Phosphorus forms in sediments of the East China Sea and its environmental significance

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Abstract: By means of SEDEX, ASPILA and XRF, depth-dependent changes of different phosphorus forms in sediment cores from specific areas of the offshore Changjiang Estuary (Yangtze Estuary) in 1998 were analyzed. Results show that contents of total phosphorus (TP), organic-phosphorus (OP) and iron-phosphorus (Fe-P) decreased down-core, while those of absorbed-phosphorus (Ad-P) and calcium-phosphorus (Ca-P) increased. The distribution tendency of detritus-phosphorus (De-P) is not obvious. Results also show that TP, Fe-P and OP contents at Meso station of the Changjiang Estuary and Hangzhou Bay are higher than that of the other stations. This suggests that the pollutants carried by the Changjiang and the Qiantang rivers from inland have affected the natural environment in offshore area. TP, Fe-P and OP contents of each station become higher from bottom to top, indicating the amount of the terrestrial pollutants carried by the two rivers has been enhanced since the last 30-50 years. Ad-P, Ca-P, Fe-P and OP are all active phosphorus in sediments, and their re-cycling in sediment is closely related to each other.

Key words: Changjiang Estuary; East China Sea; sediment column; phosphorous forms; phosphorous distribution; environmental significance

1 Introduction

Phosphorus is one of the necessary nutrient elements to marine ecosystem (Fillippelli and Delaney, 1996), but to provide too much nutrients is harmful to a stable ecosystem. Coastal sediments are important in modifying the relative availability of nitrogen and phosphorus (Boynton and Kemp, 1985) and may be important sinks for nutrients transported to the open ocean (Ruttenberg, 1993; Howarth et al., 1995), while some studies indicate that the phosphorus in sediments is regenerated to the water column and takes part in the recycle of phosphorus in water (Jensen et al., 1995). The interface exchange of phosphorus between the sediments and seawater is totally determined by the phosphorus forms in sediments. Generally, the phosphorus forms vary in different areas because of different chemical-physical conditions and biological environments (Aleya, 1992; Mohamed et al., 1994). Therefore, studies on the spatial-temporal change of different forms of phosphorus in marine sediments are essential not only to better understand the evolution of the sediment environment, but also to quantify the effects of the modern industry on the ecological system.

In recent years, eutrophication becomes a very serious environmental problem in the Changjiang Estuary and adjacent East China Sea due to a large amount of nutrient discharged from the Changjiang River. The previous research results (Pu et al., 2000) had showed the primary production in the Changjiang Estuary and adjacent East China Sea is limited by phosphorus, the provision of phosphorus is becoming a priority. This study systematically analyzes the total phosphorus and its related forms in the sediment collected in this area by the Second Institute of Oceanography in May 1998. Combining with chemical component analysis and marine ecological features, we aim to determine the geochemical characters of phosphorus

in this area and the corresponding environmental indication.

2 Sample and method

Sediment cores were collected by multi-corer device (diameter of 7.1 cm) during investigation of Chinese-Japanese cooperation of the Changjiang Estuary in May 1998 (Figure 1). The samples were sliced on board and kept at -20°C. When in laboratory, sediments were dried at 60°C and ground to past 200 meshes.
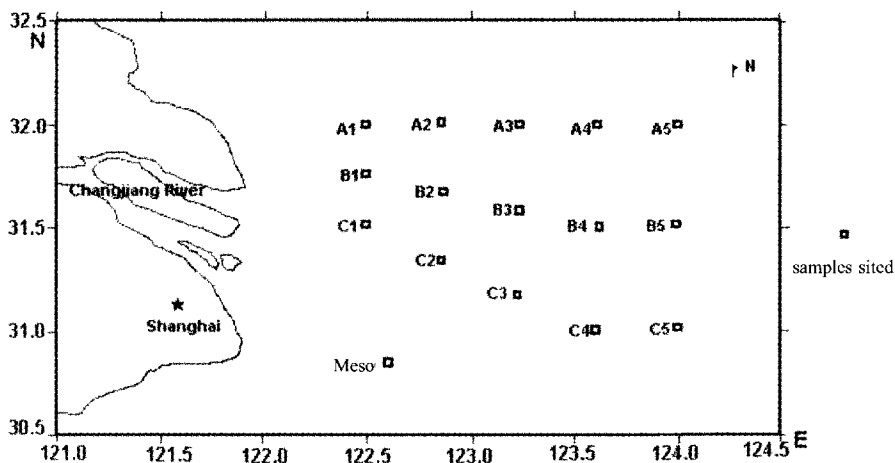

