

Spatiotemporal changes of biogenic elements in the Changjiang River Estuary and adjacent waters in summer over the last decade

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Abstract

The long-term spatiotemporal changes of surface biogenic elements in the Changjiang River Estuary and adjacent waters during the summer of 2008–2016 were analyzed in this study. The concentrations of dissolved inorganic nitrogen (DIN), soluble reactive phosphate (PO_4^{3-}) and silicate (SiO_3^{2-}) were generally stable, with a slight decrease of DIN and PO_4^{3-} , and a slight increase of SiO_3^{2-} , which mainly occurred in the estuarine waters. The grey correlation analysis was carried out between biogenic elements and chlorophyll *a* (Chl-*a*). Results showed that compared with the absolute values of biogenic elements, the correlations between the concentration ratio of nitrogen to phosphorus (N/P), ratio of silicon to nitrogen (Si/N) and Chl-*a* were closer, indicating the important influence on phytoplankton by the structure of biogenic elements. The study area was generally in a state of potential P limitation, and could have potential impact on the phytoplankton community, triggering the shift of red tide dominant species from diatoms to dinoflagellates.

Key words: Changjiang River Estuary, biogenic elements, spatiotemporal changes

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1 Introduction

The biogenic elements such as nitrogen (N), phosphorus (P), and silicon (Si) in the seawater are essential nutrients for the growth and reproduction of phytoplankton, and play a very critical role in marine ecosystem functioning (Boyce et al., 2010; Falco et al., 2010; Yang et al., 2015). Suitable biogenic elements can maintain the balance of the marine ecosystem, while the lack or surplus of biogenic elements will lead to a lack of nutrition or eutrophication of the seawater, making the marine ecosystem unbalanced and biological communities changed, as well as leading to marine ecological disasters and the exhaustion of economic species (Anderson et al., 2002; Xiao et al., 2018).

The estuary areas have been well recognized as areas of high biological productivity and interfaces of material transportation and transformation between land and ocean (Furuya et al., 2003; Bianchi and Allison, 2009). As China's largest estuary, the Changjiang River Estuary is endowed with unique geographic location, monsoon and circulation conditions and complex estuarine ecosystem (Chen et al., 2015; Dai et al., 2016; Lu et al., 2017). Continuous runoff transports abundant biogenic elements into the estuary, forming the basis for the survival and development of marine lives. Since 1980s, with the ever-expanding population and economic aggregation in the Changjiang River Basin, the nutrients have experienced a drastic increase (Li et al., 2007; Chen et al., 2011; Wang and Cao, 2012; Yang et al., 2015), leading to the exacerbation of harmful algal and the alternation of phytoplankton community (Zhou et al., 2008; Wang and Wu, 2009; Jiang et al., 2014; Xiao et al., 2018). While in recent years, due to the strengthening of ecological protection, the amounts of

pollutants have been gradually under control (Liang et al., 2016). In this study, the long-term changes of surface biogenic elements during the summer of 2008–2016 were analyzed by grids, to explore the spatial and temporal characteristics. Meanwhile the relationship with chlorophyll *a* (Chl-*a*) was further analyzed to discuss the impact of biogenic elements on phytoplankton community.

2 Materials and methods

2.1 Data sources

In this study, a square area (30.0°–31.9°N, 121.0°–122.9°E) was selected in the Changjiang River Estuary and adjacent waters (Fig. 1). A 9-year time series of surface seawater data in the summer (from June to August) of 2008–2016 were obtained from the Chinese National Marine Environmental Monitoring Program by different monitoring institutions. There were 995 samples in total, with an average of 111 samples per year. Stations were located irregularly in space, and were not all the same between years, but could basically cover all the study area.

Samples for the concentrations of nutrients (including NO_3^- , NH_4^+ , NO_2^- , PO_4^{3-} , SiO_3^{2-}) and Chl-*a* were taken to institutions qualified with China Inspection Body and Laboratory Mandatory Approval, and analyzed following the same methods of Chinese Marine Monitoring Specification (GB 17378–2007). NO_3^- and NO_2^- were determined by naphthalene ethylenediamine spectrophotometric method, and NH_4^+ was determined by indophenol blue spectrophotometric method. Dissolved inorganic nitrogen (DIN) was calculated by the sum of NO_3^- , NH_4^+ and NO_2^- . Soluble

