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Baseline

Geochemistry of phosphorus in sediment cores from Sishili Bay, China

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ABSTRACT

This paper presents the distribution of total phosphorus (P), inorganic P (IP) and organic P in sediment cores from Sishili Bay, China. Their concentrations ($\mu\text{mol g}^{-1}$) ranged from 15.04 to 21.59, 12.43 to 18.27 and 0.15 to 5.11, respectively, showing 87.6–96.9% of TP is IP. The distribution of the fractionation of IP, obtained by a sequential extraction technique, was 1.9–3.2% for soluble and loosely bound P (Ex-P), 8.5–13.1% for Al-bound P (Al-P), 7.4–9.5% for Fe-bound P (Fe-P), 5.0–12.4% for reductant-soluble P (Oc-P), 9.7–15.6% for CaCO_3 -bound P (ACa-P) and 45.9–54.6% for detritus P (Det-P). The P distribution and concentration was consistent with other Chinese coastal seas. No significant difference was found for the sedimentary P forms between scallop cultivation area and background area, indicating that shellfish aquaculture did not have significant effect on the depositional environment in the studied area, at least in case of P.

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Phosphorus (P) is an essential macronutrient for all life. On geologic timescales, P is a limiting nutrient in oceanic biogeochemical cycles (Broecker, 1982; Smith, 1984; Tyrell, 1999). In recent decades, anthropogenic activities through the form of either gaseous, liquid or solid emissions have become the cause of many of environmental issues and are responsible for major global reorganizations of the biogeochemical cycles (Mackenzie et al., 2002). It was reported that by 2000, the total overall effect of land use activities on nutrients remobilization increased to 100 Mtons nitrogen (N) and 50 Mtons P per year, with an average annual growth rate of the perturbation of 2% between 1950 and 2000 (Mackenzie et al., 2002). Besides, world fertilizer consumption puts another millions of tons of N and P each year to environment mainly in the forms of nitrate and phosphate (Mackenzie et al., 2002; Paytan and McLaughlin, 2007). Consequently, environment becomes enriched with biological available nutrients, and a significant part of which are transferred from land to coastal margin through soil erosion, mineral dissolution, surface water runoff and so on, making eutrophication become a common phenomenon in coastal water.

Because of its close relation with oceanic productivity and the marine biogeochemistry of many other key elements such as carbon and N, marine P cycle has been the subject of intense study for more than three decades (e.g., Krom and Berner, 1981; Ruttenberg, 1992;

Filippelli, 1997; Van Den Broeck and Moutin, 2002; Moutin et al., 2008; Küster-Heins et al., 2010; Wang and Morrison, 2014). Paytan and McLaughlin (2007) estimated that almost 99% of particulate and 25% of dissolved P from land are buried in coastal zone. So, understanding sedimentary P in coastal zone is a vital link for the study of its global biogeochemical cycle.

The environmental behaviors of sedimentary elements depend strongly on their specific chemical forms or method of binding. A widely-used technique for understanding element distribution in the solid phase, which is known as fractionation, is based on the application of sequential selective chemical extractions. These methods are based on the rational use of a series of more or less selective reagents chosen to solubilize successively the different mineralogical fractions thought to be responsible for retaining the larger part of the trace elements (Wang et al., 2013a). They are intended to simulate the various possible natural and anthropogenic modifications of environmental conditions. The biogeochemistry of P in sediments is complicated. Inorganic P can react with calcium (Ca), iron (Fe) and aluminum (Al) compounds to form discrete phosphates; organic P can be found in forms with varying resistance to microbial degradation. P can be transferred from water to sediment through biochemical and physical reactions, such as ion exchange, adsorption, and precipitation and also could be released from sediments as the overlying water quality changes. The behavior of sedimentary P is controlled by a number of biogeochemical processes such as microbial degradation of organic matter, desorption from iron (oxyhydr)oxides when iron reduction takes place and dissolution of P-containing mineral forms during geochemical alteration.

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Sishili Bay is a busy region in the south coast of the North Yellow Sea greatly affected by human activities mainly from urbanization. It is in the Shandong Peninsula Blue Economic Zone, the development of which is an important part of the national development strategy of China. Raft shellfish aquaculture, which has been banned since 2011, was once widespread in Sishili Bay for decades. The main objectives of this study are to assess the geochemistry of phosphorus in Sishili Bay sediment cores by determining its concentrations and chemical forms in which it occurs using the sequential extraction procedure, and provide a background estimation of baseline data for future surveys on the responses of Sishili Bay environment to anthropogenic influences.

In this study, four sediment cores were collected in Sishili Bay and its adjacent area (Fig. 1). Cores B, C and D located in the scallop cultivation area, while core E situated in a clear sea area at the outside edge of the Sishili Bay. The sampling program was carried out in June 2009. The core samples were taken by a stainless steel gravity corer equipped with PVC internal tube liners. The cores from sites B and C were about 70 cm in length, the core from site D was about 80 cm in length and the core from site E was about 100 cm in length. After collection, the cores were transported to laboratory within 3 h. In laboratory, all cores were extruded and sliced into 2 cm intervals. The subsamples were homogenized and stored at $\sim 4^{\circ}\text{C}$ in the dark until further treatment.

