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Baseline

Geochemical characteristics of phosphorus in surface sediments of two major Chinese mariculture areas: The Laizhou Bay and the coastal waters of the Zhangzi Island

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ABSTRACT

Phosphorus (P) in surface sediments of the Laizhou Bay (LB) and the coastal waters around the Zhangzi Island (ZI) was analyzed. Six forms of P were separated — exchangeable or loosely sorbed P (Ads–P), aluminum-bound P (Al–P), iron-bound P (Fe–P), authigenic apatite plus $CaCO_3$-bound P plus biogenic apatite (Ca–P), detrital apatite plus other inorganic P (De–P) and organic P (OP). The average contents of P in the LB were in the order: De–P > OP > Ca–P > Fe–P > Ads–P > Al–P; in the ZI, the corresponding order was De–P > OP > Fe–P > Ca–P > Ads–P > Al–P. Due to the high nutrient loadings from the surrounding rivers, TP contents in sediments of the LB were higher than in those of the ZI. The potential bio-available P (Ads–P and OP) accounted for 14.7% and 24.2% of TP in sediments of the LB and the ZI, respectively.

As an important biogenic element in the ocean, phosphorus (P) directly affects the primary productivity of the ocean and has a significant impact on the marine carbon cycle (Lui and Chen, 2011; Yu et al., 2012); P is also directly related to the global climate and environmental changes (Krom et al., 2004). Hecky and Kilham (1988) pointed out that P might be the element which controlled the global marine biological productivity during a long geologic time scale (>1000 years). As an important reservoir of P in marine environment, sediment not only has a buffering effect on the P content in the overlying water, but also is an important source of P in seawater (Giblin et al., 1997; Zabel et al., 1998). Fisher et al. (1982) reported that sediments provided 28–35% of P needed in the primary productivity of coastal marine ecosystems.

Both organic and inorganic forms of P are present in marine sediments. Inorganic forms of P may be adsorbed onto the surfaces of minerals, or be bound to aluminum, iron, or calcium (Föllmi, 1996; Benitez-Nelson, 2000; Łukawska-Matuszewska and Bolałek, 2008; Song, 2010). The binding forms of P in sediments have major influences on transportation, degradation, and the ultimate fate of P in marine ecosystems. Only certain forms of P can be transformed into bio-available ones after being affected by physical, chemical and biological factors, including desorption, dissolution and reduction processes (Song, 2010). After that, the bio-available forms of P are released into the overlying water. These certain forms of P become important factors affecting the trophic status of water or causing eutrophication (Eijsink et al., 2000). Therefore, research on the geochemical forms of P in sediments may help researchers understand the dynamic cycle of P in seawater and sediments, such as migration and transformation between sediments and the overlying water, and subsequent diagenesis and other geochemical processes (Zabel et al., 1998; Eijsink et al., 2000).

The Laizhou Bay and the surrounding marine area of the Zhangzi Island (hereafter referred to as the Zhangzi Island for short) are important mariculture zones in China, and they are located in the Bohai Sea and the northern North Yellow Sea, respectively. In recent years, the ecological environments of the Bohai Sea and the Yellow Sea have changed dramatically under dual influences of human activities and natural environmental factors (Pan and Wang, 2012; Gao et al., 2014a,b); especially in the water column of the Bohai Sea, P concentration displayed a decreasing tendency (Zhang et al., 2004; Liu et al., 2004a; Wang et al., 2009; Liu et al., 2011a). Xia et al. (2009) reported that the supplementation of the soluble reactive phosphate in the Laizhou Bay was not only from river input

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but also from the mineralization and regeneration of organic matter in sediments. Liu et al. (2011b) showed that nitrogen pollution was serious in the entire Laizhou Bay from 2006 to 2009, however P was inadequate. In the aforementioned four years, the average N/P value was 164, which was much higher than the Redfield ratio 16 (Redfield, 1958). In the summer of 2011, the growth of phytoplankton in the North Yellow Sea was limited by P (Li et al., 2013). The regeneration of P in sediments plays an important role in the balance and the dynamical circulation of P nutrient in the aqueous system. However, comparing with other areas in the Bohai Sea and the Yellow Sea, the information on sedimentary P in the Laizhou Bay and the Zhangzi Island is very limited.

In this study, a sequential extraction method (SEDEX) (Ruttenberg, 1992) was employed to operationally discriminate six different forms of sedimentary P in the Laizhou Bay and the Zhangzi Island. The purposes of this research are to investigate the contents and geochemical fractionation of P in surface sediments of the Laizhou Bay and the Zhangzi Island, examine factors influencing their distributions and determine the potential mobility of P from sediments to the overlaying waters of these two areas.

The Laizhou Bay (area – ~7000 km^2, coastline length – ~320 km, mean depth <10 m, max. depth – ~18 m) lies in the southern part of the Bohai Sea, accounting for up to 10% of the total area (Fig. 1). The sea floor of the Laizhou Bay is relatively flat which is caused by the accumulation of riverine sediments. There are more than a dozen of rivers running into the Laizhou Bay, such as the Yellow River and the Xiaoqinghe River. The Yellow River is characterized by high concentration of suspended sediments and high deposition rate in its delta area (Liu et al., 2004b). Most of the other rivers are small and seasonal. The Laizhou Bay is an important spawning and breeding ground for many marine organisms. However, due to the abundant seawater resources and underground brine resources, more than 400 chemical enterprises are located in the southwestern coast of the Laizhou Bay and over 150 kinds of chemical products are manufactured. Derived from many point sources such as industrial wastewaters, domestic sewage and agricultural discharges, non-purified or insufficiently purified wastewaters are discharged into the Laizhou Bay. The Laizhou Bay can be characterized as a region surrounded by areas of high population growth and economic development in China (Zhuang and Gao, 2013).