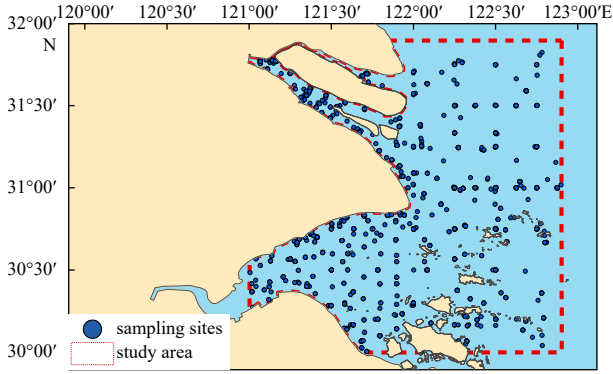


Fig. 1. Location of the Changjiang River Estuary and adjacent waters.

reactive PO_4^{3-} and SiO_3^{2-} were determined by phosphomolybdenum blue spectrophotometric method and silicon molybdenum blue spectrophotometric method, respectively. The concentration ratios of N/P and Si/N were calculated after converting to molar concentration of N, P and Si. Chl-*a* concentration was determined by the fluorescence method. Besides, different sources of data were further normalized and checked to sieve out suspicious data, so as to guarantee the accuracy (Lu et al., 2017; Xiang et al., 2018).

2.2 Data analysis

In this study, data were analyzed by $0.1^\circ \times 0.1^\circ$ grid using ArcGIS 10.3.1, considering different sites and numbers between years. The data were first preprocessed into grids, the value of each grid represented the average value of data inside.

The temporal trend of biogenic elements was quantitated by the linear regression method, and the slope was calculated to show the trend and changing extent. Positive values indicated an increasing trend, while negative values indicated a decreasing trend. The absolute values represented the changing extent, in which higher values indicated a greater change.

The relationship between biogenic elements and Chl-*a* was analyzed by the grey correlation analysis (Tosun, 2006), taking the following steps:

First, the original data were normalized by the mean method.

$$x_i(k) = \frac{X_i(k)}{\frac{1}{n} \sum_{k=1}^n X_i(k)}, \quad (1)$$

for the factors negatively related to Chl-*a* (i.e., DIN , PO_4^{3-} and SiO_3^{2-}), data were normalized otherwise as follows:

$$x_j(k) = \frac{\max(X_j(k)) - X_j(k)}{\frac{1}{n} \sum_{k=1}^n X_j(k)}, \quad (2)$$

where $x_i(k)$ and $x_j(k)$ are normalized, and $X_i(k)$ and $X_j(k)$ are original.

Secondly, the correlation coefficient $\varepsilon_{0i}(k)$ was calculated as follows:

$$\varepsilon_{0i}(k) = \frac{\Delta_{\min} + \rho \Delta_{\max}}{\Delta_{0i}(k) + \rho \Delta_{\max}}, \quad (3)$$

where $\Delta_{0i}(k) = |x_0(k) - x_i(k)|$, $x_0(k)$ denotes the reference se-

quence, and $x_i(k)$ denotes the comparability sequence. ρ is distinguishing or identification coefficient which is between 0 and 1 (taking 0.5). Δ_{\max} and Δ_{\min} are the maximum and minimum values of $\Delta_{0i}(k)$, respectively.

Finally, the grey correlation degree was calculated as the average value of the grey correlation coefficient, which was defined as follows:

$$r_i = \frac{1}{n} \sum_{k=1}^n \varepsilon_{0i}(k), \quad (4)$$

where r_i is the grey relational grade which represents the level of correlation between the reference sequence and the comparability sequence. If a particular comparability sequence is more important than the other comparability sequences to the reference sequence, then the grey correlation degree for that comparability sequence and reference sequence will be higher than others.

3 Results

3.1 Temporal change

The annual mean concentrations of DIN , PO_4^{3-} and SiO_3^{2-} during the summer of 2008–2016 ranged from 0.85 mg/L to 1.57 mg/L, 0.028 mg/L to 0.044 mg/L, and 1.40–1.87 mg/L (Fig. 2). The surface biogenic elements remained stable. While there was a slight decrease of DIN and PO_4^{3-} , and a slight increase of SiO_3^{2-} based on the linear regression method. The mean concentrations of DIN and PO_4^{3-} decreased by 0.019 mg/L and 0.001 mg/L per year, and that of SiO_3^{2-} increased 0.024 mg/L per year. The concentration ratios of N/P and Si/N were also analyzed. The annual mean N/P and Si/N during the summer of 2008–2016 ranged from 44.83 to 99.35 and 0.81 to 1.35, and the average values were 72.06 and 1.01, respectively. N/P far exceeded the Redfield ratio, while Si/N fluctuated around the Redfield ratio up and down (Redfield et al., 1963). No significant long-term trends were observed, while there was a slight increase for N/P, and a slight decrease for Si/N.

