



Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Distribution, mixing behavior, and transformation of dissolved inorganic phosphorus and suspended particulate phosphorus along a salinity gradient in the Changjiang Estuary

Jia Meng^{a,b}, Zhigang Yu^{a,c}, Qingzhen Yao^a, Thomas S. Bianchi^d, Adina Paytan^e, Bin Zhao^{a,b}, Huihui Pan^{a,b}, Peng Yao^{a,c,f,*}

^a Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao 266100, China

^b College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

^c Institute of Marine Organic Geochemistry, Ocean University of China, Qingdao 266100, China

^d Department of Geological Sciences, University of Florida, Gainesville, FL 32611-2120, USA

^e Institute of Marine Sciences, University of CA, Santa Cruz 95064, USA

^f Qingdao Collaborative Innovation Center of Marine Science and Technology, Qingdao 266100, China

ARTICLE INFO

Article history:

Received 5 July 2014

Received in revised form 27 September 2014

Accepted 29 September 2014

Available online xxx

Keywords:

Changjiang Estuary

Suspended particulate matter

Phosphorus forms

Water elutriation

Mixing behavior

Transformation

ABSTRACT

Surface water and suspended particulate matter (SPM) samples were collected along a salinity gradient in the Changjiang Estuary in June, 2011 to examine the distribution, mixing behavior and transformation of dissolved and particulate phosphorus (P) species. Particulate P was fractionated into five size fractions using a water elutriation method, followed by a sequential extraction procedure (SEDEX). Dissolved inorganic P (DIP) concentrations ranged from 0.53 to 3.02 $\mu\text{mol L}^{-1}$ with a mean of 1.44 $\mu\text{mol L}^{-1}$, while total particulate P (TPP) concentrations ranged from 20.56 to 26.90 $\mu\text{mol L}^{-1}$ (24.21 $\mu\text{mol L}^{-1}$). The variation of DIP and P species in both bulk and size fractionated particles along the salinity gradient indicated a significant transformation between different P phases, especially for labile P such as exchangeable P (Ex-P), organic P (Or-P) and Fe-bound P (Fe-P) in a particulate P pool. Among all P forms, detrital P (De-P) and Or-P in SPM were the most abundant, accounting for 43.9% and 26.1% of TPP in bulk particles. De-P increased with increasing particle grain size, with an average concentration of $8.92 \pm 2.20 \mu\text{mol g}^{-1}$ in the clay fraction ($<8 \mu\text{m}$) and $12.6 \pm 1.49 \mu\text{mol g}^{-1}$ in the sand fraction ($>63 \mu\text{m}$), whereas Or-P and other P forms decreased gradually with increasing grain size. The average concentration of Or-P in clay fraction was $6.93 \pm 1.92 \mu\text{mol g}^{-1}$ and it decreased to $1.59 \pm 0.61 \mu\text{mol g}^{-1}$ in the sand fraction. The flux of bioavailable P (BAP, sum of Ex-P, Or-P and Fe-P) in clay fraction ($<8 \mu\text{m}$), defined as “truly” suspended particles, was estimated to be $0.21 \times 10^4 \text{ t P yr}^{-1}$ and accounted for 29% of the bulk BAP flux. The particulate P to specific surface area ratios (P/SSA) was lower in fine suspended particles than in coarse particles, indicating lower preservation of P in these particles. When compared with the bed sediments of the Changjiang Estuary, the P/SSA loadings in fractionated suspended particles were maintained at the same level for De-P and Fe-P, slightly higher for authigenic P (Au-P) and refractory P (Re-P) and obviously higher for labile P such as Ex-P and Or-P, further indicating the differential behavior of P forms during particle settlement in this dynamic estuary.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Phosphorus (P) plays an important role in phytoplankton primary production (Paytan and McLaughlin, 2007 and references therein). Understanding the biogeochemical cycling of P in estuarine systems requires knowledge of the dynamics of P species, such as their physical matrix (e.g., dissolved, colloidal or particulate), chemical speciation (e.g., inorganic, organic or metal complexation) transport, transformation, and mixing behavior (Billen et al., 2001; Bianchi et al., 2007;

Boesch et al., 2009). Phosphorus is transported to the ocean primarily in particulate phases via riverine influx (Ruttenberg, 1993; Howarth et al., 1995; Guo et al., 2004; Jensen et al., 2006; Cai et al., 2008); the speciation of this particulate P is partly controlled by particle grain size (Rao and Berner, 1997; Andrieux-Loyer and Aminot, 2001; He et al., 2009). Particles of different grain sizes differ in their sedimentation, flocculation and disaggregation properties, which can be further altered across steep salinity gradients—commonly found in estuarine environments. Large-river delta-front estuaries (LDEs) (Bianchi and Allison, 2009), have been shown to be globally important interfaces in controlling the distribution and bioavailability of P in river-dominated coastal margins (Mayer et al., 1998; Cai et al., 2012; Lin et al., 2012, 2013).

* Corresponding author. Tel./fax: +86 532 66781659.
E-mail address: yaopeng@mail.ouc.edu.cn (P. Yao).

Unfortunately, studies focusing P speciation of size-fractionated suspended particles in LDEs remain sparse.

The Changjiang (Yangtze River) LDE is characterized by high productivity, largely stemming from the high amounts of nutrients discharged by the river (Zhou et al., 2008). Previous studies on P cycling in the Changjiang LDE have mainly focused on the P speciation, distribution (e.g., Fang et al., 2007; He et al., 2009) and bioavailability (e.g., He et al., 2009; Hou et al., 2009), with very few on mixing behavior and transformation of P species. Moreover, previous work focused either on dissolved P or P speciation in bulk particles/sediments in the estuary (e.g., Fang et al., 2007; Hou et al., 2009; He et al., 2009; Yu et al., 2012; Meng et al., 2014a; Yao et al., 2014a). However, P speciation in size-fractionated suspended particles and their behavior along the salinity gradient remain poorly understood in the Changjiang LDE. In this study, surface water samples and suspended particulate matters (SPM) in the Changjiang LDE were collected to examine the following: 1) distribution, mixing behavior and transformation of dissolved inorganic P (DIP) and size-fractionated suspended particulate P in the Changjiang LDE; 2) bioavailable P (BAP) concentrations in suspended particulate P and BAP fluxes associated with particle grain size from the Changjiang LDE to the East China Sea (ECS) shelf, and; 3) preservation of P associated with different particle grain sizes and specific surface areas (SSA).

2. Materials and methods

2.1. Study area and sampling

The Changjiang is one of the largest rivers in the world, where it is ranked fourth in water ($900 \text{ km}^3 \text{ yr}^{-1}$) and fifth in sediment ($4.70 \times 10^8 \text{ t yr}^{-1}$) discharge, respectively (Milliman and Farnsworth, 2011; Bianchi et al., 2014). The P flux of the Changjiang to the ECS reaches up to $1.49 \times 10^5 \text{ t P yr}^{-1}$ (Zhang et al., 2003).

The Changjiang Estuary is divided into the South Branch and the North Branch near Xuliujing, and the runoff and SPM are transported to the ocean mainly through the South Branch (Shen et al., 2008). A Turbidity Maximum Zone (TMZ) in the lower river, which migrates depending on river discharge, has been shown to play an important role in estuarine mixing processes (e.g., SPM transport and accumulation, surface sediments deposition and resuspension) in the Changjiang LDE (Shen et al., 2008), and thus provides an ideal site for studying the interactions between dissolved and particulate P species in this Estuary.

Sampling was conducted onboard the RV *Runjiang 1* (Zhoushan Runhe Co., Ltd., China) in June, 2011. Surface water and SPM samples were collected at 8 stations along a salinity gradient starting near Xuliujing and extended seaward to an area with a salinity of ca. 25 (Fig. 1). During this sampling period, the river discharge in the Changjiang Estuary was $19,100 \text{ m}^3 \text{ s}^{-1}$, based on hydrologic data from Xuliujing (<http://xxfb.hydroinfo.gov.cn>).

Surface water samples were collected by submersible pump. An aliquot of each sample (300 mL) was stored in a HDPE (high-density polyethylene) bottle for laser particle analyses. About 10 to 50 L samples were filtered through pre-cleaned and pre-weighed $0.45 \mu\text{m}$ polyether sulfone (PES) filters directly after sampling. Both water samples (about 100 mL of each sample) and filters were kept frozen prior to measurements of DIP and SPM concentrations.

About 100 to 150 L surface water was collected for particle size fractionation, using a water elutriation method (Walling and Woodward, 1993; He et al., 2009). According to hydrodynamic diameter (Stoke's diameter), suspended particle samples were separated into five size fractions, i.e. 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 ($>63 \mu\text{m}$). The size-fractionated samples were collected, filtered through pre-cleaned $0.45 \mu\text{m}$ cellulose acetate membrane filters on shipboard, and all filters were kept frozen prior to measurements of SSA and P speciation.

2.2. Analytical methods

2.2.1. Analyses of salinity, SPM concentration and DIP

Salinity of surface water was determined onboard using a Hach multi-parameter meter (HQ40d; Hach Ltd., USA). SPM concentrations were determined gravimetrically from filtered samples. DIP was measured photometrically using a nutrient auto-analyzer (Quatro, Bran-Lubbe Ltd., Germany) (Grasshoff et al., 1999). The detection limit for PO_4^{3-} was $0.01 \mu\text{mol L}^{-1}$. The relative standard deviation (RSD) of replicate analyses of a given sample was less than 3%.

2.2.2. Analyses of particle grain size and SSA

Grain size composition of the bulk SPM samples was measured using a laser particle analyzer (Mastersizer 2000, Malven Instruments Ltd., UK) following the method of Hu et al. (2009). SSA was determined using an automatic nitrogen adsorption surface area analyzer (3H-2000BET-A, Beishide Instrument-ST Co., Ltd., China), according to Waterson and Canuel (2008).

