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Distribution, partitioning and sources of dissolved and particulate nitrogen and phosphorus in the north Yellow Sea

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ABSTRACT

Little is known about characteristics of dissolved and particulate N and P forms in the north Yellow Sea (NYS). In this study, water and particulate samples were collected from the NYS to understand the biogeochemical behaviors, interactions and sources of dissolved and particulate N and P. Among the various N and P forms, dissolved organic N (DON) and P (DOP) were the predominant forms, accounting for 64% and 65% of total N (TN) and P (TP). Dissolved and particulate inorganic N and P displayed a decreasing trend from northwest region to the middle region, which was mainly influenced by riverine input along the Liaodong Peninsula coast. However, dissolved and particulate organic N and P showed higher values at northwest region and southern region, which were dominantly affected by biological activities and the Bohai Sea input. Vertical distribution patterns of dissolved and particulate N and P generally displayed the higher values at surface and bottom waters, which was the combined result of the influences by thermocline, the Yellow Sea Cold Water Mass (YC), biological activities and sediment resuspension. There were significant correlations between dissolved and particulate pools and between inorganic and organic forms, indicating their transformations through phytoplankton and bacteria activities and adsorption/desorption processes. Budgets suggested that net sink of dissolved inorganic N and P in the NYS could be mainly removed from water column. Particulate N and P were mainly from phytoplankton productivity, contributing to 84% and 74% of total particulate N (TPN) and P (TPP) influx.

1. Introduction

Nitrogen (N) and phosphorus (P) as major bioactive elements, play an essential role in the biological productivities, ecosystem functions and biogeochemical processes in marine environments (Lin et al., 2012; Loh and Bauer, 2000). In some marine ecosystems, elevated N and P inputs to aquatic environment will increase the eutrophication risk on water quality (Yu et al., 2012; Zhou et al., 2008), contrarily, the absent N and P will limit algal growth (Worsfold et al., 2008). In aquatic environments, N and P exist in both dissolved and particulate pools, each of which contains organic and inorganic forms (Loh and Bauer, 2000; Suzuki et al., 2015; Yoshimura et al., 2007).

Dissolved N and P are essential nutrients for the growth of marine primary and secondary producers (Burford et al., 2008; Carpenter and Dunham, 1985; Vegter and De Visscher, 1987). Total dissolved N (TDN) and P (TDP) occur in both dissolved inorganic N (DIN) and P (DIP) and dissolved organic N (DON) and P (DOP) (Lin et al., 2012; Loh and Bauer, 2000; Shi et al., 2015). Among them, DIN, in the form of nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+), is thought to be the major bioavailable form of N. DON mainly contains protein, free amino acids, amides, vitamin and urea (Berman and Bronk, 2003). A large fraction of DON is now known to be bioavailable and provides the majority of N requirements in certain oligotrophic systems (Doval et al., 1999; Worsfold et al., 2008; Moschonas et al., 2015). The DIP pool consists of orthophosphate (PO_4^{3-}), pyrophosphate (pyroP) and polyphosphate (polyP), in which PO_4^{3-} is the dominant form and has high reactivity and can be utilized easily by phytoplankton whereas pyroP and polyP can not be absorbed easily by some phytoplankton species (Diaz et al., 2016). DOP comprises a major fraction of dissolved P

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(Karl and Björkman, 2002) and may be utilized by marine photoautotrophs as well as by microheterotrophs (Björkman and Karl, 1994; Loh and Bauer, 2000; Orrett and Karl, 1987).

Particulate N and P, accounting for a large proportion of total N and P, are essential factors in nutrient loading and act as potential sources of dissolved nutrients in the coastal waters (Shen et al., 2008; Yu et al., 2012; Zhang et al., 2003). Total particulate N (TPN) and P (TPP) also exist in inorganic N (PIN) and P (PIP), and organic N (PON) and P (POP) forms (Labry et al., 2013; Yu et al., 2012). PIN is mainly from riverine input and marine source, such as biological debris (Yu et al., 2012). Besides, the fine suspended particles can also adsorb some forms of dissolved nitrogen and become absorbed nitrogen. At present, the study on the PIN determination method is less and mainly based on the extraction method of PIP. This method has been used to extract PIN in the East China Sea (Yu et al., 2012). PON consists of organic nitrogen debris, bacteria and phytoplankton composition, which can be readily recycled by mineralization, especially in maximum turbidity zones of estuaries (Abril et al., 2000). PIP occurs in mineral phases (i.e., orthophosphate, pyrophosphate and polyphosphate), which can be adsorbed to biotic and abiotic particles and as intracellular storage products (Yoshimura et al., 2007). POP comprises P incorporated in living and detrital organic molecules such as phosphomonoesters and diesters, phosphonates, and nucleotides (Labry et al., 2013). Dissolved and particulate organic N and P have been shown to be a significant component (~40%) of the total dissolved and particulate pools (Boynton et al., 1995; Loh and Bauer, 2000; Ormaza-González and Statham, 1996). Due to the bioavailability and turnover times between inorganic and organic forms of N and P are different, thus, it is necessary to research the characteristic and dynamic of each form of N and P, which is useful to understand their cycles in aquatic environments.