We followed the sequential extraction procedure reported by Zhang and Kovar (2000) to determine different geochemical fractions of P. The six operational defined forms of P obtained through this scheme were: (1) exchangeable or loosely sorbed P (Ex-P); (2) aluminum-bound P (Al-P); (3) iron-bound P (Fe-P); (4) reductant-soluble P (Oc-P); (5) CaCO_3 -bound P (ACa-P); (6) detritus P (Det-P). The concentration of inorganic P (IP) was calculated as the sum of the six P forms mentioned above.

Freeze-dried samples were thoroughly ground, homogenized and sieved through a 200 mesh screen. Then ~ 0.5 g of each sample was weighed and loaded to a 50 ml centrifuge tube with 10 ml solutions to perform the sequential extraction scheme. Ex-P was extracted with 1.0 M MgCl_2 ($\text{pH} = 7.0$). Al-P was extracted with 0.5 M NH_4F ($\text{pH} = 8.0$). Fe-P was extracted with 0.1 M NaOH-0.05 M Na_2CO_3 . Oc-P was extracted with CDB (0.22 M sodium citrate, 0.14 M sodium dithionite, 1.0 M sodium bicarbonate) ($\text{pH} = 7.6$). ACa-P was extracted with 1.0 M NaAc-HAc ($\text{pH} = 4$). Det-P was extracted with 1.0 M HCl. The content of total P was microwave digested. The concentration of P was determined by using an inductively coupled plasma optical emission spectrometer (Optima 7000 DV, PerkinElmer, USA). The organic P was calculated by subtracting inorganic P from total P.

Between the extraction steps, solid/liquid separation was achieved by centrifuging at 4000 rpm for 20 min, the resulting supernatant being transferred to glass bottles and analyzed in time. Residues were then washed with 10 ml de-ionized water, shaken for 15 min, and centrifuged for 20 min at 4000 rpm, the supernatant also being analyzed. The sequential extraction procedure was carried out with no interruption once started. All plastic and glassware 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. All chemicals used in the experiment were guaranteed-reagent grade. The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, analysis of reagent blanks, and analysis of replicates. All analyses of samples were carried out in triplicates and the RSDs were $<3\%$.

The sample granulometry was analyzed using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm . The percentages of the following 3 groups of grain sizes were determined: $<4 \mu\text{m}$ (clay), 4–63 μm (silt), and $>63 \mu\text{m}$ (sand). Total organic carbon (TOC) contents of the sample were determined using an Elementar vario MACRO cube CHNS analyzer after removing the inorganic carbon with 1 M HCl.

Grain size composition and TOC content were measured to get the general characteristic of sediment samples used in this study.

As shown in Fig. 2, the studied sediment cores were dominated by high silt and sand contents. For core B, the clay contents increased gradually from 2.1% at surface to 6.6% at 70 cm depth with a mean of 4.0%; for cores C and D, the clay contents were generally within the range of 5–10%, its average content in these two cores had very similar values of 8.5% and 8.3%, respectively; for core E, the clay contents were within the range of 12–20% at most depths with a mean of 15.3%. On average, except for core B, which was dominated by sand component, the other three cores were dominated by silt component. Like that of clay component, the silt content in core B increased downward from 25.6% to $\sim 70\%$ at 70 cm depth with a mean of 44.5%; the average silt contents in cores C, D and E were 58.6%, 66.5% and 63.0%, respectively. The average contents of sand component in cores B, C, D and E were 51.5%, 32.9%, 24.9% and 21.8%, respectively. The data of median grain size (D50) in the upper 20 cm depth of cores C, D and E exhibited a generally increasing trend downward, while they decreased from $\sim 105 \mu\text{m}$ at surface to $\sim 60 \mu\text{m}$ at ~ 20 cm depth for core B; the D50 data showed no clear vertically variation trends below 20 cm depth for all the four cores (Fig. 3). According to the classification of Shepard (1954), the upper 15 cm sediment of core B was silty sand and the rest part of the core was mainly

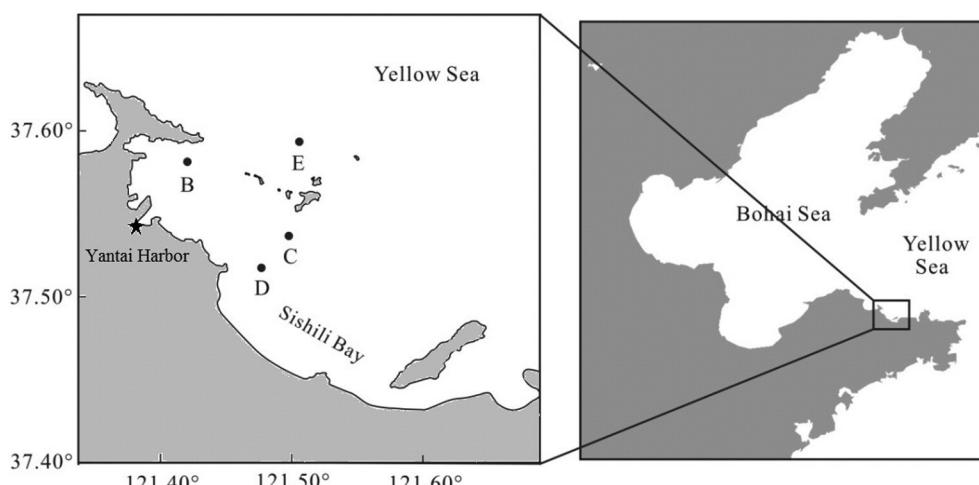


Fig. 1. Location of sampling sites (filled circles) in Sishili Bay. Filled star shows the place of Yantai Harbor.