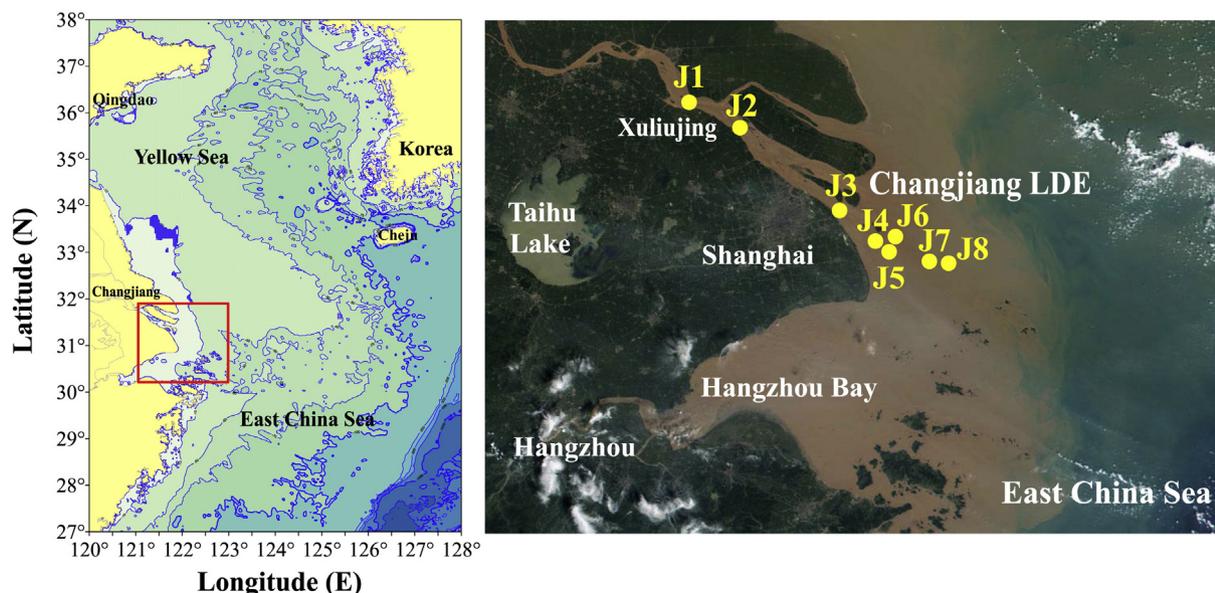


Fig. 1. Sampling locations in the Changjiang (Yangtze River) Estuary during June, 2011.

2.2.3. Sequential extraction and analysis of phosphorus

Speciation of P in freeze-dried and homogenized suspended particles (ca. 0.1 g) was determined by a sequential extraction procedure (SEDEX) modified by Vink et al. (1997), whereby the major reservoirs of P were separated into the following six pools: detrital P (De-P); authigenic P (Au-P); refractory P (Re-P); Fe-bound P (Fe-P); organic P (Or-P) and exchangeable P (Ex-P) (Table 1). All extracted phosphates were determined with the phosphomolybdate blue method by spectrophotometry (Grasshoff et al., 1999). Total particulate P (TPP) concentration was defined as the sum of these six particulate P forms. Method blanks and standard reference material (SRM) were used for data quality control. Sediment standards collected from China's off-shore region in the ECS (GB W 07314) were used for SRM. The TPP concentration for the SRM was determined as $20.55 \pm 1.82 \mu\text{mol g}^{-1}$ by our method (Relative standard deviation (RSD) < 10%, n = 6), which is very close to the established value determined by China's State Oceanic Administration ($20.85 \pm 1.97 \mu\text{mol g}^{-1}$). The RSDs of replicate analyses of a given sample were less than 4.8%, 6.3%, 8.2%, 13.0%, 5.6% and 9.1% for Ex-P, Or-P, Fe-P, Au-P, De-P and Re-P, respectively (n = 6).

In our method (Vink et al., 1997), an additional step was added to extract reactive Or-P with SDS, and Re-P was defined as non-reactive (or inert) organic P that could not be extracted by SDS. Separation of Or-P from Re-P is a critical improvement making the calculation of BAP possible, because Or-P can be easily regenerated while Re-P is difficult to be utilized by organisms (Lopez, 2004). As for De-P and Au-P, they have very slow formation kinetics and are slow to regenerate and were also widely thought of as "immobile P" (Vink et al., 1997; Coelho et al., 2004; Hou et al., 2009). In addition, it should be noted that P speciation in our method (and other methods) is just operationally defined (Table 1), for example, Ex-P is defined as loosely-sorbed P and consists of direct adsorption of phosphate and dissolved organic P (DOP) (Zhang et al., 2004). However, the concentrations of Or-P were much more abundant than Ex-P in this study (Table S1), therefore the organic P form in Ex-P may account for only a small fraction of all organic P and can be neglected.

2.3. Statistical analysis

Pearson correlation analysis with a two-tailed test of significance was performed using the IBM SPSS Statistics 20 program to study the relationship between the measured parameters. The program SPSS was also used to run one-way analysis of variance (ANOVA) to examine the statistical differences in data between two or more groups.

Table 1
Outline of P fractionation scheme.

Step	Extractant	Separated P speciation
I	1 M MgCl ₂	Ex-P; formed by direct adsorption of phosphate and dissolved organic P (DOP) onto sediments (Zhang et al., 2004)
II	Sodium dodecyl sulfate (SDS) solution	Or-P; contains orthophosphate monoesters and diesters (DNA, phospholipids), as well as polyphosphates and pyrophosphates that are inorganic storage compounds and degradation products (Lukkari et al., 2009)
III	Citrate-dithionite-bicarbonate (CDB) solution	Fe-P; P associated with oxide or oxyhydroxide of iron and manganese
IV	Acetate buffer	Au-P; includes authigenic carbonate fluorapatite (CFAP), biogenic apatite (i.e., bones, teeth), and carbonate-associated P (Ruttenberg, 1992; Hou et al., 2009; Sekula-Wood et al., 2012)
V	1 M HCl	De-P; P intrinsic to igneous or metamorphic rocks (Ruttenberg, 1992)
VI	1 M HCl (after ashing under 550 °C)	Re-P; organic P that cannot be extracted by SDS

3. Results

3.1. Variations in SPM concentrations, grain size composition and SSA along the salinity gradient

During our sampling, salinity gradually increased from 0.16 in the inner-estuary to 25 outside the estuary (Table 2; Fig. 2). SPM concentrations of bulk suspended particles, which ranged from 38 to 545 mg L⁻¹, first increased and then gradually decreased with increasing salinity, with the highest level observed at site #J4 and #J5, corresponding to salinities of 6 and 10 (Table 2; Fig. 2). The percentages of clay (<8 μm), fine silt (8–16 μm), medium silt (16–32 μm), coarse silt (32–63 μm) and sand (>63 μm) obtained by laser particle analysis were 43.8–59.2%, 23.7–34.7%, 10.9–19.4%, 2.1–7.6% and 0.4–3.2%, respectively (Table S2). The median grain sizes (MGS) ranged from 6.46 to 9.26 μm with the minimum values found in the TMZ area, where SPM concentrations were highest (Table 2; Fig. 2). Due to sample availability, only a part of the size-fractionated samples was analyzed for SSA. SSA measured in suspended particles ranged from 1.92 to 21.4 m² g⁻¹ (Table S1). The smaller-size fractions (<32 μm) were characterized by larger SSA (avg. 15.0 m² g⁻¹), while the SSA of the larger-size fractions (>32 μm) were significantly smaller (avg. 2.67 m² g⁻¹).

3.2. Variations in DIP along the salinity gradient

DIP concentrations ranged from 0.53 to 3.02 μmol L⁻¹ (avg. 1.44 μmol L⁻¹) with the maximum value observed at the inner-estuary sites (salinity ~0). The DIP concentrations slightly increased from J1 to J2/J3 first and then decreased sharply with increasing salinity between the salinities of 0.17 and 6; for salinities higher than 6, there was a gradual decreasing trend with salinity (Table 2; Fig. 3). Overall, the variation of DIP across the salinity gradient showed a strong removal behavior (Table 2; Fig. 3).

3.3. Variations in speciation of P in bulk suspended particles

The TPP concentrations ranged from 20.56 to 26.90, with an average of 24.21 μmol g⁻¹. TPP first decreased and then increased with the increasing salinity, with the relatively lower values (20.56 μmol g⁻¹) found near the river mouth (Fig. 4a). De-P and Or-P were the primary components of TPP (Table S1, Fig. 4a). The concentration of De-P varied from 8.74 to 12.58 μmol g⁻¹ with an average of 10.63 μmol g⁻¹, and Or-P had an average concentration of 6.33 μmol g⁻¹, that ranged from 4.98 μmol g⁻¹ to 7.46 μmol g⁻¹. The Or-P gradually decreased from the inner-estuary region to the river mouth, followed by an increase outside the estuary. Similar to Or-P, De-P concentrations in the river mouth were relatively low. Concentrations of Re-P, Au-P, Ex-P and Fe-P were lower compared to De-P and Or-P. The Re-P ranged from 1.90 to 5.25 μmol g⁻¹ with an average of 3.21 μmol g⁻¹ and the Au-P varied from 1.06 to 1.99 μmol g⁻¹ (avg. 1.71 μmol g⁻¹) (Table S1). Ex-P had an average concentration of 1.82 μmol g⁻¹ and ranged from 1.09 to 2.81 μmol g⁻¹. Concentrations of Fe-P were low and ranged from 0.23 to 1.00 μmol g⁻¹ (avg. 0.52 μmol g⁻¹) (Table S1). Overall, Re-P and Fe-P both exhibited a decreasing trend with increasing salinity, while Ex-P showed an increase. Au-P did not vary with salinity (Fig. 4a).

P concentrations on volume bases (in μmol L⁻¹) in bulk suspended particles showed a similar variation with SPM, and ranged from 0.98 to 13.27 μmol L⁻¹. The highest concentrations of all forms (μmol L⁻¹) were observed at the river mouth region (sites #J4 and #J5) with salinities of 6 and 10 (Table S3; Fig. 4b).

Among the six particulate P species, De-P represented the highest fraction (43.9 ± 3.6%) of TPP from all stations, followed by Or-P (26.1 ± 3.1%), Re-P (13.1 ± 3.9%), Ex-P (7.6 ± 2.7%) and Au-P (7.1 ± 1.5%) (Fig. 4c). De-P and Or-P together accounted for over 70%

Table 2

Location and bulk properties (salinity; SPM concentration; median grain size and DIP concentrations) along the salinity gradient in the Changjiang Estuary during June, 2011.

