSLME
		(2.68)	(0.05)	(2.78)	(64.45)	(2.64)	(80.30)	summer cruise
Autumn	Oct.-Nov. 1997				$7.12 - 52.4$	$0.82 - 8.58$		Wang et al. (2003)
	Oct.-Nov.				(30.7)	(8.1)	(163.6)	Gao et al.
	2000							(2004)
	Nov. 2002	(10.2)		(4.5)	$39 - 63$			Sun et al.
								(2008a)
	Oct.-Nov.	(8.78)	(0.19)	(7.16)	$12.3 - 16130$	$0.2 - 3.1$	17.5-5876.6	908 Project
	2007				(676.5)	(1.0)	(648.7)	
Winter	Jan. 1999				$6.56 - 28.8$	$1 - 2.97$		Wang et al.
								(2003)
	Jan. 2003	(8.55)		(6.3)	$22 - 34$			Sun et al.
								(2008a)
	Jan. 2007	(6.84)	(0.32)	(7.84)	$4.1 - 177.6$	$0.3 - 8.2$	$4.6 - 68.2$	908 Project
	Jan. 2008	$6.77 - 13.37$	$0.33 - 1.66$	6.89-14.07	(23.2) $5.27 - 22.80$	(1.3) $0.59 - 1.85$	(25.8) $4.80 - 28.95$	YSLME
		(9.11)	(0.73)	(9.57)	(14.91)	(1.10)	(16.35)	winter

Table 1. Nutrient concentration $(\mu \text{mol/L})$ and N:P:Si ratios in the southern Huanghai Sea

Notes: Means are denoted in parentheses; "–": no data.

Fig.2. Variation of nutrient concentration in the southern Huanghai Sea during spring.

Fig.3. Variation of nutrient ratios in the southern Huanghai Sea during spring.

Fig.4. Variation water-column averaged nutrient concentrations along the 36◦N transect [1976–2000: Lin et al. (2005); 2007 (black dot): National Comprehensive Marine Investigation Project; 2008 (black dot): YSLME joint-cruises].

showed a decreasing trend (Fig. 2).

A further comparison of nutrient variation trend was made at the particular transect of $36°$ N with the results of Lin et al. (2005) for depth-averaged nutrient concentrations for the time period 1975–2000. The DIN concentration showed an increasing trend, and the concentrations in 2007 and 2008 were much higher than the measurements before 2000 (Fig. 4). But the concentration of phosphate and silicate measured in 2007 and 2008 did not conform to the decline trend revealed before 2000, and both nutrients concentrations were significantly higher than the prediction (Fig. 4). The positive trends of DIN in the Huanghai Sea during the observation period were consistent with the rise of DIN observed throughout the global marginal seas. The results hint that changes of environmental parameters in the Huanghai Sea might deviate from the trends revealed by Lin et al. (2005). A further evaluation of environmental changes and the responses of the ecosystems of the Huanghai Sea is necessary.

On the west coast of the Huanghai Sea, the environmental changes in the Jiaozhou Bay and Sanggou Bay have received much attention. Significant increase of DIN and N:P ratio and sharp decrease of silicate and Si:N ratios were reported in these two bays during the past several decades (Zhao et al., 2005; Fu et al., 2012). This might be seen as an enlarged ecological signal of the Huanghai Sea ecosystem which means if this trend continues, the Huanghai Sea ecosystem could be similarly endangered.

3.2 *Trends in variation of phytoplankton community in the Huanghai Sea*

3.2.1 *Chlorophyll a*

The average Chl-a concentration in the surface water of the southern Huanghai Sea varied between 0.11 mg/m³ and 1.62 mg/m³ during 1983–2008. The Chl-a concentrations were lower during 1996–1998 as compared with 1983–1986, followed by the suggestion of an increasing trend through at least 2007, with the highest values of the record during 2006–2007, all higher than 1 mg/m^3 (Fig. 5).

