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Nutrient distribution and structure affect the acidification of eutrophic ocean margins: A case study in southwestern coast of the Laizhou Bay, China

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ABSTRACT

The effects of nutrient distribution and structure on the acidity of coastal waters were analyzed based on the data of 48 surface water samples collected in the southwestern coast of the Laizhou Bay and its adjacent rivers (SWLZB) which are heavily influenced by nutrient-laden discharges. The concentration and structure of nutrients varied considerably along the coast owing to different contributors. The studied inshore waters exhibited a sign of acidification. The pH was significantly negatively correlated with the concentration of NO_3-N, NO_2-N, NH_4-N and DSi, but showed no obvious correlation with the concentration of PO_4-P and the ratio of TDN/TDP, DSi/DIN and DSi/PO_4-P, respectively. The results indicated that the distribution of nutrients might well be an important environmental factor affecting the acidification of the SWLZB in warmer months.

1. Introduction

It is well-known that nutrient over-enrichment is a major environmental problem in many coastal areas around the world (Cloern, 2001; Seitzinger et al., 2005; Song, 2011). Coastal areas are regions with high population density and intense human activities, accounting for ~30% of the total net oceanic primary production (Alongi, 1998; Gattuso et al., 1998; Dürr et al., 2011; Song, 2011). Large amounts of nutrients have been transported from land to coastal areas by rivers in the past decades due to the rapid increase of human activities, resulting in environmental deterioration and biogeochemical process variation (Seitzinger et al., 2005; Halpern et al., 2008; Qu and Kroeze, 2010). The concentration and composition of nutrients could not only affect the biomass and composition of phytoplankton but also cause large-scale algal bloom when there is too much of them (Gao and Song, 2005; Song, 2011; Smetacek and Zingone, 2013; Xing et al., 2015). Benefiting from the nutrient enrichment, many microbial species are flourishing in eutrophic coastal seas, and their respiration could release much CO_2 which may lower the seawater pH in these areas (Cai et al., 2011; Wallace et al., 2014). In addition, some nutrients may exist in the form of acid or weak base, for instance, N may exist as HNO_3 or NH_3 in some particular situations, which may affect the acidity of seawaters directly. Ocean acidification (OA) induced by human activities, especially in coastal regions, has aroused great concern in recent years (Caldeira and Wickett, 2003; Canadell et al., 2007; Quéré et al., 2013). From the preindustrial period to the 1990s, the mean pH of global surface oceans had decreased from approximately 8.2 to 8.1, corresponding to a 26% increase in the acidity of the oceans as measured by the concentration of hydrogen ion (Gattuso and Hansson, 2011). With few exceptions, this change exceeded that in any period in the last 300 million years, and is projected to continue to influence the world oceans of greater depths progressively (Caldeira and Wickett, 2003). The majorities of marine bios reside in the surface ocean and are exposed to this progressive increase of seawater acidity. Microbes collectively support marine food webs, and the activities of biota influence the composition of dissolved chemicals and particulate organic materials and moderate the exchange of nutrient elements such as carbon, nitrogen, phosphorous between the ocean waters (Cooley et al., 2009), and all these processes are subject to OA. Although OA and nutrients in coastal waters have intimate interactions, at present there is little research concerning the effects of nutrient distribution and structure on OA.

The effects of nutrient distribution and structure on OA may be evidenced in waters of the southwestern coast of the Laizhou Bay (SWLZB). There are ten rivers (Yihonghe River, Guanglihe River, Zhimaihe River, Xiaoqinghe River, Mihe River, Yuhe River, Bailanghe River, Dihe River, Weihe River, and Jiaolaihe River) flowing into the Laizhou Bay from its southwestern coast, most of which are small and seasonal. Due to abundant seawater resources and underground brine resources, a chemical industrial base called the Weifang Binhai Economic Development Zone is located along its southwestern coast. Over 400 chemical enterprises are located nearby and >150 kinds of chemical products are

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manufactured in this area. Thus, large quantities of CO_2, SO_2 and NO_2 were produced in these chemical industrial activities (Qin, 2010), which may affect the acidity of the coastal waters of the SWLZB. In addition, the river waters carry large amounts of nutrients derived from many point sources such as industrial effluents and agricultural runoff, non-purified or insufficiently purified wastewaters discharged into the inshore waters of this area (SOA, 2009; SOA, 2012). Therefore, the aquatic environment of the SWLZB is in a eutrophic state (Zhang et al., 2015). Different rivers have different nutrient concentration and composition which may change the concentration and structure of nutrients in the inshore waters along the coast. Such a condition in the SWLZB provided the opportunities for the analysis of the interactions between nutrients and OA.

This study tried to determine the concentrations of total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), ammonium nitrogen (NH_4-N), dissolved organic nitrogen (DON), total dissolved phosphorus (TDP), reactive phosphorus (orthophosphate-P; PO_4-P), dissolved organic phosphorus (DOP), and dissolved silicate (DSi) in the surface waters of the SWLZB and the pH in the same sites with a purpose of attempting to analyze the interactions between the distribution or structure of nutrients and OA.

