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Geochemical forms and seasonal variations of phosphorus in surface sediments of the East China Sea shelf

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ABSTRACT

Geochemical characteristics of phosphorus (P) in the surface sediments of the East China Sea shelf (ECSS) were studied in spring and autumn, 2014. Distributions, seasonal variations, transformations and their influencing factors were discussed. Besides, burial fluxes of P in different seasons were also calculated. Five operationally defined forms of P, namely exchangeable or loosely sorbed P (Ads-P), iron-bound P (Fe-P), authigenic P (Au-P), detrital apatite plus other inorganic P (De-P) and organic P (OP), were obtained using a sequential extraction procedure. Generally, the concentrations of Ads-P, Fe-P, Au-P and OP decreased seaward and the concentrations of De-P increased seaward in both seasons. In spring, the average concentrations of Ads-P, Fe-P, Au-P, De-P and OP were 13.8 ± 5.0, 21.9 ± 7.6, 148.5 ± 44.5, 153.1 ± 55.8 and $91.7 \pm 21.5\ \mu g\ g^{-1}$, respectively. The corresponding concentrations in autumn were 11.4 ± 4.3, 20.0 ± 10.9, 170.4 ± 53.6, 225.6 ± 101.7 and $77.1 \pm 33.9\ \mu g\ g^{-1}$, respectively. The average percentages of P fractions in total P (TP) in spring and autumn were both in the order: De-P > Au-P > OP > Fe-P > Ads-P. The average concentrations of Bio-available P (Bio-P) were $127.4 \pm 31.4\ \mu g\ g^{-1}$ in spring and $108.5 \pm 47.2\ \mu g\ g^{-1}$ in autumn, accounting for 29.8% ± 7.3% and 21.5% ± 8.2% of corresponding TP, respectively. Seasonal variations of the primary production, hydrodynamic conditions, hypoxia and other environmental conditions were responsible for the seasonal variations of different phosphorus forms. The calculation of burial fluxes reflected that, in most parts of the studied area, TP had relative high burial fluxes in autumn, while Bio-P had relatively high burial fluxes in spring. The burial fluxes of other phosphorus forms also showed different seasonal variations in different parts of the studied area.

1. Introduction

Affected by human-induced excessive nutrient input, Chinese coastal environments have experienced eutrophication, frequent occurrence of Harmful Algal Blooms (HABs), elevated productivity and seasonal hypoxia in bottom water in recent decades (Yu et al., 2013; Liu et al., 2015; Xing et al., 2015; Zhou et al., 2008, 2015). Sediment is an important indicator of marine environmental changes (Meyers, 2003; Schelske et al., 1988, 2006; Yu et al., 2013). Phosphorus (P), an important biogenic element, plays an important role in the biological productivity in marine environments (Benitez-Nelson, 2000; Song, 2010; Lui and Chen, 2011; Yu et al., 2012; Samadi-Maybodi et al., 2013; Zhuang et al., 2014). Its cycle is markedly affected by processes taking place in the sediments and at the water–sediment interface (Fisher et al., 1982; Ruttenberg and Berner, 1993; Van Raaphorst and Kloosterhuis, 1994; Föllmi, 1996). Marine sediment not only has a buffering effect on the P concentration in the overlying water, but also is an important source of P in seawater (Giblin et al., 1997; Zabel et al., 1998). According to the study of Fisher et al. (1982), sediments provided 28–35% of P needed in the primary productivity of coastal marine ecosystems.

The East China Sea (ECS) is a typical epicontinental sea (Fig. 1). It has been suffering from environmental deterioration in the rapid industrialization and urbanization of China in the past few decades. Especially since the late 1970s when China's reform and opening up began, a high loading of industrial effluents, agricultural runoff and domestic sewage as well as solid wastes from various human activities were discharged into the ECS (Li and Daler, 2004; Liu et al., 2015). In recent years, much attention has been paid to the P in sediments of different ECS areas, mainly the Changjiang (Yangtze River) Estuary and its adjacent waters owing to the enormous influence of the Changjiang's discharges on the ECS's ecosystem, and a general understanding of its basic geochemistry has been achieved. It has been reported that the total concentrations of P in the surface sediments of the Changjiang