3.2.2 *Cell abundance*

Phytoplankton cell abundance (net samples) has shown great fluctuations in the past 50 a, spanning at

Fig.5. Variation of chlorophyll a concentrations in southern Huanghai Sea [1983–1986: Zhu et al. (1993); 1996–1998: Wang (2001, 2003); 1998–2001: FIO unpublished data and Huang et al. (2006); 2002: Li et al. (2004); 2005: Zheng et al. (2006); 2006–2007: National Marine Comprehensive investigation; 2008: YSLME winter and summer joint cruise].

least four orders of magnitudes over the record (Fig. 6). The highest abundance was recorded during summer 2006 (63 363×10^4 cell/m³) whereas the lowest value was only 2.59×10^4 cell/m³, recorded during May 2005. At present, no clear trend can be discerned in the historic dataset.

3.3.3 *Primary production*

The primary production varied between 7.6 $mg/(m^2 \cdot d)$ and 653.8 mg/ $(m^2 \cdot d)$ recorded in winter of 1996–1998 and summer of 2000 respectively. The

Fig.6. Variation of phytoplankton cell abundance in the southern Huanghai Sea [1959–1960: monthly average, First Institute of Oceanography; 1984–1985: Marine Atlas Editorial Committee (1993); 1985–1986, 1998–2000: Wang (2001); 2001–2002: FIO unpublished data and Wang (2003); 2005: Xu (2007); 2006–2007: National Marine Comprehensive Investigation; 2008: YSLME winter and summer joint cruise].

seasonal variations of primary production were somewhat consistent, with highest value in either spring or summer each year, and lowest values in winter (Fig. 7). Like the variation trend of chlorophyll a concentration, primary production declined from 1983–1986 to 1996–1998 and obviously increased since the end

of the 1990s. The primary production measurements during 1998–2000 were all higher than those obtained during 2006–2007. A contributing factor may be that the investigation conducted during 1998–2000 covered the northern Huanghai Sea which normally has a relatively higher primary production.

Fig.7. Variation of primary production in the southern Huanghai Sea (1983–1986, 1996: Zhu et al., 1993 and Lin et al., 2005; 1998–2000: FIO unpublished data; 2006–2007: National Marine Comprehensive investigation; 2008: YSLME winter and summer joint cruise).

3.3.4 *Relative contributions of diatom and dinoflagellates*

In spring the percentage of diatoms in the total phytoplankton abundance dropped from 88.9% in 1986 to 69.5% in 1998, while that of dinoflagellates increased from 11.1% to 30.5% in the same period in the whole Huanghai Sea (Table 2). And in the southern Huanghai Sea the contribution of diatoms further decreased to 50.89% in May of 2005. Yet we have to notice that the time of investigation is an important influence in the assessment of the phytoplankton community, for example in March and April the diatoms were still predominant (*>*98%) in the phytoplankton community (Table 2). So from the viewpoint of seasonal scale, the percentage of diatom might not decrease in spring (March to May).

3.3.5 *Occurrence of HABs*

A total of 138 HAB events were recorded since 1972 among which 95 occurred in the last 10 a. The occurrence sites of HABs along the west coast of the Huanghai Sea coincided with the most polluted and eutrophicated area (Fig. 8).

In the 1990s, Smayda summarized the dataset collected from all over the world and came to this conclusion that the increase of HABs occurrence in the coastal waters was the result of eutrophication (Smayda, 1990). Since then, much evidence supports the inferred linkage between the increase in nutrient

Table 2. Relative contribution of diatoms and dinoflagellates to total phytoplankton abundance in the Huanghai Sea during spring (net sample)

Dinoflagellate $(\%)$	Reference
88.9 11.1	Wang (2001)
30.5 69.5	Wang (2001)
0.28	Xu(2007)
49.11	Xu (2007)
0.37	Xu (2007)
98.8 $1.2\,$	National Marine Comprehensive investigation
	Diatom $(\%)$ 99.72 50.89 99.63

Fig.8. Occurrence frequency of HABs in the Huanghai Sea during 1972-2008 (left: State Oceanic Administration, China) and the occurrence sits of HABs in the west coast of the Huanghai Sea (right: courtesy of Prof. Li Ruixiang).

loading and supply ratio with the development of some HABs and changes in phytoplankton species composition, including that in the coastal region of the Huanghai Sea.

In the west coastal area of the Huanghai Sea, serious eutrophication and higher N:P ratios have been identified as the environmental conditions for the occurrence of HABs in the Haizhou Bay (Cheng et al., 2009) and the Jiaozhou Bay (Han et al., 2004). This could be seen as evidence of ecosystem response to the changes of nutrient concentration and element ratios.