Figure 1 Sampling sites and location of the investigated area in the East China Sea

Ad-P, Fe-P and Ca-P in the samples were separated and extracted according to sequential extraction method (SEDEX) (Ruttenberg, 1992). TP and total inorganic phosphorus in samples are determined by ASPILA method (Aspila et al., 1976). OP, De-P and other inorganic phosphorus (De-P) contents are determined by the following ways:

$$OP = TP - \text{total inorganic phosphorus}$$
$$De\text{-}P = TP - (Ad\text{-}P + Fe\text{-}P + Ca\text{-}P)$$

For all steps, the standard ascorbic acid molybdate blue technique was used for developing color. Sample absorbances and P concentrations were performed using a Shimadzu UV-1202 Spectrophotometer with a 5-cm cell. Sample absorbances were zeroed by glass distilled water and measured at 882 nm. Reagent blanks and standards were prepared to match the matrix of each sample step analyzed. Samples were diluted according to the P content.

In addition, the total phosphorus in sediment was alternatively determined by the X-ray fluoresescence spectrometer (Siemens Co. SRS3000) analysis method for comparison. Al_2O_3, CaO, SiO_2, TiO_2, Fe_2O_3, and S in sediments were also analyzed by XRF with fused method.

3 Results and discussion

The variations in the five kinds of phosphorus are summarized (Table 1). It is shown that contents of TP, OP and Fe-P decreased down-core (Figures 2-4), while that of Ca-P and Ad-P increased (Figures 5 and 6). The distribution tendency of De-P is not obvious (Figure 7). The factors that control the phosphorus variations are still in debates. The increments of phosphorus with time can be controlled by both degradation of organic matters and reactivation of phosphorus during early diagenesis. Alternatively, some researchers proposed that pollution sources and accumulation mechanisms are the main reason (Xu and Li, 1990; Huang and Ji, 1994). Generally, the following four factors play the most important roles: 1) the new sediment

components; 2) diagenesis; 3) accumulation; and 4) bioturbance. The effects of these factors on different forms of phosphorus are different. Each form of phosphorus can be controlled by one or more mechanisms.

3.1 Depth –dependent changes of OP

The sources of OP can stem from matters inherited from both terrestrial source and the marine planktons. These two kinds of OP correspond to refractory OP and leachable OP, respectively, depending on their origin. The refractory OP is composed of emission matters from land and changes little with time. The leachable OP is mainly composed of dead marine planktons and undergoes rapid discharges due to degradation of organic matters in transit to the sediment-water interface (Krom and Berner, 1980; McManus et al., 1997; Slomp et al., 1996), continued degradation and transformation during burial with sediments in the early diagenesis. Estuarine studies indicate that nearly 100% of the P from sedimenting organic matter is regenerated to the water column during a single year (Caraco et al., 1990). It can also change into other combined form phosphorus (Berner et al., 1993; Rutterberg, 1993; Rutterberg and Berner, 1993; Sundby et al., 1992).

Therefore, the discharge of leachable OP is an important process that can affect the composition of OP in sediments. If planktonic origin is dominated, most of planktonic OP becomes progressively impoverished in sediments and the content of OP immediately

Table 1 Contents of the total phosphorus and its different forms in sediment cores of parts of the stations (μg/g)

