

## Behavior of different phosphorus species in suspended particulate matter in the Changjiang estuary\*

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**Abstract** Suspended particulate matter (SPM) collected in the Changjiang (Yangtze River) estuary in June 2006 was separated into five fractions via water elutriation: clay-very fine silt (<8 μm), fine silt (8–16 μm), medium silt (16–32 μm), coarse silt (32–63 μm) and sand (>63 μm). The SPM and fractionated particles were sequentially analyzed by a modified SEDEX sequential extraction method to obtain six species of phosphorus: exchangeable or loosely-sorbed P, organic P, Fe-bound P, authigenic P, detrital P and refractory P. The results indicated that all particulate phosphorus species except for detrital P were negatively correlated to particle size; a high detrital P content was found in coarse silt and very coarse silt. From the inside of the river mouth to the gate of the river mouth, organic P, Fe-bound P and refractory P in the suspended particles decreased and a higher amount of exchangeable P appeared around the gate of the river mouth. From the gate of the river mouth to the sea, exchangeable P and organic P in suspended particles increased distinctly. The total particulate P flux into the estuary from the Changjiang River was about  $45.45 \times 10^8 \mu\text{mol/s}$  during sampling. Of this, about  $8.27 \times 10^8 \mu\text{mol/s}$  was associated with the “truly suspended” fraction. The bio-available particulate P flux was about  $13.58 \times 10^8 \mu\text{mol/s}$ . Of this, about  $4.24 \times 10^8 \mu\text{mol/s}$  was transported by “truly suspended” particles.

**Keyword:** Changjiang estuary; particle size fractions; particulate phosphorus species

### 1 INTRODUCTION

As a key nutrient, phosphorus (as the species phosphate) represents an important regulating factor in primary productivity, not only in freshwater but also in transient zones such as estuaries and coastal environments (Bauerfeind et al., 1990; Harrison et al., 1990). 87%–90% of river-borne phosphorus (P) that is transported into estuarine and coastal regions exists as particulate P species (Meybeck, 1982; Jensen et al., 2006). Upon delivery to estuaries from rivers, the river-borne P experiences large changes in salinity, pH and sometimes redox potential. Phosphorus mobility in these changing environments is related to the P speciation. Phosphorus in particles is present as inorganic or organic species. The particulate inorganic P includes exchangeable P, P associated with Al, Fe and Mn oxides and hydroxides, P associated with Ca and residual inorganic P (Pardo et al., 2003). The contents of the different species of

P are influenced by several factors, such as the major chemical composition, environmental chemical reaction processes and particle size (Andrieux et al., 2001; Koch et al., 2001). Of these, particle size is the most important factor. The mobility and transportation of different-sized particles differ in water (Krein et al., 2000). In general, estuarine export of suspended material is dominated by particles with low settling velocities, and these particles contribute, along with colloidal complexes, to the extensive P removal observed in the low-salinity regions of estuaries as well as the dissolved P maximum frequently observed at mid-salinity in some

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estuaries (Tappin, 2002). Although P species have been studied in estuarine sediments with respect to particle size (Andrieux et al., 2001), little information is available for SPM. Much effort has been focused on P species in the bottom sediments of estuaries and the coastal marine environment of the Changjiang estuary (Gao et al., 2001; Xu et al., 2001; Fang et al., 2007).

In the present study, dissolved P and particulate P species in suspended particles and in different size fractions in the Changjiang estuary were determined. The behavior of P in the Changjiang estuary was studied.

## 2 STUDY AREAS

The Changjiang estuary is the pathway through which the Changjiang River discharges into the East Sea. Historical data collected at the Datong Hydrological Station over the past 100 years shows that the annual water discharge to the Changjiang estuary averages  $955 \times 10^3 \text{ km}^3$ , and the annual fluvial sediment output is  $450\text{--}480 \times 10^6 \text{ tons/yr}$  (Chen et al., 2001). The estuarine region was first divided into a North Branch (NB) and a South Branch (SB), and then the SB was divided into a North Passage (NP) and a South Passage (SP). Finally, the SP was divided into a North Channel (NC) and a South Channel (SC). The Changjiang estuary is a mesotidal estuary with regular semidiurnal tides outside the mouth and non-regular semidiurnal tides inside (Tian et al., 1993). The average tidal range is 2.7 m with a maximum of 4.7 m. Average tidal currents are about 1.0 m/s but can reach more than 2.0 m/s during spring tide (Chen et al., 1988).