4 Discussion

With the process of industrialization and urbanization, massive and increasing quantities of industrial, agricultural and sewage effluents with abundant nutrients (nitrogen and phosphorus in particular) have been discharged into the coastal waters through a variety of pathways. Damming of the rivers has reduced the water and silicate flux into the coastal regions. These activities would largely alter the size and composition of the nutrient pool of the marine environments which caused eutrophication and many other negative ecological consequences especially to the phytoplankton community.

4.1 *Possible causes of changes in nutrient concentrations and ratios in the Huanghai Sea*

Riverine transportation and atmospheric deposition are the major sources of nutrient to the Huanghai Sea ecosystem (Zhang and Liu, 1994; Bashkin et al., 2002; Zhang et al., 2007). Influenced by the increasing usage of fertilizer and domestic discharge, the concentration and composition of nutrient sources to the rivers have been significantly changed (Paerl, 2006; Fan and Huang, 2008; Gao and Wang, 2008). For example, in the Changjiang River watershed, the usage of chemical fertilizer increased three times in the past 20 a from 3.02*×*10⁶ t in 1980 to 9.37*×*10⁶ t in 1996 (Cai and Chen, 1997). According to Yan and Zhang (2003), the flux of nitrogen entering the Changjiang River was 7.8*×*10⁶ t in 1997 which was about three times of 1968.

In addition, the N:P ratio in the river was much higher than in the ocean, for instance, the N:P ratio in the rivers entering the Huanghai Sea was about 106:1 (Zhang and Liu, 1994). Atmosphere deposition was another source of nutrient input to the Huanghai Sea by which the flux of DIN and phosphate was in the same magnitude as from the river. And the N:P ratio in the atmospheric deposit was about 84:1, which was also significantly higher than in the ocean. So the increase of DIN concentrations was mainly due to the combined contributions of riverine nitrogen input and atmosphere deposition.

The transportation of silicate by atmospheric deposition was negligible compared with DIN and phosphate. The decrease of silicate in the Huanghai Sea was attributed to the damming of river systems which led to a net decrease in the amount of silicate reaching the coast. However, for phosphate, no evidence showed the input through the river transport decreased in the last several decades. Some researchers suggested that the decrease of phosphate might be due to the increasing load of DIN which increased the primary production of phytoplankton thus enhanced the consumption of phosphate (Gao and Li, 2009).

4.2 *Relationships between nutrient change and ecosystem responses*

4.2.1 *Recent general increasing trend of primary production*

Phytoplankton growth depends largely on the availability of inorganic nutrients. Thus, one of the nutrient enrichment effects may increase the phytoplankton productivity (Hodgkiss and Lu, 2004). This has been evidenced by the high primary production distribution along the nutrient-rich coastal region and upwelling area. In the Huanghai Sea, the phytoplankton primary production obviously increased since the end of the 1990s (Fig. 5) which was coincident with the increase of DIN concentrations during the last 10 a (Fig. 2 and Table 1).

Besides the nutrient increase caused by anthropogenic activities, during the last century, the winter monsoon has enhanced and this would increase the material transportation to the Huanghai Sea through coastal currents and atmospheric deposition (Lin et al., 2005; Xing et al., 2009). At the same time, the enhanced winter monsoon would increase the mixing extent of water column which would bring more nutrients from the deep waters to the euphotic zone. In addition, the N:P ratio in the river and atmospheric deposition entering the Huanghai Sea were both much higher than in the ocean as mentioned in Section 4.1. This would help to relax the N-limitation of the ocean environment and enhance the primary production (Gao and Wang, 2008). The observations in the Changjiang River Estuary have verified the enhancement of biological production due to the material flux change of Changjiang River (Gao and Wang, 2008; Zhou et al., 2008). So the change of primary production in the Huanghai Sea was caused by the changes of nutrient concentrations and composition induced by both human activity and climate change.

4.2.2 *Nutrient ratio and phytoplankton community structure*

The nutrient supply and its ratios have a decisive effect on the species composition of the phytoplankton since different algal species have different nutrient requirements (Hodgkiss and Lu, 2004). Diatoms are in general fast growing species under non-limiting conditions and demonstrate a higher growth rate than flagellates at similar volumes (Banse, 1982). Given sufficient nutrients and silicate concentration higher than a threshold concentration of approximately $2 \mu \text{mol/L}$ silicate (Egge and Aksnes, 1992), diatoms have been observed to dominate the phytoplankton community. In addition, the mesocosm experiment conducted in the North Sea suggests that diatoms are poor competitors at low phosphate concentrations (on the average 0.1 *µ*mol/L) (Egge, 1998).