Station	TP	OP	Ad-P	Fe-P	Ca-P	De-P
A1 0-1*	541.9	138.9	4.66	29.73	11.06	357.01
A1 4-6	488.0	55.3	5.48	29.03	12.20	385.99
A1 10-12	502.0	72.3	3.95	23.08	12.50	390.16
A1 23-26	512.0	62.4	5.63	26.04	17.30	400.63
A3 2-3	566.0	98.5	6.35	23.11	14.30	423.74
A3 3-4	504.0	46.0	4.75	17.04	14.20	422.01
A3 14-17	531.0	41.7	7.47	38.28	14.47	429.07
A3 26-29	493.6	17.2	5.74	22.50	38.90	409.27
A4 0-1	522.2	113.7	3.95	20.44	10.50	373.61
A4 3-4	434.9	18.9	3.35	22.84	17.50	372.31
A4 8-10	422.5	18.6	3.64	17.61	18.40	364.25
A4 14-17	472.8	48.3	5.58	16.99	19.00	382.93
C1 0-1	483.3	95.9	5.39	25.59	8.20	348.22
C1 1-2	436.5	37.0	5.25	18.55	8.90	366.80
C1 2-3	436.8	41.9	4.31	23.82	14.20	352.57
C1 6-8	429.4	24.8	7.14	20.12	14.70	362.65
C3 0-1	544.0	120.5	5.65	26.55	22.30	368.99
C3 3-4	524.0	27.0	4.93	17.28	15.80	458.99
C3 8-10	484.3	64.5	2.43	14.66	22.10	380.60
C3 20-23	503.1	25.1	1.10	11.15	34.70	431.05
C4 1-2	416.5	50.5	1.70	18.01	13.70	332.50
C4 3-4	441.8	114.8	5.96	23.17	16.50	281.36
C4 6-8	461.5	78.7	2.54	14.69	13.87	351.70
C4 14-17	432.8	41.7	2.55	9.82	15.90	362.83
Meso 0-2	595.9	148.7	6.20	52.10	10.70	377.48
Meso 2-5	638.5	174.6	7.88	49.52	14.80	391.70
Meso 8-11	565.2	118.4	7.03	48.41	12.70	378.66
Meso14-17	602.1	93.3	6.86	46.39	13.90	441.65
Meso20-23	586.3	123.4	8.62	48.40	14.80	391.08
Meso26-29	590.9	86.3	5.73	43.20	9.40	446.27
Meso35-36	597.8	120.0	13.64	40.05	37.80	368.01

*depth (cm)

Table 2 Correlation coefficients of phosphorus types and chemical components in sediments

	TP	OP	Ad-P	Fe-P	Ca-P	De-P
TP	1.00	0.71**	0.59*	0.79**	-0.13	0.55*
OP	0.71**	1.00	0.45*	0.66**	-0.39*	-0.18
Ad-P	0.59*	0.45*	1.00	0.74**	-0.25	0.20
Fe-P	0.79**	0.66**	0.74**	1.00	-0.33	0.22
Ca-P	-0.13	-0.39*	-0.25	-0.33	1.00	0.19
De-P	0.55*	-0.18	0.20	0.22	0.19	1.00
SiO$_2$	-0.75*	-0.38	-0.48	-0.77**	0.23	-0.12
CaO	0.13	-0.02	0.10	0.02	-0.19	-0.47
Al$_2$O$_3$	0.76**	0.32	0.44	0.81**	-0.01	0.36
Fe$_2$O$_3$	0.79**	0.38	0.49	0.85**	-0.01	0.38
DIP in pore water	-0.45	-0.53	-0.81	-0.74**	0.70*	0.14
S	-0.17	-0.47	-0.61	-0.71*	-0.37	0.35
TiO$_2$	0.83**	0.45	0.60*	0.88**	0.08	0.58*

N=30; **. Correlation is significant at the 0.01 level; *. Correlation is significant at the 0.05 level.

decreases with the depth increasing. However, in this study, there are no apparent changes in the OP concentration throughout the whole profiles (Figure 3). Correlation analysis shows that OP content in sediments is independent of dissolved inorganic phosphorus (DIP) in pore water (Table 2). This suggests that in the analyzed samples, OP is mainly of terrestrial origin.