## 3 MATERIALS AND METHODS

### 3.1 Sampling

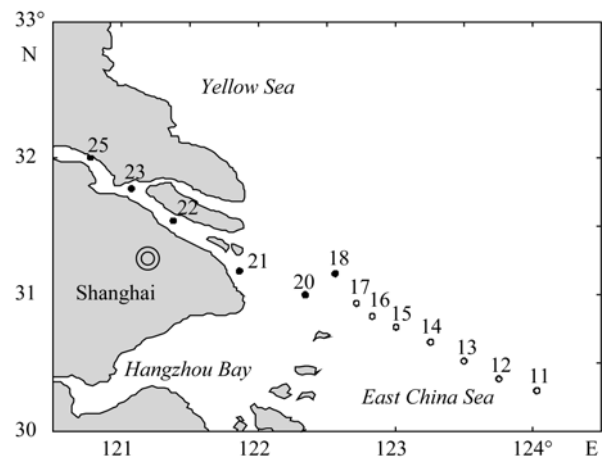
Surface water samples were collected along the direction of Changjiang River runoff in June 2006 (Fig.1). Surface water was filtered through pre-cleaned  $0.45 \mu\text{m}$  Millipore filters within 8 hours of collection and stored frozen before the measurement of dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP). The filters were kept frozen until the analyses of SPM concentrations and particulate P species were performed (Pacini et al., 1999). About 100 L to 150 L of surface water was collected for particle size fractionation at stations 25, 23, 22, 21, 20 and 18.

Water salinity was measured in situ using a Sea-Bird CTD set. The suspended particle size distributions were also measured in situ at stations

18–25 using a Lisst-100 (Type C, SEQUOLA).

### 3.2 SPM, Chl-*a*, DIP and DOP

Suspended particulate matter was determined gravimetrically. Chlorophyll *a* (Chl-*a*) was extracted by 90% acetone in darkness for 24 h, and the extractions were measured on a fluorescence spectrophotometer with a standard deviation of 5%–10%. DIP was measured photometrically by auto-analyzer (AAIII, BRAN+LUEBBE) with a precision of 5%–10%. Total dissolved phosphorus (TDP) was determined using the ultraviolet photooxidation-persulphate oxidation method (Yu, 1999). DOP was operationally defined as the difference between the TDP and DIP concentrations.



**Fig.1 The locations of sampling stations in the Changjiang estuary**

Suspended particulate matter and water samples were collected at all stations; fractionated suspended particulate matter was only sampled at stations indicated by filled circles; the gate of the river mouth is located between stations 20 and 21

### 3.3 Particle size fractions

In this study a custom-built water elutriation apparatus, built according to Walling et al., (1993) as illustrated in Fig.2, was used to separate suspended particles into clay-very fine silt ( $<8 \mu\text{m}$ ), fine silt ( $8\text{--}16 \mu\text{m}$ ), medium silt ( $16\text{--}32 \mu\text{m}$ ), coarse silt ( $32\text{--}63 \mu\text{m}$ ) and sand ( $>63 \mu\text{m}$ ) (Udden, 1914; Wentworth, 1922). The apparatus consists of four organic glass sedimentation chambers linked by organic glass tubes, a peristaltic pump with variable speed control and a 50-L capacity outflow container (V). The internal diameters of the cylindrical portions of sedimentation chambers I, II, III and IV are 25, 50, 100 and 200 mm, respectively. The SPM samples are imported to the system through an organic glass tube (8 mm i.d.), flowed through the

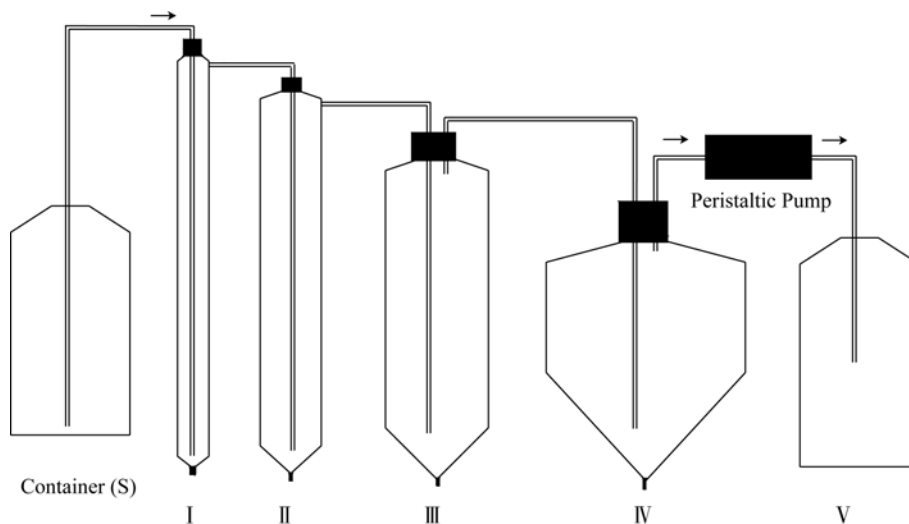


Fig.2 Water elutriation apparatus

sedimentation chambers and peristaltic pump, and finally collected in the 50-L container (V). In each chamber, samples enter at the bottom via a “long” organic glass tube and flow to the next chamber at the top. The peristaltic pump is positioned after the 200 mm sedimentation chamber to maintain a constant flow for the system.