In the Huanghai Sea, the seasonal succession of the phytoplankton community during spring of 2005 showed a similar trend (Table 2). Based on the observational data, from March to May, the nutrient concentrations decreased due to the consumption by phytoplankton. Because nitrogen was generally in excess, the N:P ratio tended to increase and P-limitation was likely to occur as nutrients were drawn down. At the same time, the contribution of diatoms declined from 99.72% to 50.89%, possibly caused by the changes of N:P ratios.

Another reason might be the possible change of silicate concentration and the Si:N ratio. According to the literature, long time series analysis of phytoplankton abundance and composition in coastal areas indicates that flagellates have become more abundant compared with diatoms (Smayda, 1990) and the decrease in the Si:N ratio has probably been responsible for this tendency (Officer and Ryther, 1980; Egge and Aksnes, 1992). The influence of Si:N ratio on the phytoplankton species composition was verified in the Changjiang River Estuary through oceanographic investigations conducted during 1998–2004 (Gong et al., 2006). Diatoms used to be the most abundant phytoplankton species in the Changjiang Diluted Water influenced area, yet after the construction of Three Gorges Dam, the Si:N ratio declined from 1.5 to 0.4 and the flagellates (e.g., prymnesiophytes, cryptophytes and chryophytes) became the dominant species in 2003. The authors proposed that the phytoplankton community changes because of Si limitation (Gong et al., 2006). In the Huanghai Sea, although the change of Si:N ratio was not obvious, the source of silicate was believed to be reduced due to the damming of the rivers. Thus, although the data collected so far cannot support a clear variation trend of phytoplankton species composition, a declining ratio of diatoms might be predicted due to the deficiency of phosphate and silicate of the Huanghai Sea.

4.2.3 *Nutrient ratio and occurrence of HABs*

In the past few decades there has been accumulating evidence from around the world to suggest that coastal marine phytoplankton blooms have increased in frequency, intensity and geographic distribution (Hodgkiss and Ho, 1997). Undoubtedly, a potential relationship exists between red tides and the N and P load of coastal waters, and the linkage between HAB occurrence and accelerated eutrophication have been noted within the past three decades. However, more and more studies suggest that compared with the absolute nutrient concentrations, nutrient ratios (such as N:P and Si:P) are far more important regulators in the bloom forming and species compositions of HABs (Hodgkiss and Ho, 1997; Anderson et al., 2002).

As mentioned above, human activities have largely altered the size and composition of nutrient pools in coastal areas, which might create a more favorable nutrient environment for certain HAB species. And several toxic flagellate blooms have occurred in water masses characterized by high N:P ratios and phosphate deficiency (Maestrini and Granéli, 1991; Kaartvedt et al., 1991).

HABs in Tolo Harbor in Hong Kong showed a distinct relationship with nutrient ratios. Hodgkiss and Ho (1997) demonstrated that the number of dinoflagellate red tides increased as the annually averaged N:P ratio fell from 20:1 to 11:1 between 1982 and 1989. Another example is in the coastal area of the North Sea. A 23-a time series of survey data off the German coast showed a 4-fold increase in the N:Si and P:Si ratios which was accompanied by a decrease in the diatom community and an increase in the occurrence of foam-producing *Phaeocystis* blooms (Radach et al., 1990). On the west coast of the Huanghai Sea, the occurrence of HABs increased substantially during the last 10 a (Fig. 8) and more nondiatom species blooms were recorded such as *Alaxandrium tamarence, Gymnodinium catenatum, Noctiluca scintillans, Alaxandrium affine*, and *Gonyaulax polygramma*. This process was accompanied by the accelerated eutrophication and alteration of nutrient ratios (Han et al., 2004; Cheng et al., 2009). This could be seen as the evidence of ecosystem response to the changes of nutrient concentration and element ratios.