3.2 Depth−dependent changes of Fe−P

Fe-P extracted by SEDEX method (Ruttenberg, 1992) includes ferric phosphorus and aluminum phosphorus (Francoise and Alain, 1997). Fe-P was known as potential variable component in sedimentary phosphorus. In surface sediment, Fe-P can be used to determine the source of phosphorus, and also to indicate the extent of environment pollution (Hisashi, 1983). At the MESO station located in Huaniaoshan sea area, the contents of all kinds of phosphorus, especially Fe-P and OP, are higher than that of the other stations. For example, the highest Fe-P content in MESO station (52.10 μg/g) is three times the lowest one in C4 station (18.01 μg/g) (Table 1). For that the MESO station is situated off the Changjiang Estuary and Hangzhou Bay, receiving terrestrial material from both the Changjiang and Qiantang rivers. Pollutants caused by human activities along the two rivers have great impacts on the offshore environment of the East China Sea.

In sediment cores, the results show that the concentration of Fe-P decreased slowly down the core (Figure 4). Fe combined with P should exist as oxide in

Figure 2   Distribution of TP in sediment columns of the East China Sea
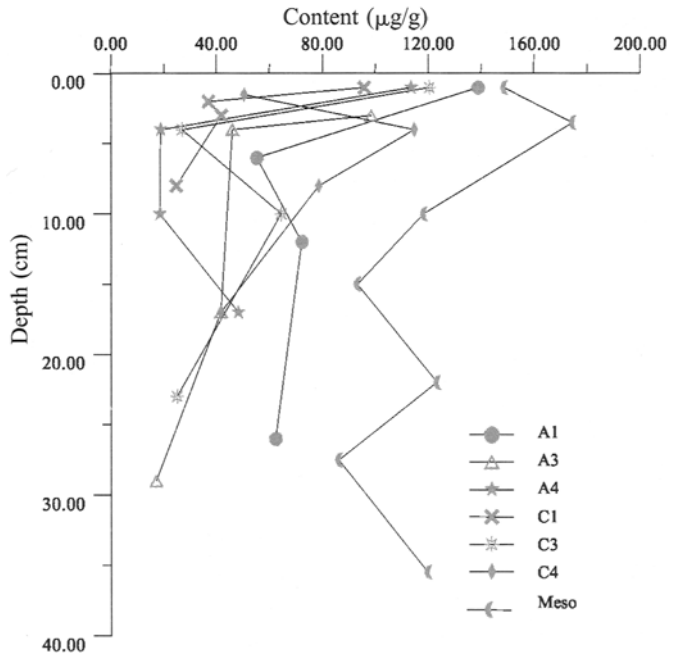
Figure 3   Distribution of OP in sediment columns of the East China Sea

sediments and will be affected by oxidation-reduction condition changing often with depth and time. Meanwhile, Fe-P is also closely related to the relevant ions concentration in pore water.
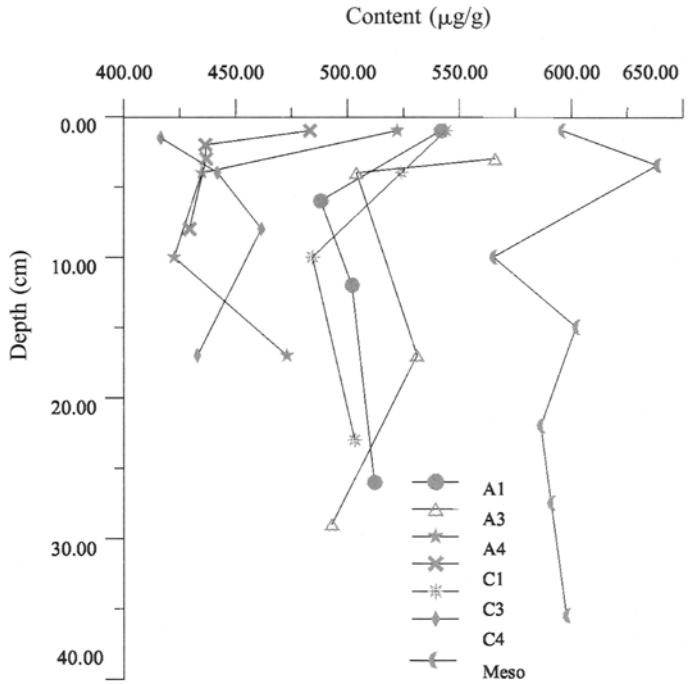
(Jensen and Thamdrup, 1993; Sundby et al., 1992; Mohamed et al., 1994). The distribution tendency of Fe-P decreasing down-core is most probably caused by the concentration gradient of ferric and ferrous irons in the sediments (Jensen and Andersen, 1992; Jensen and Thamdrup, 1993; Jensen et al., 1995; Schuffert, 1994). Ferrous ion is often mobilized in sediments under anoxic conditions, which would suggest mobilization of Fe-P to take place.