About 100 to 150 L of surface water sample was collected. After settling for about 24 hours, the clear water was sucked out and stored for use as carrier water in the elutriation process. The sediments remaining in the container were used for elutriation. When a sampling run was initiated, the water elutriator was filled with the clear water previously sucked from the containers. After enough slurry was drawn into the apparatus, the clear water flowed through the system until the sedimentation chambers were completely flushed. The sediment samples collected from each sedimentation chamber were collected on filters and frozen. The slurry collected in the outflow container was left to settle for about 72 h and the upper clear water was then decanted. The sediments remaining in the outflow container were collected on filters and frozen.

### 3.4 Sequential extraction of particulate P

Suspended particles were freeze-dried and then crushed and ground. The species of particulate phosphorus (PP) were determined using a modified sequential extraction scheme based on the SEDEX scheme of Ruttenberg (Ruttenberg, 1992; Vink et al. 1997). The six-step extraction scheme separated the major reservoir of PP into six pools: loosely exchangeable P, organic P, Fe-bound P, authigenic apatite P, detrital fluorapatite P and refractory P. The

acid extractions were neutralized with 1 mol/L NaOH. The molybdenum blue method was used as a final detection method for soluble reactive phosphorus extracted by the scheme (Murphy et al., 1962). Phosphorus in citrate-dithionite-bicarbonate (CDB) extraction was determined using the solvent extraction method after the following treatment: 0.25 ml 1 mol/L  $\text{FeCl}_3$  was added to 25 ml CDB + rinse solution and allowed to sit for 1 week in order to destroy the excess dithionite (Ruttenberg, 1992; Anschutz et al., 1998). The P in the supernatant was analyzed by a Unico™ 2000 spectrophotometer. The reproducibilities of exchangeable P, organic P, Fe-bound P, authigenic apatite P, detrital fluorapatite P and refractory P were 4.47%, 6.88%, 8.73%, 13.0%, 5.94% and 9.94%, respectively.

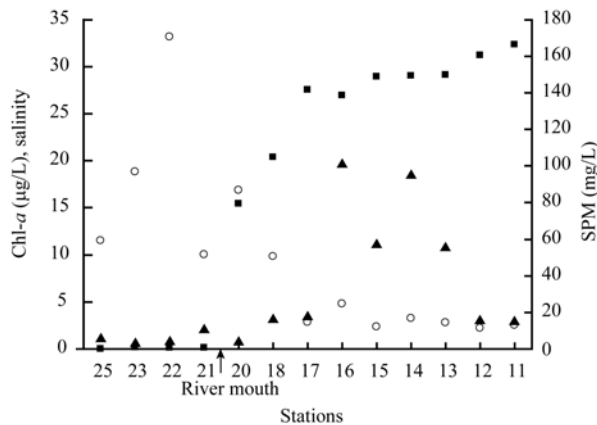
## 4 RESULTS

### 4.1 Salinity, SPM, Chl-*a* and suspended particle size distribution

The salinity, SPM and Chl-*a* values are shown in Fig.3. The results indicate that the estuary is dominated by fresh water inside the river mouth and the salinity increases gradually outside the river mouth. SPM values ranged from 10 to 170 mg/L. They increased from the inside to the gate, reached their highest level at station 22, and decreased gradually towards the outside of the river mouth. Chl-*a* values ranged from 0.56 to 19.56  $\mu\text{g/L}$ . Chl-*a* concentrations were less than 3  $\mu\text{g/L}$  inside the river mouth, increased toward the sea and then decreased again, with the highest Chl-*a* levels being found at stations 13 to 16 (above 10  $\mu\text{g/L}$ ).