3.2 Spatiotemporal change

The spatiotemporal changes of biogenic elements are shown in Fig. 3. The concentrations of DIN , PO_4^{3-} and SiO_3^{2-} changed by -0.126 – -0.151 mg/(L·a), -0.019 – -0.004 mg/(L·a), -0.226 – -0.219 mg/(L·a). The concentrations of DIN decreased significantly in the Hangzhou Bay and PO_4^{3-} decreased in the Changjiang River Estuary. The concentrations of SiO_3^{2-} increased significantly both in the Changjiang River Estuary and Hangzhou Bay. N/P and Si/N changed by -47.93 – -43.59 and -0.66 – -3.46 per year. N/P mostly decreased in the Hangzhou Bay, due to the decrease of DIN and increase of PO_4^{3-} . While Si/N mostly increased in the Changjiang River Estuary and Hangzhou Bay, due to the increase of SiO_3^{2-} and the decrease of DIN .

3.3 Spatial distribution

The spatial distributions of biogenic elements in the study area are shown in Fig. 3. Concentrations of biogenic elements (DIN , PO_4^{3-} , SiO_3^{2-}) all showed a downward trend from near-shore waters to far-shore waters. Higher concentrations were found inside the Changjiang River Estuary, the Hangzhou Bay and their confluence area. The maximum concentrations of DIN and PO_4^{3-} occurred inside the Hangzhou Bay, while that of SiO_3^{2-} occurred inside the Changjiang River Estuary. The values of N/P and Si/N increased from near-shore waters to far-shore waters.

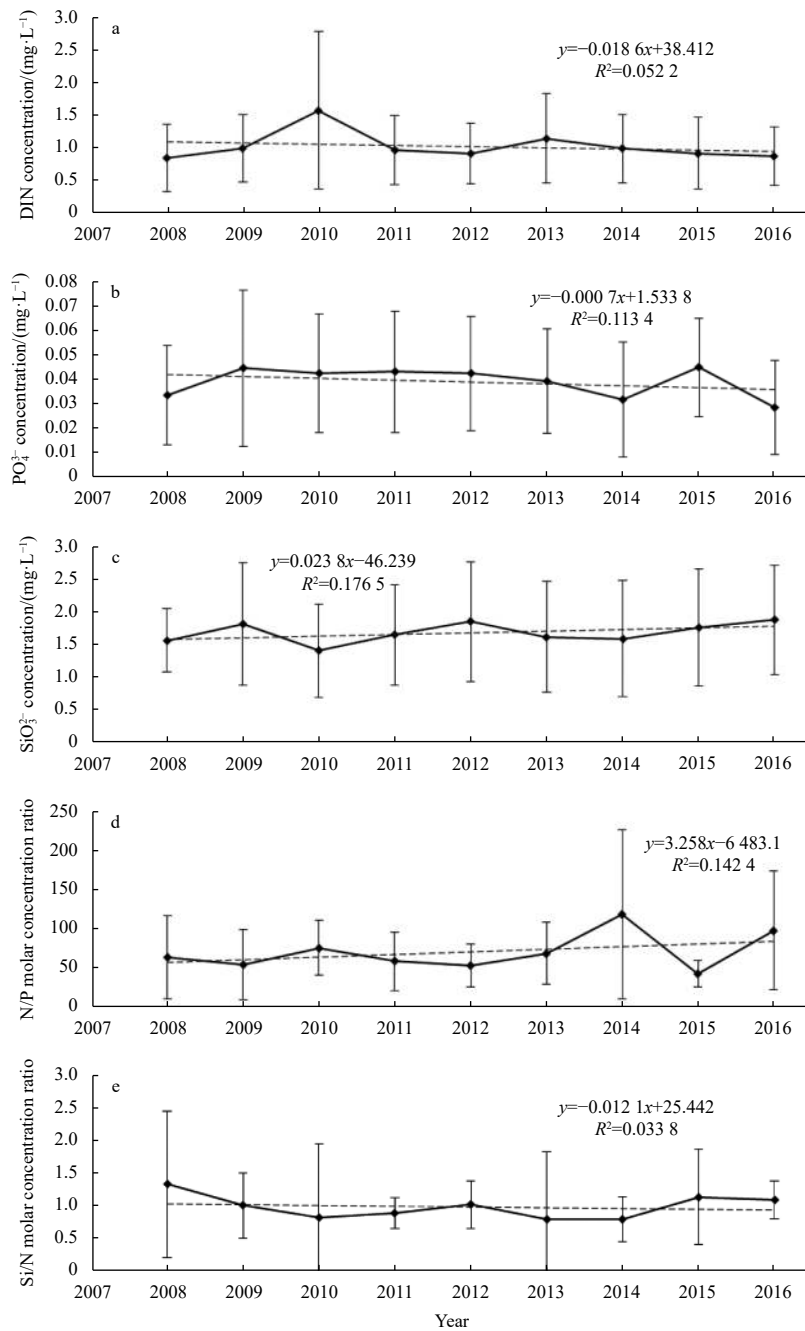


Fig. 2. Temporal changes of surface biogenic elements in the Changjiang River Estuary and adjacent waters during the summer of 2008–2016.