5 Conclusions

Changes in nutrient concentrations and ratios, and their possible ecological consequences in the Huanghai Sea were studied in this work. Although in the whole region, the nutrient concentrations and N:P:Si ratios revealed great annual and seasonal fluctuations and no clear pattern were observed—perhaps due to the scarcity of dada—an increase of DIN concentration and N:P ratio as well as the decrease of phosphate and silicate concentrations and Si:N ratios were displayed on seasonal scale and in coastal regions. Many pelagic ecosystem changes have been strongly related to the changes of the inorganic nutrient supplies, such as the recent increase of primary production, changes of phytoplankton biomass and abundance, increase of eutrophication, and occurrence of HABs. In addition, a fairly clear temporal trend in nutrient conditions has been detected on the transect at 36◦N, which suggests that long-term and systematic ecosystem monitoring in the Huanghai Sea is necessary.

Acknowledgements

The author would like thank Prof. John Cullen from Department of Oceanography, Dalhousie University, Canada for his valuable comments and language improvement for the manuscript. Comments provided by the two anonymous reviewers are acknowledged.

References

- Anderson D M, Glibert P M, Burkholder J M. 2002. Harmful algal blooms and eutrophication: nutrient source, composition, and consequences. Estuaries, 25(4b): 704–726
- Banse K. 1982. Cell volumes, maximal growth rates of unicellular algae and ciliates, and the role of ciliates in the marine pelagial. Limnology and Oceanography, 27: 1059–1071
- Bashkin V, Park S, Choi M, et al., 2002. Nitrogen budgets for the republic of Korea and the Yellow Sea region. Biogeochemistry, 57(1): 387–403
- Belkin I M, Cornillon P C, Sherman K. 2009. Fronts in large marine ecosystems. Progress in Oceanography, 81: 223–236
- Chai Chao, Yu Zhiming, Shen Zhiliang, et al. 2009. Nutrient characteristics in the Yangtze River Estuary and the adjacent East China Sea before and after impoundment of the Three Gorges Dam. Science of the Total Environment, 407: 4687–4695
- Cheng Junli, Zhang Ying, Zhang Dong, et al. 2009. Analysis of ecological environment elements during the red tide occuring in Haizhou Bay. Advances in Marine Science (in Chinese), 27(2): 217–223
- Cai Shenglin, Chen Wanli. 1997. China Agriculture Yearbook (in Chinese). Beijing: China Agriculture Press
- Conley D, Stålnacke P, Pitkänen H, et al. 2000. The transport and retention of dissolved silicate by rivers in Sweden and Finland. Limnology and Oceanogra phy, 45(8): 1850–1853
- Correll D L. 1998. The role of phosphorus in the eutrophication of receiving waters: A review. Journal of Environment Quality, 27: 261–266
- Dong Zhijun, Liu Dongyan, Keesing J K. 2010. Jellyfish blooms in China: Dominant species, causes and consequences. Marine Pollution Bulletin, 60: 954–963
- Egge J K. 1998. Are diatoms poor competitors at low phosphate concentrations? Journal of Marine Systems, 16: 191–198
- Egge J K, Aksnes D L. 1992. Silicate as a regulating nutrient in phytoplankton competition. Marine Ecology Progress Series, 83: 281–289
- Fan Hui, Huang Haijun. 2008. Response of coastal marine eco-environment to river fluxes into the sea: A case study of the Huanghe (Yellow) River mouth and adjacent waters. Marine Environmental Research, 65: 378–387
- Fu Mingzhu, Pu Xinming, Wang Zongling, et al. 2012. Integrated assessment of marine aquaculture ecosystem health of Sanggou Bay. Acta Ecologicia Sinica (in Chinese), doi: 10.5846/stxb201106270960
- Gao Lie, Li Daoji. 2009. Changes of nutrient concentrations in western areas of Yellow Sea and East China Sea in recent several decades. Marine Science (in Chinese), 33(5): 64–69