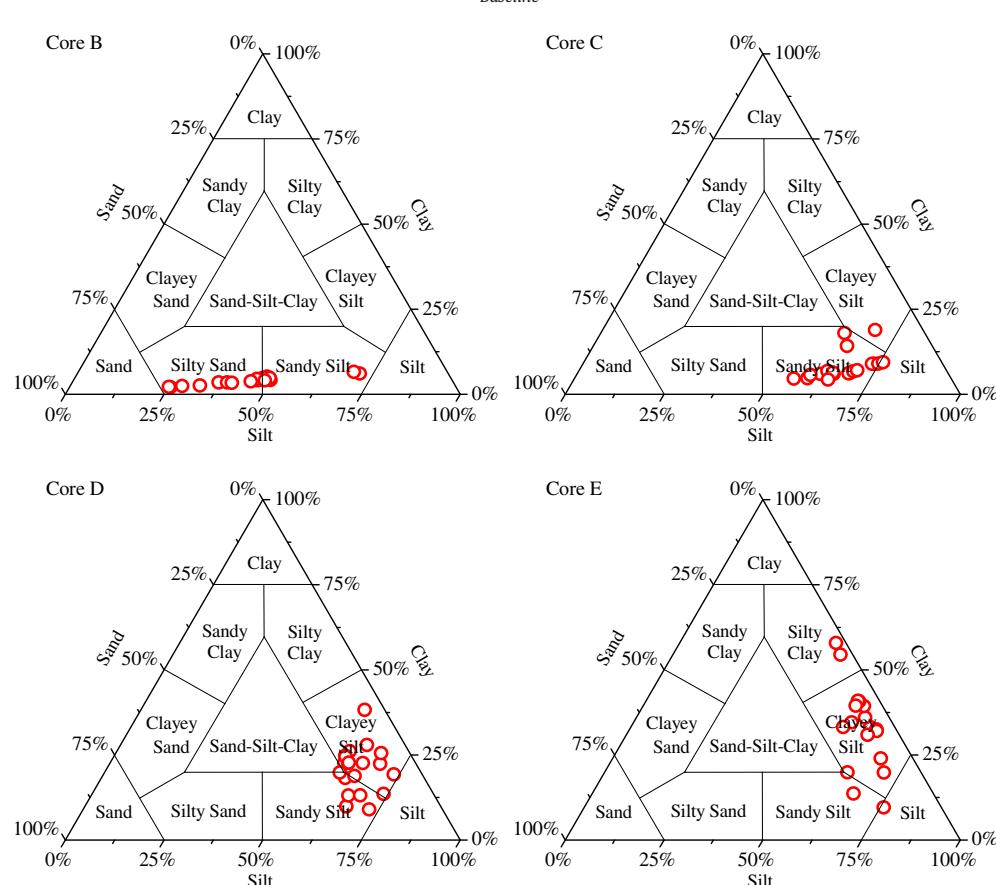


Fig. 2. Grain size compositions of the cores.

sandy silt; the sediments of cores C and D were almost clayey silt and sandy silt, respectively; the sediments of cores E were mainly clayey silt with some sandy silt layers (Fig. 2).

Reverse to that of D50, the TOC contents in cores C, D and E were highest at top layers and took on a decreasing trend downward in the upper 20 cm depth; below this depth, the TOC contents varied mainly within the relatively narrow range of 0.2–0.4% (Fig. 3). In core B, TOC

contents in the upper 40 cm were apparently lower than that of the other three cores and varied with the range of 0.1–0.2% with an exceptional high value of 0.3% at 15 cm depth, which was similar to the TOC contents below this depth (Fig. 3).

The water contents for cores B, C, D and E show little vertical variation and the average values are 25.3%, 31.1%, 31.1%, and 33.3%, respectively.