Their spatial distributions were quite similar, which higher values were located in the eastern far-shore waters of the study area, and lower values were located in the Hangzhou Bay.

3.4 The relationship between biogenic elements and Chl-*a*

In this study, concentrations of Chl-*a* were analyzed to study the relationship between Chl-*a* and biogenic elements. The spatial distribution of Chl-*a* was similar to those of N/P and Si/N (Figs 4 and 5). High-value areas were located in the far-shore waters on the eastern waters of Zhoushan Islands, while low-value areas were in the Changjiang River Estuary.

The grey correlation analysis was carried out among DIN, PO₄³⁻, SiO₃²⁻, N/P, Si/N and Chl-*a*. Results showed that the grey

correlation degrees were all above 0.5, showing a relatively high correlation between biogenic elements and Chl-*a* (Table 1). Among them, the degrees of N/P (0.924) and Si/N (0.922) were higher than those of DIN (0.744), PO₄³⁻ (0.566), SiO₃²⁻ (0.854).

4 Discussion

4.1 Temporal trends of biogenic elements

Since the 21st century, Chinese government has paid full attention on the ecological environment protection, and the total amounts of pollutants entering the river and the sea have been effectively controlled. Though the concentrations of DIN and PO₄³⁻ were still quite high compared with those before 1980s,

