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Phosphorus speciation and availability in sediments off the eastern coast of Hainan Island, South China Sea



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ABSTRACT

Surface and core sediments were collected off the eastern coast of Hainan Island (South China Sea), and a sequential extraction method (SEDEX) was used to separate and quantify five sedimentary phosphorus (P) reservoirs: exchangeable or loosely sorbed P (Ex-P), iron-bound P (Fe-P), authigenic P (Ca-P), detrital P (De-P) and organic P (OP). Total P (TP) in the surface and core sediments ranged from 7.96 to 22.34 μ mol g⁻¹, and was dominated by inorganic P (IP). De-P and Ca-P were the main chemical species of P in surface and core sediments. The distribution of the P species in surface and core sediments was governed by various factors, including terrigenous input, biological processes, Fe oxides/hydroxides, organic matter degradation, and sediment grain size. The organic carbon (OC)/OP ratio ranged from 37 to 293 (average, 107 ± 58) in surface sediments, suggesting that the organic matter in sediments had been subject to degradation and comprised mostly refractory compounds. The OC/P_{reactive} ratio (37–69) was relatively low in the core sediments, suggesting an excess of sedimentary reactive P compared with OC. The Fe/P ratio ranged from 2 to 19 in surface and core sediments, which indicates that the higher proportions of the crystalline phases occurred in estuarine areas relative to the offshore areas. The potential bioavailable P accounted for 20.3–54.2% of TP in the surface and core sediments.

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1. Introduction

Phosphorus (P) is an essential nutrient for marine phytoplankton growth, and plays a significant role in the global biogeochemical cycling of biogenic elements in estuarine and coastal ecosystems (Howarth et al., 1995; Slomp et al., 2013; Meng et al., 2015). P is also critical to the global climate and environmental changes because of the relationship between atmospheric carbon dioxide and marine photosynthetic productivity (Broecker, 1982; Krom et al., 2004; Ni et al., 2015). Numerous studies have indicated that estuaries and adjacent seas are important sinks for P, which can be captured in large quantities in these ecosystems (Nixon, 1996; Fang, 2000; Slomp, 2011; Yang et al., 2015), and that the fate of P in sediments is mainly dominated by the reactivity of the various P fractions (Ruttenberg, 1992; Andrieux and Aminot, 1997; Coelho et al., 2004). Moreover, P cycling and bioavailability in estuarine and coastal areas depend on P speciation (Lebo, 1991;

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http://dx.doi.org/10.1016/j.csr.2016.03.003 0278-4343/© 2016 Elsevier Ltd. All rights reserved. Andrieux-Loyer and Aminot, 2001; Wang et al., 2009). Therefore, knowledge of P speciation in marine sediments is necessary for understanding P cycling, evaluating its response to environmental changes, assessing P bioavailability in estuarine and coastal environments, and clarifying its involvement in linking the cycles of carbon, nitrogen, oxygen, and sulfur (Jensen et al., 1998; Schenau and De Lange, 2001; Hou et al., 2009; Berbel et al., 2015).

The Wanquan River estuary and a number of lagoons (e.g., Bamen Bay; Fig. 1) enclosed by coral reefs are located on the eastern Hainan Island coast (Huang et al., 2013). The Wanquan River is the island's third longest river (163 km) with a drainage area of 3693 km² (Zhu et al., 2003). The river conveys average freshwater discharge of 163.9 m³ s⁻¹ that annually carries 3.9×10^6 t of sediment to the estuary and adjacent coastal areas (Wang et al., 2006). The rapid population growth and economic development in its catchment has resulted in the Wanquan River receiving high loads of nutrients and untreated wastewater (Ge et al., 2003; Yu et al., 2005), and this has resulted in numerous pollution problems in the downstream estuarine and coastal ecosystems (Wang et al., 2006). For instance, in recent years, largescale aquaculture in coastal areas of Hainan Island has affected the coastal marine ecosystem, and eutrophication has occurred

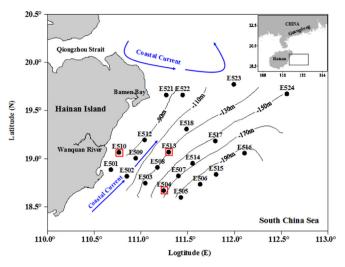


Fig. 1. Sampling stations for surface sediments (dots) and core sediments (squares), and the isobaths (m) in the study area. The arrows indicate the current directions off the eastern coast of Hainan Island, abstracted from Yu and Liu (1993) and Hu et al. (2000).

(Pan et al., 2007). P is the potential limiting element for phytoplankton growth in the Wanquan River estuary and coastal ecosystem (Li et al., 2013, 2014). Nutrients sequestered in estuarine and coastal sediments can be an important source of P for pelagic primary production (Sundby et al., 1992; Nizzoli et al., 2007), which mainly depends on the P speciation in sediments (Coelho et al., 2004; Spears et al., 2006). Thus, the study of sedimentary P speciation is important in understanding eutrophication in the marine ecosystem.