The redox status is in good agreement with the color changes of sediment cores, which is mainly controlled by the iron components, in turn, is related to certain geological settings. The surface layer of several centimeters at this area is relatively light while that of the deeper part is darker, indicating the formation of FeS (Jensen and Andersen, 1992), may be also with Fe_2S (Hammond et al., 1999). Iron and sulphur are very active elements in marine sediments, especially near the oxidation-reduction interface. Supporting evidence comes from relation between Fe-P and chemical components. As Table 2 shows, Fe-P is positively correlated with Al_2O_3 ($R^2 = 0.81$) and Fe_2O_3 ($R^2 = 0.85$) contents, but negatively with S content ($R^2 = -0.71$) and DIP ($R^2 = -0.74$) in pore water, suggesting at the transition from oxic to anoxic conditions, Fe-P is liberated to diffuse out of the sediments at the sediment-water interface.

3.3 Depth−dependent changes of TP

The TP contents in each sediment column are between 416.5-638.5 µg/g and gradually increased from the bottom to the surface layer (Figure 1). The tendency is comparable to that of
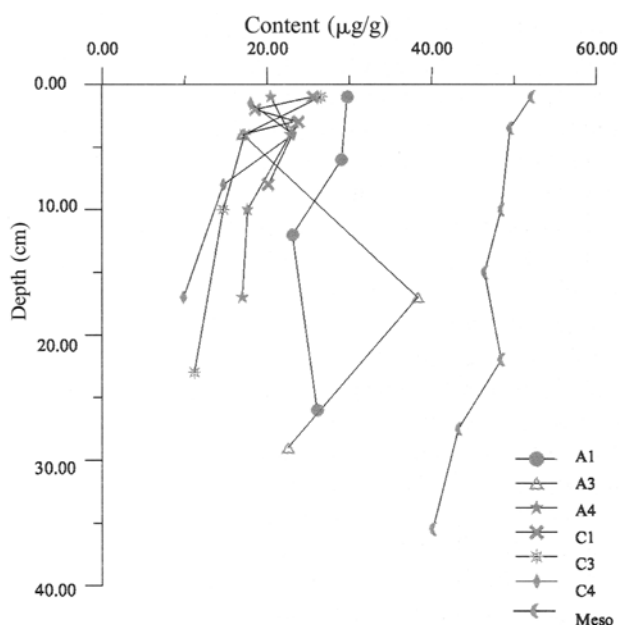

Figure 4   Distribution of Fe-P in sediment columns of the East China Sea
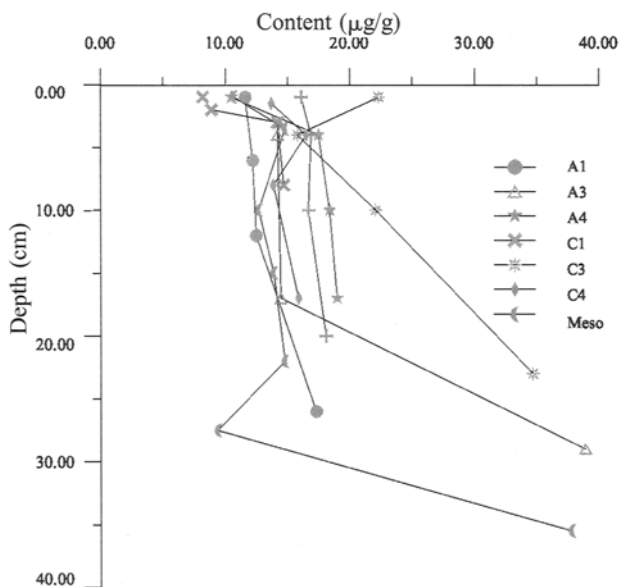
Figure 5   Distribution of Ca-P in sediment columns of the East China Sea

Fe-P and OP, which account for 20% of TP content. This is also well in corresponding with correlation analysis results. TP concentration is positively correlated with both Fe-P ($R^2 = 0.79$) and OP ($R^2 = 0.70$) (Table 2). The changes in TP content can be dominantly controlled by Fe-P and OP contents (Jesnen et al., 1995; Hammond et al., 1999; Schuffert, 1994).