TP slightly varied between 15.85 and 16.50 $\mu\text{mol g}^{-1}$ with a mean of 16.24 $\mu\text{mol g}^{-1}$ in core B, increased from 16.10 $\mu\text{mol g}^{-1}$ at top to 19.26 $\mu\text{mol g}^{-1}$ at 10 cm and then decreased monotonously to 15.04 $\mu\text{mol g}^{-1}$ at bottom in core C, ranged from 12.66 to 21.59 $\mu\text{mol g}^{-1}$ (mean: 17.14 $\mu\text{mol g}^{-1}$) with a maximum value at 8 cm depth in core D, and from 16.09 to 18.56 $\mu\text{mol g}^{-1}$ (mean: 17.42 $\mu\text{mol g}^{-1}$) with a maximum value at 10 cm depth in core E

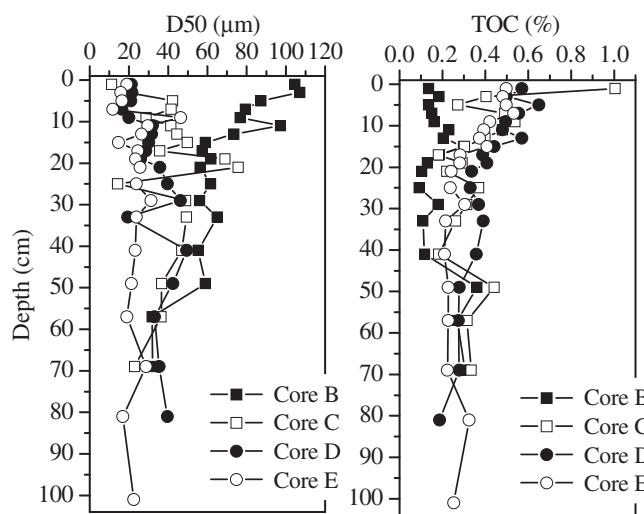


Fig. 3. Median grain size (D50) and TOC of the cores.

Table 1
Concentration of F1–F6, TOC and TP in cores B, C, D and E ($\mu\text{mol g}^{-1}$).

		F1	F2	F3	F4	F5	F6	TOP	TP
Core B	Min.	0.21	1.29	0.97	1.13	1.12	7.21	0.22	15.85
	Max.	0.27	1.60	1.68	2.03	1.68	9.99	3.10	16.50
	Mean	0.25	1.38	1.21	1.58	1.47	8.86	1.50	16.24
Core C	Min.	0.22	1.57	1.30	1.51	1.39	6.68	0.15	15.04
	Max.	0.52	2.79	1.77	2.75	1.97	10.07	0.99	19.26
	Mean	0.32	2.22	1.47	2.12	1.65	8.71	0.52	17.01
Core D	Min.	0.41	1.42	0.76	0.59	1.83	6.74	0.23	12.66
	Max.	0.61	2.48	2.50	1.16	2.81	9.07	5.11	21.59
	Mean	0.47	1.82	1.63	0.86	2.29	7.95	2.13	17.14
Core E	Min.	0.47	1.29	0.90	0.91	2.34	6.27	0.52	16.09
	Max.	0.67	2.39	1.93	1.26	3.10	9.23	3.63	18.56
	Mean	0.55	1.70	1.37	1.08	2.72	7.99	2.01	17.42

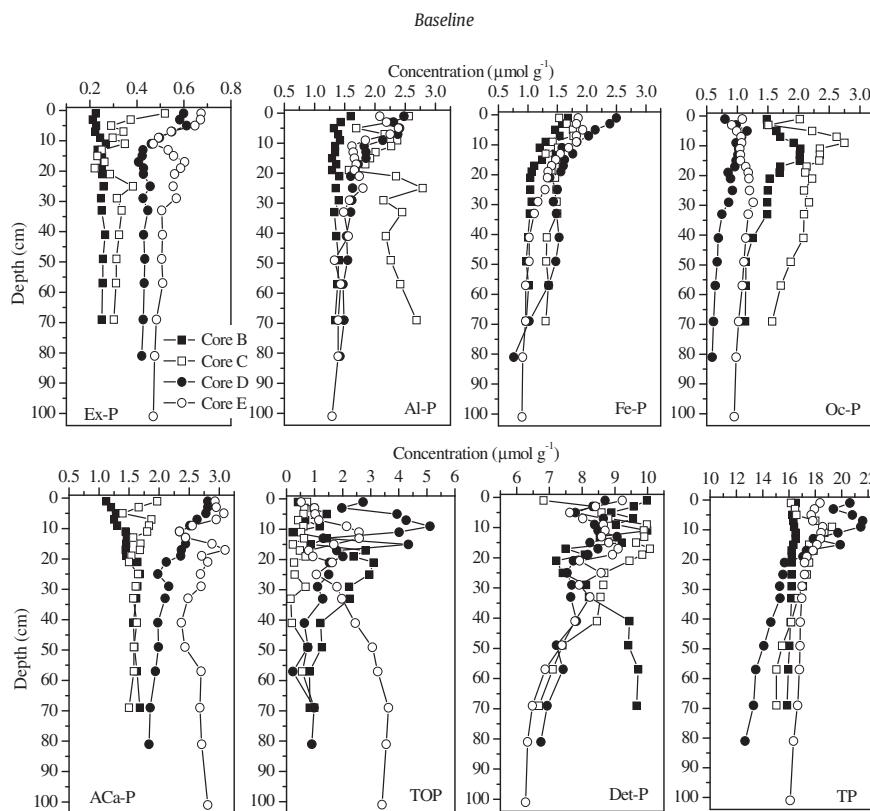


Fig. 4. Vertical distributions of F1–F6, TOP and TP.