Relative to other marginal seas, information about the P fractions in sediments on the continental shelf of the northern South China Sea (SCS) is very limited, especially offshore to the east of Hainan Island. To fill this knowledge gap and provide a comprehensive overview of the geochemistry of P in the study area, we used the sequential extraction method (SEDEX) developed by Ruttenberg (1992) to discriminate the various chemical species of P in sediments off Hainan Island. The objectives of this work were: (a) to quantify the main P species in surface and core sediments off the eastern coast of Hainan Island; (b) to explore factors influencing the distribution and geochemical behavior of the various P fractions in sediments and (c) to assess the potential bioavailability of this element in the study area. This study provides a better understanding of the biogeochemical cycling of P in tropical estuarine and coastal areas.

2. Materials and methods

2.1. Study area and sample collection

Hainan Island is located in the northwest of the SCS with a diverse in tropical ecosystems (e.g., mangroves and coral reefs), and has 33,920 km² in surface area and 7.5×10^6 inhabitants (Liu et al., 2011; Zhang et al., 2013). Typhoons and tropical storms frequently affect this area in August and September, and the island receives abundant rainfall, approximately 80% of which occurs annually from May to October during the wet season (Wang, 2002; Mao et al., 2006). Upwelling near Hainan Island is concentrated on the eastern side, between 18.5–20.5°N and 110–111.5°E, which is consistent with the southerly and southwesterly wind circulation in the SCS (Deng et al., 1995; Su and Pohlmann, 2009). The isobaths off the eastern Hainan Island coast are parallel to the coastline (Fig. 1). The coastal current travels from east to west

along the Guangdong coastline in winter, and forms an anticlockwise loop current; off the eastern coast of Hainan Island the coastal current travels from south to north in the summer (Yu and Liu, 1993; Hu et al., 2000; Fig. 1). The field observations in this study were undertaken in August 2008, off the eastern coast of Hainan Island. The sampling stations are shown in Fig. 1. Surface sediments (0–2 cm) were collected at 21 stations using a stainless steel grab sampler. Three core sediments (17–25 cm long) were taken at stations E504, E510 and E513 using a box-corer. The core sediments were immediately sliced at 1-cm intervals on board the research vessel, and immediately frozen at -20 °C. In the laboratory the sediment samples were freeze-dried, homogenized, and ground to a fine powder for sieving (< 200 mesh, 74 µm) using an agate mortar and pestle prior to analysis.

2.2. Sequential extraction of P

The species of P in the sediment were chemically fractionated using a sequential extraction method (SEDEX) developed by Ruttenberg (1992) and modified by Huerta-Diaz et al. (2005) for marine sediments (Fig. 2). Briefly, the technique involves separation of the main reservoirs of sedimentary P into five pools: exchangeable or loosely sorbed P (Ex-P), iron-bound P (Fe-P), authigenic P (Ca-P; this includes authigenic carbonate fluorapatite, biogenic apatite, and CaCO₃-associated P), detrital P (De-P), and organic P (OP). We made two modifications to the original SEDEX scheme. First, to avoid the interference by the citrate-dithionitebicarbonate (CDB) reagent in reduction of the molybdate complex (Ruttenberg, 1992), in this study Fe-P was determined using a method (Huerta-Diaz et al., 2005) involving a combination of buffered CDB reducing solutions with CDB-MAGIC (magnesiuminduced co-precipitation). Second, we determined organic phosphorus (OP) in a separate procedure, as the OP concentration can be underestimated when using the SEDEX procedure (Ruttenberg, 1992; Berner et al., 1993). OP was analyzed non-sequentially as the difference between 1 M HCl extractable P (24 h) prior to and following high-temperature combustion (550 °C, 2 h) of the sediment (Aspila et al., 1976). Total P (TP) concentrations were calculated as the sum of OP and inorganic P (IP), determined using the SEDEX method (Slomp et al., 1996a). The IP concentrations, which were calculated as the sum of Ex-P, Fe-P, Ca-P, and De-P (derived using the SEDEX method), were consistent (correlation coefficient, 0.9978) with independent measurement of IP in the same samples, determined using 1 M HCl extraction in the single-step procedure (Fig. 3); this demonstrated that there was excellent recovery of the IP fractions using the SEDEX procedure. Therefore data on the organic P fraction in the Ex-P and Ca-P phases are not presented here and because they involved extremely low concentrations, excellent recovery of the IP fractions also indicated negligible organic P fraction in the two phases, although these organic P data are significant in sequential extraction (Zhang et al., 2010a). Furthermore, there was no significant difference in the IP concentrations determined using the two different methods (ANOVA, p > 0.05). The TP concentration measured for the Chinese standard for coastal marine sediment (GBW07314) was $19.51 \pm 0.13 \mu$ mol g^{-1} , which is consistent with the certified value for this standard (20.85 \pm 1.97 μ mol g⁻¹). The TP concentration calculated from the sum of five P species showed no significant variation from the TP values determined for the same samples using the high-temperature combustion method (Aspila et al., 1976) (ANO-VA, p > 0.05). The relative standard deviations were better than 1.0%, 2.4%, 3.7%, 1.5%, and 2.8% for Ex-P, Fe-P, Ca-P, De-P, and OP, respectively.

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