The Zhangzi Island (coastline length – 60 km) is located in a national first-class clean sea area in the northern North Yellow Sea which is ~100 km away from Dalian City, Liaoning Province (Fig. 1). The Zhangzi Island is one of the islands of Changshan Archipelagos, composed of more than a hundred islands and islets. The offshore area of the Zhangzi Island is the largest aquaculture base for artificial breeding, larval rearing and cultivating of seafood with high economic value added in China, which produces scallops, sea cucumbers, abalones, sea urchins, conchs and so on. The only national original seed field for *Patinopecten yessoensis* is located in this area. Fodder–feeding has been banned from seafood farming for many years in this area, and the cultivation of crops on the islands is also prohibited. Therefore, its coastal environmental quality is generally better than other typical Chinese coastal seas such as the Laizhou Bay; meanwhile, the phosphorus in the water

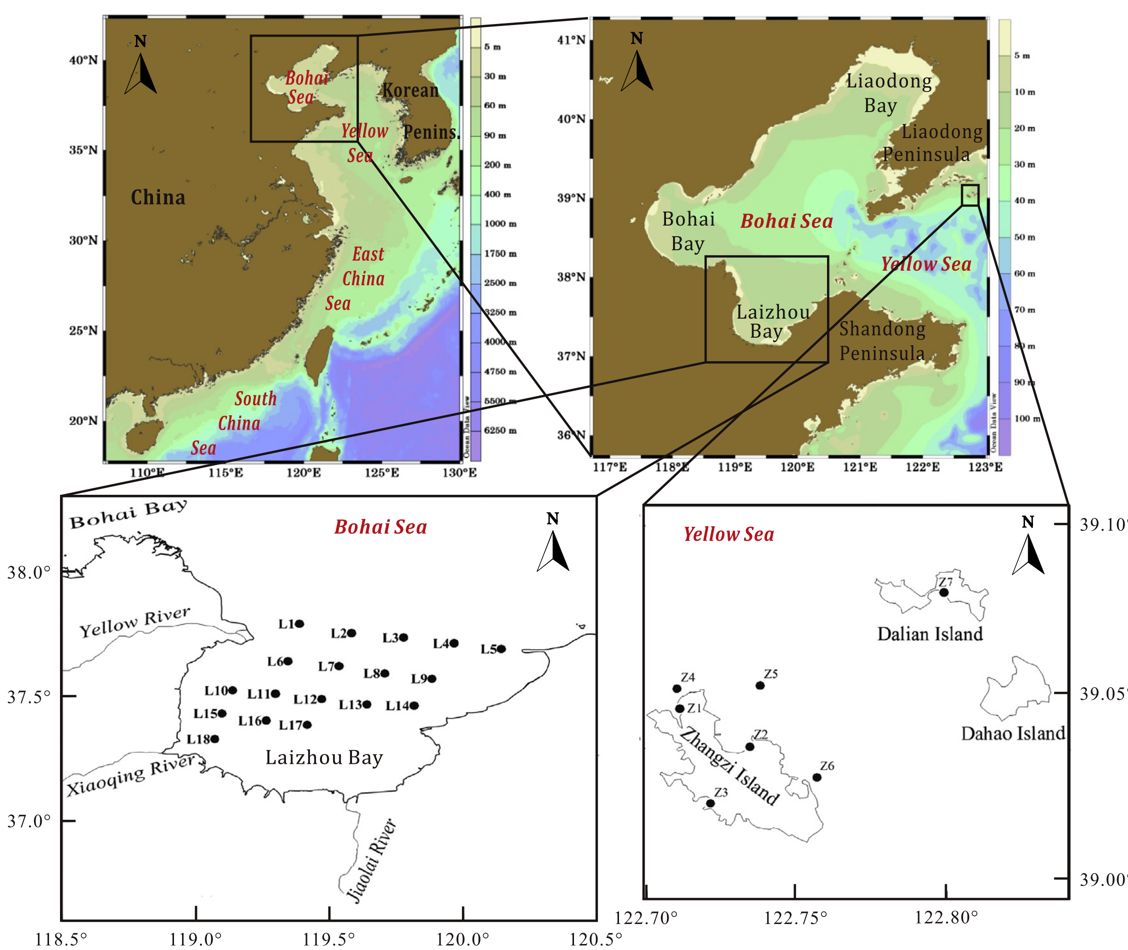

Fig. 1. Location of sampling stations in the Laizhou Bay and the coastal waters of the Zhangzi Island.

column of this kind of area may be insufficient for the needs of primary producers.

A total of 18 surface sediment samples were collected from the Laizhou Bay in October 2011 and 7 surface sediment samples were collected from the Zhangzi Island in November 2011 to investigate the geochemical characteristics and environmental quality of biogenic elements and trace metals (Fig. 1; Gao et al., 2013, 2014a,b; Zhuang and Gao, 2014). In the Laizhou Bay, sampling stations L1 and L6 were near to the new and old estuaries of the Yellow River, respectively; station L18 was near to the estuary of the Xiaoqinghe River. In the surrounding marine area of the Zhangzi Island, three stations were located in the intertidal zone (Z1 – Z3); three were in the coastal waters (Z4 – Z6), among which Z4 and Z5 were located in the mariculture areas where sea cucumbers and scallops were farmed, respectively. Station Z7 was in the intertidal zone of an outer island called Dalian Island. Surface sediment samples of the top ~5 cm were collected by a stainless steel grab sampler and/or a plastic spatula, and were placed in acid-rinsed polyethylene bags. They were transported to the laboratory in a cooler box with ice packs and stored at −20 °C until further treatment.

Fractionation of P in sediments is often quantified by operationally defined sequential extraction techniques such as the SEDEX method (Ruttenberg, 1992). This method has been widely accepted and found to be robust in strikingly different sediments from different sedimentary environments including lakes, rivers, soils, continental margins and deep-sea sediments (Ruttenberg, 1992; Ruttenberg and Berner, 1993). Authigenic carbonate fluorapatite (CFAP) could be chemically separated from detrital apatite (FAP) by using SEDEX method. CFAP represents an oceanic sink for reactive P whereas FAP does not (Liu et al., 2004b). In this study, we employed the SEDEX method originally developed by Ruttenberg (1992) and modified by adding an aluminum-bound P extracting step to determine different phosphorus phases (Gunduz et al., 2011). The six operationally defined forms of reactive phosphorus phases which were separated under this scheme are: (i) exchangeable or loosely sorbed phosphorus (Ads–P); (ii) aluminum-bound phosphorus (Al–P); (iii) iron-bound phosphorus (Fe–P); (iv) authigenic apatite plus $CaCO_3$-bound phosphorus plus biogenic apatite (Ca–P); (v) detrital apatite plus other inorganic phosphorus (De–P) and (vi) organic phosphorus (OP). Total phosphorus (TP) content was the sum of OP and inorganic phosphorus (IP) contents.