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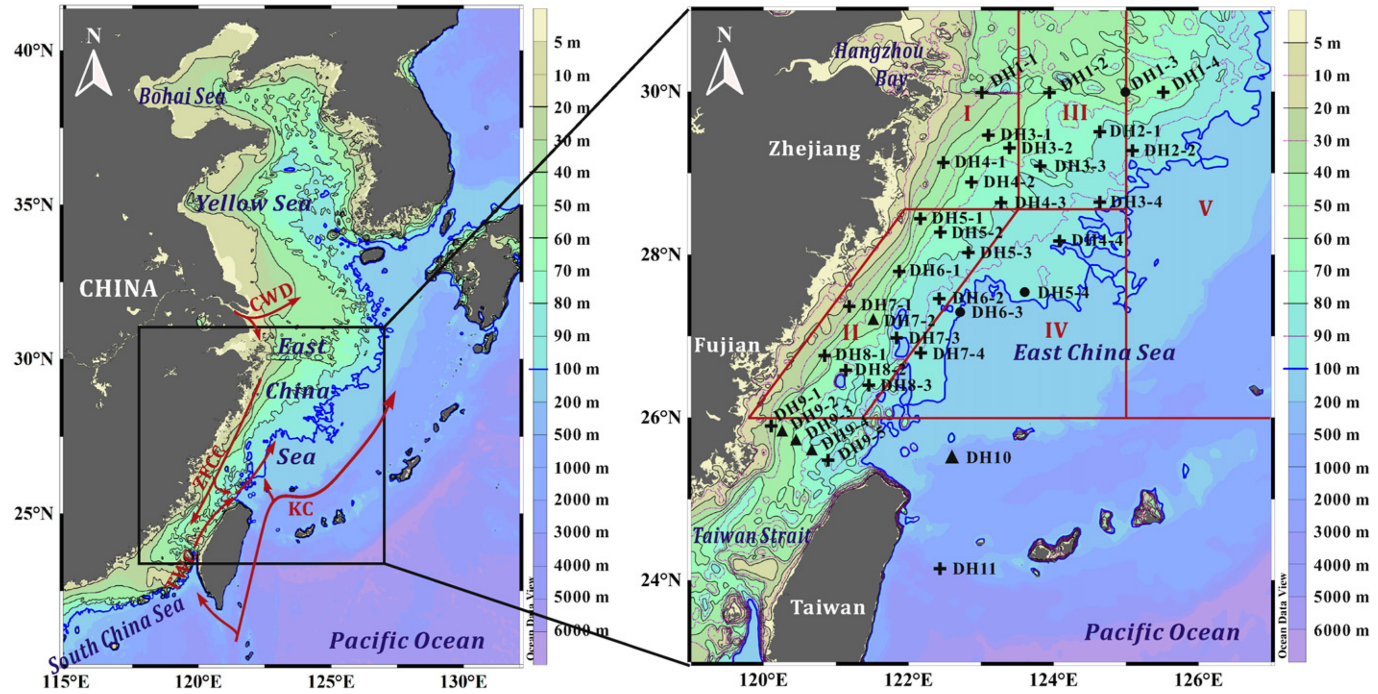

Fig. 1. Locations of sampling sites in the East China Sea shelf. + indicates the locations of sediment samples collected in both spring and autumn; ▲ indicates the locations of sediment samples collected only in spring; ● indicates the locations of sediments samples collected only in autumn. The studied area was divided into five subregions according to the study of Fang et al. (2007): (I) estuary, (II) inner shelf, (III) and (IV) middle shelf, and (V) outer shelf. Based on the principle of proximity, sites DH9-1, DH9-2, DH9-3, DH9-4, and DH9-5 were classified into subregion II and sites DH10 and DH11 were classified into subregion V, respectively. The major currents in the East China Sea are schematically shown. CDW, ZFCC, TWC and KC represent the Changjiang Diluted Water, the Zhejiang–Fujian Coastal Current, the Taiwan Warm Current and the Kuroshio Current, respectively.

