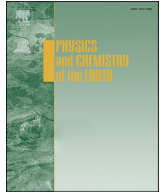




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Phosphorus fraction and phosphate sorption-release characteristics of the wetland sediments in the Yellow River Delta

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ABSTRACT

The aim of this study was to investigate phosphorus (P) fractions and phosphate sorption-release characteristics of the surface sediments regarding the wetland restoration in the Yellow River Delta (YRD). Sediments samples were collected from three typical sample plots: *Phragmites australis* community (p), *Suaeda salsa* community (s), and bare land (b) both in natural wetland (N) and restored wetland (R). The results showed that the mean content of TP was 541.58 mg/kg, and the rank order of P fractions were: inorganic phosphorus (IP) (65.6%) > residual phosphorus (RP) (24.9%) > organic phosphorus (OP) (9.5%). For sediments under the same land cover, TP and OP contents were significantly higher in natural wetlands than those in restored wetlands. This indicated that the restoration project really made a difference in TP content of sediments, and the decreased TP might result from decreased OP. For P kinetics sorption, a quick sorption mainly occurred within 0.5 h. The maximum phosphorus adsorption capacities (Q_{max}) ranging from 139.40 mg/kg to 224.06 mg/kg and the bonding energy constant (K) ranging from 0.33 mg/L to 1.37 mg/L were both obtained using a Langmuir model. In addition, Q_{max} , P release (P_r) and P release rates (P_{rr}) were in the order of Nb > Np > Ns > Rb > Rp > Rs, Np > Rp > Ns > Rs = Nb > Rb and Rp > Ns > Rs > Rb > Np > Nb, respectively. This indicated that sediments from natural wetland could adsorb more P as well as release more P into overlying water, moreover, more content of P were left in sediments comparing to restored wetland. Sediments from bare land were more likely to retain P as a pool because of the highest sorption capacity while lowest release potential. Our study showed that P sorption-release and the quick sorption processes were mainly affected by sediment moisture, amorphous iron and aluminum oxides (Fe_{ox} and Al_{ox}). Besides, Q_{max} was related to background value of sediments P. OP was the major P fraction adsorbed by sediments, and the P adsorbed by sediments was mainly adsorbed on Fe_{ox} and Al_{ox} .

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1. Introduction

Coastal wetland in China play an important role in regulating flood, storing and purifying wastewater, as well as providing habitats for more than 200 water bird species that annually migrate along the East Asian-Australasian Flyway, one of the eight primary migratory flyways around the world (Ma et al., 2009). However, most of the coastal wetlands have been severely damaged and degraded due to the tremendous demand for nature resource with the development of economics in China (Han et al., 2006). The Yellow River Delta (YRD), one of the three major river deltas in China, is well protected for wintering, breeding, or stopover sites

and the habitats for the birds in China (Fan et al., 2011, 2012; Yu et al., 2014). However, the YRD have been deteriorated and lost considerably because of the great potential of exploitation (Wang et al., 2012b) and reduction of freshwater (Li et al., 2009; Yang et al., 2010; Wang et al., 2012a; Guan et al., 2013). In order to restore degraded wetland, a restoration project—drawing water from Yellow River to the coastal wetland has been done by government in the YRD since 2002 (Wang et al., 2011; Hua et al., 2012; Jiang et al., 2015). As a result, the ecological environment has been improved to a certain extent, with lower contents of nitrogen and total phosphorus (TP) in water, and lower salinity and higher organic matter (OM) in sediments, and more birds due to the growth of vegetation providing a better habitat for them (Cui et al., 2009).

Phosphorus (P), as the most limited nutrition element, is important for wetland ecosystem, while its excess supply can lead

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to eutrophication. Sediments as the base of the wetland ecosystem can regulate the concentration of P by adsorbing it as a sink from overlying water and releasing it as a source under certain physicochemical and biological conditions (Zhang et al., 2016). Therefore, study on the distribution of P fractions and its sorption-release characteristics is the basis for the study of the risk of P release. P fractions and its distribution (Xu et al., 2012b; Yu et al., 2014), as well as the capacity of P retention and release (Sun et al., 2012) in sediments from the YRD had been studied. However, no study has reported the distribution of P fraction and its sorption-release characteristics regarding the restored wetland, and little is known about the relationship between P fractions and the characteristics of P sorption-release of sediments in the YRD. According to previous studies, not all of the P fractions can be released from sediments to overlying water (Kaiserli et al., 2002; Katsaounos et al., 2007), which means that there is a probable relationship between P sorption-release and P fractions. Therefore, the aims of this study were to: (1) investigate the distribution of P fractions, the maximum P adsorption capacity (Q_{\max}) and P released contents (P_r) in the sediments, and the differences between natural and restored wetland, (2) describe the processes of P dynamic sorption in sediments, and (3) analyze their influence factors and the relationship between P sorption-release and P fractions. The results of this study will contribute to the further study on evolution of P sink or source function in coastal wetland.