Freeze-dried samples were thoroughly ground, homogenized and sieved through a 200 mesh screen. The sequential extraction scheme was performed by using 0.1 g sediment in a 50 ml extractant solution volume. Ads–P was extracted with 1 M $MgCl_2$ (pH = 8.0). Al–P was extracted with 0.5 M NH_4F. Fe–P was extracted with CDB (0.22 M sodium citrate, 0.14 M sodium dithionite, 1.0 M sodium bicarbonate) (pH = 7.6). Ca–P was extracted with acetate buffer (pH = 4.0). De–P was extracted with 1 M HCl. Finally, OP in the residual sediment samples was extracted with 1 M HCl after ashing the samples at 550 °C for 2 h.

Analyses of P concentration were performed with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP–OES) (Optima 7000DV, PerkinElmer, USA) and the analytical conditions followed Gunduz' study (Gunduz et al., 2011). The selection of instrumental parameters and optical wavelength was based on obtaining good sensitivity, reasonable detection limits, and eliminating interferences (Aydin et al., 2009). In this study, 213.617 nm was chosen as spectral wavelength for P analyses (Gunduz et al., 2011).

The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, and analysis of replicates. The precision of the analytical procedures was expressed as the relative standard deviation (RSD). The precision of the analysis of standard solution was better than 5%; all analyses of samples were carried out in duplicate and the RSD were less than 10%, and the results were expressed as the mean. Duplicate for 10 samples were also made in the SEDEX process, and the RSD were less than 10%. All reagents were analytical or guaranteed grade; all the labwares (bottles, tubes, etc.) were pre-cleaned by soaking in 10% HNO_3 (v/v) for at least 2 days, followed by soaking and rinsing with de-ionized water.

The organic carbon (OC) in sediments was obtained by determining the total carbon using an Elementar vario MACRO cube CHNS analyzer after removing the inorganic carbon with 1 M HCl. The substance contents of sediments were expressed in dry weight basis based on the results of moisture contents, which were determined gravimetrically by comparing the weight differences before and after heating an aliquot of sediment at 105 °C until constant weight was obtained.

The particle size of bulk samples was analyzed by a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of the following three groups of grain sizes were determined as in the work of Gao et al. (2008, 2010, 2013, 2014a,b), Gao and Chen (2012), Zhuang and Gao (2013, 2014) and so on: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand).

The sediments in the Laizhou Bay were mainly composed of fine components (clay + silt) with the percentages of more than 80% for most of the samples (Fig. 2). Sediments of the stations in the east-central area of the Bay had relatively less clay or silt than those of other stations except L18. L18 was close to the estuary of the Xiaoqinghe River, and the percentage of sand was up to 59.2%. Sediments in the Zhangzi Island were mainly composed of sand with percentages of coarse fraction more than 70% for most of the samples (Fig. 2). Stations Z4, Z5 and Z6 located at coastal waters had relatively lower sand contents but higher clay and silt contents than other stations located at the intertidal zone. In summary, the studied surface sediments of the Laizhou Bay were predominantly composed of clayey silt and sandy silt; the surface sediments of the Zhangzi Island were dominated by sand and silty sand (Gao et al., 2014a,b).

OC contents in sediments of the Laizhou Bay varied between 0.14% and 1.51% with an average of 0.67%. In the Zhangzi Island, OC contents varied between 0.12% and 2.18% with an average of 0.73%. The differences among the samples were significant. Generally, sediments with higher percentages of fine components (clay and silt) had higher OC contents (Fig. 2). Similar results were found in sediments of coastal areas by other researchers (Duan et al., 2012; Gao and Chen, 2012; Wang et al., 2012).

Spatial variations of IP and TP in surface sediments of the Laizhou Bay and the Zhangzi Island were shown in Fig. 3. TP contents in surface sediments of the Laizhou Bay ranged from 315.9 $\mu g\ g^{-1}$ to 582.7 $\mu g\ g^{-1}$, with an average value of 485.7 $\mu g\ g^{-1}$ (Fig. 3; Table 1). The maximum TP content appeared in L12 and the minimum in L14. TP contents in surface sediments of the Zhangzi Island ranged from 81.3 $\mu g\ g^{-1}$ to 401.3 $\mu g\ g^{-1}$, with an average value of 275.6 $\mu g\ g^{-1}$. The maximum TP content appeared in Z6 and the minimum in Z2. The average TP content in the Laizhou Bay was about 1.8 times the average TP content of the Zhangzi Island.

IP contents in surface sediments of the Laizhou Bay ranged from 272.5 $\mu g\ g^{-1}$ to 491.8 $\mu g\ g^{-1}$, with an average value of 423.6 $\mu g\ g^{-1}$, which accounted for 87.4% of the TP content. Both TP and IP contents decreased from the west to the east of the Bay (Fig. 3). However, the maximum value appeared in the central zone of the Bay (Fig. 3). IP contents in surface sediments of the Zhangzi Island ranged from 58.5 $\mu g\ g^{-1}$ to 323.2 $\mu g\ g^{-1}$, with an average value of 226.4 $\mu g\ g^{-1}$, which accounted for 80.3% of the

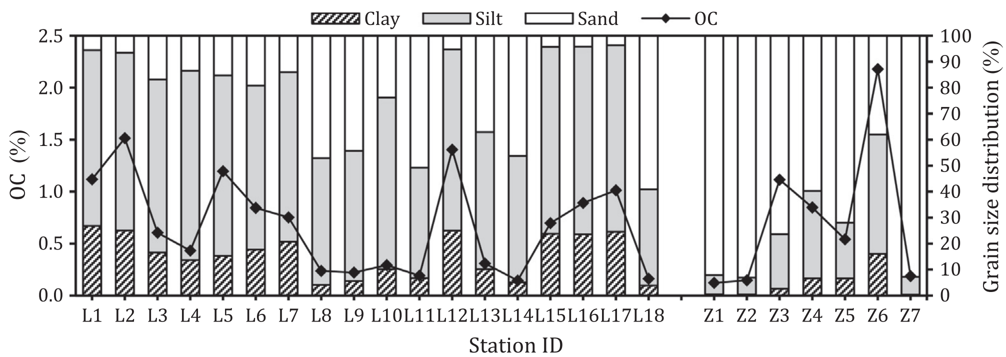

Fig. 2. Spatial variations of grain size distribution and OC concentration in surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China.