2. Materials and methods

2.1. Sample collection

The research was carried out during 23 September to 1 October 2012, which is after the peak period of the rainy season. The sampling stations were arranged in the flowing direction of the major rivers in this area covering about 15–20 km from the high tide mark to the land and about 10 km from the high tide mark to the sea, and keeping about 2–3 km from each other (Fig. 1). The river stations arranged in ten rivers of the SWLZB coast, which are Yihonghe River (YHH), Guanglihe River (GLH), Zhimaihe River (ZMH), Xiaoqinghe River (XQH), Mihe River (MH), Yuhe River (YH), Bailanghe River (BLH), Dihe River (DH), Weihe River (WH), and Jiaolaihe River (JLH). The sampling sites in the inshore waters formed five transects, here named as L-transect (sites L1, L2, L3, L4 and L5), K-transect (sites K1, K2 and K3), J-transect (sites J1, J2, J3 and J4), I-transect (sites I1, I2 and I3) and H-transect (sites H1, H2 and H3). A total of 48 water samples were collected from the surface (depth of ~0.5 m) using well cleaned polyethylene bottles (pre-conditioned for 24 h in 1:10 nitrate acid solution and rinsed well with 18.2 MΩ-cm deionized water). The samples were stored in a cooler box with ice bags, and then refrigerated at 4 °C within 12 h until further analysis. All the samples were filtered with cellulose acetate membrane filters (Whatman®, 0.45 μm) before nutrient determination.

2.2. Analytical methods

TDN, NO_3-N, NO_2-N, NH_4-N, TDP, PO_4-P and DSi were measured using continuous flow analyzer (SEAL AutoAnalyzer 3, German). The analytical precision for TDN, NO_3-N, NO_2-N, NH_4-N, TDP, PO_4-P and DSi was assessed by multiple analysis of standards and replicates. The precision of the analyses of standard solution was better than 5%, which was consistent with the previous report of Liu et al. (2011); all analyses of the samples were carried out in duplicate and the relative standard deviations were $<10\%$, and the results were expressed as the means. The concentrations of dissolved inorganic nitrogen (DIN) were the sum of NO_3-N, NO_2-N and NH_4-N. The concentrations of dissolved organic nitrogen (DON) and phosphorus (DOP) were estimated by the subtractions of DIN from TDN and PO_4-P from TDP, respectively.

The pH values were determined in situ using a portable Orion Star-A combined instrument equipped with an Orion® 8107UWMMD Ross combination electrode (Thermo Scientific, Singapore) for the precision of pH analysis. The pH buffers adopted were three NIST (National Institute of Standards and Technology, the US Department of Commerce)-traceable pH buffers. According to the results of Zhai et al. (2012), in the Bohai Sea, the pH values on the total-hydrogen-ion scale (pH_T) were lower than the NIST-traceable pH values by 0.143 ± 0.006 pH units (mean ± standard deviation, $n = 73$). Based on this result, we transferred the NIST-traceable pH data to the total-hydrogen-ion scale (pH_T).

2.3. Statistical analysis

All data were tested for normality with the Shapiro–Wilk test before analysis. The Spearman correlation-coefficient was used to analyze the relationship between pH_T and nutrient concentrations or ratios. In this research, a value of $P < 0.05$ was considered to indicate a significant difference in all statistical analysis. Multiple regression analysis was used to estimate the coefficients of the linear equation, based on which the value of the dependent variable could be well predicted. The analyses were performed through the Origin statistical package version 7.0.

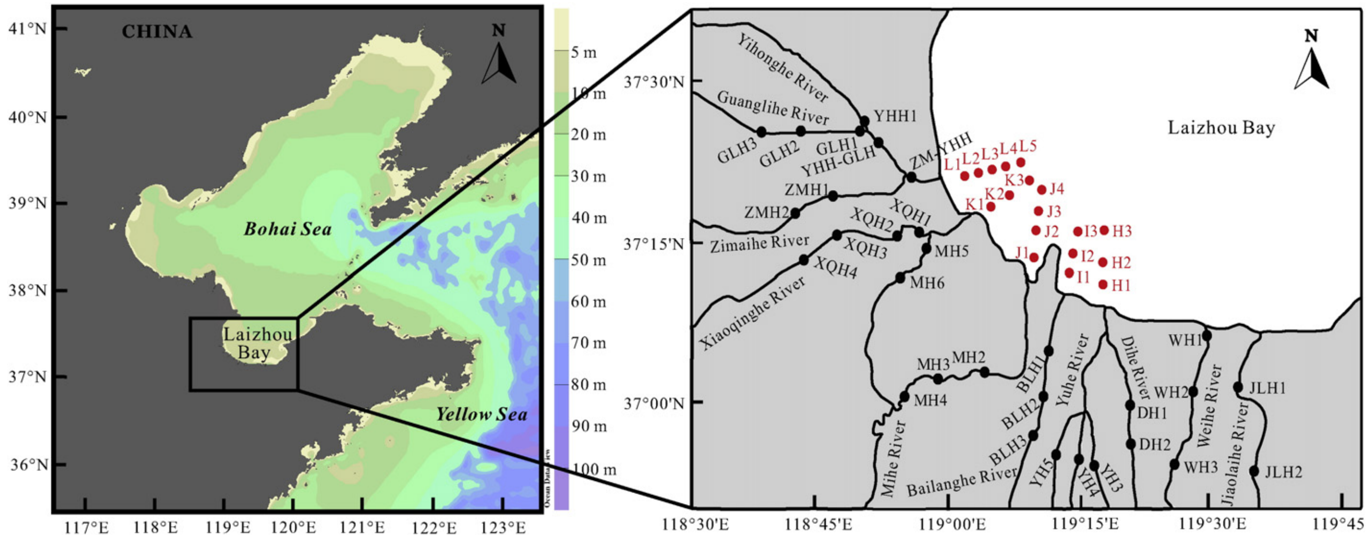

Fig. 1. Location of sampling stations in the coastal waters of the SWLZB. The marine sampling stations were shown in red dots and the riverine ones were shown in black.