Estuary and its adjacent waters varied within a wide range and it existed dominantly in inorganic forms (Fang et al., 2007; Yu et al., 2013; Meng et al., 2014; Yang et al., 2015). The seaward decreasing trends of some P forms revealed their terrestrial origins (Yu et al., 2013; Meng et al., 2014; Yang et al., 2015), and the concentrations of bio-available forms of P (Bio-P) in the northern part of the ECS were slightly lower than in the Yellow Sea (Song and Liu, 2015). The results obtained from the analysis of a sediment core from the ECS inner shelf mud area indicated that the geochemical information of detrital P (De-P) may provide insight into the linkages between regional climate change and flooding events in this region (Meng et al., 2015a).

However, studies on the seasonal variations of P in the surface sediments of the ECS have been largely ignored. The ECS has obvious seasonal variation characteristics, including the seasonal variations of freshwater discharge from coastal rivers, hypoxia outbreak time, nutrient concentrations, chlorophyll *a* (Chl *a*) concentrations, the primary production and so on (Chen et al., 2001, 2004; Rabouille et al., 2008; Wang, 2009; Li et al., 2014). As P has close relations to these parameters, there may be some seasonal variations for P in the surface sediments of the ECS. Besides, knowledge about P in the sediments of the ECS was mainly from the Changjiang Estuary and its adjacent areas, and few studies have focused on P in the sediments of the other parts of the ECS that is relatively far away from the Changjiang Estuary.

Therefore, this study aimed to investigate the concentrations and geochemical fractionations of P in the surface sediments of the ECS shelf (ECSS) generally between 25.5°N and 30°N based on the investigations of two cruises in spring and autumn, to analyze its seasonal variation characteristics and influencing factors, and calculate its burial fluxes.

2. Materials and methods

2.1. Study site and sample collection

The ECSS is bordered by Chinese mainland on the western side (Fig. 1). It is a dynamic system governed by the riverine input and currents (Fig. 1). The Changjiang, the third largest river in the world in its length and runoff, is the major source of materials to the ECSS (Fig. 1). The current system in the ECSS primarily consists of the Changjiang Diluted Water (CDW), the Zhejiang–Fujian Coastal Current (ZFCC), the Taiwan Warm Current (TWC), and the Kuroshio Current (KC) (Zhu et al., 2011) (Fig. 1).

The eco-environment of the ECSS has many obvious seasonal variation characteristics. The discharge of Changjiang is highly seasonal with its peak in summer and 75% of the river runoff occurring during the flood/rainy season between May and October (Rabouille et al., 2008). The hypoxia adjacent to the Changjiang Estuary, which is one of the largest coastal low-oxygen areas in the world (Chen et al., 2007), always occurs in summer and its zone has increased in recent decades (Rabouille et al., 2008; Wang, 2009). Wang et al. (2012) also noted that the increasing trend of hypoxia would continue in next two decades. The primary production in the coastal zone influenced by the Changjiang ranges from 1.5 to 4.5 $\mathrm{g\ C\ m^{-2}\ d^{-1}}$ (Chen et al., 2004) during summer. The high primary production is highly seasonal with values falling to 0.04 $\mathrm{g\ C\ m^{-2}\ d^{-1}}$ during winter (Chen et al., 2001). The nutrient levels in the Changjiang Estuary and the adjacent area generally peak during autumn and winter (or in early spring), and the lowest value usually occurs in mid-summer which is linked to the phytoplankton growth (Li et al., 2014). The Chl *a* concentrations in the Changjiang River Estuary and the adjacent area are high in summer and low in autumn and winter (Li et al., 2014). The HAB outbreak timing in the ECS has obvious seasonal variation (Li et al., 2014). During the 1980s, the peak of HABs for each year appeared in June to August. However, the frequency peak occurred from May to July in both the 1990s and 2000s (Li et al., 2014).

Sediment samples of this study were collected by a stainless steel box corer during two cruises carried out from May 22–June 11 (spring) and October 18–November 30 (autumn), 2014 on board R/V Science I in the ECSS with water depths generally <100 m, extending approximately from the east of Zhoushan Archipelago to the north of the Taiwan Strait (Fig. 1). The top ~2 cm sediments were gathered with a plastic spatula