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Phosphorus speciation, transformation, and preservation in the coastal area of Rushan Bay

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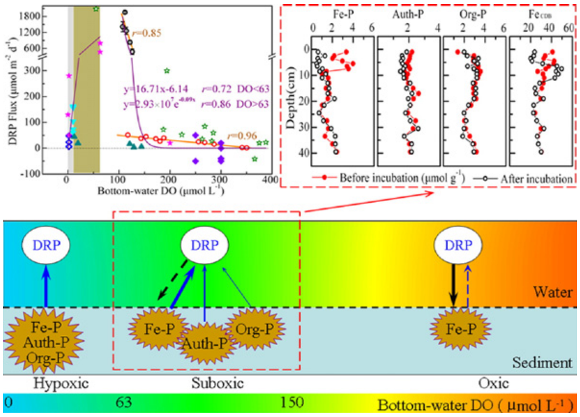
HIGHLIGHTS

- Benthic processes of phosphorus in a seasonal coastal low-oxygen zone were assessed.
- Bottom-water DO between 63 and 150 μM can enhance the diffusive DRP flux.
- Increasing diffusive DRP fluxes mainly originates from Fe–P and Auth-P.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphorus (P) speciation, burial, and transformation are poorly constrained under low-oxygen conditions. Sequential chemical extraction techniques, in-situ incubation, and laboratory incubation were employed to explore P cycling in the low-oxygen area of coastal Rushan. The study determined that the total P concentrations in the coastal area of Rushan Bay were higher than those of other China shelf seas, and largely affected by anthropogenic activities. The phosphate (DRP) fluxes in the study area calculated using an incubation method (0–1960 μmol m^{-2} day^{-1}) and measured based on pore water gradients (1.5–50.4 μmol m^{-2} day^{-1}) were both highly correlated with oxygen conditions. Sediment incubations showed that DRP diffusion from the sediment mainly originates from Fe–P and Auth-P dissolution and that Org-P recycling contributed only a small portion of the total released P pool. The benthic phosphate flux can be 60 times higher under low bottom-water oxygen levels of 63–150 μmol L^{-1} than under oxygen levels exceeding 150 μmol L^{-1} in the study area. The P accumulation rates and burial efficiencies in this study area ranged from 16.5–33.3 μmol cm^{-2} $year^{-1}$ and 81.1–83.4%, respectively, and were regulated by the oxygen level and diffusive DRP flux. This study indicates that low oxygen levels between 63 and 150 μmol significantly govern P transformation and preservation in the sediment and P pools in the water column.

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1. Introduction

Human activities have negatively influenced coastal water quality and ecosystem functions. Coastal eutrophication has had a profound impact on environmental ecosystems attributable to anthropogenic activities (Conley et al., 2009), with increasing terrestrial nutrient loading (Rabalais et al., 2010), which may induce or accelerate hypoxia, anoxia (Diaz and Rosenberg, 2008; Rabalais et al., 2010) or algal blooms (Carstensen et al., 2007).

Phosphorus (P) is generally considered a limiting nutrient for algae growth in many coastal zones (Lewandowski et al., 2003), especially in Chinese coastal waters (Liu et al., 2004; Jiang et al., 2014). Sediment plays a key role in regulating the P concentration in the water column (Jin et al., 2013; Leote and Epping, 2015). The transformation, preservation, and recycling of P at the sediment-water interface are largely controlled by the reactivity of different forms of P (Ruttenberg, 1992; Slomp et al., 1996a; Mort et al., 2010), and driven by a number of biological, physical and geochemical processes (Schenau and De Lange, 2001; Slomp et al., 2013). Numerous studies have shown that estuarine and coastal areas are important P sinks and function as P filters (Fang et al., 2007; Raimonet et al., 2013; Bonaglia et al., 2014) due to their fairly high sedimentation rate and phosphorus burial efficiency. However, sediments can also provide a significant source of P for the water column (Lewandowski et al., 2003; Krom et al., 2010; Zaaboub et al., 2014).

Phosphorus cycling and bioavailability in sediments of coastal systems are largely dependent on P speciation since the non-refractory fraction of P can be regenerated from the organic matter degradation and Fe-(oxyhydr)oxides reduction (Ruttenberg, 1992; Slomp et al., 1996a). Previous observations have shown that dissolved reactive phosphate (DRP) is preferentially released from the sediments into pore water and the overlying water under hypoxic and anoxic conditions (Jahnke, 1990; Ingall and Jahnke, 1997; Mort et al., 2010). In general, DRP is dominantly generated from Fe-(oxyhydr)oxide-bound P and organic matter-hosted P under hypoxic and anoxic conditions (Ingall and Jahnke, 1997), resulting in lower P burial efficiencies in oxygen-depleted bottom waters (Ingall and Jahnke, 1994; Schenau and De Lange, 2001). Although P cycling is closely linked to oxygen levels, it remains poorly characterized in low-oxygen systems, especially in Chinese continental shelves.