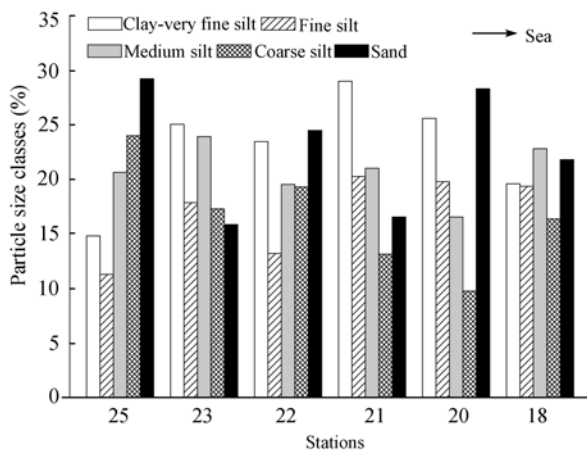
The percentages of clay-very fine silt, fine silt,

medium silt, coarse silt and sand ranged from 15% to 29%, 11% to 20%, 17% to 24%, 10% to 24% and 16% to 29%, with averages of 23%, 17%, 21%, 17% and 23%, respectively, at stations 18 to 25 (Fig.4). Compared with stations that were dominated by fresh water inside the river mouth, there was more sand and less medium silt and coarse silt around the river mouth at station 20.



**Fig.3 Salinity and suspended particulate matter concentrations (SPM) along a Changjiang estuary transect**

■ Salinity; ○ SPM; ▲ Chl-a

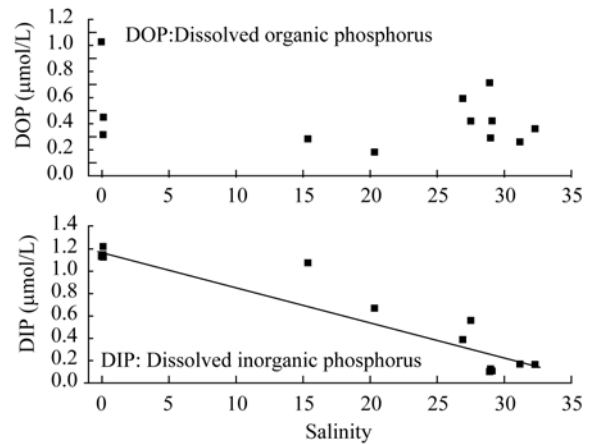


**Fig.4 Distribution of various particle size classes along a Changjiang estuary transect**

**4.2 Dissolved phosphorus**

Plots of nutrients versus salinity clearly illustrate the variation in the nutrient concentration along the estuary profile (Fig.5). DIP did not change obviously inside the river mouth, which was dominated by fresh water, with a concentration of 1.02–1.22  $\mu\text{mol/L}$ . At a salinity of about 14, the DIP was higher than its conservative value, indicating the addition of DIP to the water. At a salinity of about 30 (stations 13 to 16), the DIP was lower than its conservative value, indicating the removal of DIP from the water.

The DOP varied greatly in the freshwater region of the estuary (Fig.5). DOP was 1.02  $\mu\text{mol/L}$  at freshwater station 25 and these values decreased in the seaward direction, with values of 0.45, 0.31 and 0.28  $\mu\text{mol/L}$  at stations 23, 22 and 20, respectively. At a salinity of about 30, the DOP ranged from 0.26 to 0.71  $\mu\text{mol/L}$  with an average of 0.43  $\mu\text{mol/L}$ , which was higher than the corresponding value at the gate.



**Fig.5 Dissolved inorganic phosphorus and dissolved organic phosphorus concentrations along a Changjiang estuary salinity transect**

The line represents the conservative value

**4.3 Particulate P species in suspended particles**

Particulate organic P contents at stations 25, 23, 22, 21, 20 and 18 were 6.59  $\mu\text{mol/g}$ , 5.28  $\mu\text{mol/g}$ , 4.56  $\mu\text{mol/g}$ , 2.83  $\mu\text{mol/g}$  and 3.36  $\mu\text{mol/g}$ , respectively; the contents of Fe-bound P were 6.12  $\mu\text{mol/g}$ , 4.80  $\mu\text{mol/g}$ , 4.33  $\mu\text{mol/g}$ , 2.79  $\mu\text{mol/g}$  and 2.64  $\mu\text{mol/g}$ , respectively; and the contents of refractory P were 6.18  $\mu\text{mol/g}$ , 5.77  $\mu\text{mol/g}$ , 4.70  $\mu\text{mol/g}$ , 1.76  $\mu\text{mol/g}$  and 0.76  $\mu\text{mol/g}$ , respectively (Fig.6). The contents of organic P, Fe-bound P and refractory P decreased gradually from the freshwater region (station 25) to the river mouth (station 20). The average exchangeable P inside the river mouth (stations 22 to 25) was 1.87  $\mu\text{mol/g}$ , which was lower than the corresponding value around the gate of the river mouth (2.54  $\mu\text{mol/g}$ ). From the gate to the sea, a distinct change in particulate P species was observed: exchangeable P and organic P in suspended particles increased greatly and predominated with concentrations of 5.76–23.66  $\mu\text{mol/g}$  and 2.43–11.88  $\mu\text{mol/g}$ , respectively, which made up 38.46%–63.75% and 26.99%–48.75%, respectively, of particulate P.