Table 2Comparison of concentrations of TP and TOP in different Chinese coastal areas ($\mu\text{mol g}^{-1}$).

Area	TP	TOP	References
Core B in Sishili Bay	15.85–16.50	0.22–3.10	This study
Core C in Sishili Bay	15.04–19.26	0.23–0.99	This study
Core D in Sishili Bay	12.66–21.59	0.23–5.11	This study
Core E in Sishili Bay	16.09–18.56	0.52–3.63	This study
Jiaozhou Bay	6.4–10.1	0.32–5.00	Dai et al. (2006)
Bohai Sea	10.8–20.3	1.00–6.77	Jiang and Liu (2013)
Southwest Yellow Sea	8.97–24.8	0.11–8.61	Hong et al. (2010)
Yellow Sea	14.4–18.3	2.45–2.65	Cao and Liu (2010)
East China Sea shelf	10.5–26.1	1.28–4.66	Zhou et al. (2016)
East Sea	13.4–22.5	1.35–4.80	Zheng et al. (2003)
East Sea	13.7–19.9	2.11–3.81	Cao and Liu (2010)
Changjiang Estuary	9.7–21.8	0.76–5.68	Yang et al. (2015)
Changjiang Estuary	15.0–21.4	2.56–7.84	Meng et al. (2014)
Changjiang Estuary	14.3–21.7	≤0.37	Yu et al. (2013)
Pearl River Estuary	11.0–18.7	2.81–7.80	Yue et al. (2007)

(Table 1, Fig. 4). These results were comparable with those reported for the Jiaozhou Bay, the Bohai Sea, the Yellow Sea, the East China Sea, the Changjiang Estuary, and the Pearl River Estuary (Table 2).

Ex-P followed the order of core B ($0.25 \pm 0.04 \mu\text{mol g}^{-1}$) < core C ($0.32 \pm 0.06 \mu\text{mol g}^{-1}$) < core D ($0.47 \pm 0.06 \mu\text{mol g}^{-1}$) < core E ($0.55 \pm 0.06 \mu\text{mol g}^{-1}$). It varied at upper 30 cm and then kept almost constant below for cores C, D and E, while varied relatively little from top to bottom for core B.

Al-P in cores B, D and E decreased downward and then merged at a value about $1.50 \mu\text{mol g}^{-1}$. In core C, Al-P varied in a zig-zag form between 1.57 and $2.79 \mu\text{mol g}^{-1}$ at the top 40 cm and then increased downward slightly from 2.25 to $2.70 \mu\text{mol g}^{-1}$.

Fe-P decreased rapidly from top to 20 cm depth in all four cores, and then slightly below 20 cm, making vertical distribution of Fe-P in cored D more like a right-leaning slim "S" than the other three ones do. The

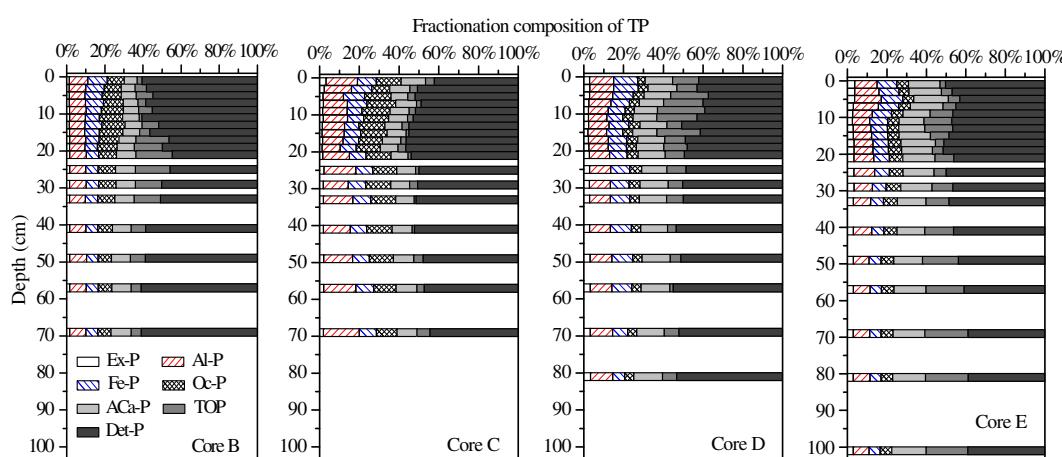


Fig. 5. Fractionation composition of TP in each studied core.