Sampling site	Latitude (°N)	Longitude (°E)	Salinity	SPM (mg L ⁻¹)	Median grain size (μm)	DIP (μmol L ⁻¹)
J1	120.98	31.79	0.16	40	7.62	2.19
J2	121.27	31.65	0.17	38	8.67	3.02
J3	121.77	31.24	0.58	107	6.64	2.40
J4	121.95	31.11	6	529	6.47	1.01
J5	122.03	31.08	10	545	6.46	0.88
J6	122.04	31.14	16	227	6.97	0.86
J7	122.18	31.04	21	188	9.26	0.53
J8	122.28	31.04	25	114	9.02	0.64

of TPP. Fe-P was the least abundant particulate P species, and only accounted for $2.1 \pm 1.2\%$ of the TPP.

3.4. Variations in speciation of P of size-fractionated suspended particles

In general, concentrations of Ex-P, Fe-P, Or-P, Au-P and Re-P in size-fractionated suspended particles decreased gradually with increasing particle size, while De-P exhibited an increase with increasing grain size (Fig. 5). De-P was the most abundant particulate P species in all size-fractionated suspended particles except at site #J4 (Table S1). In the clay fraction (<8 μm), concentrations of De-P and Or-P averaged in 8.92 ± 2.20 and 6.93 ± 1.92 μmol g⁻¹, respectively, followed by Re-P (4.21 ± 0.59 μmol g⁻¹), Au-P (1.92 ± 0.44 μmol g⁻¹), Ex-P (1.71 ± 0.38 μmol g⁻¹) and Fe-P (0.57 ± 0.33 μmol g⁻¹). In the sand fraction (>63 μm), De-P increased to 12.56 ± 1.49 μmol g⁻¹, while Re-P, Or-P and Fe-P decreased to 2.27 ± 0.80 μmol g⁻¹, 1.59 ± 0.61 μmol g⁻¹, and 0.37 ± 0.21 μmol g⁻¹, respectively. With the exception of De-P, concentrations of different P species in size-fractionated suspended particles were more similar with increasing grain size, and unlike bulk suspended particles, Or-P was no longer the second abundant P species in some size fractions. Ex-P varied little with grain size, and ranged from 1.23 ± 0.20 μmol g⁻¹ to 2.22 ± 1.39 μmol g⁻¹, which was close to its concentrations in bulk suspended particles (1.82 ± 0.63 μmol g⁻¹).

4. Discussion

4.1. Distribution and mixing behavior of P in dissolved and particulate phases

The range of DIP concentrations in the Changjiang LDE were extremely broad with values found between pristine to eutrophic estuaries. For example, the end-member river DIP concentrations

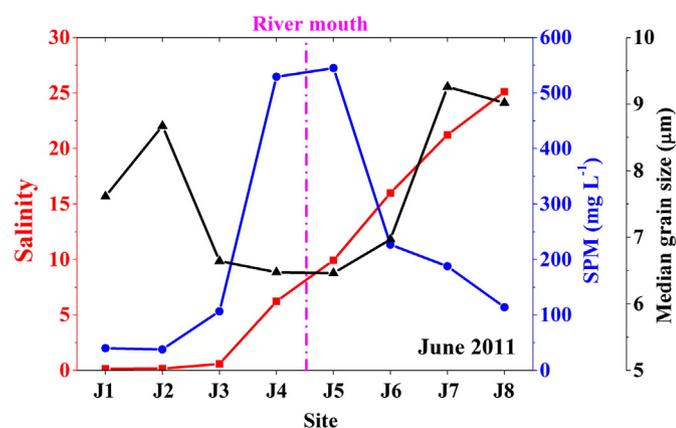


Fig. 2. Variations in salinity, median grain size and suspended particulate matter (SPM) concentrations along the salinity gradient in the Changjiang Estuary during June, 2011.

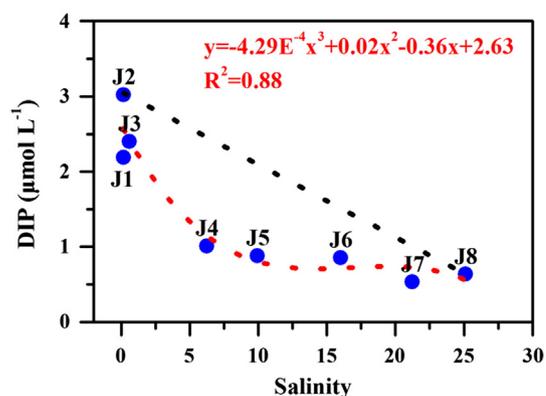


Fig. 3. Variations in DIP concentrations with salinity in the Changjiang Estuary during June, 2011.

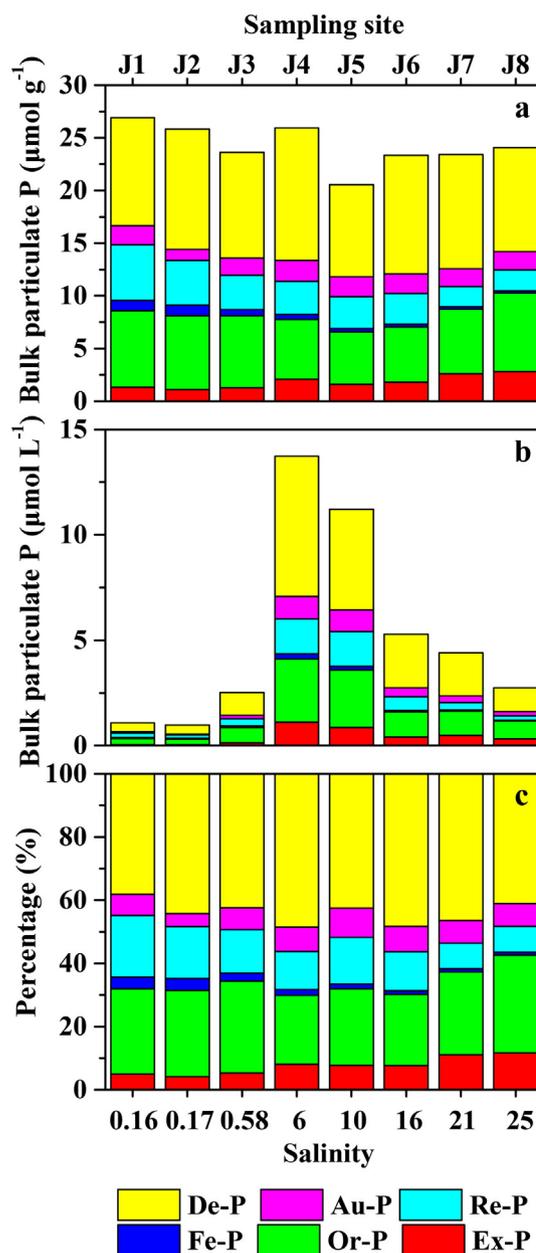


Fig. 4. Variations in abundance and percentages (c) of different particulate P species (in μmol g⁻¹ (a) and μmol L⁻¹ (b)) in bulk suspended particles with salinity in the Changjiang Estuary during June, 2011. Ex-P: exchangeable P; Or-P: organic P; Fe-P: Fe-bound P; Re-P: refractory P; Au-P: authigenic P; De-P: detrital P.

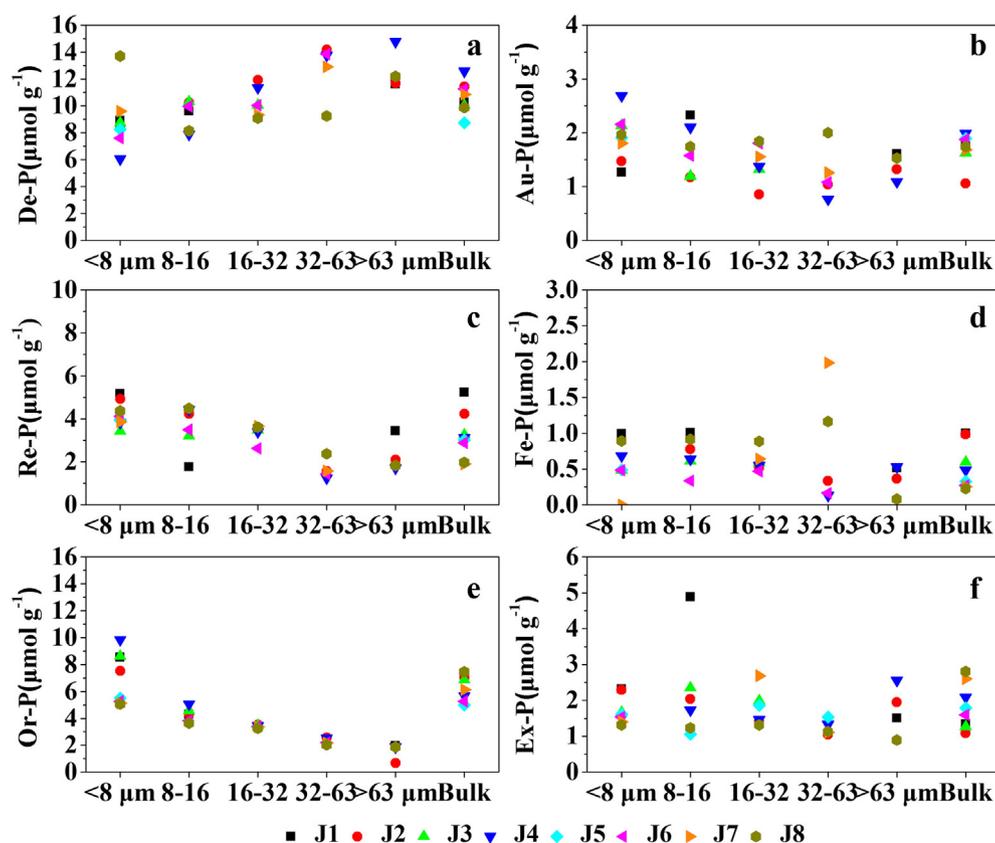


Fig. 5. Variations in abundance of different particulate P species in size-fractionated suspended particles by size fractions in the Changjiang Estuary during June, 2011.

