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Nutrient fluxes across sediment-water interface in Bohai Bay Coastal Zone, China

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ABSTRACT

Sediment cores and overlying water samples were collected at four sites in Tianjin Coastal Zone, Bohai Bay, to investigate nutrient (N, P and Si) exchanges across the sediment-water interface. The exchange fluxes of each nutrient species were estimated based on the porewater profiles and laboratory incubation experiments. The results showed significant differences between the two methods, which implied that molecular diffusion alone was not the dominant process controlling nutrient exchanges at these sites. The impacts of redox conditions and bioturbation on the nutrient fluxes were confirmed by the laboratory incubation experiments. The results from this study showed that the nutrient fluxes measured directly from the incubation experiment were more reliable than that predicted from the porewater profiles. The possible impacts causing variations in the nutrient fluxes include sewage discharge and land reclamation.

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1. Introduction

The sediment-water interface is one of the most important boundaries in shallow water bodies, such as coastal and estuarine waters (Ignatieva, 1999). It can affect the circulation, transformation and storage of substances in the environment. Nutrient flux across the sediment-water interface is a crucial factor affecting nutrient balance and maintenance of primary productivity in the water (Callender and Hammond, 1982). Under certain conditions it serves as an internal source of pollutants, as excessive nutrients could be released to the overlying water from the contaminated sediments through particle resuspension, bioturbance, turbulent and molecular diffusion, which can result in increased nutrient concentrations in the water column. Hence, how to effectively control the secondary pollution due to release of nutrients from the contaminated sediment can be a key to a successful water protection program (Pitkänen et al., 2001; Conley et al., 2002).

Several methods have been developed for benthic nutrient flux measurement in the marine environment in the last few decades. In-situ incubation is one of the most accurate and commonly used methods nowadays (Hammond et al., 1985; Pratihary et al., 2009; Oehler et al., 2015). This method includes a specially designed chamber/lander where the sediment captured is incubated and the exchange at the sediment-water interface is measured in-situ, which is good at simulation of the natural conditions. The technical requirement of laboratory

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http://dx.doi.org/10.1016/j.marpolbul.2016.10.056 0025-326X/© 2016 Elsevier Ltd. All rights reserved. incubation (another method) includes laboratory incubation of the sediment cores in a controlled environment in order to test the mechanisms hypothesized. Therefore, this method is still widely used in benthic flux research (Liu et al., 2003; Engelsen et al., 2008; Liu et al., 2011; Aigars et al., 2015; Leote and Epping, 2015; Zhou et al., 2016). Benthic nutrient fluxes can also be estimated through porewater profiles based on Fick's laws (Woulds et al., 2009; Percuoco et al., 2015). In a diffusion controlled environment, the flux is proportional to the concentration gradient. In other cases, modifications should be made to better account for the effects of other processes (Kristensen and Hansen, 1999; Feng, 2006).

In shallow water environment, nutrient and carbon cycles are driven by a close benthic–pelagic coupling process. Shallow bays are habitats for high productivity due to an increased nutrient supply from sediments (Engelsen et al., 2008). Therefore, many studies focused on the contributions of sediment nutrient supply to the primary production in the water column. According to Jørgensen (1983), coastal and continental margin sediments receive about 80% of the freshly produced organic matter that reaches the sediment in the world's oceans, which amounts to 10–50% of the annual primary production in the overlying waters. However, the processes are complicated, site-specific and time-variant. (Boynton and Kemp, 1985; Berelsona et al., 1998; Liu et al., 2003; Engelsen et al., 2008; Pratihary et al., 2009).

Mechanisms controlling the benthic nutrient fluxes are another important research topic. According to literatures, the actual retention, transformation or recycling of nutrients in coastal or enclosed marine ecosystems is dependent on a series of factors including the amount

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and bioavailability of land based nutrient loads, sediment characteristics, near-bottom water oxygen regime, temperature and intensity of sediment bioturbation (Aigars et al., 2015).

Located in the west Bohai Sea, the Bohai Bay is a large-scale semienclosed shallow water body. Previous studies have shown that the water exchange between the Bohai Bay and the central area of the Bohai Sea is weak (Lv et al., 2015; Sun and Tao, 2006). Therefore, this area is susceptible to problems of pollution and eutrophication. However, instead of being protected, the area is one of the most heavily exploited and polluted areas in China (Peng, 2015). The Bohai Bay is surrounded by the metropolitan areas, such as Beijing, Tianjin, Hebei Province, and Shandong Province, which together form one of the major economic rims - the Bohai Economic Rim, with a population over 100 million. Tianjin Coastal Zone is located at the head of the Bohai Bay, where is a heavily exploited area due to increasing development of petro-chemical industry, shipping, mariculture, tourism and sea salt industries along the coast (Zheng et al., 2007).

In the last few decades, anthropogenic activity has become a major threat to the ecosystem of the Bohai Bay and has changed the environment dramatically. Eutrophication has become a prominent issue since large amount of urban, industrial and agricultural discharge enriched in nutrients empty into the bay. For example, annual discharges of DIN from Haihe River Basin total about 9×10^4 ton (Zhang et al., 2015). Annual fluxes of DIN and DIP to the Bay are closely correlated with the river discharges (Zheng et al., 2007).

On the other hand, since the sediment of the Bohai Bay is dominated by fine grains of silt and clay, which have high specific surface area and can easily adsorb aquatic substances sinking to sediment and release the substances back into the water column under certain conditions. Moreover, the water exchange capacity of this area with the outer sea is weak. Therefore, pollutants tend to be trapped within this area for a long time and produce more serious consequences. What make this situation even more complicated are the decrease of river water discharges (Lei et al., 2007; Liu and Liu, 2004; Wang et al., 2006; Feng and Zhang, 1998) and the increase of large-scale sea reclamation projects (Yuan et al., 2014; Nie and Tao, 2008). These phenomena cause changes in riverine input and the transport of the nutrients (CRAES, 2007).