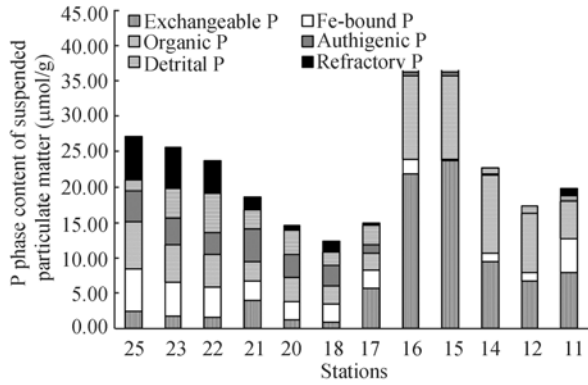


Fig.6 P phase content of suspended particulate matter along a Changjiang estuary transect

4.4 Particulate P species in various particle size classes

The variation of different species of particulate

P in different particle sizes is shown in Fig.7. In general, exchangeable P, organic P, Fe-bound P, authigenic P and refractory P were concentrated in small particle size classes, such as clay-very fine silt and fine silt, while more detrital P was found in medium silt and coarse silt fractions.

Also, as shown in Fig.7, the variations of different particulate P species differed from each other. The content of exchangeable P was relatively high around the river mouth (stations 20 and 21), especially for the clay-very fine silt fraction. The average exchangeable P in clay-very fine silt increased from about 1.44 µmol/g inside the river mouth (stations 22, 23 and 25) to about 7.57 µmol/g around the gate of the river mouth (stations 20 and 21) and then decreased to 0.45 µmol/g outside the river mouth (station 18). In contrast to exchangeable P, the content