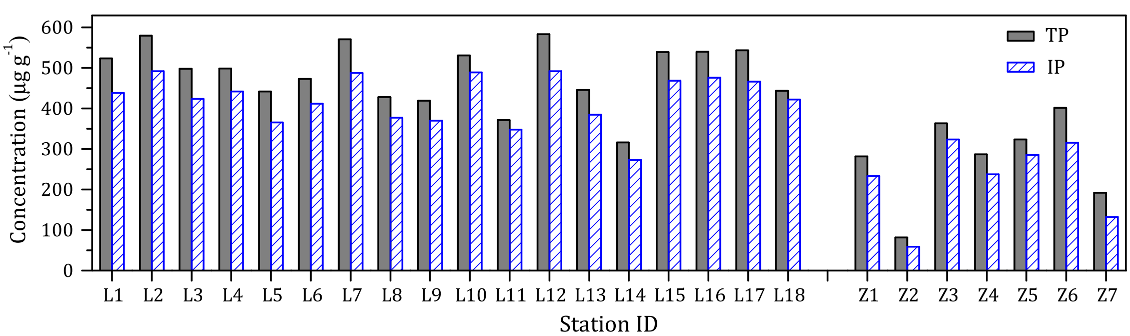

Fig. 3. Spatial variations of IP and TP in surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China.

Table 1
Contents of phosphorus forms in surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China. The values were expressed as $\mu g\ g^{-1}$ dry sediment weight and the percentages of TP, respectively.

Location		Ads–P	Al–P	Fe–P	Ca–P	De–P	OP	TP
Laizhou Bay	Min. ($\mu g\ g^{-1}$)	1.1	<0.01	5.6	18.9	230.1	21.4	315.9
	Max. ($\mu g\ g^{-1}$)	18.4	3.4	50.9	100.3	408.0	90.9	582.7
	Mean ($\mu g\ g^{-1}$)	10.7	1.1	31.7	60.2	320.0	62.1	485.7
	RSD (%)	51.5	83.3	39.7	46.3	13.4	33.6	15.3
	Min. (%)	0.4	<0.1	1.1	5.2	55.0	4.8	
	Max. (%)	3.4	0.6	9.4	19.2	83.6	17.3	
	Mean (%)	2.1	0.2	6.5	11.9	66.7	12.6	
Zhangzi Island	Min. ($\mu g\ g^{-1}$)	2.2	0.6	19.8	8.6	16.3	22.8	81.3
	Max. ($\mu g\ g^{-1}$)	34.4	18.5	49.9	96.9	203.6	85.8	401.3
	Mean ($\mu g\ g^{-1}$)	13.1	3.6	33.0	31.4	145.4	49.1	275.6
	RSD (%)	81.1	184.1	30.3	98.0	46.6	40.4	39.4
	Min. (%)	2.3	0.3	9.1	3.1	20.0	11.0	
	Max. (%)	9.5	5.7	27.9	24.1	65.8	31.1	
	Mean (%)	4.5	1.3	13.7	11.3	49.5	19.7	

TP content (Table 1). The maximum content of IP was observed in Z3 and the minimum in Z2 (Fig. 3).

Spatial variations of phosphorus forms in surface sediments of the Laizhou Bay and the Zhangzi Island were shown in Fig. 4. Ads–P contents in surface sediments of both areas were very low. In the Laizhou Bay, the contents of Ads–P ranged from 1.1 to 18.4 $\mu g\ g^{-1}$, which accounted for 0.4–3.4% of the TP contents (Table 1). In the Zhangzi Island, the corresponding data were 2.2–34.4 $\mu g\ g^{-1}$ and 2.3–9.5%, respectively.

In the Laizhou Bay, contents of Al–P and Fe–P ranged from <0.01 to 3.4 $\mu g\ g^{-1}$ and 5.6 to 50.9 $\mu g\ g^{-1}$, respectively, which accounted for <0.1–0.6% and 1.1–9.4% of TP contents, respectively. In the Zhangzi Island, the corresponding data were 0.6–18.5 $\mu g\ g^{-1}$, 19.8–49.9 $\mu g\ g^{-1}$, 0.3–5.7% and 9.1–27.9%, respectively (Table 1). Generally, sediments in the southern area contained more Al–P than in the northern area of the Laizhou Bay. In the Zhangzi Island, the proportion of Al–P was higher, and extremely high Al–P content was found in Z5.

In the Laizhou Bay, Ca–P contents ranged from 18.9 to 100.3 $\mu g\ g^{-1}$, which represented 5.2–19.2% of the TP contents. In the Zhangzi Island, the corresponding data were 8.6–96.9 $\mu g\ g^{-1}$ and 3.1–24.1%, respectively (Table 1). In the Laizhou Bay, the maximum Ca–P content was recorded in L1 which was located at the Yellow River Estuary. Ca–P content decreased in the outflow direction of the Yellow River. In the Zhangzi Island, stations Z3, Z4 and Z6 which were relatively richer in OC and contained more fine fractions were relatively richer in Ca–P compared with other stations. In the Laizhou Bay, contents of De–P ranged from 230.1 to 408.0 $\mu g\ g^{-1}$, which represented 55.0–83.6% of the TP contents. In the Zhangzi Island, the corresponding data were 16.3–203.6 $\mu g\ g^{-1}$ and 20.0–65.8%, respectively (Table 1).