In the investigated area, TP content in sediment is also closely related with the main chemical components. The correlation coefficients between TP and SiO_2, Al_2O_3, CaO are -0.75,

0.76, 0.13 respectively. For TP and TiO$_2$, the coefficient is as great as 0.83. Since SiO$_2$ stands mainly for the coarse mineral like quartz, and Al$_2$O$_3$ for fine components like clay, this means that TP content in sediments is related with mineral composition and grain size of the sediments. That is, TP in sediments is diluted by quartz sand, and is associated with clay components. Positive correlation between TP and TiO$_2$ means that phosphorus in the sediment from the offshore area is terrestrial, like TiO$_2$. TP independent of CaO refers to that marine bio-clastics is not an important source for phosphorus.

3.4 Depth–dependent changes of other phosphorus forms

To obtain more information, we clearly distinguish the De-P from Ca-P. The De-P, which represents the apatite of igneous or metamorphic origin and other non-dissolved inorganic phosphorus, accounts for 61.3-87.6% of TP. The De-P in sediments is sensitive to the micro-environmental factors (e. g., water temperature and pH value). Our results show that the De-P content does not obviously change with the depth (Figure 7). This indicates that the matter source and sediment environment are relatively steady in this area.

However, the Ca-P, including the authigenic carbonate, fluorapatite, CaCO$_3$-associated P and biogenic apatite, represents an oceanic sink for reactive P (Ruttenberg, 1992). In estuary and coastal sedimentary condition, sediment Ca-P originates from not only terrestrial but also marine resource. Figure 5 shows that the
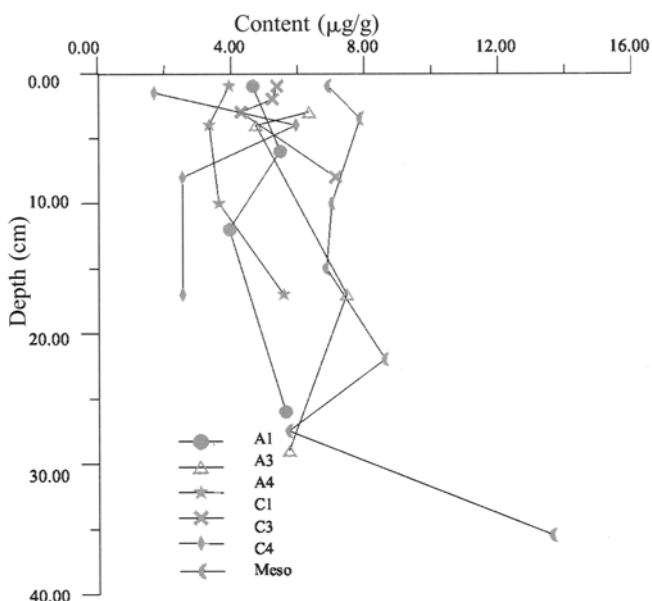

Figure 6 Distribution of Ad-P in sediment columns of the East China Sea
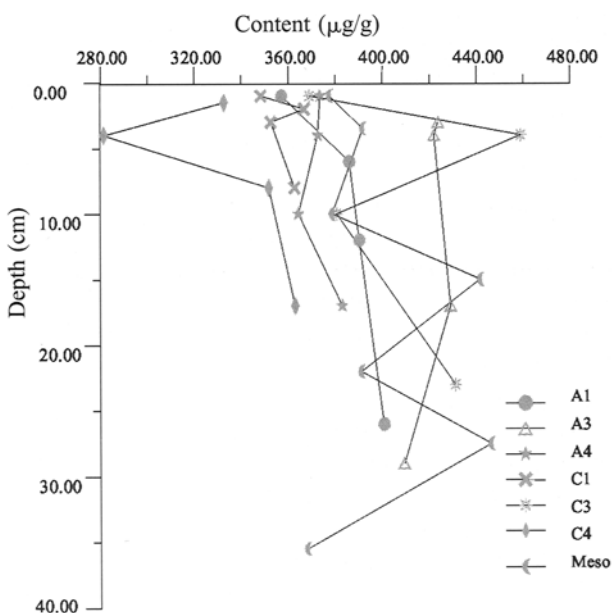