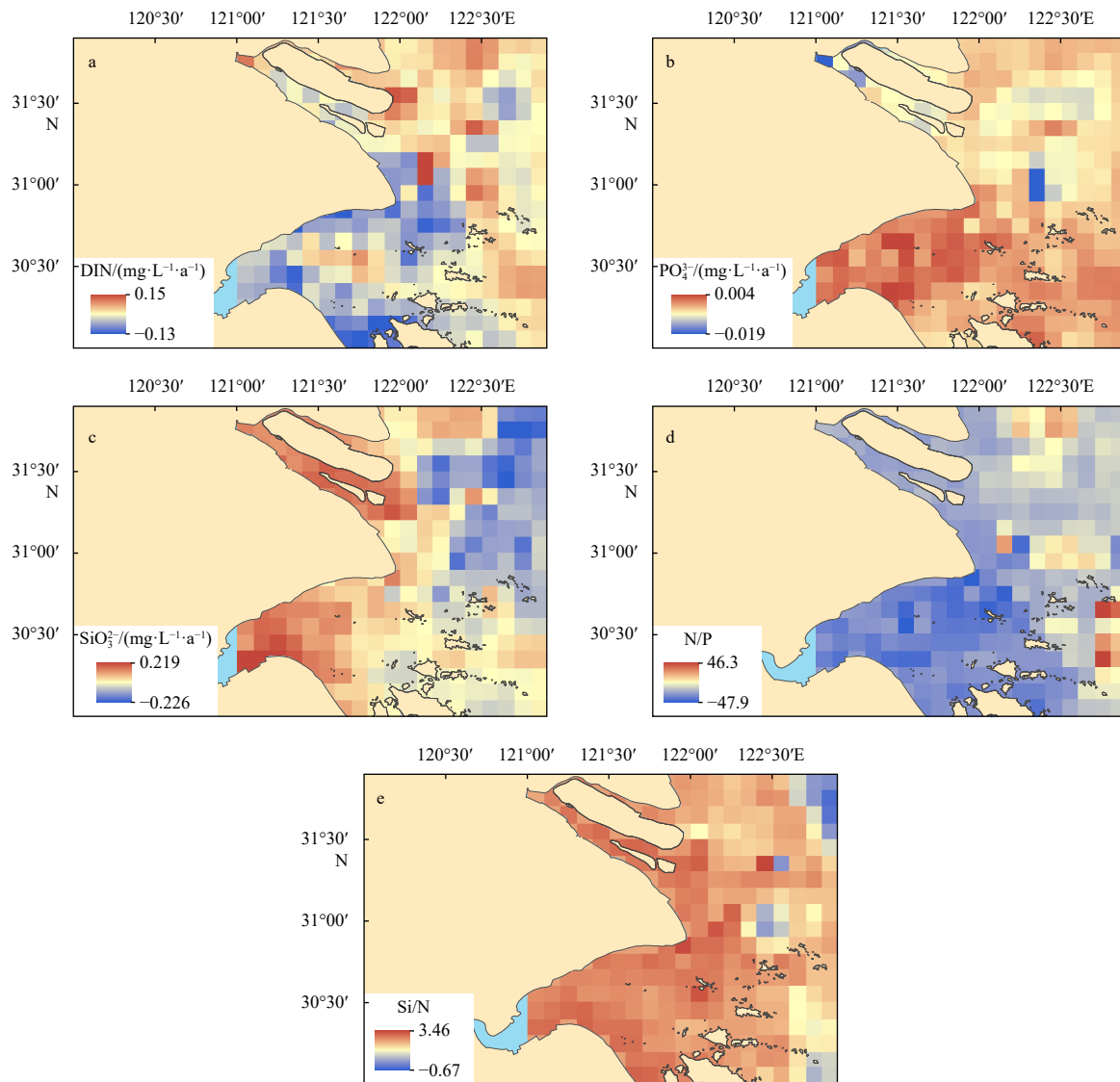


Fig. 3. Spatiotemporal changes of surface biogenic elements in the Changjiang River Estuary and adjacent waters by grids during the summer of 2008–2016. a. DIN concentration change; b. PO_4^{3-} concentration change; c. SiO_3^{2-} concentration change; d. N/P molar concentration ratio change; e. Si/N molar concentration ratio change.

they have gradually stabilized, and fluctuated within a narrow range (Zhou et al., 2006; Chen et al., 2011; Wang and Cao, 2012; Yang et al., 2015). In this study, similar conclusions were made, that the concentrations of DIN and PO_4^{3-} remained stable and showed a slight decrease (Figs 2a, b).

The concentration of SiO_3^{2-} decreased compared with the end of last century (1985–1986) and earlier in this century (2002–2003) (Wang and Cao, 2012; Yang et al., 2015). On one hand, it was related to the decrease of sand in the Changjiang River due to the water retention by Three Gorges Dam on the upper reaches of the Changjiang River. On the other hand, it was also due to more consumption of phytoplankton by severe eutrophication. But during 2008–2016, the concentration of SiO_3^{2-} stayed stable and turned to show a slight increase, which was consistent with former research (Yang et al., 2015). It was likely to be attributed to the alleviation of eutrophication.

Historical research found that N/P in the study area was seriously uncoordinated since the late 1980s (Zhou et al., 2006; Wang and Cao, 2012; Yang et al., 2015). It increased from 14 in 1959, to

the highest 580 in 1987 (Chen et al., 2011). By 2016, the average of N/P was still above 80, deviated significantly from the Redfield ratio (16). The uncoordination of N/P was mainly due to the excessively high concentrations of DIN (Wang et al., 2002; Yin et al., 2016). It may also relate to the decrease of sand and runoff of Changjiang River (Chen et al., 2011). The decrease of sand could cause the decrease of suspended materials in the Changjiang River, thus weakening the supplementation of N. Meantime, the decrease of runoff may result in the invasion of Taiwan Warm Current, strengthening the supplementation of P. Si/N showed the trend of decrease, attributed for the decrease of Si and the increase of N (Yang et al., 2015).

4.2 Spatial distributions of biogenic elements

The study area is mainly influenced by the eastern Taiwan Warm Current system and the western coastal current system (Sun, 2006). The concentrations of DIN, PO_4^{3-} and SiO_3^{2-} showed a downward trend from near-shore waters to far-shore waters (Fig. 4), indicating the important influence of coastal current sys-