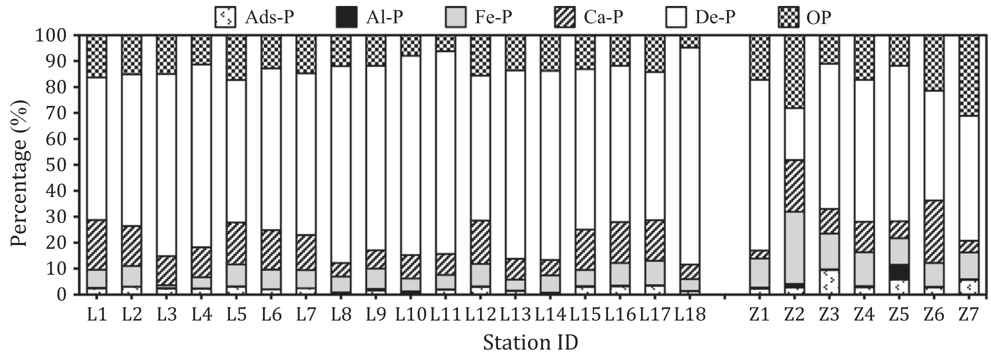

Fig. 4. Spatial variations of phosphorus forms in surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China.

OP contents in the Laizhou Bay ranged from 21.4 $\mu g\, g^{-1}$ to 90.9 $\mu g\, g^{-1}$, with an average value of 62.1 $\mu g\, g^{-1}$, which accounted for 12.6% of the TP content. Contents of OP in the Zhangzi Island ranged from 22.8 $\mu g\, g^{-1}$ to 85.8 $\mu g\, g^{-1}$, with an average value of 49.1 $\mu g\, g^{-1}$, which accounted for 19.7% of the TP content (Table 1).

The average contents of different forms of P in surface sediments of the Laizhou Bay were in the order: De–P > OP > Ca–P > Fe–P > Ads–P > Al–P; in the Zhangzi Island, the corresponding order was De–P > OP > Fe–P > Ca–P > Ads–P > Al–P.

Generally, TP contents in surface sediments of the Laizhou Bay were much higher than those of the Zhangzi Island (Table 1). Previous studies showed that physicochemical properties of sediments, oxygen conditions in water and sediments, and depth of the water column all have significant impacts on the spatial variability of contents of TP and fractionations (Łukawska-Matuszewska and Bolałek, 2008). High TP content in sediments of the Laizhou Bay was the combined results of the complex geological structure within the basin, river input, chemical plants discharge and agriculture activities in the coastal zone. In the Zhangzi Island, fodder–feeding has been banned from seafood farming for many years, and the cultivation of crops on the islands is also prohibited. Moreover, the surrounding marine area of the Zhangzi Island is relatively farther from the mainland. Therefore, a lower level of P loaded from anthropogenic sources is expected, indicating that sources of P may be mainly of biogenic origin in the surrounding marine area of the Zhangzi Island, due to the deposition of P after the death of fish, shellfish, plankton and other marine organisms.

Both TP and IP contents decreased from the west to the east in the Laizhou Bay and this was due to the fact that a large amount of P was brought in by rivers from the west and the southwest zone of the Bay (Fig. 3). Previous study found that the high contents of IP and TP in the Yellow River Estuary were due to the high content of P in loess, which was eroded over the drainage basin and carried by the Yellow River (Liu et al., 2004b). It also may be due to the formation of P and iron compounds with the sorption of phosphate ions, which may cause the increase of TP content in sediments (Murphy et al., 2001). However, the maximum value was observed in the central zone of the Bay (L12) (Fig. 3), which may be due to tides and currents that can promote the content of P in the central zone of the Bay. In the Zhangzi Island, station Z6 was located near the mariculture area and was relatively rich in organic and inorganic P compared with other stations in the Zhangzi Island. In the intertidal zones where coarse fractions were dominant, P contents were much lower, due to the considerable dynamics of the bottom water and intensive sea floor transport (Łukawska-Matuszewska and Bolałek, 2008). Z2 located at an intertidal zone with sandy sediments was a typical example; both IP and OP contents were the lowest in Z2. The results indicated that IP was the dominant part of TP. Similar results were found by other researchers (Lai and Lam, 2008).

The distributions of OP were different from IP, indicating that the sources of OP were different from those of IP. OP can be more affected by biological and physical factors than IP. In addition, it can be bio-available partly, and is more associated with anthropogenic activities than most of IP forms (Ruban et al., 2001). OP mainly derives from terrestrial input and biological processes such as the food chain. Content level of OP may directly affect dissolved P in the primary productivity (Vaalgamaa, 2004). By the combined effects of input, deposition characteristics, early diagenesis and biological effects, OP contents in surface sediments of the Laizhou Bay were much higher than those of the Zhangzi Island. However, percentages of OP to TP in surface sediments of the Zhangzi Island were much higher than those in the Laizhou Bay, and this could be explained by some reasons. The Zhangzi Island is situated at the latitude somewhat higher than the Laizhou Bay, so the annual average seawater temperature is relatively lower; under this condition the accumulation rate might be rapid and the degradation of organic matter might be less efficient (Nyenje et al., 2010). In addition, the Zhangzi Island is located at a transition zone from an inner shelf dominated by detrital sediments to an outer shelf dominated by biogenic sediments (Lin et al., 2002). The Zhangzi Island is rich in aquaculture resources, thus the deposition of OP is in a higher proportion after the death of marine lives.

Values of TP, IP and OP of the Zhangzi Island were lower than those of the Laizhou Bay. The surrounding coastal waters of the Zhangzi Island are relatively farther from the mainland with less anthropogenic influences such as agricultural activities, so less land-based sources of P are expected. The discharge of continental groundwater along beaches and through the seafloor is also an important transportation pathway of nutrients to coastal waters (Moore, 1999; Burnett et al., 2006; Spiteri et al., 2008; Smith and Swarzenski, 2012). A possible enrichment of P in the Laizhou Bay and the surrounding marine area of the Zhangzi Island also could be supplied by submarine groundwater discharge (SGD). However, up to now no information is available for this specific case study. In order to ascertain if SGD delivers phosphorous in the seawater, further multidisciplinary investigations are necessary, both in the mainland and marine areas, where freshwater and seawater interact and biogeochemical reactions play an important role.