- Gao Shengquan, Lin Yian, Jin Mingming, et al. 2003. Distribution of nutrient and its relationship with anchovy spawning ground in the southern waters of Shandong Peninsula. Acta Oceanologica Sinica (in Chinese), 25 (Suppl 2): 157–166
- Gao Shengquan, Lin Yian, Jin Mingming, et al. 2004. Distribution features of nutrients and nutrient structure in the East China Sea and Yellow Sea in spring and autumn. Donghai Marine Science (in Chinese), 22(4): 38–50
- Gao Shu, Wang Yaping. 2008. Changes in material fluxes from the Changjiang River and their implications on the adjoining continental shelf ecosystem. Continental Shelf Research, 28: 1490–1500
- GEF/UNDP. 2007. Reducing environmental stress in the Yellow Sea Large Marine ecosystem. Transboundary Diagnostic Analysis
- Geider R, La Roche J. 2002. Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. European Journal of Phycology, 37: 1–17
- Gong G C, Chang J, Chiang K P, et al. 2006. Reduction of primary production and changing of nutrient ratio in the East China Sea: Effect of the Three Gorges Dam? Geophysical Research Letters, 33: L07610
- Han Xiaotian, Zou Jingzhong, Zhang Yongshan. 2004. Harmful algae bloom species in Jiaozhou Bay and the features of distribution. Marine Sciences (in Chinese), 28(2): 49–54
- Harrison P H, Conway H, Holmes W, et al. 1977. Marine diatoms grown in chemostats under silicate or ammonium limitation: III. Cellular chemical compostion and morphology of *Chaetoceros debilis, Skeletonema costatum*, and *Thalassiosira gravida*. Marine Biology, 43(1): 19–31
- Heileman S, Jiang Y. 2009. Yellow Sea LME. In: Sherman K, Hempel G, eds. The UNEP Large Marine Ecosystem Report: A Perspective on Changing Conditions in LMEs of the World's Regional Seas. 441–451
- Hodgkiss I J, Ho K C. 1997. Are changes in N:P ratios in coastal waters the key to increased red tide blooms? Hydrobiologia, 352: 141–147
- Hodgkiss I J, Lu S H. 2004. The effects of nutrients and their ratios on phytoplankton abundance in Junk Bay, Hong Kong. Hydrobiologia, 512: 215–229
- Huang Bangqin, Liu Yuan, Chen Jixin, et al. 2006. Temporal and spatial distribution of size-fractionized phytoplankton biomass in East China Sea and Huanghai Sea. Acta Oceanologica Sinica (in Chinese), 28(2): 156–164
- Humborg C, Ittekkot V, Cosiasu A V, et al. 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature, 386: 385–387
- Jickells T D. 1998. Nutrient biogeochemistry of the coastal zone. Science, 281: 217–222
- Justić D, Rabalais N N, Turner R E, et al. 1995. Changes in nutrient structure of river-dominated coastal waters: stoichiomitric nutrient balance and its consequences. Estuarine, Coastal and Shelf Science, 40: 339–356
- Kaartvedt S, Johnsen T M, Aksnes D L. 1991. Occurrence of the toxic phytoflagellate *Prymnesium parvum* and associated fish mortality in a Norwegian fjord system. Can J Fish Aqua Sci, 48: 2316–2323
- Li Hongbo, Xiao Tian, Liu Guimei, et al. 2004. Impact of the tidal front on the distribution of baterioplankton biomass in the southern Yellow Sea. Acta Ecologica Sinica (in Chinese), 24(11): 2608–2615
- Lin Chuanlan, Ning Xiuren, Su Jilan, et al. 2005. Environmental changes and the responses of the ecosystems of the Yellow Sea during 1976–2000. Journal of Marine Systems, 55: 223–234
- Maestrini Y, Granéli E. 1991. Environmental conditions and ecophysiological mechanisms which led to the 1988 *Chrysocromulina polylepis* bloom: an hypothesis. Oceanologica Acta, 14: 397–413
- Marine Atlas Editorial Committee. 1993. Atlas of Bohai Sea, Huanghai Sea and East China Sea (in Chinese). Beijing: Ocean Press
- Nixon S W, Ammerman J W, Atkinson L P, et al. 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry, 35: 141–180
- Officer C B, Ryther J H. 1980. The possible importance of silicon in marine eutrophication. Mar Ecol Prog Ser, 3: 83–91
- Paerl H W. 2006. Assessing and managing nutrientenhanced eutrophication in estuarine and coastal waters: Interactive effects of human and climate perturbations. Ecological Engineering, 26(1): 40–54