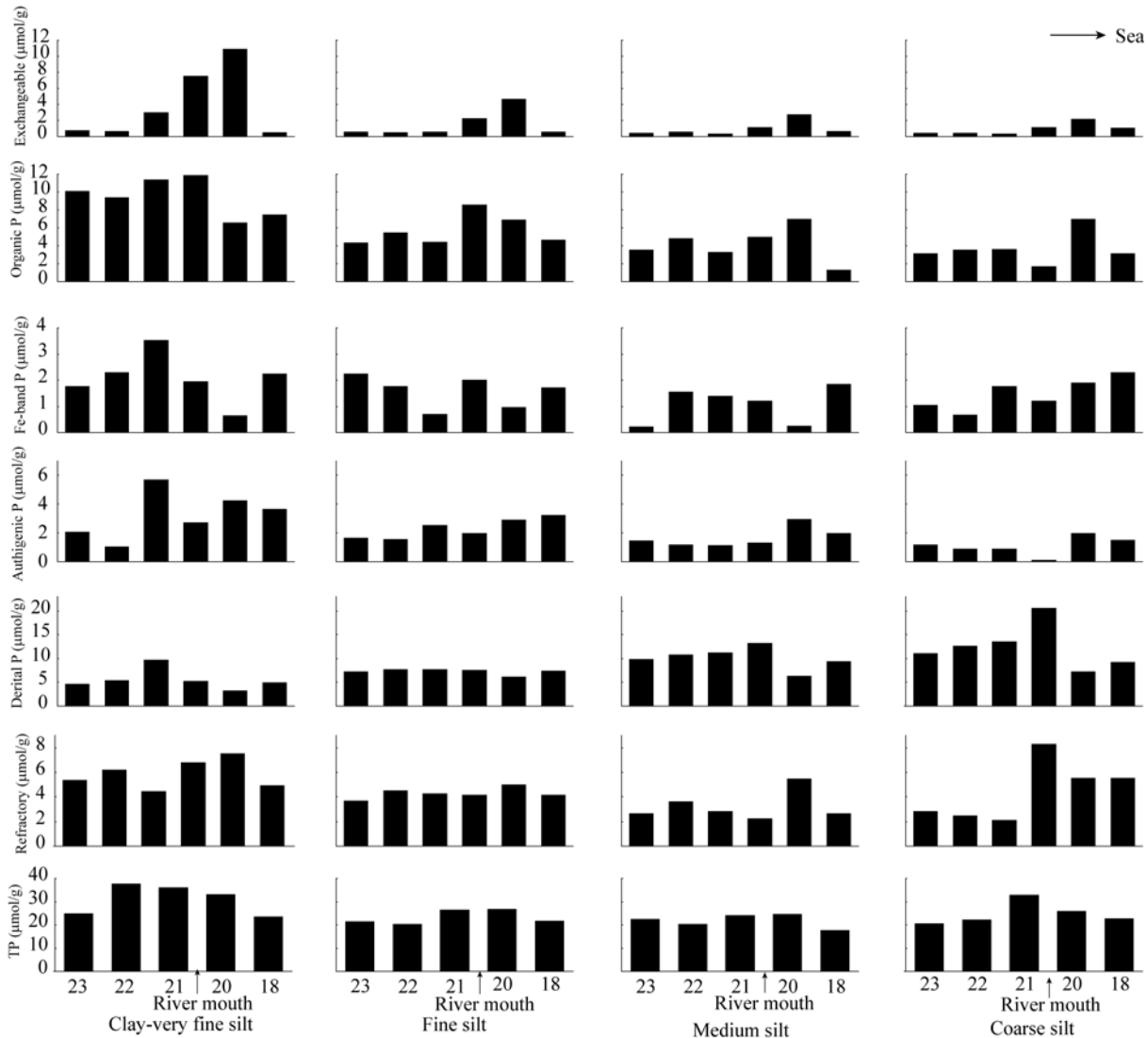


Fig.7 Variation of particulate P forms in different particle size classes by station in Changjiang estuary in June, 2006

The sand fraction was unavailable

of Fe-bound P and organic P in clay-very fine silt was low around the gate of the river mouth, with averages of 1.52  $\mu\text{mol/g}$  and 8.58  $\mu\text{mol/g}$ , respectively.

## 5 DISCUSSION

### 5.1 Effect of particle size on particulate P species

The results reported here indicate that exchangeable P, organic P, Fe-bound P, authigenic P and residual P are concentrated in clay and silts with finer particles while detrital P is concentrated in silts and sand with coarser particles (Fig.7). There are several possible explanations for this observation. First, it is known that the increased ratio of particle surface area/volume associated with decreased particle size can enhance the sorption of metals and other contaminants (Turner et al., 1994), and the particulate P content is significantly related to the adsorptive capacity of particles (Froelich, 1988; Aminot et al., 1996). In addition, Fe and Al oxides are often regarded as P scavengers which are known to associate with surfaces and become enriched in small particles (Horowitz, 1991). Stone et al. (1993) observed that particle size was correlated with the relative contributions of various particulate P fractions to the P content of the sediment, which contributed to the observed increase in Fe and Al oxides with decreasing particle size. Second, some small particles with low settling velocities may in fact be organisms such as bacteria or phytoplankton, which has been proved by the relationship between organic matter and particle size (Alber, 2000; Coppola et al., 2005, 2007). The smaller the particle, the more particulate organic carbon was observed (Bergamaschi et al., 1997; Keil et al., 1997).

### 5.2 Behavior of particulate P in the Changjiang estuary

From inside the river mouth to the gate of the river mouth (salinity 0–15), the DOP concentration decreased gradually and organic P, Fe-bound P and refractory P contents in suspended particles decreased obviously, while more DIP was observed and more exchangeable P appeared around the gate of the river mouth (Figs.5–7). This phenomenon indicates that DOP was mineralized and some of the P that was present in suspended particles as organic P, Fe-bound P and refractory P were released from the particles. Some of the mineralized P from the DOP and the released P from particles was released into the water as DIP, and some of it was re-adsorbed by suspended particles as exchangeable P.

The mineralization of DOP and the release of particulate organic P, Fe-bound P and refractory P are attributable to changes in the water environment (such as ion strength and redox potential) (Froelich, 1988; Gardolinski et al., 2004; Deborde et al., 2007). With an increasing salinity, particulate organic P was decomposed and rapidly released into the water body, due to plasmolysis of particle bacteria (Gardolinski et al., 2004).

The higher exchangeable P around the river mouth is probably due to the aggregation of SPM which was observed when the particles sampled at station 20 were water elutriated. Salinity was one of the most important factors influencing the aggregation of suspended particles in the estuary, and the salinity of surface water at station 20 was 15, which is close to the favorable salinity range for aggregation in the Changjiang estuary (3–15, Shen et al., 1985; Qiu et al., 1988). The phenomenon of dissolved inorganic P being adsorbed into particles in low-salinity regions has been observed in many estuaries (Lucotte et al., 1983; Lucotte et al., 1988; Fox, 1990; Balls, 1994; Zwolsman, 1994). Most authors have attributed this to the aggregation of organic humus or the co-precipitation of iron (hydro) oxides (Forsgren et al., 1992; Forsgren et al., 1996; Hyacinthe et al., 2004). The “fresh” estuarine particles include aggregations of organic matter, iron and manganese oxides and carbonates (Turner et al., 2002). In the mixing experiment of Changjiang River water with East China Sea water, newly formed iron oxides and organic aggregation were observed (Fan et al., 2008). The surface areas of these “fresh” aggregated particles were highly reactive, and the particles were chemically more reactive, and thus could adsorb dissolved constituents faster. Particles with these characteristics contribute to the extensive removal observed in the low salinity regions of estuaries (Tappin, 2002), which results in the increase of exchangeable P at station 20 (Fig.7). In contrast, the aggregation should reduce inorganic particulate P in large size particle classes, especially for detrital P (Fig.7), since more organic matter tends to be associated with these classes.