TP and OP contents in sediments of the Laizhou Bay and the Zhangzi Island were compared with values of other industrialized coastal zones found in the literature (Table 2). TP values obtained from the Laizhou Bay and the Zhangzi Island were higher than those from Wadden Sea and Adriatic Sea, but lower than those from Seto Inland Sea, Kieler Bucht, Aarhus Bay and Gulf of St. Laurent. This could be explained by the higher dissolved inorganic N/P ratios, and it is also related to the lower concentrations of phosphate in Chinese rivers (e.g. the Yellow River (Huanghe) and the Yangtze River (Changjiang)) than most of other rivers in the world (e.g. the Seine River and the Rhine River) (Liu et al., 2003). Contents

Table 2
Comparison of concentrations of total phosphorus (TP) and organic phosphorus (OP) found in literature for some coastal sediments and the present study (μg g^{-1}).

Study area	Sediment nature	TP	OP	Reference
Wadden Sea	Silt	93–155	15.5–77.5	De Jonge et al. (1993)
Seto Inland Sea	Silty clay	496–682	186–310	Yamada and Kayama (1987)
Kieler Bucht, Western Baltic	Clayey sand – clay	310–1240	31–372	Balzer (1986)
Adriatic Sea	Silt to clay	155–217	15.5	Giordani and Astorri (1986)
Aarhus Bay	Silt	930–1550	155	Jensen and Thamdrup (1993)
Gulf of St. Laurent		1627.5	105.4	Sundby et al. (1992)
Bay of Seine	Sand	155–651	1.55–248	Andrieux and Aminot (1997)
North Sea	Sand – silt	93–806	52.7–279	Slomp et al. (1998)
Bohai Sea	Silt – clay	310–620	21.7–217	Liu et al. (2004b)
East China Sea		418–690	34–182	Fang et al. (2007)
NW East China Sea		444.2–672.4		Yu et al. (2013)
The Gulf of Gdańsk (southern Baltic Sea)	Clay-silt-sand	54–29672	2–16291	Łukawska-Matuszewska and Bolałek, (2008)
Southwest Yellow Sea		278–768	160–653	Hong et al. (2010)
Laizhou Bay	Clayey silt – sandy silt	315.9–582.7	21.4–90.9	This study
Zhangzi Island	Sand – silty sand	81.3–401.3	22.8–85.8	This study

of TP and OP in this study are consistent with the data obtained from the Bohai Bay in other studies (Liu et al., 2004b). In general, both TP and OP contents in the two studied areas were below the medium level comparing with other sea areas in the literature.

The atomic ratio of the organic carbon (OC) to OP (OC/OP) is commonly used to indicate the sources of organic matters in sediments. In general, the atomic ratio of OC to OP in marine phytoplankton is 106 (Anderson and Sarmiento, 1994). If the value in sediment is lower than 106, there will be more reactive P than OC in sediments, and the OP will be well-preserved. If the value in sediments is higher than 106, the organic matter in sediments would be mainly from the foreign source input. Except station L14 of the Laizhou Bay and Z1 and Z7 of the Zhangzi Island, OC/OP in all the sediments of the other stations were above 106, which indicated that organic matters in sediments of the Laizhou Bay and the Zhangzi Island were mainly from the foreign source input (Fig. 5). Organic matter in the Laizhou Bay may be mainly brought by river input, and organic matter in the Zhangzi Island may be brought by sewage (residual feeds, excrement and suspended particles, etc.) discharged during the process of seedling raising or by ships during the process of fishing and seeding.

Ads–P represents the loosely sorbed and exchangeable P in sediments; it may include dissolved P in pore water (Kaiserli et al., 2002). It is also a seasonally variable pool of P compounds (Rydin, 2000). Ads–P in sediments is the reactive P. The main carriers of Ads–P are oxides, hydroxides and clay mineral particles in sediments. Physical–chemical factors such as temperature, pH, water dynamic conditions, bioturbation and the redox characteristics can lead to the release of Ads–P into the water column (Chen et al., 2011). In the two studied areas, the mean contents of Ads–P in sediments were the second lowest among the five IP fractions, and exhibited high variability in various sampling sites. In the Laizhou Bay, the maximum Ads–P content was observed in the central zone of the Bay (L17) (Fig. 4), which may be due to tides and currents that carry Ads–P into the central zone of the Bay. Particle size is also an important factor in controlling the contents of Ads–P in sediments. Sediments with smaller particle size would have stronger adsorption capacity due to greater specific surface area. This explained that the Ads–P contents were higher in fine-grained sediments (Figs. 2 and 4). Sand component of the sediment of Z2 was up to 93.1%; therefore, its Ads–P content was the lowest (2.2 μg g^{-1}).

Al–P and Fe–P combining with oxides of Al, Fe and Mn and their hydrates are considered to be bio-available P. Al–P and Fe–P are closely related to anthropogenic activities and are considered to be originated mainly from domestic sewage and industrial wastewater (Jensen et al., 1995). Fe/Al–P is considered to be easily resolved constituent of sediments, since they may change with the redox changes in the environment. When redox potential (Eh) is lower, iron ions are reduced, and P is released, P concentrations in water may increase. When Eh increases, active iron is oxidized and rapidly adsorbs P from the water column, P concentrations in water may decrease; thus P exchange occurs at the sediment–water interface (Zhou et al., 2005; Smolders et al., 2006). P is transported primarily in organic forms or adsorbed onto iron oxides in riverine waters. In the estuaries of the rivers, the residence time of riverine water extends, and this may promote the sedimentation of suspended matters, which can enrich the sediment with iron and phosphorus (Lebo, 1991; Zwolsman, 1994). This process explains well why Fe–P contents increased gradually in the outflow direction of the river and then decreased after a certain distance. Fe/Al–P is often used as an important indicator of sediment quality (Wang et al., 2006). Active Fe and Al (hydrated) oxides are widely regarded as the main adsorbent for P in natural sediments. Fe/Al–P