found in the Changjiang LDE ($2.19 \mu\text{mol L}^{-1}$ (J1)) was generally higher than other pristine LDEs such as the Yukon River Basin ($\sim 0.053 \mu\text{mol L}^{-1}$) (Guo et al., 2004), Chena River ($\sim 0.15 \mu\text{mol L}^{-1}$) (Cai et al., 2008), Amazon shelf water ($\sim 0.7 \mu\text{mol L}^{-1}$) (DeMaster and Pope, 1996), and lower than those from eutrophic LDEs, such as the River Po ($\sim 2.9 \mu\text{mol L}^{-1}$) (Vignati et al., 2003) and lower Mississippi ($\sim 3.2 \mu\text{mol L}^{-1}$) (Sutula et al., 2004) (Fig. 6). This range in DIP was comparable to other eutrophic LDEs in China such as the Jiulong LDE ($\sim 2.1 \mu\text{mol L}^{-1}$) (Lin et al., 2013) and the Pearl LDE ($\sim 2.7 \mu\text{mol L}^{-1}$) (Dai et al., 2014). Furthermore, DIP concentrations in the Changjiang LDE have risen over two-fold since the 1960s ($\sim 0.5 \mu\text{mol L}^{-1}$) (Jiang

et al., 2010), further demonstrating the effects of recent economic development increasing nutrient inputs from the Changjiang drainage basins. While average TPP concentrations ($24.21 \pm 2.00 \mu\text{mol g}^{-1}$) in the Changjiang LDE were generally lower when compared to other LDEs around the world, such as the Chena LDE (average in $85.48 \mu\text{mol g}^{-1}$) (Cai et al., 2008), the Po LDE (average in $60.49 \mu\text{mol g}^{-1}$) (Vignati et al., 2003), as well as the global average of $38.71 \mu\text{mol g}^{-1}$ (Froelich, 1988), they were comparable to those of the lower Mississippi (Sutula et al., 2004) (Fig. 6).

These differences in TPP concentrations (in $\mu\text{mol g}^{-1}$) between the Changjiang LDE and other estuarine systems are likely in part controlled

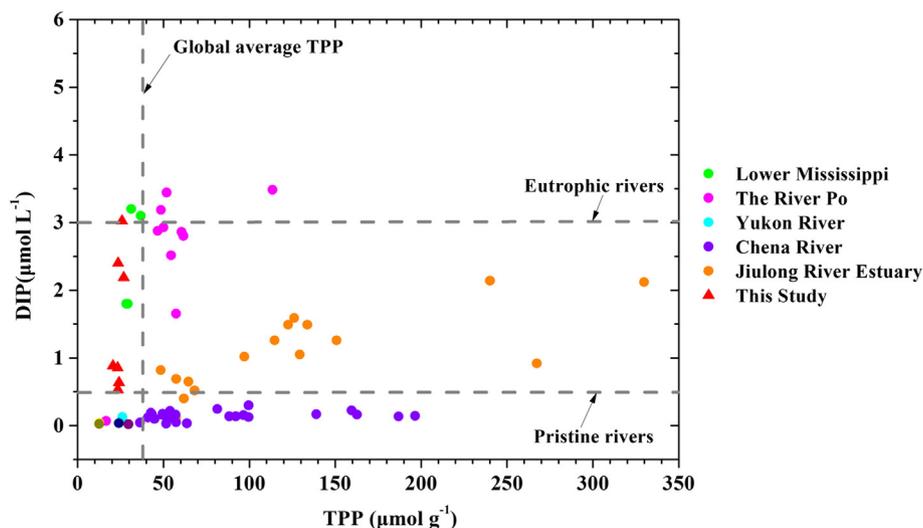


Fig. 6. Plots of TPP and DIP from the Changjiang Estuary and comparing with other rivers and estuaries around the world such as the Lower Mississippi (Sutula et al., 2004), River Po (Vignati et al., 2003), Yukon River (Guo et al., 2004), Chena River (Cai et al., 2008), and Jiulong River Estuary (Lin et al., 2013).

by differences in mineralogical composition and associated biomass of SPM (e.g., Froelich, 1988; Vignati et al., 2003; Sutula et al., 2004; Cai et al., 2008). Moreover, this variability of SPM content in the river could also influence the TPP concentrations (in $\mu\text{mol L}^{-1}$). For example, it is well known that the annual suspended sediment discharge of the Changjiang has decreased since 1950s because of the construction of dams in the upstream (Milliman and Farnsworth, 2011). This has become more serious after the construction of the Three Gorges Dam since part of the SPM and associated nutrients (Si and P) have been trapped within the dam reservoir (Zhang et al., 1999; Liu et al., 2003; Ran et al., 2013). The retention of nutrients by reservoirs and their potential effects on biogeochemistry and aquatic food webs in coastal environments have become a serious global issue in part due to stoichiometric shifts in macronutrients (Conley et al., 1993; Humborg et al., 2000, 2006; Ragueneau et al., 2009).

Most P species clearly showed non-conservative behavior in the Changjiang LDE, which is also common for other anthropogenically-altered LDE systems, such as the Mississippi River Delta and Loire Estuary (Meybeck et al., 1988; Shim et al., 2012). The slight increase of DIP concentration in the low salinity region ($S < 6$) from J1 to J2/J3 was likely caused by the local inputs of high-concentration DIP from the municipal sewage of Shanghai and the Huangpu River ($0.95\text{--}4.85 \mu\text{mol L}^{-1}$) (Zhang et al., 2007). Nevertheless, there was a considerable decline in DIP concentration across the salinity gradient (from $3.02\text{--}0.64 \mu\text{mol L}^{-1}$) which indicated the removal of P during early mixing stages in the estuary (Fig. 3), which further supported similar trends of dissolved organic P removal shown in prior work. For example, DOP decreased from $\sim 1.0 \mu\text{mol L}^{-1}$ in the freshwater region to $\sim 0.28 \mu\text{mol L}^{-1}$ in the outer estuary (He et al., 2009). The behavior of DIP and DOP in the Changjiang LDE was again similar to the Mississippi River LDE (e.g., Shim et al., 2012), but distinctly different from LDEs less impacted by eutrophication, such as the Amazon Estuary. In fact the Amazon appears to have a very narrow dissolved phosphate range due to an intensive “P-buffering” mechanism (Fox et al., 1986). Thus, in the context of Amazon, the buffering of dissolved P concentrations by particulate P during early estuarine mixing may have been reduced in the Changjiang LDE due to increasing DIP inputs and decreasing TPP inputs. This reduction in buffering capacity of particulate P is also likely to alter the mixing behavior and transformation of P species in the Changjiang LDE, as suggested by previous work (Shen et al., 2008). Other estuarine systems such as the Scheldt Estuary (Van der Zee et al., 2007) and Jiulong River Estuary (Lin et al., 2013), have further documented effects of such human drivers on the biogeochemical behavior of P in estuaries (Nixon, 2003; Guo et al., 2004; Grosse et al., 2010; Dai et al., 2014).

Recent work has shown that particulate P forms and their spatial distribution along salinity gradients were mainly controlled by particle sources, grain size composition, and their behavior in the estuary (He et al., 2009; Yu et al., 2012; Lin et al., 2013). More specifically, local inputs of water/sediment (e.g., settlement of suspended particles and resuspension of bed sediments) can modify the sample composition, particularly in the turbidity maxima zone where the most of the suspended particles are not from the upper stream but from local resuspension induced by the tidal action. In the Changjiang Estuary, concentrations of TPP ($\mu\text{mol g}^{-1}$) first decreased and then increased with the relatively low values near the river mouth (Fig. 4a). Prior work has also shown that the samples collected at different locations did not have the same origin/composition of TPP for a non-Lagrangian sampling (Schroeder et al., 2012), but did reflect the influence of particles from different sources. In the low-salinity region, suspended particles are mainly derived from the Changjiang River that had high concentrations of TPP ($\sim 31 \mu\text{mol g}^{-1}$) (Liu et al., 2003; Yu et al., 2012). In the mid-salinity region near the river mouth, lower TPP concentrations ($\mu\text{mol g}^{-1}$) were likely attributed to the re-suspension of sediments and removal of fine-grained suspended particles in the TMZ area. Sediment re-suspension has been shown to contribute significantly (55.7%) to the turbidity maximum in the Changjiang LDE (Li and

Zhang, 1998; Shen et al., 2008). In fact, the sediments in this area were characterized as having lower TPP concentrations ($17.0 \mu\text{mol g}^{-1}$) than suspended particles (Meng et al., 2014a). In the region of high salinity, where light was no longer a limiting factor for primary production, phytoplankton contributed to SPM with a large fraction of “fresh” living P being represented in the TPP of this area (Yu et al., 2012). The greater importance of phytoplankton in the TPP has been further supported by the increased $\delta^{13}\text{C}$ and decreased C/N ratios from the river mouth to this area (Pan et al., in press).

The TMZ in the medium-low salinity area of the estuary (stations #J4 and #J5 with salinities of 6–10, Fig. 1), showed the greatest change in the concentration of the particulate P species ($\mu\text{mol L}^{-1}$) (Fig. 4), which was largely due to changing SPM concentrations. The flocculation and deflocculation of fine-grained suspended particles greatly influenced the SPM concentrations in the Changjiang LDE and thus had a major role in controlling the addition and removal behavior of TPP ($\mu\text{mol L}^{-1}$) (Prastka and Malcolm, 1994). For example, TPP concentrations in $\mu\text{mol L}^{-1}$ were positively correlated with SPM changes ($R^2 = 0.97$, $p < 0.01$) in the estuary indicating that SPM concentration strongly influenced TPP (Figs. 2, 4b). In the TMZ, near the river mouth, the dramatic change in ionic strength of water (e.g., Patra et al., 2012) likely contributed to altering the surface charge of suspended particles as well the hydrophilic and/or hydrophobic properties – further contributing to the flocculation formation and sedimentation (Li, 1998; Li et al., 2001). This was also supported by the relatively smaller MGS (Fig. 2), indicative of the accumulation of fine suspended particles in this region. SPM concentrations decreased with increasing MGS across an increasing salinity gradient, indicating that the flocculation of fine-grained suspended particles that settled in the TMZ were not likely transported further in the system. This high sedimentation of flocs, not only scavenged fine-grain suspended particles, but also removed the associated biogenic components (e.g., TPP in $\mu\text{mol g}^{-1}$), forming an effective “estuarine filter” (Tian et al., 1991).

