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Speciation, bioavailability and preservation of phosphorus in surface sediments of the Changjiang Estuary and adjacent East China Sea inner shelf

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ABSTRACT

The speciation, potential bioavailability and preservation of phosphorus (P) in surface sediments of the Changjiang (Yangtze River) Estuary and adjacent East China Sea (ECS) inner shelf were investigated through the analyses of P fractions and sediment bulk properties. A sequential extraction method (SEDEX) was used to separate and quantify the following six sedimentary P reservoirs: exchangeable P (Ex–P), authigenic P (Au–P), detrital P (De–P), organic P (Or–P), refractory P (Re–P) and Fe-bound P (Fe–P). Total P (TP) in surface sediments ranged from 15.0 to 21.4 μmol g^{-1} and was highest near the Changjiang river mouth. The average contribution of each form of P to TP was 55.6% (De–P), 17.8% (Re–P), 16.1% (Or–P), 5.5% (Au–P), 2.5% (Ex–P) and 2.5% (Fe–P), respectively. De–P showed relatively higher concentrations in the river mouth and the ECS shelf region, off the Changjiang Estuary. High concentrations of Or–P were found mainly in mud areas showing a similar distribution pattern with silt, sediment surface area (SSA), and total organic carbon (TOC). Re–P was mainly distributed near the estuarine area and the Zhe–Min coast. Bioavailable P (BAP), accounted for 9.5–32.0% of TP (with a mean of 21.2%) and showed a similar distribution pattern to that of Or–P. De–P/SSA and TOC/SSA loadings both decreased with increasing of SSA, while Or–P/SSA loadings varied little with SSA, indicating that Or–P may have reached an adsorption–desorption equilibrium on mineral surfaces. TOC to total organic P (TOP; sum of Re–P and Or–P) ratios less than the Redfield ratio (84 in average) may have indicated efficient remineralization of organic matter in mobile muds of the Changjiang Estuary and adjacent ECS inner shelf. Furthermore, the relatively high TOC/Or–P ratios (72–422 with a mean of 188) likely suggest a higher degree of preferential regeneration of labile Or–P over TOC in sediments.

1. Introduction

Phosphorus (P) is an essential nutrient and plays a key role in biogeochemical cycles of biogenic elements in estuarine and coastal environments (Slomp, 2011), especially for large-river delta-front estuaries (LDE) (Bianchi and Allison, 2009). The sources of P in these environments mainly include particulate inorganic/organic materials derived from riverine inputs, marine autotrophic production and atmospheric dusts (Slomp, 2011, and references therein). Past work has shown that burial of P in marine sediments is an important sink and that the fate of P in sediments is largely controlled by the reactivity of different forms of P (e.g. Ruttenberg, 1992; Andrieux-Loyer and Aminot, 1997; Coelho et al., 2004; Hou et al., 2009). Refractory P phases, such as detrital apatite (Detrital P, De–P) and other P-containing minerals (derived mainly from rivers) have slow formation kinetics, are buried directly and are slow to regenerate (Ruttenberg, 1992; Anschutz et al., 1998; Coelho et al., 2004). Significant partitioning and transformation of reactive P phases occur during burial processes driven by a number of biological, physical, and geochemical processes (Schenau and de Lange, 2001; Fang et al., 2007). The interactions of these complex biogeochemical processes will affect the retention and ultimate

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form of buried P (Ruttenberg, 1992; Andrieux-Loyer and Aminot, 1997). For example, microbial breakdown of labile sedimentary organic matter (SOM) results in the release of phosphate, together with dissolved organic phosphorus (DOP), nitrate, methane and carbon dioxide, to the overlying water column where it is available for primary production (Andrieux-Loyer and Aminot, 1997). These linkages with marine primary productivity and sediment biogeochemical cycling, in part highlight the importance of studying the speciation and preservation of P in marine sediments (Andrieux-Loyer and Aminot, 1997; Schenau and de Lange, 2001; Fang et al., 2007; Hou et al., 2009).

Rapid development of the local economy in the Changjiang River drainage basin has changed land-use practices which has partly resulted in large increases in nutrient inputs to the Changjiang LDE. Moreover, P has been shown to be a limiting nutrient for phytoplankton growth in the Changjiang LDE and the East China Sea (ECS) shelf (Liu et al., 2003). Thus, any increase in the release of P from surface sediments to overlying waters could have a significant impact on phytoplankton production and community composition. As mentioned earlier, this release from sediments is largely governed by the speciation of P in sediments (Ruttenberg, 1992; Coelho et al., 2004). Previous work on P cycling in sediments of the Changjiang LDE and adjacent shelf have mainly focused on the distribution of P forms and their relationships with grain size composition (Rao and Berner, 1997; He et al., 2009a) and bioavailability of particulate P (He et al., 2009b; Hou et al., 2009), with very few on the preservation of P (Fang et al., 2007). In addition, previous results either focused on the Changjiang Estuary (intertidal flat) (Xu et al., 2001; Hou et al., 2009) or from further offshore (middle shelf) (Zheng et al., 2003; Fang et al., 2007) in the ECS, with very few on the outer estuary and inner shelf regions (He et al., 2009b). More specifically, studies on the unique roles of mud deposits in determining the source and fate of different forms of P in the highly-reactive mud regions of the Changjiang LDE (Liu et al., 2007) and/or the ECS inner shelf, have been largely ignored.