Coastal waters are active interfaces between terrestrial and oceanic environments that have a large discharge of fluvial materials, complex biogeochemical processes and anthropogenic inputs. The north Yellow Sea (NYS), as a semi-closed marginal sea and one of the world's most representative shallow continental shelf oceans (Yang et al., 2010), is rich in natural resources and plays an important role in human life and economic exploitation of the Chinese eastern littoral. It is also the link for material and energy exchange between the Bohai Sea and South Yellow Sea (Lu et al., 2005). Thus, the NYS is a dynamic system governed by riverine input, currents and anthropogenic input. At present, due to their high reactivity and easy uptake by marine organisms, DIN and DIP and their bioavailability in the NYS have been studied (Li et al., 2013; Zhao et al., 2012). However, compared with dissolved inorganic N and P, little is known about the corresponding organic and particulate N and P characteristics and fluxes in the NYS. In addition, studies examining both dissolved and particulate, and inorganic and organic N and P in the NYS are even scarcer. Therefore, this paper investigated inorganic and organic N and P in both dissolved and particulate forms in the NYS. The aim was to explore the behaviors, variations, interactions and sources of dissolved and particulate N and P in the NYS. This study will provide the data base for the future research on N and P cycles in the NYS.

2. Materials and methods

2.1. Study area

The NYS is a semi-closed marginal sea bordered by the Chinese mainland and the Korean peninsula (Fig. 1). It is one of the world's most representative shallow continental shelf oceans with an average depth of about 38 m (Yang et al., 2010). It is separated from the Bohai Sea (BS) to the west by the Bohai Strait, and from the South Yellow Sea (SYS) to the south by a line connecting the Chengshanjiao of the Shandong Peninsula and the Changshanchuan of the Korean Peninsula. Thus, the NYS is the link for material and energy exchange between the BS and SYS (Lu et al., 2005). Major rivers discharging into the NYS include rivers along the Liaodong Peninsula coast (e.g., the Yalu, Dayang, Zhuang, Biliu and Dengsha Rivers) with sediment discharge of 250×10^4 t/yr, and rivers along the Shandong Peninsula coast (e.g., the Jia River and Jie River) with sediment discharge of 140×10^4 t/yr (Cheng, 2000).

The circulation patterns in the NYS are dominated by the Yellow Sea Cold Water Mass (YC), Yellow Sea Warm Current (YSWC) and coastal currents along the northern and eastern coasts of the NYS. The YC is a mixed water of outer seawater and coastal water and has low temperature. The YSWC is a branch of the Tsushima Current that flows northwestward into the SYS and carries warm and salty water into the Yellow Sea, roughly following the Yellow Sea Trough (Song, 2009). Coastal currents include the Liaonan Coastal Current (LCC), west Korean Coastal Current (KC) and Yellow Sea Coastal Current (YSCC). The LCC is formed by the flowing water from Yalu River southwestward along the south coast of Liaodong Peninsula and has low temperature. The KC flows southward along the west coast of Korean Peninsula and has low temperature and low salinity. The YSCC is formed by the cold water masses of Bohai Bay and Laizhou Bay converging at the effect of north wind and flows eastward along the north coast of Shandong Peninsula and then turns southward in Chengshantou.

2.2. Sampling

Seawater and suspended particle samples were collected in September 2012 from cruise of “Kexue 3” in the NYS. Thirty-six sampling sites in the NYS were set (Fig. 1). In all the sampling sites, seawaters and suspended particles were collected from surface and bottom (2 m above sediment) layers. Besides, seawaters and suspended particles at nine stations in two sections (BX-5 and NYS1) were collected for determining nutrients at six depths (surface, 5 m, 10 m, 20 m, 30 m and bottom layers) according to the water depth. Transect BX-5 located in the YC and crossing the Zhangzi Island shellfish farms, was typical to present the influence of YC and organic detritus discharge of shellfish on the NYS; transect NYS1 located between the BS and NYS, was typical to present the influence of Bohai Sea input on the NYS. Seawater samples were collected by a CTD-Rosette system using Teflon coated bottles (10 L, Sea Bird Inc., USA) equipped with temperature, salinity and fluorescence sensors. Immediately after collection, about 100 ml seawaters were directly collected in acid-cleaned HDPE bottles and stored at -20 °C for total N (TN) and P (TP) determination; about 2 L seawaters were filtered through pre-acid-cleaned and precombusted (450 °C for 4 h), 47 mm diameter Whatman GF/F glass fiber filters. The filtrate samples for DIP and DIN were collected in acid-cleaned HDPE bottles and stored at -20 °C until analysis in the laboratory. The filters were rinsed with distilled water to remove dissolved nutrients after filtration, then were folded twice with the loaded surface inside, returned to the plastic Petri dishes, and stored at -20 °C for particulate sample analysis. Data of environment conditions, including temperature (T), salinity (S) and chlorophyll *a* (Chl a) were continuously determined by temperature, salinity and fluorescence probes installed in CTD.

2.3. Measurement of dissolved, particulate and total N and P

Nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and DIP were measured with a Skalar nutrient autoanalyzer using the standard colorimetric methods according to Aydin-Onen et al. (2012). The detection limits were 0.02, 0.02, 0.03 and 0.01 μM for NO_3^-, NO_2^-,