2. Materials and methods

2.1. Sample collection

The study area (37°43.640'N– 37°49.804'N and 119°3.152'E– 119°13.100'E) is located in the YRD in Shandong province, China. It has a warm temperate continental monsoon climate, and the mean annual temperature, precipitation and evaporation were 12.3 °C, 555.9 mm and 1962.1 mm, separately. Fluvo-aquic soil and saline soil were major soil types in study area. *Phragmites australis* and *Suaeda salsa* were dominant plant species (Yao et al., 2016). In natural wetland, the average plant height, plant coverage and plant biomass of *Phragmites australis* were 2.0 m, 95% and 388.08 g/m², and these of *Suaeda salsa* were 0.30 m, 30% and 120.88 g/m². In restored wetland, the average plant height, plant coverage and plant biomass of *Phragmites australis* were 2.2 m, 98% and 451.52 g/m², and these of *Suaeda salsa* were 0.55 m, 75% and 321.6 g/m². Moreover, *Suaeda salsa* community of natural wetland is located in high convex region.

All sediment samples were collected from the salt marsh in the YRD National Nature Reserve (Fig. 1) during August 2013. The restored wetland (R) of the YRD was selected as the main research area, while the nearby natural wetland (N) as the reference area. In addition, three typical sample plots: *Phragmites australis* community (p), *Suaeda salsa* community (s), and bare land (b) both in restored and natural area had been selected to explore P fractions and sorption-release of sediment in different vegetation communities. Surface sediments (0–20 cm) from six representative sampling sites were collected in triplicate with a soil core sampler (60 mm in diameter). Samples were taken to the laboratory in sealed plastic bags for further treatment and analysis.

2.2. Sample analyzes

The distribution of soil aggregate size classes was measured by wet sieving method (Elliott, 1986) and the percentages of macro-aggregate (>0.25 mm), micro-aggregate (0.25–0.053 mm) and clay (<0.053 mm) were recorded. Sediment pH and EC were measured by a pH electrode (Hanna Instruments, Woonsocket, RI,

USA) and an electric conductivity meter (VWR Scientific, West Chester, PA, USA) in a 1:5 (w/v) sediment-to-distilled water suspension, separately. Organic matter (OM) was measured by the potassium dichromate-dilution heat method (Nelson et al., 1982). Amorphous iron oxides (Fe_{ox}), amorphous aluminum oxides (Al_{ox}) and amorphous phosphorus oxides (P_{ox}) of sediments were extracted by ammonium oxalate separately (Dong et al., 2011), and then measured by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

2.3. Phosphorus fractions

P fractions in sediment was determined by chemical sequential extraction method (Reddy and Wang, 1998) and that was, inorganic phosphorus (IP) was extracted by HCl, whereas organic phosphorus (OP) was then extracted by NaOH, and residual phosphorus (RP) was determined by treating the sample at 250°C for 30 min and 550 °C for 45 min separately, followed by HCl extraction, the sum of three P fractions was regarded as total phosphorus (TP). The concentrations of P fraction extractions were analyzed by the flow analyzer (Auto Analyzer III, 161 Bran + Luebbe GmbH, Germany), accordingly.

2.4. Phosphorus sorption kinetics experiments

Dried sediment samples (0.5 g) were added in a series of 100 mL conical flasks with 25 mL P solution (KH₂PO₄, containing 2 mg/L). Two drops of chloroform were added to inhibit bacterial activity. The conical flasks were shaken in a water bath shaker of 150 rpm at 25 ± 1 °C for different time intervals, varying within 24 h (0, 0.25, 0.5, 1, 2, 3, 5, 8, 12, 16, and 24 h). Solutions filtered through 0.45 μm filter membrane, and filtrates were then measured by using the molybdenum blue colorimetric method (Gilcreas, 1998). The content of P adsorbed by sediments was calculated as the difference between the mass of P initially added and that recovered in solution after sorption. Triplicate samples were analyzed and the data were expressed as the average.

2.5. Phosphorus sorption isotherm experiments

Sediment samples of 0.5 g were put into a series of conical flasks with plug. Each experiment consisted of 50 mL P solution with a series of initial P concentrations of 0.2, 0.5, 1, 2, 3, 4, and 5 mg/L obtained. The conical flasks were shaken in a water bath shaker of 150 rpm at 25 ± 1 °C for 24 h. Solutions filtered through 0.45 μm filter membrane, and filtrates were then measured by using the molybdenum blue colorimetric method. The content of P adsorbed by sediments was calculated as the difference between the mass of P initially added and that recovered in solution after sorption. Triplicate samples were analyzed and the data were expressed as the average.

2.6. Phosphorus release experiments

The sediments were washed with 95% alcohol after the P isotherm experiments to remove the residual phosphate solution. The sediments were then delivered into a 50 mL centrifuge tube with 50 mL KCl solution (containing 0.01 mol/L). Two drops of chloroform were added to inhibit bacterial activity. The cubs were shaken in a water bath shaker of 150 rpm at 25 ± 1 °C for 24 h. The suspensions were then centrifuged at 4000 rpm for 30 min, and the concentrations of P were measured by the molybdenum blue colorimetric method.

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