4.2. Transformation of dissolved and particulate P

The behavior of different P phases along the Changjiang LDE salinity gradient likely indicated an intensive transformation between dissolved P and particulate P species (Figs. 3, 4b). First of all, the removal of dissolved P during early mixing in the estuary was likely due to a variety of processes such as biological uptake and adsorption onto particles (Huang and Zhang, 2010, 2011; Lin et al., 2013; Meng et al., 2014b). The adsorption capacity of P by particles can be strengthened at low salinity, compared with freshwater and high salinity regions (Liu et al., 2002; Meng et al., 2014b). At low salinities (< 6), the ionic strength increased with increasing salinity, resulting in the aggregation of the particles. Dissolved P may be capsulated and protected in newly formed aggregates, allowing for enhanced adsorption and consequently a sharp decrease of DIP/DOP concentrations (Liu et al., 2002; Meng et al., 2014b). With further increases in salinity, enough anions (e.g. Cl^- , SO_4^{2-} , HCO_3^- , OH^- and Br^-) would compete for the adsorption sites on particle surfaces, thereby decreasing adsorption, and enhancing the release of sorbed phosphate from particle surfaces (Wang et al., 2006; Millero et al., 2001; Zhang and Huang, 2011), which would explain for the gradual change of DIP in the high salinity region of the Changjiang LDE.

The release of P from suspended particles is governed by many other factors beyond adsorption, such as the level of DIP in water and EPC_0 (zero equilibrium phosphate concentration) of particles (Zhang and Huang, 2007, 2011), particularly in the context of speciation of particulate P (Ruttenberg, 1992; Coelho et al., 2004). The speciation of particulate P, as determined by sequential extraction, has been shown to provide more detailed information of sources of particulate P and its relationship with dissolved P in aquatic environments (Lin et al., 2013). For example, De-P is stable and experiences little to no decomposition in coastal systems, and thus has the potential to be a good tracer

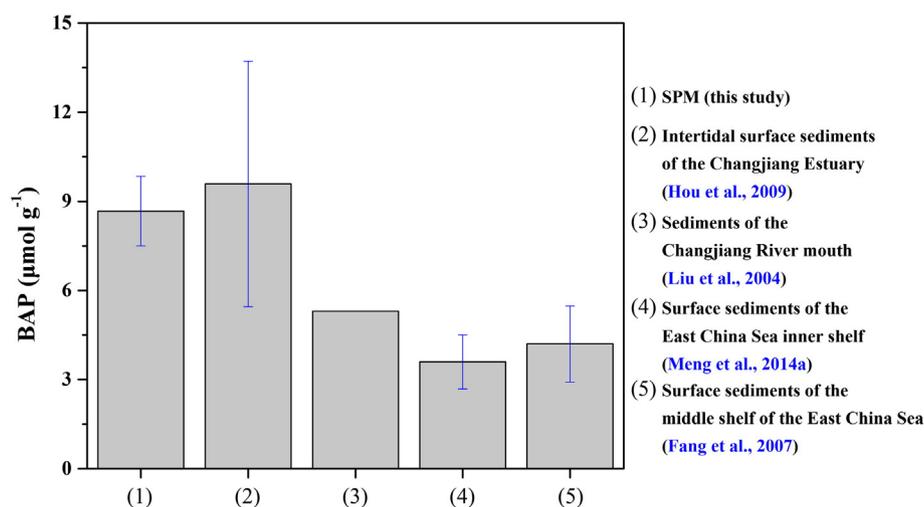


Fig. 7. Bioavailable P of SPM in the Changjiang Estuary and comparing with those of the intertidal surface sediments of the Changjiang Estuary (Hou et al., 2009), the sediments of the Changjiang River mouth (Rao and Berner, 1997), the surface sediments of the East China Sea inner shelf (Meng et al., 2014a), and the surface sediments of the middle shelf of the East China Sea (Fang et al., 2007).

for terrestrial inputs (Ruttenberg, 1992; He et al., 2009; Yu et al., 2012). On the other hand, Or-P has been used to demonstrate the influence of biological production and/or activities on natural waters (Zhang et al., 2004; Lin et al., 2013), in contrast to Ex-P which was formed by direct adsorption of phosphate and/or DOP on to sediments and revealed a direct correlation with dissolved P (Zhang and Chi, 2002; Zhang et al., 2004; Zhang and Huang, 2007). The dominance of De-P in TPP in the Changjiang LDE is similar to that in the Yellow River Estuary (Liu et al., 2004) and the Mackenzie River Delta (Zhang et al., 2010), but totally different from that in the Amazon Estuary, where De-P accounted for only about 6% of TP (Berner and Rao, 1994). One possible explanation for the high De-P fractions in the Changjiang LDE is that the eroded soils in the Changjiang upstream basins, which are the primary sources for particles in the river, are characterized by high De-P but low reactive P contents (He et al., 2009; Meng et al., 2014a). This also explains the low concentrations of Fe-P in this region, which was also mainly controlled by terrestrial sources. In contrast, rivers like the Amazon, mainly flowing through tropical rain forests, tropical grasslands and alpine plant regions (with fertile soils), have a more limited De-P contribution (Berner and Rao, 1994; Liu et al., 2006). As for Or-P, both terrestrial inputs and autochthonous phytoplankton production control its concentrations.

In the oligohaline region, where the SPM concentrations are relatively lower than the TMZ, light becomes less limiting and with sufficient nutrients from the Changjiang LDE, phytoplankton growth is enhanced, which should result in the consumption of DIP and the generation of Or-P. In addition, DIP may be adsorbed on to particle surfaces forming Ex-P or co-precipitated with Fe-oxyhydroxides forming easily reducible or reactive Fe-P (Ruttenberg, 1992; Ruttenberg and Berner, 1993; Monbet et al., 2007). As shown in Fig. 4b, an increase in these P forms (Ex-P, Or-P

and Fe-P) was observed. Interestingly, the total increase of Ex-P, Or-P and Fe-P between station J2 and J3 ($0.57 \mu\text{mol L}^{-1}$) could be balanced out by the decline in DIP ($0.62 \mu\text{mol L}^{-1}$). From J3 to J4, SPM concentrations sharply increased, light became the limiting factor for phytoplankton growth, and thus biological uptake was not likely the main reason for the observed decrease in DIP (from 2.40 to $1.01 \mu\text{mol L}^{-1}$). As mentioned previously, the adsorption capacity of P by particles could be strengthened in the TMZ, the total increase of Ex-P and Fe-P between stations J3 and J4 ($1.17 \mu\text{mol L}^{-1}$) may account for the decrease in DIP. For other P speciation, the flocculation of fine suspended particles in the TMZ seemed to dominate the sharp increase (in $\mu\text{mol L}^{-1}$) (Li, 1998; Li et al., 2001). In middle and higher salinity areas (from J4 to J8), the decrease in DIP concentrations was no longer accompanied by an increase in the concentrations of any particulate P speciation. Thus, the general decrease in both DIP and particulate P concentrations, as observed in other estuaries (e.g., Jiulong River Estuary), was mainly controlled by increasing salinity and physical dilution (Lin et al., 2013).

4.3. Evaluation of bioavailable P concentrations and BAP fluxes associated with particle grain size

P has been shown to be a limiting nutrient for phytoplankton growth in the Changjiang LDE (Liu et al., 2003). Therefore, any increase in the release of P from SPM into the water column could have a significant impact on phytoplankton production. Ex-P, Or-P and Fe-P have been recognized as potential BAP, representing the upper limit of P that can be released into seawater and available for organisms (Andrieux-Loyer and Aminot, 1997; Hou et al., 2009). BAP concentrations were 6.90 – $10.49 \mu\text{mol g}^{-1}$ and the average contribution of BAP to TPP was 35.8% in the Changjiang LDE. Or-P was the main form of BAP in this study area and thus BAP also decreased inside the river mouth, followed by an increase along the salinity gradient outside the river mouth. Compared with BAP in sediments from the Changjiang LDE and the ECS shelf, BAP in SPM was more abundant with a higher potential to be released into the water column (Fig. 7) (Rao and Berner, 1997; Fang et al., 2007; Hou et al., 2009; Meng et al., 2014a). Therefore, based on the average BAP concentrations in bulk SPM ($8.67 \mu\text{mol g}^{-1}$) of this study and in bed sediments ($3.60 \mu\text{mol g}^{-1}$) of this area in previous study (Meng et al., 2014a), about 58.5% of BAP on particles was estimated to be lost, via consumption, sedimentation, and/or transport from the estuary to the coast. This estimate was much higher than that for the Amazon LDE where only ~16% of BAP was lost, mainly caused by a decrease

Table 3

Percentages of BAP in size-fractionated particles collected from the Changjiang Estuary during June, 2011. – : not available.