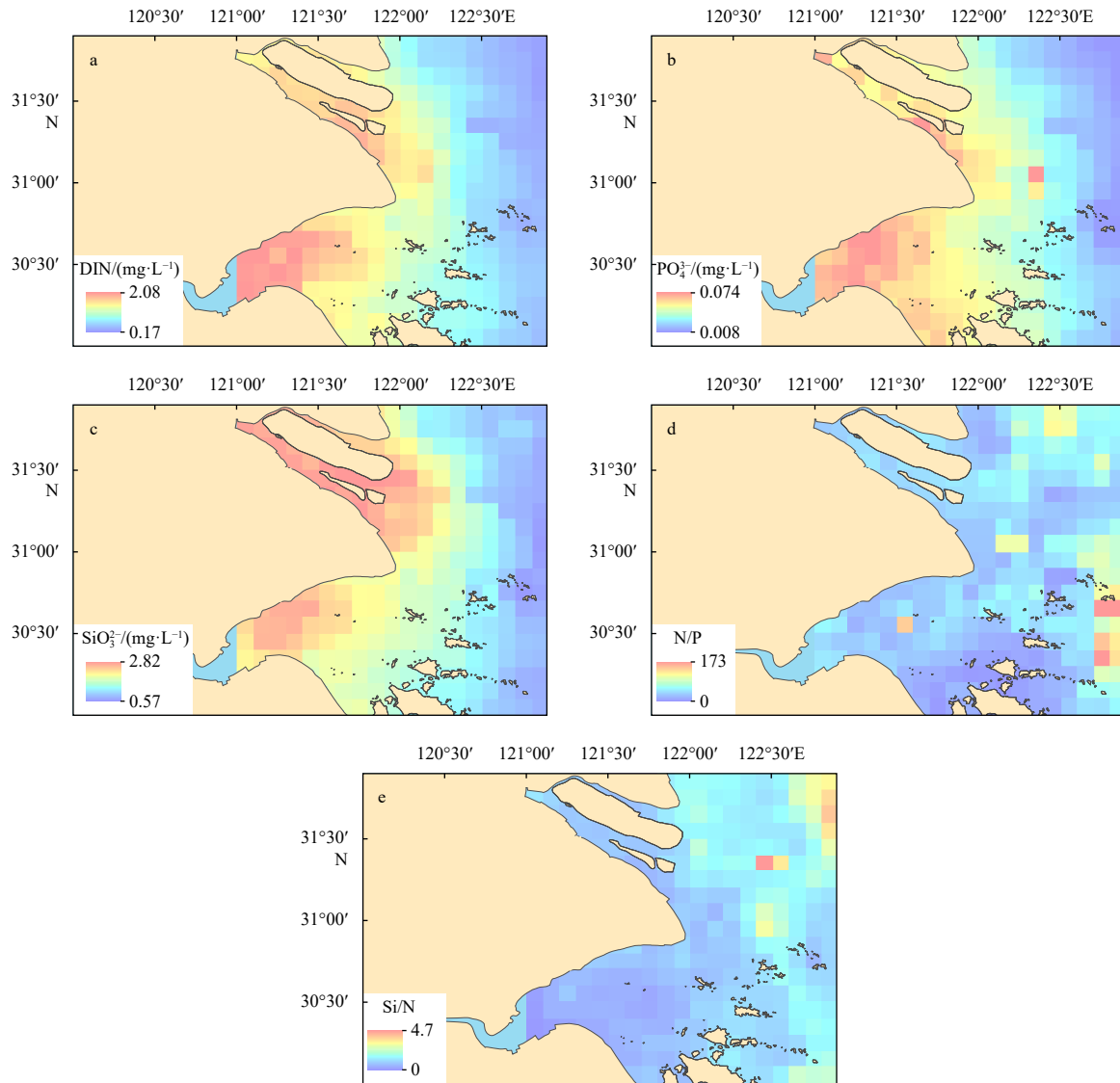


Fig. 4. Spatial distribution of surface biogenic elements in the Changjiang River Estuary and adjacent waters during the summer of 2008–2016. a. DIN concentration; b. PO_4^{3-} concentration; c. SiO_3^{2-} concentration; d. N/P molar concentration ratio; e. Si/N molar concentration ratio.

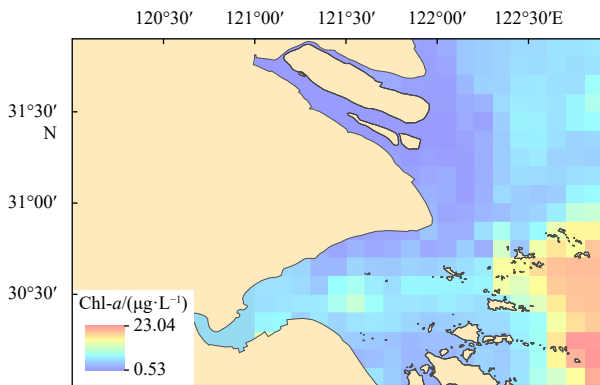


Fig. 5. Spatial distribution of surface chlorophyll *a* (Chl-*a*) in the Changjiang River Estuary and adjacent waters during the summer of 2008–2016.