Flocs in estuaries and coastal waters are fragile (Fennessy et al., 1994). Additional turbulence and shock waves can break them apart into smaller flocs and single particles (Li et al., 1999). Consequently, phosphorus associated with the flocs would be released into the water, and redistributed in different particle size classes (Figs.6 and 7). The sample collected from outside the river mouth (station 18)

showed a lower exchangeable P than those collected around the river mouth (stations 20 and 21). The DIP was also higher than its conservative value at station 18. It can be inferred that, during transportation from the gate of the river mouth to the sea (from station 21 to station 18), particulate aggregations broke up, and the P that had been adsorbed to particles as exchangeable P around the gate of the river mouth was released into the water again.

At about salinity 30, DIP was lower than its conservative value, while DOP, exchangeable P and organic P in suspended particles were higher than those around the gate of the river mouth. The behavior of P was closely related to the activity of marine plankton. At stations 11 to 17, due to the pronounced sedimentation of suspended particles, SPM was lower than 25 mg/L. Therefore, light was no longer a limiting factor for growth of phytoplankton, and nutrient removal from the Changjiang River was abundant because of phytoplankton thriving (Ning et al., 1988; Tian, 1993), which resulted in higher Chl-*a* (Fig.3). The P related to phytoplankton was extracted as exchangeable P and organic P in modified SEDEX, (Ruttenberg, 1992; Vink et al., 1997), so the contents of exchangeable P and organic P were higher in this area.

### 5.3 Riverine fluxes of particulate P to the Changjiang estuary

With the lower velocity of water flow, most riverine suspended particles are deposited in the estuary, and due to differences in settling velocities, suspended particles with different particle sizes are deposited in different parts of the estuary (Gibbs et al, 1989): coarse suspended particles (such as sand and coarse silt) would be deposited close to the land, fine suspended particles (such as fine silt) would be transported a greater distance toward the sea, and some small suspended particles (such as clay) would be delivered to the sea. The estuarine front could also act as a sieve within the estuarine sediment transportation system (Reeves et al., 2001; Neil, 2009). Thus, the distribution and behavior of some elements in the estuary that were closely related to particles, such as phosphorus, were greatly influenced by particle size. In order to understand the behavior of P in the estuary, the relationship between particle size and particulate P species should be studied. This study could benefit from the physical size separation of suspended particles.

Although numerous works have studied the role of

particle size in particulate matter transported from the land to the sea, most of them have been devoted to organic matter (Turner et al., 1994; Milligan, 1995; Dyer et al., 1996; Wolfstein, 1996; Coppola et al., 2005, 2007), and little was known about phosphorus (Andrieux et al., 2001). Alber (2000) operationally separated suspended particles into “truly suspended” and “settleable” fractions with a cut-off velocity of 0.006 m/s and found that all measured parameters (Chl-*a*, organic carbon and nitrogen, phaeopigment) were largely associated with the “truly suspended” fraction. Alber hypothesized that the more organic-rich, biologically-active material associated with the suspended fractions likely had a different fate in the estuary, as “truly suspended” particles will be readily transported while “settleable” particles will settle and be resuspended with each tide. According to the diameters of the elutriator chambers and the flow rate, settling velocity ranges for particles with size ranges <8  $\mu\text{m}$ , 8–16  $\mu\text{m}$ , 16–32  $\mu\text{m}$ , 32–63  $\mu\text{m}$  and >63  $\mu\text{m}$  were <0.004 cm/s, 0.004–0.016 cm/s, 0.016–0.064 cm/s, 0.064–0.256 cm/s and >0.256 cm/s, respectively. Thus, the <8  $\mu\text{m}$  particle fraction could be regarded as “truly suspended” particles. At station 25 (a station located in the freshwater part of the Changjiang estuary), which was representative of the particles delivered from the Changjiang River to the estuary, almost half of particulate P was organic P in “truly suspended” particles while detrital P, ranging from 37% to 54%, was an especially significant contributor to total particulate P in “settleable” fractions. These results indicate that there were qualitative differences between the “truly suspended” and “settleable” fractions in the distribution of particulate P and that these differences should be considered in order to understand the fate of particulate P exported to the Changjiang estuary.