This study examined the sources, distribution patterns, potential bioavailability and preservation of different forms of P, and their effects on the Changjiang LDE and the ECS inner shelf, with particular emphasis on the mobile-mud belts. The primary goal of this work was to better constrain the biogeochemical processes in P cycling in the Changjiang LDE, by determining how several sediment bulk parameters, such as grain size and mineral compositions, total organic carbon (TOC), and sediment surface area (SSA) interacted with P speciation.

2. Materials and methods

2.1. Study area and sample collection

The Changjiang River is the largest river in China, ranked third in length (6300 km), fifth in freshwater discharge (9.0×10^{11} m^3 yr^{-1}), and fourth in sediment discharge (4.8×10^8 t yr^{-1}) in the world (Dagg et al., 2004). The Changjiang LDE is characterized by high productivity that largely stems from the high amounts of nutrients discharged by the river (Zhou et al., 2008). An increase in the loading of nutrients has also caused severe eutrophication in the Changjiang LDE, resulting in the frequent occurrence of harmful algal blooms and seasonal hypoxia in bottom waters (Zhou et al., 2008). However, recent work has suggested that these eco-environmental issues were caused mainly by an imbalance in the nutrient structure, rather than simply high nutrient loadings (Jiang et al., 2010).

The hydrographic regimes of the Changjiang LDE and the ECS inner shelf are very complex and are mainly controlled by the Yellow Sea Coastal Current (YSCC) in the north, the Zhe–Min Coastal Current (ZMCC), and the Taiwan Warm Current (TWWC) in the south – as well as the Changjiang Diluted Water (CJDW) (Fig. 1) (Liu et al., 2007). All of the aforementioned currents play a key role in the transport and burial of sediments from the Changjiang. Previous investigations have shown that about 40% of the sediments are deposited in the near-shore just off the river mouth, forming the Changjiang LDE mud area with high sedimentation rates ranging from 1 to 6 cm yr^{-1}(Guo et al., 2003; Liu et al., 2007). Much of the remaining sediment is transported southward along the Zhe–Min coast by the CJDW and littoral currents (YSCC and ZMCC), where it is deposited west of 123°E due to a barrier and/or shear effect of the northward flowing TWWC, forming the mobile-mud belt on the ECS inner shelf (Fig. 1) (Qin et al., 1996; Liu et al., 2007). Only a small portion of this sediment escapes to the northeast of the estuary in summer due to enhanced northeastward flow of the CJDW and TWWC (Liu et al., 2006b).

Sampling was conducted onboard the *R/V Runjiang 1* (Zhoushan Runhe Co., Ltd., China) from late July to early August in 2011 (Fig. 1). Surface sediment samples (approx. 5 cm) were collected using a stainless-steel box-corer in the Changjiang LDE and the ECS inner shelf. Sediment cores were extruded, cut into sections homogenized, and stored at −20 °C until analysis. Most of the samples were collected within the Changjiang LDE and Zhe–Min coastal mud areas.

2.2. Analyses of sediment grain size, surface area and mineral composition

Grain size composition of the samples was measured using a laser particle size analyzer (Mastersizer 2000, Malven Instruments Ltd., UK), following the method of Hu et al. (2009). Sediment surface area (SSA) was determined using an automatic nitrogen

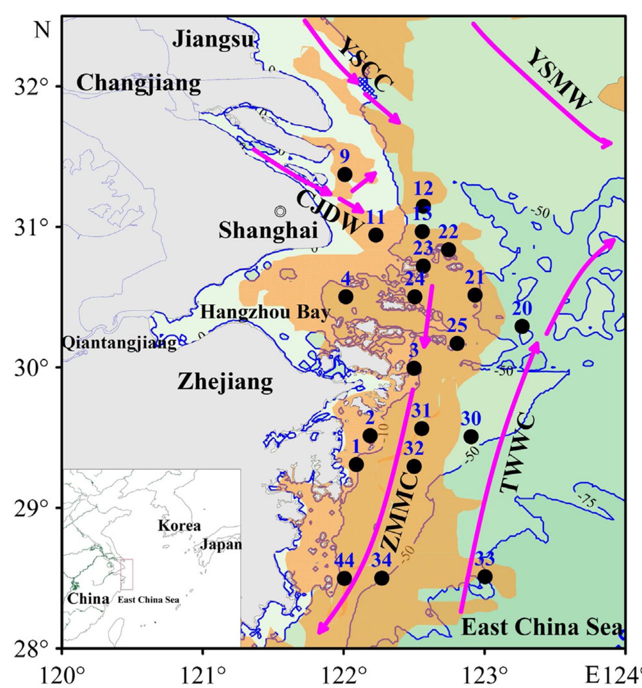

Fig. 1. Sampling locations at the Changjiang (Yangtze River) Estuary and adjacent East China Sea (ECS) inner shelf. Arrows indicate the direction of the currents (from Liu et al., 2007). YSCC: Yellow Sea Coastal Current; TWWC: Taiwan Warm Current; YSMW: Yellow Sea Mixing Water; ZMCC: Zhe–Min Coastal Current; CJDW: Changjiang Diluted Water. The mud deposits (in shade of orange) are displayed according to Qin et al. (1996). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)