Sampling site	<8 μm	8–16 μm	16–32 μm	32–63 μm	>63 μm
J1	43.6%	42.6%	–	–	19.3%
J2	55.2%	31.3%	25.1%	19.0%	16.5%
J3	42.9%	33.8%	28.9%	–	–
J4	49.0%	34.0%	25.3%	20.1%	22.0%
J5	34.8%	–	–	–	–
J6	34.7%	25.8%	28.4%	19.2%	–
J7	29.3%	–	31.5%	25.0%	–
J8	26.6%	28.7%	27.3%	24.1%	15.5%

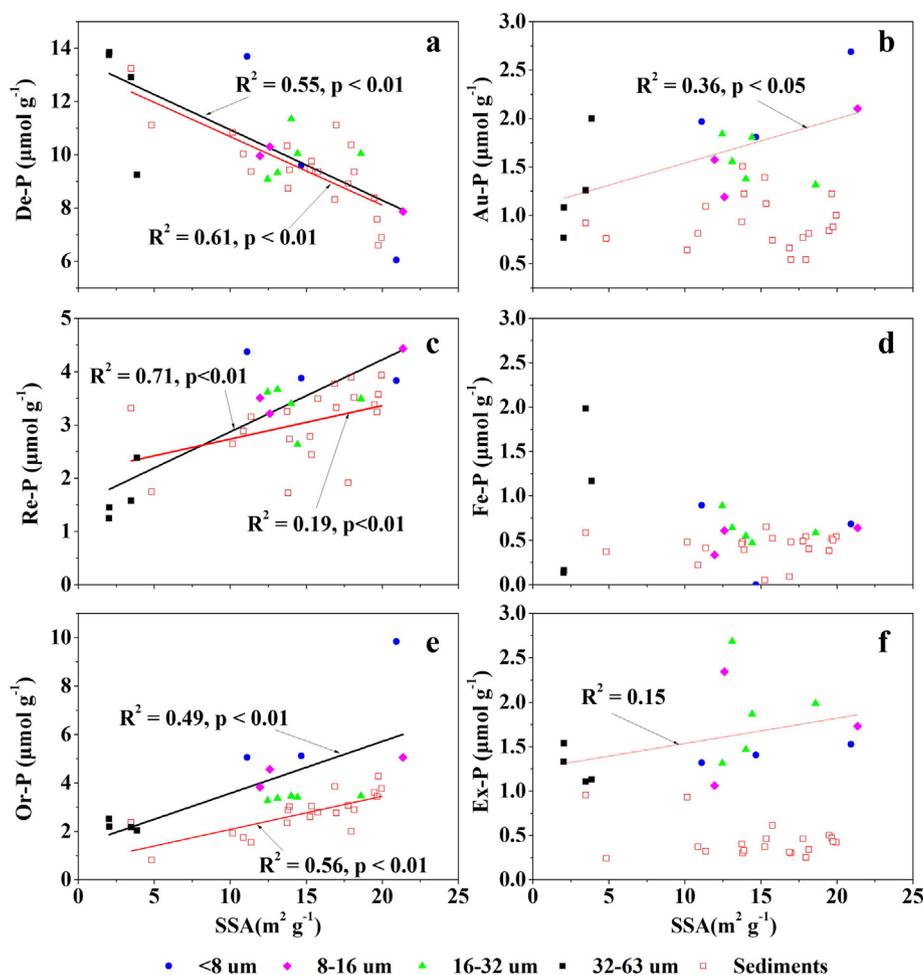


Fig. 8. Relationships between De-P (a), Au-P (b), Re-P (c), Fe-P (d), Or-P (e) and Ex-P (f) with SSA in size-fractionated suspended particles in this study and in bulk bed sediments collected from the Changjiang Estuary (Meng et al., 2014a).

in Or-P after deposition of suspended sediment on the estuarine portions of the shelf (Bernier and Rao, 1994).

The flux of “truly” suspended (BAP_e) (see more below), estimated to be 0.21×10^4 tP yr⁻¹ (based on the BAP concentrations in the clay fraction and the mass fraction of clay, about 24% according to the unpublished data from another cruise), accounted for 29% of bulk BAP, indicating that fine-grained suspended particles played an important role in the BAP transport in the Changjiang LDE. The percentages of BAP in TPP decreased with increasing grain size (Table 3). Fine fractions of abundant BAP could be delivered longer distances, potentially reaching the open seas while coarse fractions rich in De-P likely settled near the river mouth (Alber, 2000). The hydrodynamic sorting of particles has been shown to play a major role in transporting material and in controlling spatial variability in sedimentation rates (e.g. Bianchi et al., 2007; Wakeham et al., 2009). For example, settling velocities for suspended particles with grain sizes <8 μm, 8–16 μm, 16–32 μm, 32–63 μm and >63 μm were <0.004 cm s⁻¹, 0.004–0.016 cm s⁻¹, 0.016–0.064 cm s⁻¹, 0.064–0.256 cm s⁻¹ and >0.256 cm s⁻¹, respectively (He et al., 2009). According to Alber (2000), the cut-off velocity for the truly suspended fraction was 0.006 cm s⁻¹. We used this <8 μm particle fraction as the cut-off for the “truly suspended” particles, since the BAP in the “truly” suspended particles were most likely to be transported to the coastal ocean. As mentioned previously, this portion of BAP was defined as BAP_e. Thus, based on the BAP concentrations in bulk suspended particles, river discharge and SPM concentrations at salinity of around 0 (J1), the flux of BAP from the Changjiang LDE was 0.72×10^4 tP yr⁻¹. This suggests that fine suspended particles, which are transported further offshore, can have a significant impact on

offshore primary production, particularly if the LDE has experienced eutrophication issues.

4.4. Preservation of P associated with particle grain size and SSA

Relationships between P forms and SSA of particles further revealed the sources and preservation of P in the Changjiang Estuary. Negative relationship was found between De-P and SSA of size-fractionated particles (R² = 0.55, p < 0.01) (Fig. 8a), which can be attributed to the fact that De-P is mainly composed of primary minerals (Dai et al., 2007). Those minerals are the major components of coarse silt, sand and other particles that have large sizes and low SSA. Fine-grained particles usually have relatively larger SSA, which can increase the sorption of organic matters, metals and other materials (e.g., Turner et al., 1994; Zhang et al., 2012; Tang et al., 2014), and thus Or-P, Re-P and other P forms (with the exception of Fe-P) showed positive correlations with SSA (Fig. 8). The variations of De-P, Re-P and Fe-P vs. SSA in particles and sediments showed no significant difference (p = 0.25, 0.27 and 0.02 for De-P, Re-P and Fe-P, respectively), while other P forms such as Or-P, Au-P and Ex-P showed a clear decrease from particles to sediments (p < 0.001 for all three P forms) (Fig. 8). These variations are further illustrated by the plots of P/SSA loadings vs. salinity (Fig. 9). The physical meaning of P/SSA loading is defined as the binding strategy of P with particles/sediments through either adsorption or aggregation (Meng et al., 2014a), similar to that of TOC/SSA loading which has generally been used to characterize the relationship between organic matter (OM) and particle grain size (in terms of SSA), and thus for evaluating OM/mineral associations and OM preservation, albeit by

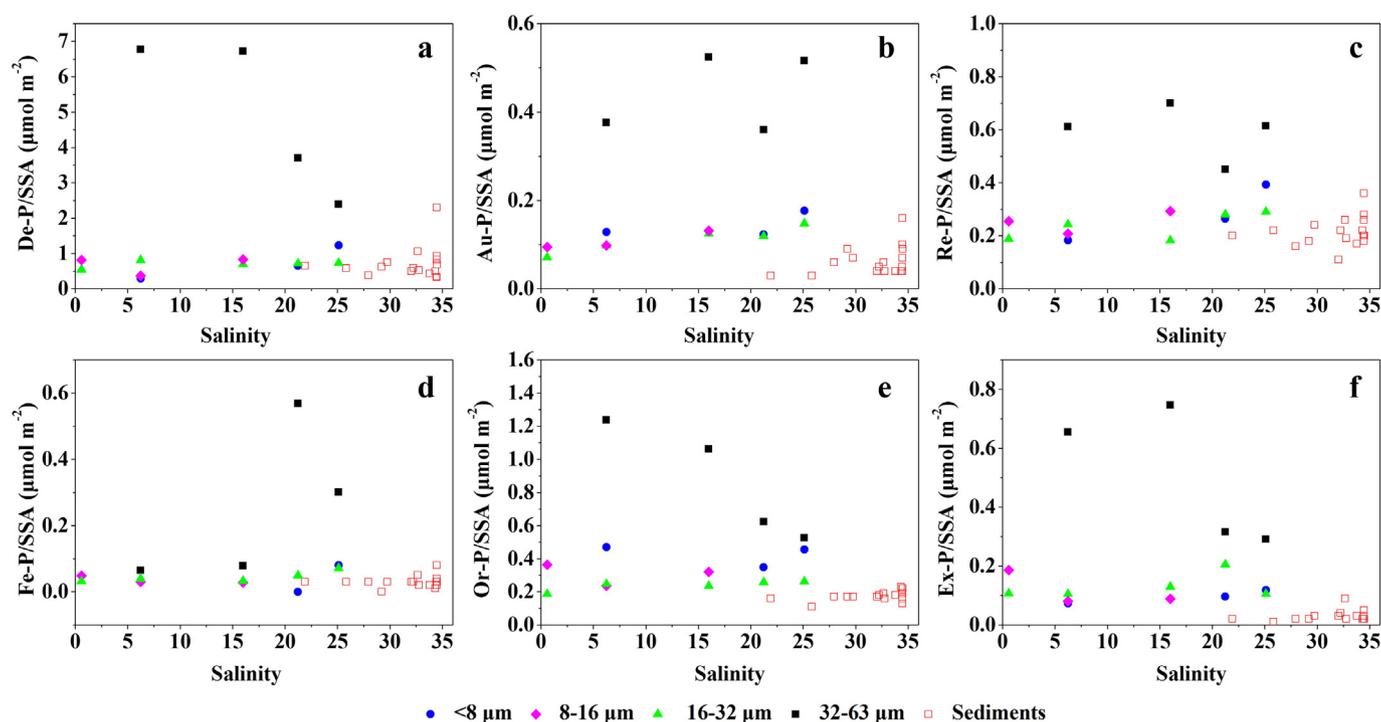


Fig. 9. Variations of De-P/SSA (a), Au-P/SSA (b), Re-P/SSA (c), Fe-P/SSA (d), Or-P/SSA (e) and Ex-P/SSA (f) vs. salinity in size-fractionated suspended particles in this study and in bulk bed sediments collected from the Changjiang Estuary (Meng et al., 2014a). The salinity for sediments is derived from CTD (conductivity, temperature, and depth profiler) determination of bottom water at each sampling site (unpublished data).

inference (Wakeham et al., 2009; Blair and Aller, 2012; Yao et al., 2014b). Due to the complexity of the nature of the mineral surface and the chemical structure of associated OM, the mechanistic controls on the preservation of OM remain largely unclear. Nevertheless, P/SSA loading has been used to describe the associations between P species and mineral grains and the preservation status of P in surface sediments of the Changjiang Estuary (Meng et al., 2014a). High P/SSA loadings were mainly found in coarse-grained suspended particles (32–63 μm), while in fine-grained suspended particles P/SSA changed very little (Fig. 9). The fine-grained suspended particles with higher SSA, have been shown to promote rapid equilibrium with the P species on particles in the Changjiang, but were less favorable in preserving P in sediments compared to coarse-grained particles (Meng et al., 2014a). Lower P/SSA loadings in fine suspended particles compared with coarse particles indicated losses of P on these particles, suggesting more efficient transformation and remobilization of different forms of P on fine particles in the Changjiang LDE.