Based on particulate P speciation in various particle size classes, the suspended particle size distribution, SPM at freshwater station 25 and water discharge during sampling, riverine fluxes of particulate P to the Changjiang estuary could be calculated in terms of total suspended particles and of various particle size classes. The results are shown in Table 1. The detrital P was the predominant fraction of P (46.76% of particulate P fluxes) among the pools of particulate P. The organic P and refractory P were the second largest pool and accounted for 21.89% and 16.25% of particulate P fluxes, respectively. The exchangeable P, Fe-bound P and authigenic P made up less than 10% of particulate P fluxes.

**Table 1 Flux of various particulate P forms in terms of total suspended particle matter and different particle size classes transported from the Changjiang River to the estuary ( $\times 10^8 \mu\text{mol/s}$ )**

	Exchangeable P	Fe-bound P	Organic P	Authigenic P	Detrital P	Refractory P	Bio-P**	TPP**
Clay-very fine silt	0.25	3.40	0.59	0.70	1.55	1.79	4.24	8.27
Fine silt	0.14	1.11	0.58	0.42	1.84	0.94	1.83	5.02
Medium silt	0.20	1.63	0.10	0.68	4.63	1.24	1.93	8.47
Coarse silt	0.23	1.72	0.57	0.65	5.97	1.54	2.52	10.68
Sand*	0.28	2.09	0.69	0.79	7.27	1.87	3.07	13.00
T-SPM**	1.11	9.95	2.53	3.23	21.25	7.39	13.58	45.45

\*With the assumption that coarse silt and sand have the same particulate P forms

\*\* T-SPM: Total Suspended Particle matter; TPP: Total Particulate Phosphorus; Bio-P: Bio-available P

**Table 2 Flux of total particulate phosphorus (TPP) and bio-available P (Bio-P) in total suspended particle matter (T-SPM), “truly suspended particle matter” and “settleable particle matter” fractions, transported from the Changjiang River to the estuary ( $\times 10^8 \mu\text{mol/s}$ )**

	T-SPM	Truly suspended particle matter	Settleable particle matter
TPP	45.45	8.27	37.17
Bio-P	13.58	4.24	9.34

According to the DIP and DOP concentrations at freshwater station 25 and the water discharge during sampling, DIP and DOP fluxes during sampling were  $0.43 \times 10^8$  and  $0.39 \times 10^8 \mu\text{mol/s}$ , respectively. The total particulate P flux delivered from the main channel of the Changjiang River to the estuary was about  $45.45 \times 10^8 \mu\text{mol/s}$  (Table 2). About  $8.27 \times 10^8 \mu\text{mol/s}$  of particulate P was associated with the “truly suspended” fraction, and  $37.17 \times 10^8 \mu\text{mol/s}$  was transported with the “settleable” fraction. In other words, 18% of particulate P was readily transported to the sea. Exchangeable P, organic P and Fe-bound P are considered to be bio-available (Andrieux et al., 1997; Zhang et al., 2004). Thus, the bio-available P flux during sampling was about  $13.58 \times 10^8 \mu\text{mol/s}$  (30% of particulate P flux), which was much greater than the fluxes of DIP and DOP. Of the bio-available P flux, about  $4.24 \times 10^8 \mu\text{mol/s}$  was associated with the “truly suspended” fraction and about  $9.34 \times 10^8 \mu\text{mol/s}$  was transported by “settleable” particles. Thus about 31% of the bio-available P was readily transported to the sea, which was about 10 times higher than the flux of DIP.

## 6 CONCLUSION

Particulate P species in suspended particles and in separated particle size classes collected from the Changjiang estuary were analyzed. The results indicate that: (1) Exchangeable P, organic P, Fe-bound P, authigenic P and refractory P were

concentrated in the small particle size classes, while more detrital P was found in the coarse silt and very coarse silt fractions. (2) From the inside to the gate of the river mouth, DOP and DIP decreased with increasing salinity, but the DIP was higher than the conservative value. Particulate organic P, Fe-bound P and refractory P decreased with increasing salinity, but a higher level of exchangeable P was found around the gate of the river mouth. From the gate to the outside of the river mouth, the DIP decreased and was lower than the conservative value. Due to the abundant phytoplankton, higher DOP, particulate exchangeable P and particulate organic P values were found outside the river mouth (3) About 30% of particulate P transported from the Changjiang River to the estuary was bio-available ( $13.58 \times 10^8 \mu\text{mol/s}$ ), which was higher than the flux of dissolved phosphorus ( $0.82 \times 10^8 \mu\text{mol/s}$ ).

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