Rushan Bay has recently become a seasonal low-oxygen area in summer due to increased human activities (Ran et al., 2011). The maintaining mechanism of low-oxygen condition is related to the water column stratification and some biogeochemical processes e.g. sediment oxygen demand (Ran et al., 2011). Environmental alternations, like the formation of low-oxygen benthic environment, have significantly influenced the distribution, transformation, and preservation of biogenic elements. Although the area provides an ideal location for studying coastal P cycling under oxygen-deficient conditions, few studies have investigated P-related processes in the sediment. This study investigates the biogeochemical processes of P in sediments of coastal area of Rushan Bay via a series of in-situ and laboratory sediment incubations. The specific objectives of this study are as follows: (1) to identify P speciation in sediments using sequential chemical extraction techniques, (2) to quantify the speciation factors relative to the P fraction distributions, (3) to determine P transformation at the sediment-water interface under low-oxygen conditions, and (4) to evaluate P preservation in the coastal area.

2. Materials and methods

2.1. Study area

The Rushan Bay coastal area of the Southern Shandong Peninsula is connected to the South Yellow Sea. The depth of the study area out Rushan Bay ranges from 5 to 30 m (Fig. 1). The Rushan River is the major source of silt entering Rushan Bay, contributing $30 \times 10^4 - 40 \times 10^4$ t year^{-1} (Compile committee of Chinese gulfs gazetteers ed., 1993). The mean annual river discharge is approximately 2.5×10^8 m^3 year^{-1} (0.5% of the water volume in this study area). The shallow coastal area is dominantly influenced by the regular semidiurnal tidal current. The Yellow Cold Water Mass (YSCWM, Fig. 1(a)) can extend to the edge of study area in summer, which locates in the central Yellow Sea at the depths deeper than 50 m. The Yellow Sea Coastal Current is close to the survey area, which flows southeastward in the surface and bottom layers in the north part of Southern Yellow Sea along the Southern Shandong Peninsula. Additionally, the area is significantly impacted by the marine aquaculture (especially shellfish mudflat cultures), urban and industrial effluents. Rushan Bay has witnessed significant changes for the past few decades. For example, the sediment total P concentration in Rushan Bay is about 2 times higher than that in the Yellow Sea (Wang et al., 2008). Such an increase of P is attributed to the mariculture in the recent decades. Low-oxygen begins to develop in early summer, reaches its maximum in August, and finally disappears in autumn (Ran et al., 2011).

2.2. Sample collection, pretreatment and analyses

Four surveys were conducted in Rushan Bay and adjacent areas during late spring, summer and winter from 2014 to 2015 (Table 1). The water column depth, bottom-water temperature, salinity and dissolved oxygen (DO) were measured using an oceanography instrument (JFE Co. Ltd, AAQ122, Japan). The current speed was obtained using an acoustic Doppler current profiler (ADCP, RD instrument, WS-600, America). Bottom-water samples were collected using Teflon coated Go-Flo bottles. The DO concentration was determined on board using the Winkler titration method.

Sediment core samples from three locations were obtained using a gravity corer (KC-Denmark Ltd., Denmark) (Fig. 1). The samples were collected by inserting 55 cm long polymethyl methacrylate (PMMA) tubes (internal diameter: 5 cm) into the sediment. At each site, overlying water samples were taken from top-cores and filtered through 0.45 μm pore size polyethersulfone filters with N_2 purging. The samples were then stored in 10 mL polypropylene (PS) bottles for dissolved nutrient (stored at −20 °C) and dissolved iron (acidified with 0.1 mL or 2% v/v of HNO_3 and stored at 4 °C) analyses in the laboratory. The cores were subsequently inserted into a nitrogen-filled glove box before the remaining overlying water was removed.

The sediment cores were then sliced at intervals of 1.0 cm (0–10 cm in depth), 2 cm (10–30 cm in depth) and 3 cm (>30 cm in depth) on the basis of the general variation of P profiles in sediments of Rushan Bay and Yellow Sea (Liu et al., 2004; Wang et al., 2008). An aliquot of each wet sediment sample was transferred to a 50 mL plastic centrifuge tube for pore-water extraction. The tubes were capped, removed from the glove box and centrifuged at 4000 rpm for 20 min. The centrifuge tubes were then returned to the glove box. The supernatant water from each sample was dispensed via a 10 mL plastic syringe through a 0.45 μm polyethersulfone filter and collected in a 10 mL PS bottle. Sub-samples were collected and pretreated for the dissolved nutrient and dissolved iron analyses, as described above. The residual centrifuge material was capped and stored in a nitrogen-filled glove box for phosphorus species analyses. Other core sediments were sealed and stored at −20 °C until being sliced for total organic carbon, grain size, ^{210}Pb, and δ^{13}C determinations.

At the site C2, two additional sediment cores were sampled using 1 cm diameter holes at 1 cm intervals. The Eh values and oxygen concentrations of these cores were analyzed using an oxidation reduction potential (ORP) meter (AZ 8651, pH/OPR METER) and dissolved oxygen microelectrode (Field Microsensor Multimeter, Denmark), respectively, with the necessary precalibrations.