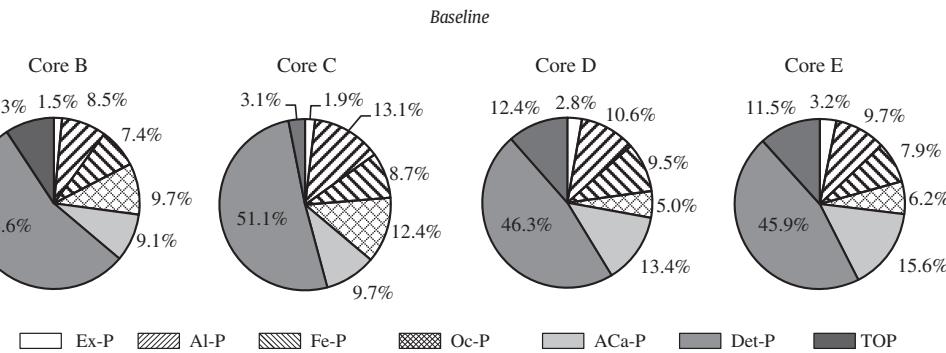


Fig. 6. Phase partitioning of different sedimentary phosphorus species in the Sishili Bay, including F1–F6 and TOP, based on average data.

mean values for cores B, C, D and E were $1.21 \mu\text{mol g}^{-1}$, $1.47 \mu\text{mol g}^{-1}$, $1.63 \mu\text{mol g}^{-1}$ and $1.37 \mu\text{mol g}^{-1}$, respectively.

Oc-P peaked at 12.5 cm blow surface with a value of $2.03 \mu\text{mol g}^{-1}$ in core B, at 9 cm with a value of $2.75 \mu\text{mol g}^{-1}$ in core C, at 5 cm with a value of $1.16 \mu\text{mol g}^{-1}$ in core D, and 30 cm with a value of $1.26 \mu\text{mol g}^{-1}$ in core E. The average values followed the same order as that of peak values do, i.e. C ($2.12 \mu\text{mol g}^{-1}$) > B ($1.58 \mu\text{mol g}^{-1}$) > E ($1.08 \mu\text{mol g}^{-1}$) > D ($0.86 \mu\text{mol g}^{-1}$).

ACa-P generally increased downward from $1.12 \mu\text{mol g}^{-1}$ at top to $1.68 \mu\text{mol g}^{-1}$ at bottom in core B, while decreasing from $2.81 \mu\text{mol g}^{-1}$ at top to $1.83 \mu\text{mol g}^{-1}$ at bottom in core D. In core C, ACa-P varied between 1.39 and $1.97 \mu\text{mol g}^{-1}$ at top 12 cm and then kept almost constant downward at $1.65 \mu\text{mol g}^{-1}$. In core E, ACa-P varied between 2.34 and $3.10 \mu\text{mol g}^{-1}$, more vigorously in the top 20 cm than below.

Det-P had a minimum value of $9.99 \mu\text{mol g}^{-1}$ at 21 cm depth in core B, while maxima of $10.07 \mu\text{mol g}^{-1}$, $9.07 \mu\text{mol g}^{-1}$ and $9.23 \mu\text{mol g}^{-1}$ for C, D and E, respectively. Det-P was the most abundant fraction in sedimentary P of the study area. This result was in line with the findings in Changjiang estuary, Jiaozhou Bay, and East China Sea.

Summarizing the contents of Ex-P, Al-P, Fe-P, Oc-P, ACa-P, and Det-P mentioned above, we get the content of IP, i.e. 13.55 – $16.15 \mu\text{mol g}^{-1}$ in core B, 13.33 – $18.34 \mu\text{mol g}^{-1}$ in core C, 13.70 – $18.05 \mu\text{mol g}^{-1}$ in core D, and 12.65 – $17.71 \mu\text{mol g}^{-1}$ in core E. These IP contents correspond to 74%–91% of TP in core B, 56%–92% of TP in core C, 65%–92% of TP in core D, and 62%–88% of TP in core E. These results indicate that IP was the major constitute of TP, leaving OP the minor one.

TOP had a peak value of $3.10 \mu\text{mol g}^{-1}$ at 22 cm in core B, varied slightly between 0.15 and $0.99 \mu\text{mol g}^{-1}$ in core C, varied between 0.23 and $5.11 \mu\text{mol g}^{-1}$ with peak value at 10 cm depth in core D, and

Table 3
Correlation coefficients among various fractions of phosphorus.

Core	Ex-P	Al-P	Fe-P	Oc-P	ACa-P	Det-P	TIP	TOP
B	Ex-P							
	Al-P							
	Fe-P	-0.83**	0.469*					
	Oc-P							
	ACa-P	0.704**		-0.91**				
	Det-P				0.585**			
	TIP					0.586*		
	TOP						-0.474*	
C	TP			0.782**	0.776**	0.733**		
	Ex-P							
	Al-P	0.636**						
	Fe-P							
	Oc-P							
	ACa-P	0.578*						
	Det-P	-0.548*	-0.552*					
	TIP				0.688**			
D	TOP				0.844**			
	TP					0.839**		
	Ex-P						0.889**	
	Al-P	0.916**						
	Fe-P	0.837**	0.915**					
	Oc-P	0.484*	0.690**	0.633**				
	ACa-P	0.790**	0.944**	0.920**	0.768**			
	Det-P	0.648**	0.728**	0.715**	0.776**			
E	TIP	0.738**	0.920**	0.939**	0.795**	0.968**	0.881**	
	TOP	0.507*	0.708**	0.517*	0.739**	0.690**	0.549*	
	TP	0.691**	0.899**	0.815**	0.840**	0.919**	0.797**	0.675**
	Ex-P							0.930**
	Al-P	0.755**						0.899**
	Fe-P	0.608**	0.886**					
	Oc-P							
	ACa-P	0.685**	0.574**					
	Det-P	0.525*	0.478*	0.666**				
	TIP	0.747**	0.797**	0.872**				
	TOP	-0.841**	-0.773**	-0.690*				
	TP		0.614**	0.883**				

Note: Only the values with $P < 0.05$ were shown.