The differences of P/SSA between the suspended particles and bed sediments further indicated that dynamic loss of labile P occurs as suspended particles settled down and/or in estuarine and coastal mobile muds. In the Changjiang Estuary and Zhe-Min coastal mud areas, the surface bed sediments are composed mainly by fine-grained particles, and the contribution from coarse particles is very limited (He et al., 2009; Yao et al., 2014b), indicating that the bed sediments in this region are largely derived from the settlement of fine suspended particles. According to the results of this study and prior work by Meng et al. (2014a), De-P/SSA loadings in fine suspended particles ($0.70 \pm 0.25 \mu\text{mol m}^{-2}$) were basically the same compared with those in bed sediments ($0.70 \pm 0.45 \mu\text{mol m}^{-2}$) ($p = 0.55$) (Fig. 9a). As De-P is inert and hard to regenerate, no release of De-P was expected as these suspended particles settle in the water column (Vink et al., 1997; Coelho et al., 2004). Au-P has very slow formation kinetics and belongs to the category of “Immobile P (Imm-P)” (Vink et al., 1997; Coelho et al., 2004). Nevertheless, Au-P/SSA loadings showed a decrease from suspended particles ($0.12 \pm 0.03 \mu\text{mol m}^{-2}$ for fine particles) to bed

sediments ($0.06 \pm 0.03 \mu\text{mol m}^{-2}$) ($p < 0.01$) (Fig. 9b), possibly because of decomposition of some biogenic apatite compositions (Van der Zee et al., 2002). Re-P is also categorized as an Imm-P (Lopez, 2004; Lukkari et al., 2009). There is also no significant differences in Re-P/SSA loadings between the fine particles and bed sediments ($p = 0.88$), although a slight decrease was observed (from $0.25 \pm 0.06 \mu\text{mol m}^{-2}$ to $0.21 \pm 0.05 \mu\text{mol m}^{-2}$) (Fig. 9c), which may be attributed to the presence of a part of low degradable organic P compounds in this phase (Lukkari et al., 2009). Similar with De-P/SSA and Re-P/SSA, no significant difference in Fe-P/SSA loadings between the SPM ($0.04 \pm 0.02 \mu\text{mol m}^{-2}$ for fine particles) and the bed sediments ($0.03 \pm 0.02 \mu\text{mol m}^{-2}$) was observed ($p = 0.82$) (Fig. 9d), consistent with the ANOVA results of De-P, Re-P and Fe-P between suspended particles and bed sediments (Fig. 8). As mentioned before, the low Fe-P concentrations in the Changjiang LDE resulted in the relatively low Fe-P/SSA loading in both suspended particles and bed sediments. This further suggests that there was no obvious addition or loss of Fe-P as suspended particles settle down in the water column. It seemed that the formation of Fe-P was limited to regions inside the estuary-proper of the Changjiang LDE, as observed in other near-shore plume regions on the coast (e.g., Chen et al., 2007; Hou et al., 2009; Zhang et al., 2012).

In contrast, Ex-P/SSA and Or-P/SSA loadings were both lower in bed sediments from the Changjiang Estuary and Zhe-Min coastal mud areas ($0.04 \pm 0.02 \mu\text{mol m}^{-2}$ and $0.17 \pm 0.03 \mu\text{mol m}^{-2}$, respectively) than in SPM ($0.12 \pm 0.04 \mu\text{mol m}^{-2}$ and $0.31 \pm 0.09 \mu\text{mol m}^{-2}$ for fine particles, respectively), respectively ($p < 0.01$) (Meng et al., 2014a) (Fig. 9e and f). It seemed that some portion of Ex-P and Or-P carried by suspended particles were released into the water column during particle settlement. Suboxic diagenetic conditions, caused by frequent physical reworking of sediments in the Changjiang LDE and Zhe-Min coastal mud areas may have also played a key role in P preservation, particularly for Or-P (Meng et al., 2014a; Yao et al., 2014b). This supports the idea that remineralization of organic matter is effectively enhanced in the mobile muds, causing lower Or-P/SSA loadings in the bed sediments than in SPM. Finally, based on the average BAP/SSA

values in size-fractionated SPM ($0.83 \mu\text{mol m}^{-2}$) found in this study and the bed sediments in this region ($0.28 \mu\text{mol m}^{-2}$) (Meng et al., 2014a), the loss of BAP per SSA during the sedimentation of SPM was estimated to be $0.55 \mu\text{mol m}^{-2}$, which accounted for 65.9% of the average BAP/SSA in SPM. Interestingly, this is consistent with the aforementioned estimate of 58.5% loss of BAP on bulk SPM from the Changjiang LDE.

5. Conclusions

The overall variation of DIP across the salinity gradient showed a strong trend of DIP removal. TPP contents ($\mu\text{mol L}^{-1}$) varied significantly with increasing salinity in medium-low salinity region, indicating intensive transformation between dissolved P and particulate P species, especially for Ex-P, Or-P and Fe-P, whereas TPP contents in $\mu\text{mol g}^{-1}$ were lowest in the medium salinity region near the river mouth, possibly because of re-suspension of low-TPP sediments and removal of fine-grained suspended particles in the TMZ area. Overall, the particulate P sources and grain size composition of suspended particles and their mixing behavior largely controlled the speciation and distribution of P in the Changjiang LDE. Clay fraction ($<8 \mu\text{m}$), the truly suspended particles accounted for 29% of the bulk BAP flux, indicating that the fine-grained suspended particles played an important role in the BAP transport. P/SSA loadings were very low in fine suspended particles, suggesting low preservation of P in these particles. De-P and Fe-P in fine particles and bed sediments of the Changjiang LDE were basically maintained at the same level, whereas Au-P and Re-P slightly decreased when moving from SPM to bed sediments. Ex-P and Or-P were lower in bed sediments than in SPM, suggesting a dynamic loss of labile P as the suspended particle settled down and/or active remineralization of P in the estuarine and coastal mobile muds.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 2011CB403602, 41221004, and 41176063) and the 111 Project (B13030). We thank the crews of the R/V *Runjiang* 1 for sampling assistance. Xiaojing Wang is also appreciated for analytical supports. We thank the editor and two anonymous reviewers for their constructive comments. This is MCTL Contribution No. 52.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2014.09.016>.

References

Alber, M., 2000. Settleable and non-settleable suspended sediments in the Ogeechee River estuary, Georgia, USA. *Estuar. Coast. Shelf Sci.* 50 (6), 805–816.

Andrieux-Loyer, F., Aminot, A., 1997. A two-year survey of phosphorus speciation in the sediments of the Bay of Seine (France). *Cont. Shelf Res.* 17 (10), 1229–1245.

Andrieux-Loyer, F., Aminot, A., 2001. Phosphorus forms related to sediment grain size and geochemical characteristics in French coastal areas. *Estuar. Coast. Shelf Sci.* 52 (5), 617–629.

Berner, R.A., Rao, J., 1994. Phosphorus in sediments of the Amazon River and estuary: implications for the global flux of phosphorus to the sea. *Geochim. Cosmochim. Acta* 58, 2333–2339.

Bianchi, T.S., Allison, M.A., 2009. Large-river delta-front estuaries as natural “recorders” of global environmental change. *PNAS* 106 (20), 8085–8092.

Bianchi, T.S., Galler, J.J., Allison, M.A., 2007. Hydrodynamic sorting and transport of terrestrially derived organic carbon in sediments of the Mississippi and Atchafalaya rivers. *Estuar. Coast. Shelf Sci.* 73 (1–2), 211–222.

Bianchi, T.S., Allison, M.A., Cai, W.J., 2014. *Biogeochemical Dynamics at Major River-Coastal Interfaces*. Cambridge University Press, pp. 118–137.

Billen, G., Garnier, J., Ficht, A., Cun, C., 2001. Modeling the response of water quality in the Seine river estuary to human activity in its watershed over the last 50 years. *Estuaries* 24 (6), 977–993.

Blair, N.E., Aller, R.C., 2012. The fate of terrestrial organic carbon in the marine environment. *Annu. Rev. Mar. Sci.* 4, 401–423.

Boesch, D.F., Boynton, W.R., Crowder, L.B., Diaz, R.J., Howarth, R.W., Mee, L.D., Nixon, S.W., Rabalais, N.N., Rosenberg, R., Sanders, J.G., Scavia, D., Turner, R.E., 2009. Nutrient enrichment drives Gulf of Mexico hypoxia. *Eos* 90 (14), 117–118.

Cai, Y.H., Guo, L.D., Douglas, T.A., Whitledge, T.E., 2008. Seasonal variations in nutrient concentrations and speciation in the Chena River, Alaska. *J. Geophys. Res.* 113 (G3), G030035.

Cai, Y.H., Guo, L.D., Wang, X.R., Mojzic, A.K., Redalje, D.G., 2012. The source and distribution of dissolved and particulate organic matter in the Bay of St. Louis, northern Gulf of Mexico. *Estuar. Coast. Shelf Sci.* 96 (1), 96–104.

Chen, C.C., Gong, G.C., Shiah, F.K., 2007. Hypoxia in the East China Sea: one of the largest coastal low-oxygen areas in the world. *Mar. Environ. Res.* 64, 399–408.

Coelho, J.P., Flindt, M.R., Jensen, H.S., Lillebø, A.I., Pardal, M.A., 2004. Phosphorus speciation and availability in intertidal sediments of a temperate estuary: relation to eutrophication and annual P-fluxes. *Estuar. Coast. Shelf Sci.* 61 (4), 583–590.

Conley, D.J., Schelske, C.L., Stoermer, E.F., 1993. Modification of the biogeochemical cycle of silica with eutrophication. *Mar. Ecol. Prog. Ser.* 101, 179–192.

Dai, J.C., Song, J.M., Li, X.G., Yuan, H.M., Zheng, G.X., Li, N., 2007. Sediment record of phosphorus and the primary study of its bioavailability in Jiaozhou Bay sediments. *Environ. Sci.* 28 (5), 9292–9361 (in Chinese with English abstract).

Dai, M., Gan, J., Han, A., Kung, K.S., Yin, Z., 2014. Physical dynamics and biogeochemistry of the Pearl River plume. In: Bianchi, T.S., Allison, M.A., Cai, W.J. (Eds.), *Biogeochemical Dynamics at Major River-Coastal Interfaces*. Cambridge University Press, pp. 118–137.