Table 1. Correlation between biogenic elements and chlorophyll *a*

Factors	Grey correlation degree	Rank
DIN concentration	0.744	4
PO_4^{3-} concentration	0.566	5
SiO_3^{2-} concentration	0.854	3
N/P molar concentration ratio	0.924	1
Si/N molar concentration ratio	0.922	2

waters flowed out of the two rivers, met outside of the Changjiang River Estuary and west of Zhoushan Islands, and then gradually mixed into the East China Sea. The changes of biogenic elements were analyzed in two sections of the Changjiang River Estuary (31.55°N) and Hangzhou Bay (30.55°N) (Fig. 6). Results showed that the biogenic elements behaved conservatively in the Changjiang River Estuary, but not in the Hangzhou Bay. Concentrations of biogenic elements (DIN , PO_4^{3-} , SiO_3^{2-}) remained stable inside the Changjiang River Estuary and then decreased linearly in the East China Sea. A slight decrease of PO_4^{3-} could be seen,

tem, especially the diluted water of Changjiang River and Qiantang River (Chen et al., 2010; Gao et al., 2011). Two streams of

perhaps because parts of P were sequestered in sediments of the Changjiang River Estuary (Yang et al., 2015). While concentrations of biogenic elements inside the Hangzhou Bay fluctuated, due to the open trumpet-shaped topography (Gao et al., 2011). The concentrations generally decreased inside the estuaries as the space being larger, and the slope was a little smaller than that outside the estuary. While there was a slight increase of PO_4^{3-} from the river up halfway the estuary, likely due to other sources of PO_4^{3-} , such as anthropogenic input, organic matter regeneration (Chen et al., 2010).

4.3 Relationship between biogenic elements and Chl-*a*

The distributions of N/P, Si/N and Chl-*a* all showed similar patterns, which increased from near-shore waters to far-shore waters. Through the grey correlation analysis, we also found that N/P and Si/N had a closer correlation with Chl-*a*, compared with DIN, PO_4^{3-} and SiO_3^{2-} . Sharp (2003) pointed out that the ratio of nutrients and certain physical conditions were more important to the regulation of eutrophication in the estuary than single nutrient concentration.

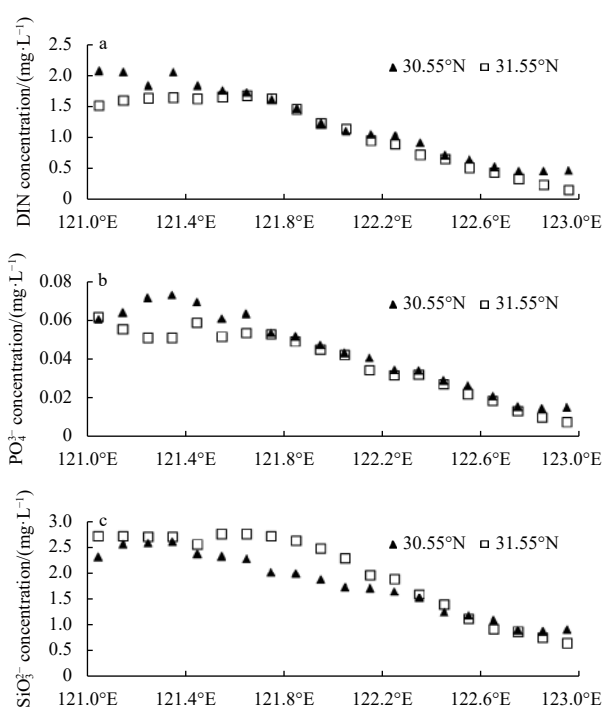


Fig. 6. Changes of surface biogenic elements along the longitude of the Changjiang River Estuary and adjacent waters during the summer of 2008–2016.

In the study area, N/P far exceeded the Redfield ratio, and Si/N fluctuated between the upper and lower Redfield ratios. It was generally believed that potential P limitation occurred when $\text{N/P} > 22$ and $\text{Si/P} > 22$, potential N limitation occurred when $\text{N/P} < 10$ and $\text{Si/P} > 1$, and potential Si limitation occurred when $\text{Si/N} < 1$ and $\text{Si/P} < 10$ (Justić et al., 1995). Accordingly, the study area was generally in a state of potential P limitation (Table 2) (Wang et al., 2013; Ye et al., 2015), especially on the southeast side of study area with N/P above 100 and Si/P above 50. As this area is where the famous Zhoushan fishing ground is located, plankton is distributed in large quantities, resulting in excessive consumption of P in the area, and N/P was much higher than the input area of biogenic elements in the Changjiang River Estuary and Hangzhou Bay. The spatial distribution of Chl-*a* (Fig. 5) also confirmed this. Phosphorus transported to the far-shore waters was greatly absorbed and utilized by phytoplankton, causing potential P limitation in this area (Gao et al., 2004; Wang and Cao, 2012; Wang et al., 2016).

