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Long-term changes in nutrients, chlorophyll *a* and their relationships in a semi-enclosed eutrophic ecosystem, Bohai Bay, China

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A B S T R A C T

As the representative semi-enclosed bay of China, Bohai Bay has experienced severe eutrophication in recent decades. Monitoring data from 1995 to 2013 were analysed by generalized additive models (GAMs) to explore the temporal variations in nutrients concentrations, nutrient ratios, chlorophyll *a* (Chl *a*) concentrations and the responses of Chl *a* to the changes in nutrients in the spring and summer. The results showed that dissolved inorganic nitrogen (DIN) decreased from 1995 to 2000 but increased after 2000 in both the spring and summer, and soluble reactive phosphorus (SRP) decreased while the molar nitrogen/phosphorus (N/P) ratios (DIN to SRP) increased over the last two decades. Generally, P-limited phytoplankton growth was observed in the spring and summer and DIN was identified as the main pollutant constituent in Bohai Bay. Furthermore, negative correlations were found between DIN and Chl *a* in summer in Bohai Bay.

1. Introduction

While undergoing urbanization and industrialization, coastal areas can become pollutant collection zones, resulting in environmental change that threaten to the ecosystem sustainability (Lim et al., 2012) and the eutrophication of coastal waters is recognized as one of the most common impacts of human activities and coastal development (Cloern, 2001; Cole et al., 2006; Nishikawa et al., 2010). Inorganic pollutants in seawater result from the decomposition of agricultural organic pollutants, which are due to the excess use of nutrients during cultivation (Carroll et al., 2003; Ferreira et al., 2014; Holmer et al., 2002; Hu et al., 2013; Maroni, 2000). Nutrients can stimulate phytoplankton blooms and impact the phytoplankton community, as individuals die, they sink, decompose and enhance the biological oxygen demand in deeper waters (Diaz and Rosenberg, 2008; Smith et al., 2001). These anthropogenic nutrient inputs can also alter nutrient ratios (Justić et al., 1995; Turner, 2002), impacting higher trophic levels (Philippart et al., 2000; Smith, 1983; Turner, 2002; Turner et al., 1998) and causing considerable damage to coastal ecosystems (Smith and Schindler, 2009), and these effects spread through the food chain (Rissik et al., 2009). It is generally believed that marine phytoplankton dynamics system are either regulated by biological mechanisms that are limited by the nutrients required for related physical and chemical processes (bottom-up control) or biological and nutrient interactions (top-down control), the relationships between consumers and resources are controlled by top-down or bottom-up forces (Hulot et al., 2014; Jaschinski and Sommer, 2008; Lotze et al., 2001; Reid et al., 2000; Smith and Lancelot, 2004; Verity et al., 2002; Ward et al., 2014).

Anthropogenic actions have an significant effect on the semi-enclosed bays, one of the most important coastal ecosystems over the last decades (Caddy, 2000; Peng et al., 2012; Shi and Wang, 2011). Bohai Bay, which is situated in the western Bohai Sea of northern China and is a typical semi-enclosed bay. Approximately 1 billion tons of wastewater are discharged into the bay every year from the surrounding areas (Duan et al., 2010) and increases in port construction, the chemical and shipbuilding industries, and aquaculture development have accompanied the urbanization of the Tianjin coastal area over the last two decades. Seawater quality has deteriorated rapidly in recent years according to the China Ocean Environmental Quality Bulletin (http://www.soa.gov.cn). Nitrogen and phosphate are considered the primary pollutants, and increases in their levels will lead to eutrophication and more and more frequent algal blooms in Bohai Bay.

The plankton community in Bohai Bay has been radically damaged in recent decades. Most studies of Bohai Bay have focused on short-term survey data (Bai et al., 2012; Cai et al., 2014; Duan et al., 2010; Huang et al., 2013; Peng, 2015; Peng et al., 2012), and phytoplankton-nutrient interactions are rarely addressed (Qin et al., 2005; Sun et al., 2003; Yang et al., 2012). Additionally, the effects of human interference (including pollutant control measures) can only be explained by long-term data. The objectives of this study are understanding the present status of eutrophication due to anthropogenic activities and the relationship

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between the phytoplankton population and nutrient levels in Bohai Bay. The results of this study provide the basis for predicting red tide outbreaks.

2. Materials and methods

2.1. Study area and data sourcing

Tianjin city is situated in the western part of Bohai Bay in China, and the study area was the Tianjin coastal zone (117°37′E–118°05′E, 38°20′N–39°11′N) (Fig. 1). The data were obtained from the Tianjin Marine Environment Monitoring Center of the State Oceanic Administration of the People's Republic of China which measured and analysed the concentrations of nutrients, such as ammonium, nitrite, nitrate nitrogen and SRP, in a long time series spanning from 1995 to 2013 in the spring and 1995 to 2012 in the summer, although data were missing in some years (the spring of 1999, 2001, 2004, 2008, 2010 and the summer of 1998, 2008, and 2010). In addition, except for the spring of the years 2012 and the summer of 2004, the chlorophyll *a* (Chl *a*) were analysed beginning in 2002. The sampling sites of each survey were generally uniformly distributed within the study area with different amounts because of the gradually improved monitoring system. The sampling and measurements followed standard methods (GB3097, 1997).

2.2. Statistical analysis

The long-term trends and relationships between the Chl *a* concentrations and various environmental, nutrient and physical parameters were explored with generalized additive models (GAMs). GAMs can predict nonlinear relationships as a flexible regression technique that by using nonparametric smoothers (Wood, 2010), and GAMs are suitable for describing complex ecological interactions because they do not require the function to be specified.