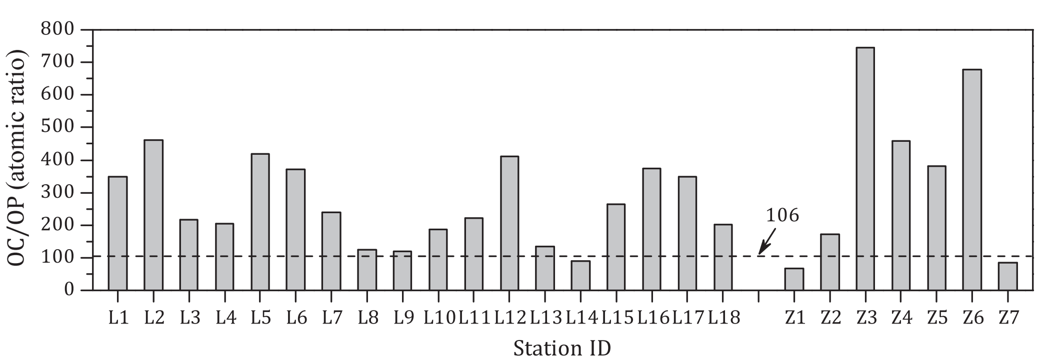

Fig. 5. Atomic ratios of OC and OP in surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island.

contents in the Zhangzi Island were higher than those in the Laizhou Bay, and extremely high Al–P content was found in Z5 which implied a potential contamination. The high Al–P content may be caused by sewage discharged during the process of seedling raising. However, the real cause has not been clear and further research is needed.

Ca–P is mainly originated from the detritus of biological bones, P combined with calcium carbonate and carbonate fluorapatite which can precipitate in interstitial water. In the two studied areas, the mean content of Ca–P was the second highest among the five IP fractions. Soil in northern China is generally calcareous, and the Yellow River sediments contain large amounts of detrital apatite, hence the contents of calcium bound phosphorus were expected to be high in sediments (Liu et al., 2004b). Ranges of Ca–P content in the Laizhou Bay and the Zhangzi Island were similar. L1 was located at the spot near to the Yellow River Estuary, so it was explicable that Ca–P content was the highest. Ca–P content decreased in the outflow direction of the Yellow River. Station Z6 located near the mariculture area was relatively rich in Ca–P compared with other stations in the Zhangzi Island, indicating that Ca–P in surface sediments was mainly derived from the bone detritus of marine organism.

De–P is mainly derived from magma and metamorphic rocks as well as marine sediments under strong riverine influence, i.e. terrestrial material which contains spherical detrital particles with smooth edges and a small specific area (Ruttenberg, 1992; Ruttenberg and Berner, 1993). De–P was the most abundant form of IP in this study (Table 1; Fig. 4). The results indicated a higher proportion of diagenesis of calcium phosphate. This result is in good agreement with studies over the Yangtze River Estuary (Rao and Berner, 1997), the Bohai Sea and the Yellow Sea (Liu et al., 2004b) and the East China Sea (Fang et al., 2007; Yu et al., 2013). However, De–P has been found to be a minor form (<1% of TP) in deep-sea sediments in the equatorial Pacific (Filippelli and Delaney, 1996) and can be 40–76% of TP in the river/estuary sediments (Rao and Berner, 1997). De–P contents decreased from the southwest to the northeast in sediments of the Laizhou Bay. This partially explained the relatively higher proportions of De–P in estuary sediments. De–P accounted for a smaller part of TP in the Zhangzi Island compared with the Laizhou Bay. The Zhangzi Island is relatively farther from the mainland, thus P content is less affected by terrestrial input.

Although the contents of P in sediments of the Laizhou Bay and the Zhangzi Island were relatively plentiful, the seawater was close to or at the state of P limitation in recent years. In the summer of 2009, the contents of dissolved inorganic nitrogen (DIN) in surface seawater of the Laizhou Bay were 2–51.43 μmol l^{-1} with the average value of 14.21 μmol l^{-1}; the contents of PO_4^{3-}–P were 0.03–0.29 μmol l^{-1} with the average value of 0.07 μmol l^{-1} (Liu et al., 2011b). The average molar ratios of DIN to PO_4^{3-}–P (N/P) in surface seawater of the Laizhou Bay rose from 115 in 2006 to 199 in 2009 (Liu et al., 2011b). This was mainly influenced by nitrogen sources in rivers of the southwest coast, in which, the influence of Xiaoqinghe River was obviously the most (Liu et al., 2011b). Li et al. (2013) found that the average content of DIN was 1.99 μmol l^{-1} while the average content of PO_4^{3-}–P was 0.15 μmol l^{-1} in surface seawater of the North Yellow Sea in the summer of 2011 with the range of N/P ratios of 4–66. The highest N/P value (66) was recorded near the bottom of Liaodong Peninsula, which was significantly affected by terrigenous input. In general, P restricted the growth of phytoplankton in the North Yellow Sea in summer (Li et al., 2013). The Laizhou Bay and the Zhangzi Island are two major mariculture areas in China, therefore, measures should be taken to reduce the input of nitrogen caused by human activities and increase the content of P in their water bodies (whether through putting in the bait or by making use of P in sediments).

Results of Pearson correlation analysis were shown in Table 3. There was a significant positive correlation between Fe–P and OC ($r = 0.663$, $p < 0.001$), Fe–P and OP ($r = 0.445$, $0.01 < p < 0.05$). In riverine water, organic forms or those adsorbed onto iron oxides were the primary forms of P in transporting (Lebo, 1991; Zwolsman, 1994). The extended residence time of riverine water in the estuary of the rivers surrounding the Laizhou Bay promoted sedimentation of riverine suspended matters, which enriched sediments with iron and phosphorus. There was no correlation between Ads–P and OP, indicating that they had no common source. There were significant positive correlations between Ca–P and IP ($r = 0.697$, $p < 0.001$), and between Ca–P and TP ($r = 0.768$, $p < 0.001$), which indicated that Ca–P was an important source for IP and TP. De–P had the highest significant positive correlations with IP ($r = 0.935$, $p < 0.001$) and TP ($r = 0.893$, $p < 0.001$), which indicated that IP and TP were mainly from the physical weathering and/or erosion of material from continents (Table 3).