The variations of biogenic elements could result in the variations of phytoplankton bloom dynamics. The study area has always been high-incidence areas of red tides in China. During 2008–2016, 5.8 red tide events were recorded annually, of which the most was 12 times in 2008, and the least was 2 times in 2011 (State Oceanic Administration, 2008–2016) (Fig. 7). Many studies have pointed out that the imbalance of regional biogenic elements was one of the important reasons for severe eutrophication and frequent occurrence of red tides (Gao et al., 2004). Judging from the dominant red tide species, 4 out of 5 red tide events in 2010 were caused by diatoms and only one was caused by dinoflagellates, while in 2016, 4 out of 7 red tide events were caused by dinoflagellates and only 2 were diatoms. The total amount of dinoflagellates red tide has exceeded 50% in 9 a. Studies found that the species of dinoflagellates in the phytoplankton community in the Changjiang River Estuary increased significantly compared with diatoms (Jiang et al., 2014; Lin and Li, 2017).

Table 2. Biogenic elements limitation in the Changjiang River Estuary and adjacent areas

Year	N limitation	P limitation	Si limitation
2008	0.3%	98.0%	0.6%
2009	0.8%	93.8%	2.0%
2010	0	86.3%	0
2011	0	99.2%	0
2012	0	96.9%	0
2013	0.3%	97.8%	0.3%
2014	0	99.7%	0
2015	0.3%	91.9%	0.3%
2016	0	99.2%	0

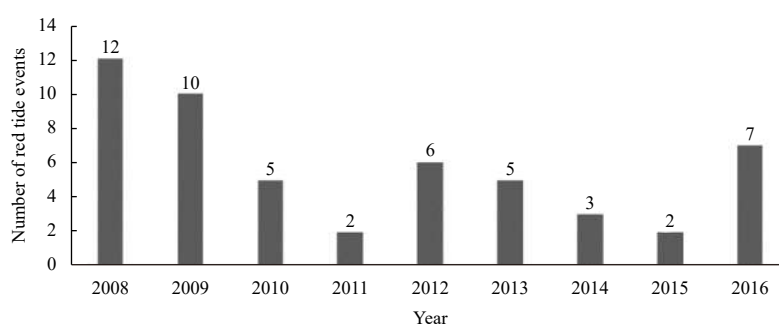


Fig. 7. Red tide events in the Changjiang River Estuary and adjacent waters from 2008 to 2016.

In general, diatoms are the dominant species due to their rapid growth and strong competitiveness when the biogenic elements are sufficient; dinoflagellates are more likely to be the dominant species under P-limited conditions (Örnólfssdóttir et al., 2004; Liang et al., 2016; Xiao et al., 2018). When P is depleted in the environment and N is still relatively sufficient, the dinoflagellates can adapt to the environment with lower biogenic elements content thus blooming in large quantities, and triggering the succession of dominant red tide species (Wang and Cao, 2012; Li et al., 2015).

5 Conclusions

This paper analyzes the spatiotemporal changes of surface biogenic elements in the Changjiang River Estuary and adjacent waters during the summer of 2008–2016, and main conclusions are as follows:

During the summer of 2008–2016, the surface biogenic elements in the study area were generally stable. The concentrations of DIN and PO_4^{3-} remained stable at a relatively high level, but showed a slight decrease, and concentrations of SiO_3^{2-} showing a slight increase. In the estuarine waters did the concentrations of DIN and PO_4^{3-} decrease significantly, and those of SiO_3^{2-} increase significantly.

Concentrations of biogenic elements (DIN, PO_4^{3-} , SiO_3^{2-}) showed a downward trend from near-shore waters to far-shore waters, indicating the important influence of coastal current system, especially the diluted water of Changjiang River and Qiantang River. Moreover the Changjiang River had a greater influence on the transportation of biogenic elements in the study area.

The biogenic elements behaved conservatively in the Changjiang River Estuary, and nonconservatively in the Hangzhou Bay. Concentrations of biogenic elements (DIN, PO_4^{3-} , SiO_3^{2-}) remained stable inside the Changjiang River Estuary, but generally decreased inside the Hangzhou Bay due to its open trumpet-shaped topography.

The distributions of N/P, Si/N and Chl-*a* all showed similar patterns, which increased from near-shore waters to far-shore waters. Compared with the absolute values of biogenic elements, the correlation between the structure of biogenic elements and Chl-*a* was closer, indicating the important influence of phytoplankton on the structure of biogenic elements in the study area.

N/P far exceeded the Redfield ratio, while Si/N fluctuated around the Redfield ratio. The study area was generally in a state of potential P limitation, and could have potential impact on the phytoplankton community, triggering the shift of red tide dominant species from diatoms to dinoflagellates.

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