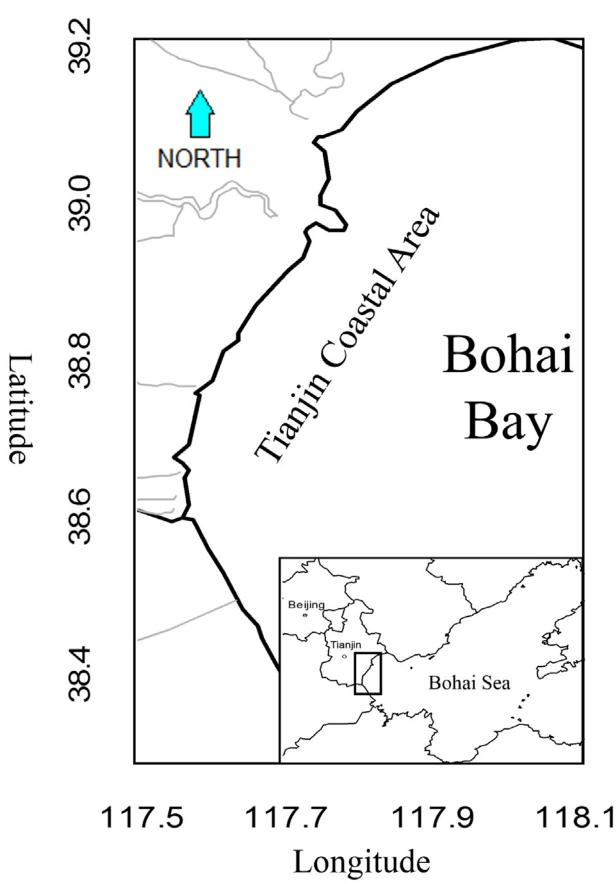

Fig. 1. Map showing the study area that Tianjin coastal area of Bohai Bay.

Linear correlations between environmental factors and species characteristics never occur in ecological research, so the normality assumption is often violated by several variables. Therefore, GAMs are often-applied and useful in ecological studies (Salmaso et al., 2012; Tao et al., 2012).

The general formula of a GAM is:

$$g(\mu_i) = \beta + \sum_{j=1}^{p} f_j(X_i) + \varepsilon_i \quad (1)$$

where the function $g(\mu_i)$ relates the response variable to the given explanatory variables, and the term β is recognized as any strictly parametric component in the model, such as the intercept. The components $f_j(X_i)$ are designated as the variable explained by the nonparametric smoothing function, and ε_i is identically and independently distributed as a normal random variable (Wood, 2010, 2012).

In this study, nutrient concentrations, nutrient ratios and phytoplankton biomass over time were modelled using a GAM.

$$\text{NutConc.} = \beta + f_1(\text{Year}) + \varepsilon \quad (2)$$

A GAM was utilized to identify the responses of phytoplankton to the various concentrations of DIN and SRP. DIN, SRP, and Chl *a* concentrations were computed from the model after normalizing the concentrations by log transformation.

$$\log(\text{Chl } a) = \beta + f_1(\log(DIN)) + f_2(\log(\text{SRP})) + \varepsilon \quad (3)$$

Nonlinear time-series data were fitted by a generalized additive model (GAM) using the package of "mgcv" in R 3.1.1 (R Development Core Team, 2014) (Wood, 2004; Wood, 2012; Wood and Augustin, 2002). The GAM procedure automatically selects the smoothing parameters that reflect the degree of linearity of the curve on account of the generalized cross-validation (GCV) score. From the results of the model, we obtained fitted values, residuals, model R^2, *p* values for the F-statistics and % deviance explained (DE).

3. Results and discussion

3.1. The variations in nutrient and chlorophyll a concentrations

Table 1 shows the average values and ranges of dissolved nutrients concentrations. In springs, the DIN (nitrite + nitrate + ammonia) concentrations varied from 0.156 to 0.641 mg/L in 2000 and 2012, respectively, and the SRP concentrations varied from 0.0068 mg/L in 2007 to 205.48 mg/L in 1997. In summer, the highest annual average DIN and SRP concentrations (1.045 and 0.0417 mg/L, respectively) occurred in 1995, while the lowest values of 0.139 and 0.0049 mg/L occurred in 2003. The molar nitrogen/phosphorus (N/P) ratios varied from 7.45 to 136.88 in the summer and from 13.33 to 205.48 in the spring, and the results indicated that Chl *a* in the spring varied from 2.38 to 13.01 μg/L in 2013 and 2007, respectively. The highest and lowest average Chl *a* values in the summer occurred in 2012 (14.01 μg/L) and 2007 (3.31 μg/L), respectively. The variations in nutrient concentrations were analysed to assess the degree of eutrophication (Fig. 2), and from 1995 to 2013, most of the DIN concentrations in the spring ranged from 0.1 to 0.6 mg/L (Fig. 2a) which were lower than the summer DIN concentrations, from 0.1 to 1.0 mg/L (Fig. 2b). Most of the spring SRP concentrations from 1995 to 2013 were lower than 0.05 mg/L, except for 1997 (Fig. 2c and d), and the average molar N/P ratios from 1995 to 2013 ranged from 10.0 to 350.0 (Fig. 2e and f). The range in Chl *a* in the spring was similar to the summer during the study period, with values below 25 μg/L. The DIN and SRP concentrations were much higher than those of the Eastern Seto Inland Sea observed by