- Schindler D W. 1974. Eutrophication and recovery in experimental lakes: implications for lake management. Science, 184: 897–899
- She J. 1999. Pollution in the Yellow Sea Large Marine Ecosystem: monitoring, research and ecological effects. In: Tang Qisheng, Sherman K, eds. Large Marine Ecosystems of the Pacific Rim: Assessment, Sustainability and Management. Malden, U.S.: Blackwell Science, 419–426
- Smayda T J. 1990. Novel and nuisance phytoplankton blooms in the sea: evidence for a global epidemic. In: Granéli et al., eds. Toxic Marine Phytoplankton. New York: Elsevier, 29–40
- Sterner R W, Andersen T, Elser J J, et al. 2008. Scaledependent carbon: nitrogen: phosphorus seston stoichiometry in marine and freshwaters. Limnology and Oceanography, 52(3): 1169–1180
- Sun Shan, Liu Sumei, Ren Jingling, et al. 2008a. Distribution of nutrients on anchovy spawning ground and overwintering ground in the Yellow Sea. Marine Science (in Chinese), 23(10): 45–50
- Sun Song, Wang Fang, Li Chaolun, et al. 2008b. Emerging challenges: Massive green algae blooms in the Yellow Sea. Nature Precedings: hdl:10101/npre. 2008.2266.1
- Turner R E, Quereshi N, Rabalais N N, et al. 1998. Fluctuating silicate: nitrate ratios and coastal plankton food webs. Proc Nat Acad Sci USA, 95: 13048– 13051
- Wang Jun. 2001. Study on phytoplankton in Yellow Sea in spring. Marine Fishery Research (in Chinese), 22: 56–61
- Wang Jun. 2003. Study on phytoplankton in the Yellow Sea in autumn and winter. Marine Fishery Research (in Chinese), 24: 15–13
- Wang Baodong, Zhan Run, Zang Jiaye, 2003. A preliminary study on the nutrient limitation of phytoplankton growth in the Huanghai Sea and the East China Sea. Acta Oceanologica Sinica (in Chinese), 25(Supp 2): 190–195
- Xing Lei, Zhao Meixun, Zhang Hailong, et al. 2009. Biomarker records of phytoplankton community structure changes in the Yellow Sea over the last 200 years. Periodical of Ocean University of China (in Chinese), 39(2): 317–322
- Xu Zongjun. 2007. The effect of atmosphere nitrogen deposition on phytoplankton community and marine primary productivity in Yellow Sea and South China Sea in spring [dissertation]. Qingdao: Ocean University of China
- Yan Weijin, Zhang Shen. 2003. The composition and bioavailability of phosphorus transport through the Changjiang (Yangtze) River during the 1998 blood. Biogeochemistry, 65: 179–194
- Zhang Jing, Liu Mingguang. 1994. Observations on nutrient elements and sulphate in atmospheric wet depositions over the northwest Pacific coastal oceans— Yellow Sea. Marine Chemistry, 47: 173–189
- Zhang Guiling, Zhang Jing, Liu Sumei. 2007. Characterization of nutrients in the atmospheric wet and dry depositon observed at the two monitoring sites over Yellow Sea and East China Sea. Journal of Atmospheric Chemistry, 57(1): 41–57
- Zhang J, Huang W W, Letolle R, et al. 1995. Major element chemistries of the Hanghe (Yellow River), China-weathering processes and chemical fluxes. Journal of Hydrology, 168: 173–203
- Zhao Shujiang, Jiao Nianzhi, Shen Zhiliang, et al. 2005. Causes and consequences of Changes in nutrient structure in the Jiaozhou Bay. Journal of Intergrative Plant Biology, 47(4): 396–410
- Zheng Guoxia, Song Jinming, Dai Jicui, et al. 2006. Distributions of chlorophyll-a and carbon fixed strength of phytoplankton in autumn of the southern Huanghai Sea Waters. Acta Oceanologica Sinica (in Chinese), 28(3): 109–118
- Zhou Mingjiang, Shen Zhiliang, Yu Rencheng. 2008. Response of a coastal phytoplankton community to increased nutrient input from the Changjiang (Yangtze) River. Continental Shelf Research, 28: 1483–1489
- Zhu Mingyuan, Mao Xinghua, Lv Ruihua. 1993. Chlorophyll and primary production level in the Yellow Sea. Journal of Oceanography of Huanghai & Bohai Seas (in Chinese), 11: 46–50