* $0.01 < P < 0.05$ (two-tail test).

** $P < 0.01$ (two-tail test).

increased from $0.52 \mu\text{mol g}^{-1}$ at top to $3.63 \mu\text{mol g}^{-1}$ at near bottom in core E. The contents of OP in Sishili Bay were consistent with those in the other Chinese coastal areas (Table 2). Compared to IP, TOP was a minor constitute of TP.

The fractionation composition of TP in every core showed little vertical variation (Fig. 5). The exchangeable fraction was always the least (1.5%–3.2%) and the Det-P always the highest (46.3–54.6%, Fig. 5).

The column-averaged values followed the order of Ex-P (1.5%) < Fe-P (7.4%) < Al-P (8.5%) < ACa-P (9.1%) < TOP (9.3%) < Oc-P (9.7%) < Det-P (54.6%) in core B, Ex-P (1.9%) < TOP (3.1%) < Fe-P (8.7%) < ACa-P (9.7%) < Oc-P (12.4%) < Al-P (13.1%) < Det-P (51.1%) in core C, Ex-P (2.8%) < Oc-P (5.0%) < Fe-P (9.5%) < Al-P (10.6%) < TOP (11.5%) < ACa-P (13.4%) < Det-P (46.3%) in core D, and Ex-P (3.2%) < Fe-P (7.4%) < Al-P (8.5%) < ACa-P (9.1%) < TOP (9.3%) < Oc-P (9.7%) < Det-P (54.6%) in core E (Fig. 6).

Among different forms of sedimentary P, Ex-P, Al-P, Fe-P and TOP may be readily released to ambient water through desorption, reductive dissolution and degradation, making them bioavailable. The mean values of potential bioavailable P in cores B, C, D and E is 6.09, 7.90, 8.78, $9.34 \mu\text{mol g}^{-1}$, respectively, corresponding to 26.7%, 26.8%, 35.3% and 32.3% of TP. The bioavailable P in this study is much higher than those in the Changjiang Estuary ($3.60\text{--}5.35 \mu\text{mol g}^{-1}$, Meng et al., 2014; Yang et al., 2015) and East China Sea shelf ($3.50\text{--}4.10 \mu\text{mol g}^{-1}$, Zhou et al., 2016).

Pearson correlation matrix is presented in Table 3. For core D, the positive relationship among all the P species means that they have common external sources, probably from terrestrial industrial effluents and domestic sewage inputs since it is the closest site to the coastal populated residence. For core E, positive relationship was found among IP species, while TOP was negative related to the other species, indicating that the IP species mainly come from the mineralization of TOP. Compared to cores D and E, cores B and C present weak correlation among different P species. The negative relationships between Ex-P and Fe-P, Fe-P and ACa-P in core B and between Ex-P and Det-P, Al-P and Det-P in core C indicate that they can transform between each other, while the positive relationships indicate that they may have common sources.

De-P is usually found to be concentrated in sand fraction, while other P fractions concentrated in clay and silt fractions (Yu et al., 2011, 2013; Meng et al., 2014, 2015; Zhuang et al., 2014; Zhou et al., 2016). In core D, all P species are positively related to water content, TOC and silt and negatively related to sand (Table 4), which confirms that all P species have common external sources delivered by silt, instead of sand. Furthermore, the bury rate may exceed the mineralization rate of OP to IP. In core E, All IP species and TP exhibit positive relationship with water content and TOC, and negative relationship with silt. TOP negatively related to water content and TOC, but positively related to silt. These results show that TOP was mainly buried in silt and mineralized to IP which was favored under high water content. The produced IP species was not contained in silt again. Besides the mineralization produced IP, there are some minor external input of IP along with TOC.

TP values in the cores of Sishili Bay varied from $12.66 \mu\text{mol g}^{-1}$ to $21.59 \mu\text{mol g}^{-1}$, falling within the range defined by those in Chinese coastal seas. Furthermore, no significant difference was found among the sedimentary P forms between Scallop cultivation area (core B, core C, and core D) and background area (core E). These results indicate that shellfish aquaculture did not have significant effect on the depositional environment, at least in case of P. Given a sedimentation rate of $0.78\text{--}0.91 \text{ cm/year}$ (Wang et al., 2013a, 2013b), the increase of TP in the upper 20 cm (Fig. 4) is coincident with a time span from mid-1980s to the sampling date. During this period, the quickly-developed human activities around Sishili Bay including fertilizer use, marine dumping and sewage discharge have contributed to the eutrophication (Wang et al., 2013a, 2013b), which includes enrichment of TP.