Nowadays, the concentrations and compositions of nutrients are dramatically different from that in the past. During 1959-2010, DIN concentration increased by 5 folds, DIP concentration increased first and then gradually dropped back as the usage of P containing detergents in the coastal regions were banned one after another since 2002. The molar ratios of N/P increased almost 8 times from 11.3 to 86.2 (Mu et al., 2012). However, the concentration of DISi has shown a constant decline as the fluxes of freshwater and sand declines. During 2004–2007, the annual concentration of DISi decreased by 2/3 and the Si/N ratios dropped to 0.5 (Kan et al., 2010). Such a change in nutrient composition has had a profound influence on phytoplankton composition in the Bohai Bay as the cell abundance of phytoplankton increased, biodiversity decreased and the spatial and temporal distribution became very uneven (Yang et al., 2007). Eutrophication is drastically increased as evidenced by red tide. During 1989 to 2002, over 15% of the red tide events occurred in Bohai Sea originated from the Bohai Bay. Red tides were reported each year from 1997 to 2002 in the head of the Bohai Bay with an average occurrence of 1.3 per year (Zhang et al., 2005). The decline of the Bohai Bay ecosystem poses a threat to the sustainable development of the coastal region.

In recent years, the degradation of the Bohai Sea ecosystem is gaining more and more attention. Several national restoration programs have been implemented such as "Bohai blue sea action plan". A concerted effort has been made by the surrounding regions. In 2012 Tianjin started to establish its watershed pollution control and integrated disposal system. Under this system, urban sewage treatment rate was raised to 90% and above and no untreated sewage discharge can end up into the sea. In Hebei Province, imported devices for the recycling and processing of waste water, oil and solids will be fully installed in large and medium-sized ports so that sewage will not be discharged into coastal waters until it is processed (Wang, 2013).

Today, the pollution control efforts of the Bohai Bay have achieved some success. According to the State Oceanic Administration (SOA) report (SOA, 2015), the polluted areas showed a continuous decline during 2012–2014. However, the pollution caused by inorganic nitrogen is still salient. In addition, as the external sources decrease, the internal sources, e.g. release of nutrients from the sediment, could delay the improvement of the water quality within a certain time period. Unfortunately, our understanding of sediment nutrient exchange is still limited due to lack of investigations in this area in the past (Zhang J. et al., 2009; Deng, 2004).

This study reports the results of biogeochemical investigation conducted in the Tianjin Coastal Zone, Bohai Bay in 2012. Field investigation and laboratory incubation experiment were conducted to study benthic nutrient fluxes at four representative sites and the associated impact factors. The temporal and spatial variations in nutrient fluxes are discussed in this study. The purpose of this work is to estimate the nutrient fluxes across the sediment-water interface in this area and address the role of benthic fluxes in the nutrient cycling and primary production in the Bohai Bay. Information derived from this study can be used for proper management and protection of this area.

2. Study site

Bohai Bay, located in the west of Bohai Sea (approximately 117.5°E-119°E and 39.25°N–38°N, Fig.1), covers an area of 159,000km² with an average water depth of 12.5 m. This area has a marked continental monsoon climate characterized by a clear division between seasons. Rainy season is short and 64-68% of the rainfall is concentrated in July and August. The average annual rainfall in Bohai Bay is 4.64 cm \cdot y⁻¹ (Li et al., 2006). The major rivers flowing into Bohai Bay are Haihe River, Huanghe River and Luanhe River. The average annual freshwater discharge to the western Bohai Bay is 2.429×10^9 m³ in the 1990s (Lei et al., 2007). The main tidal constituents in the Bohai Bay are M2 (semi-diurnal tide) and K1 (diurnal tide) with the M2 being the most predominant. The average tidal range in this area is 2–3 m with a peak of 4 m during spring tide. The tide is asymmetric with longer ebbing (7 h) and shorter flooding (5 h). The tidal current is characterized by alternating flow (west/east direction) and weak residual current. Waves are mainly wind-induced surface wave with an average wave height of ~0.6 m and the maximum height could reach 4–5 m. In winter, there are strong wind surges in the Bohai Bay (Feng et al., 1999). The terrain of the bay is rather flat and inclines towards the central Bohai Sea. The sediment of Bohai Bay is dominated by silt and clay.

The Bohai Bay is a typical semi-enclosed shallow water system with mild bottom slope and muddy sea bed. Transport of contaminants under wave-induced long-shore currents is noticeable. The water exchange between Bohai Bay and the external water body is poor, which makes it difficult for contaminants to be diluted and carried out. Thus, it is important to study the characteristics of the nutrient exchanges at the sediment-water interface to prevent the eutrophication and to improve the water quality. Tianjin Coastal Zone is located in the west end of the Bohai Bay, stretching about 150 km along the coast (Zheng et al., 2007). In recent years, the economic development in this area is gaining new momentum with the implementation of a series of new policies. Several large-scale land reclamation projects have been conducted to ease the land shortage, which not only significantly altered the coastal morphology and topography, but also led to great changes in offshore sediment transport and water circulation (Nie and Tao, 2008).

In May 2012, a basin scale field investigation was conducted in Bohai Bay with 32 sites sampled for the first time. Nutrients in the water column were sampled at all sites. As a subset, four representative sites (D2, E1, E3 and E4) were selected for sediment study based on the site

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