Figure 7 Distribution of De-P in sediment columns of the East China Sea

concentration of Ca-P gradually increases with the increment of the sediment depth. Ca-P has no relation with CaO in sediment cores, indicating complexity of Ca-P's origin. Although Ca-P is active, some researchers have shown that biologically active P, including Ca-P, may be permanently retained in coastal sediments by the formation and burial of authigenic P minerals. (Ruttenberg and Berner, 1993). In the investigated area, it is quite likely that the

depth-dependent changes of Ca-P are related to early diagenesis (Schuffert, 1994; Ruttenberg and Berne, 1993).

As for reactive phosphorus, Ad-P in sediments is one of the important forms of inorganic phosphorus and can be easily released to water and be absorbed by photoplankton. In each column, Ad-P increases down-cores (Figure 6). In our study, Ad-P exhibits an excellent negative correlation with productivity DIP in pore water ($R^2 = -0.81$), indicating the occurrence of adsorption and anti-adsorption of PO_4^{3-}. The adsorption and anti-adsorption are just partially reversible depended on environmental condition, such as pH and Eh. Other correlation analysis results show Ab-P exhibits a positive correlation with Fe-P ($R^2 = 0.74$) and OP ($R^2 = 0.45$) (Table 2). Compared to Fe-P's and OP's, the opposite changing tendency of Ad-P suggests that the cycle of Ad-P is closely related to that of Fe-P and OP.

3.5 Environmental significance

For all P forms, only Ad-P can be directly used by marine life-forms, but it is possible that other types of phosphorus can be transformed into absorbed P. It is essential to understand in what condition phosphorus in sediments changes from one into another. For example, Fe-P will be released under reduction condition, while OP will be released by the degradation of organic matters. Consequently, releasing of P in sediments and suspended materials could cause phytoplankton blooming.

At the MESO station located in Huaniaoshan sea area, the contents of all kinds of phosphorus, especially Fe-P and OP, are higher than that of the other stations. Because the MESO station is suited near the Changjiang River mouth and Hangzhou Bay, the terrestrial pollutants carried by both the Changjiang and the Qiantang rivers have strong impact on offshore environment of the East China Sea. We assign the effects directly to the increment of the frequency of the red tide at this area. The average sediment speed in our target areas is less than 2 cm/y (^{210}Pb), indicating about the geological history of the past 30-50 years in sediment cores. The upward increasing tendency of TP, Fe-P and OP in sediments can be explained by the increment of the pollution strength caused by human activity.

4 Conclusions

Based on the above discussion, the main conclusions are:

(1) With the increment of the sediment depth, the contents of TP, OP and Fe-P gradually decrease while those of Ca-P and Ad-P increase. There is no significant pattern for De-P.

(2) The observed variations of TP, OP and Fe-P in sediment cores may have been caused by (i) increased river input; (ii) mobilization of OP with decomposition of organic matter; and (iii) liberation of Fe-P which occurred with changes of redox status of the sediments. Because of the reduction dissolution and biological degradation, Fe-P and OP in sediments tend to be discharged into bottom seawater and pore water or added to Ad-P, then join in the re-circulation of phosphorus.

(3) Down-core increase in Ad-P and its relations with DIP in pore water show evidently that there are adsorption and anti-adsorption functions between Ad-P and pore water. So, its cycle is related to other phosphorus forms' cycle. The depth-dependent changes of Ca-P are related to early diagenesis.

(4) The contents of phosphorus at the Meso station near the Changjiang River entrance and Hangzhou Bay are higher than those of the other stations, indicating that the land pollutants had contaminated the costal environment of the East China Sea. The upward increasing tendency of TP, Fe-P and OP also indicates that pollutants are the main causes for the red tides outside the Changjiang River entrance.

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