Bioavailable P has higher concentration, while TOP has relative lower concentration and is similar to those in other Chinese coastal areas. This finding was consistent to the previous result reported

Table 4

Correlation coefficients between various fractions of phosphorus and the main geochemical parameters of sediments.

Core	Fraction of P	Water content	TOC	Clay	Silt	Sand
B	Ex-P					
	Al-P					
	Fe-P			-0.757**	-0.763**	0.765**
	Oc-P	-0.820**		-0.482*	-0.536*	0.533*
	ACa-P			0.778**	0.778**	-0.78**
	Det-P					
	TIP					
	TOP					
	TP	-0.707**	-0.430	-0.849**	-0.890**	0.889**
	Ex-P	0.548*	0.748**	0.482*	0.654**	-0.666**
C	Al-P		0.709**			-0.561*
	Fe-P					
	Oc-P					
	ACa-P	0.551*	0.743**	0.095	0.621**	-0.485*
	Det-P			-0.656**		
	TIP			-0.516*		
	TOP				-0.488*	
	TP					
	Ex-P	0.820**	0.731**		0.654**	-0.678**
	Al-P	0.867**	0.885**		0.802**	-0.807**
D	Fe-P	0.809**	0.860**		0.643**	-0.664**
	Oc-P	0.682**	0.817**		0.646**	-0.616**
	ACa-P	0.799*	0.915**		0.818**	-0.808**
	Det-P	0.553*	0.804**		0.575**	-0.589**
	TIP	0.803**	0.938**		0.753**	-0.760**
	TOP	0.553*	0.690*		0.736**	-0.730**
	TP	0.753**	0.901**		0.813**	-0.815**
	Ex-P	0.782**	0.535*			
	Al-P	0.625**	0.820**		-0.490*	
	Fe-P	0.689**	0.885**		-0.580**	
E	Oc-P	0.529*	0.475*			
	ACa-P	0.512*	0.453*			
	Det-P	0.705**	0.488*		-0.660**	0.528*
	TIP	0.813**	0.661**		-0.624**	
	TOP	-0.765**	-0.492*		0.514*	
	TP	0.657**	0.711**		-0.607**	0.483*

Note: Only the values with $P < 0.05$ were shown.

* $0.01 < P < 0.05$ (two-tail test).

** $P < 0.01$ (two-tail test).

by Li et al. (2013) and demonstrated that IP is the primary factor affecting the trophic state of seawater in Sishili Bay. The bioavailable P may come from the industrial wastewater and domestic sewage from surrounding land. In addition, surface runoff caused by heavy rainfall in June (wet season) may contain large quantities of bioavailable P when it flows through surrounding land and finally pours into the Sishili Bay. The high concentration of bioavailable P may play an important role in the summer peak of chlorophyll *a* observed by Shen et al. (2014).

The molar ratios of TOC to TOP (TOC/TOP) of marine phytoplankton are close to the Redfield ratio 106 (Redfield et al., 1963), while the ratios of TOC/TOP of terrestrial plants have much higher values (Wang et al., 2010; Sardans et al., 2012). So it can be used to assess the influence of terrestrial organic matter inputs, i.e. TOC/TOP higher than 106 are usually attributed to the dominance of terrestrial sources. In this study, the ratio of TOC/TOP was 23–214 with a mean of 60 in core B, 32–217 with a mean of 98 in core C, 45–118 with a mean of 79, and 26–172 with a mean of 57 in core E (Fig. 7). For core E, ratios of TOC/TOP are higher than the Redfield ratio in the top 2 cm, then decrease sharply to around 35 and keep constant below. This profile indicates that the terrestrial inputs influence only the surface sediment therein and that the abundance of P relative to carbon during organic matter deposition keeps a long history record. For the other cores, ratios of TOC/TOP varied irregularly from top to bottom, probably due to the frequent disturbance caused by annual channels dredge for the Yantai harbor or bottom trawling.

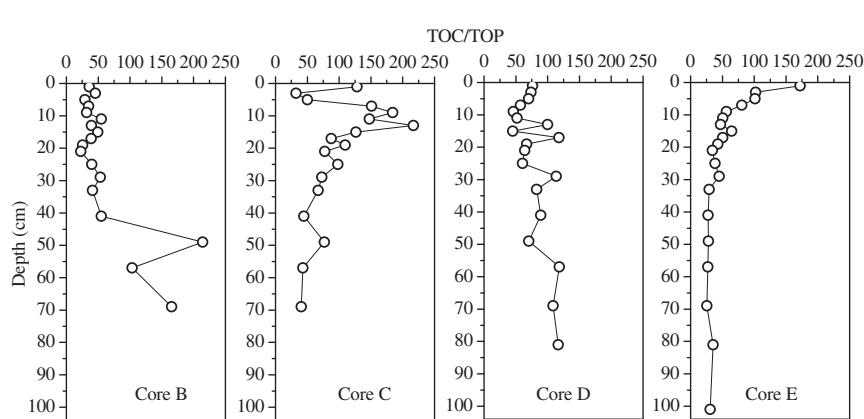


Fig. 7. Ratio of TOC/TOP in the studied cores.

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