There were significant positive correlations between OC and Ads–P, Fe–P, Ca–P, OP, TP respectively (Table 3). This indicated that organic matters played significant roles in shaping the distribution of geochemical fractionation of P in sediments (Łukawska-Matuszewska and Bolałek, 2008). Due to the high nutrient loadings in the water column and substantial organic input from rich biota, the Laizhou Bay also recorded appreciable contents of TP and OC in sediments. There were significant negative correlations between sand fraction and Ca–P, De–P, OP, IP, TP, OC, respectively. Over 70% of variation of TP content in sediments in the Gulf of Gdańsk could be explained by changes of proportion of the fine fraction (Łukawska-Matuszewska and Bolałek, 2008). The situation in this study was the same.

Ads–P is the most bio-available form of P in sediments. When P concentration in the overlying water column is low, Ads–P can be released into the overlying water very easily through sediment–water interface and utilized by the plankton. Fe–P/Al–P has the potential of bio-availability. Fe–P/Al–P could be reduced to release P when they are deposited in anoxic, reducing environments. This process usually occurs in deeper anoxic sediment layers; the free iron/aluminum and phosphorus ions diffuse towards the oxygenated surficial sediment layer, where they are re-precipitated (Jensen et al., 1995; Pettersson, 1998). However, in the relatively well-oxygenated seawaters like the Bohai Sea, Fe–P/Al–P is considered to be insoluble and non-reactive (Liu et al., 2004b). OP is more suitable for biological use after mineralizing and degrading into soluble IP (Andrieux and Aminot, 1997). In the offshore area, activities of Ca–P and De–P are very low in the weak alkaline aquatic environment. They will dissolve partly only when there is a sudden drop in pH, therefore it is difficult for them to transform into the bio-available P, and thus they have a minor contribution to the accumulation of P in the sediment pore or overlying water (Jiang et al., 2007).

Based on the above-mentioned properties of the different forms of P in marine sediments and the data of the present study, the bio-available forms of P in surface sediments of the Laizhou Bay and the Zhangzi Island were dominated by Ads–P and OP. The contents of bio-available P in surface sediments of the Laizhou Bay were 27.0–108.2 $\mu g\ g^{-1}$, which accounted for 6.1–20.3% of the TP, with an average of 14.7%, indicating that bio-available P accounted for only a small part of sedimentary P pool. The contents of bio-available P in surface sediments of the Zhangzi Island were 25.0–96.9 $\mu g\ g^{-1}$, which accounted for 17.5–36.7% of the TP, with an average of 24.2%. The proportion of the bio-available P content in the Zhangzi Island was higher than that in the Laizhou Bay. In the present study, Ca–P and De–P accounted for 71.1–89.1% of the TP in surface sediments of the Laizhou Bay, and for 39.9–68.9% in surface sediments of the Zhangzi Island. These kinds of sedimentary P have limited bioavailability, and they might be

Table 3
Pearson correlation matrix for the phosphorus species in sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China.

	Ads–P	Al–P	Fe–P	Ca–P	De–P	OP	IP	TP
OP	0.362	−0.244	0.445[c]	0.822[a]	0.275	1		
IP	0.287	−0.134	0.325	0.697[a]	0.935[a]	0.507[b]	1	
TP	0.320	−0.161	0.368	0.768[a]	0.893[a]	0.625[a]	0.990[a]	1
%OC	0.571[b]	−0.082	0.663[a]	0.802[a]	0.028	0.724[a]	0.339	0.427[a]
%Clay	0.384	−0.149	0.504[c]	0.956[a]	0.525[b]	0.812[a]	0.758[a]	0.821[a]
%Silt	0.128	−0.248	0.239	0.783[a]	0.790[a]	0.621[a]	0.882[a]	0.902[a]
%Sand	−0.209	0.228	−0.327	−0.862[a]	−0.739[a]	−0.700[a]	−0.876[a]	−0.909[a]

[a] $p < 0.001$.
[b] $0.001 < p < 0.01$.
[c] $0.01 < p < 0.05$.

buried in coastal sediments or transported to the deposition zones of open seas.

TP contents in surface sediments of the Laizhou Bay and the Zhangzi Island were 315.9–582.7 $\mu g\ g^{-1}$ and 81.3–401.3 $\mu g\ g^{-1}$, respectively. The average percentages of various geochemical forms of P in the Laizhou Bay were in the order: De–P (66.7%) > OP (12.6%) > Ca–P (11.9%) > Fe–P (6.5%) > Ads–P (2.1%) > Al–P (0.2%). The data for the Zhangzi Island followed the same sequence: De–P (49.5%) > OP (19.7%) > Fe–P (13.7%) > Ca–P (11.3%) > Ads–P (4.5%) > Al–P (1.3%). Inorganic forms of P accounted for the most part of the TP content. In the sediments from the sampling sites of the Laizhou Bay near to river mouths, relatively higher levels of P content were observed, reflecting the influence from the land-source input. In the Zhangzi Island, a smaller part of P was contributed by anthropogenic activity and land-source input. The Zhangzi Island is richer in fishery resources and therefore the deposition of OP is in a higher proportion after the death of marine lives.

Contents of TP, IP and OP in surface sediments in the Zhangzi Island were all lower than those in the Laizhou Bay, but the percentages of bio-available phosphorus (Ads–P and OP) were higher. The potential bio-available P accounted for 14.7% and 24.2% of TP in sediments of the Laizhou Bay and the Zhangzi Island, respectively. Although P in sediments of the Laizhou Bay and the Zhangzi Island was abundant, only a small part of it could be released into the overlying water under certain conditions. As two important mariculture areas in China, reducing the input of nitrogen to the water bodies of the Laizhou Bay and the Zhangzi Island and increasing the content of P have become urgent to relieve the shortage of P for the primary producers.

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