DeMaster, D.J., Pope, R., 1996. Nutrient dynamics in amazon shelf waters: results from AMASSED. *Cont. Shelf Res.* 16 (3), 263–289.

Fang, T.H., Chen, J.L., Huh, C.A., 2007. Sedimentary phosphorus species and sedimentation flux in the East China Sea. *Cont. Shelf Res.* 27 (10–11), 1465–1476.

Fox, L.E., Sager, S.L., Wofsy, S.C., 1986. The chemical control of soluble phosphorus in the Amazon estuary. *Geochim. Cosmochim. Acta* 50, 783–794.

Froelich, P.N., 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. *Limnol. Oceanogr.* 33 (4), 649–668.

Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. *Methods of Seawater Analysis*. Wiley-VCH Verlag, Weinheim.

Grosse, J., Bombar, D., Doan, H.N., Nguyen, L.N., Voss, M., 2010. The Mekong River plume fuels nitrogen fixation and determines phytoplankton species distribution in the South China Sea during low and high discharge season. *Limnol. Oceanogr.* 55 (4), 1668–1680.

Guo, L.D., Zhang, J.Z., Guéguen, C., 2004. Speciation and fluxes of nutrients (N, P, Si) from the upper Yukon River. *Glob. Biogeochem. Cycles* 18 (1), GB1038.

He, H.J., Chen, H.T., Yao, Q.Z., Qin, Y.W., Mi, T.Z., Yu, Z.G., 2009. Behavior of different phosphorus species in suspended particulate matter in the Changjiang estuary. *Chin. J. Oceanol. Limnol.* 27 (4), 859–868.

Hou, L.J., Liu, M., Yang, Y., Ou, D.N., Lin, X., Chen, H., Xu, S.Y., 2009. Phosphorus speciation and availability in intertidal sediments of the Yangtze Estuary, China. *Appl. Geochem.* 24 (1), 120–128.

Howarth, R.W., Jensen, H.S., Marino, R., Postma, H., 1995. Transport to and processing of P in near-shore and oceanic waters. In: Tiessen, H. (Ed.), *Phosphorus in the Global Environment: Transfers, Cycles and Management*. Wiley, West Sussex, pp. 323–346.

Hu, L.M., Guo, Z.G., Feng, J.L., Yang, Z.S., Fang, M., 2009. Distributions and sources of bulk organic matter and aliphatic hydrocarbons in surface sediments of the Bohai Sea, China. *Mar. Chem.* 113 (3–4), 197–211.

Huang, X.L., Zhang, J.Z., 2010. Spatial variation in sediment–water exchange of phosphorus in Florida Bay: AMP as a model organic compound. *Environ. Sci. Technol.* 44 (20), 7790–7795.

Huang, X.L., Zhang, J.Z., 2011. Phosphorus sorption on marine carbonate sediment: phosphonate as model organic compounds. *Chemosphere* 85 (8), 1227–1232.

Humborg, C., Conley, D.J., Rahm, L., Wulff, F., Cociasu, A., Ittekkot, V., 2000. Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *Ambio* 29 (1), 45–50.

Humborg, C., Pastuszak, M., Aigars, J., Siegmund, H., Mörtz, C.M., Ittekkot, V., 2006. Decreased silica land–sea fluxes through damming in the Baltic Sea catchment – significance of particle trapping and hydrological alterations. *Biogeochemistry* 77 (2), 265–281.

Jensen, H.S., Bendixen, T., Andersen, F.O., 2006. Transformation of particle-bound phosphorus at the land–sea interface in a Danish estuary. The Interactions Between Sediments and Water. Springer Netherlands Press, pp. 183–191.

Jiang, T., Yu, Z.M., Song, X.X., Cao, X.H., Yuan, Y.Q., 2010. Long-term ecological interactions between nutrient and phytoplankton community in the Changjiang estuary. *Chin. J. Oceanol. Limnol.* 28 (4), 887–898.

Li, D.J., 1998. *Organic Characteristics and Dynamic Sedimentation of Suspended Matter and its Biogeochemical Behavior in the Changjiang Estuary* (Ph.D. Thesis) East China Normal University, China (in Chinese with English abstract).

Li, J., Zhang, C., 1998. Sediment resuspension and implications for turbidity maximum in the Changjiang Estuary. *Mar. Geol.* 148 (3–4), 117–124.

Li, D.J., Zhang, J., Zhang, L.H., Chen, B.L., Chen, J.Y., 2001. Primary study on surface properties of suspended particles in the Changjiang Estuary. *J. Sediment. Res.* 5, 37–41 (in Chinese with English abstract).

Lin, P., Chen, M., Guo, L.D., 2012. Speciation and transformation of phosphorus and its mixing behavior in the Bay of St. Louis estuary in the northern Gulf of Mexico. *Geochim. Cosmochim. Acta* 87 (15), 283–298.

Lin, P., Guo, L.D., Chen, M., Cai, Y.H., 2013. Distribution, partitioning and mixing behavior of phosphorus species in the Jiulong River estuary. *Mar. Chem.* 157 (20), 93–105.

Liu, M., Hou, L.J., Xu, S.Y., Ou, D.N., Zhang, B.L., Liu, Q.M., Yang, Y., 2002. Phosphate adsorption characteristics of tidal flat surface sediments and its environmental effect

- from the Yangtze Estuary. *Acta Geograph. Sin.* 57 (4), 397–406 (in Chinese with English abstract).
- Liu, S.M., Zhang, J., Chen, H.T., Wu, Y., Xiong, H., Zhang, Z.F., 2003. Nutrients in the Changjiang and its tributaries. *Biogeochemistry* 62 (1), 1–18.
- Liu, S.M., Zhang, J., Li, D.J., 2004. Phosphorus cycling in sediments of the Bohai and Yellow Seas. *Estuar. Coast. Shelf Sci.* 59, 209–218.
- Liu, J.P., Li, A.C., Xu, K.H., Velozzi, D.M., Yang, Z.S., Milliman, J.D., DeMaster, D.J., 2006. Sedimentary features of the Yangtze River-derived along-shelf clinoform deposit in the East China Sea. *Cont. Shelf Res.* 26, 2141–2156.
- Lopez, P., 2004. Spatial distribution of sedimentary phosphorus pools in a Mediterranean coastal lagoon 'Albufera d'es Grau' (Minorca Island, Spain). *Mar. Geol.* 203 (1–2), 161–176.
- Lukkari, K., Leivuori, M., Vallius, H., Kotilainen, A., 2009. The chemical character and burial of phosphorus in shallow coastal sediments in the northeastern Baltic Sea. *Biogeochemistry* 94 (2), 141–162.
- Mayer, L.M., Keil, R.G., Macko, S.A., Joye, S.B., Ruttenberg, K.C., Aller, R.C., 1998. Importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones. *Glob. Biogeochem. Cycles* 12 (4), 573–579.
- Meng, J., Yao, P., Yu, Z.G., Bianchi, T.S., Zhao, B., Pan, H.H., Li, D., 2014a. Speciation, bioavailability and preservation of phosphorus in surface sediments of the Changjiang Estuary and adjacent East China Sea inner shelf. *Estuar. Coast. Shelf Sci.* 144 (1), 27–38.
- Meng, J., Yao, Q.Z., Yu, Z.G., 2014b. Particulate phosphorus speciation and phosphate adsorption characteristics associated with sediment grain size. *Ecol. Eng.* 70, 140–145.
- Meybeck, M., Gauwet, G., Dessery, S., Somville, M., Gouleau, D., Billen, G., 1988. Nutrients (organic C, P, N, Si) in the eutrophic river Loire (France) and its estuary. *Estuar. Coast. Shelf Sci.* 27, 595–624.
- Millero, F., Huang, F., Zhu, X., Liu, X., Zhang, J.Z., 2001. Adsorption and desorption of phosphate on calcite and aragonite in seawater. *Aquat. Geochem.* 7 (1), 33–56.
- Milliman, J.D., Farnsworth, K.L., 2011. *River Discharge to the Coastal Ocean: A Global Synthesis*. Cambridge University Press, New York, p. 62.
- Monbet, P., Brunskill, G.J., Zagorskis, I., Pfützner, J., 2007. Phosphorus speciation in the sediment and mass balance for the central region of the Great Barrier Reef continental shelf (Australia). *Geochim. Cosmochim. Acta* 71 (11), 2762–2779.
- Nixon, S.W., 2003. Replacing the Nile: are anthropogenic nutrients providing the fertility once brought to the Mediterranean by a Great River? *Ambio* 32 (1), 30–39.
- Pan, H.H., Yao, P., Zhao, B., Meng, J., Li, D., Wang, J.P., 2014. Sources, distribution, and preservation of size-fractionated particulate organic carbon in the turbidity maximum zone of the Changjiang Estuary based on water elutriation. *Acta Oceanol. Sin.* (in Chinese with English abstract, in press).
- Patra, S., Liu, C.Q., Wang, F.S., Li, S.L., Wang, B.L., 2012. Behavior of major and minor elements in a temperate river estuary to the coastal sea. *Int. J. Environ. Sci. Technol.* 9 (4), 647–654.
- Paytan, A., McLaughlin, K., 2007. The oceanic phosphorus cycle. *Chem. Rev.* 107 (2), 563–576.
- Prastka, K.E., Malcolm, S.J., 1994. Particulate phosphorus in the Humber estuary. *Neth. J. Aquat. Ecol.* 28 (3–4), 397–403.
- Ragueneau, O., Regaudie-de-Gioux, A., Moriceau, B., Gallinari, M., Vangriesheim, A., Baurand, F., Khrifounoff, A., 2009. A benthic Si mass balance on the Congo Margin: origin of the 4000 m DSI anomaly and implications for the transfer of Si from land to ocean. *Deep-Sea Res.* II 56 (23), 2197–2207.
- Ran, X.B., Yu, Z.G., Yao, Q.Z., Chen, H.T., Guo, H.B., 2013. Silica retention in the Three Gorges reservoir. *Biogeochemistry* 112 (1–3), 209–228.
- Rao, J.L., Berner, R.A., 1997. Time variations of phosphorus and sources of sediments beneath the Chang Jiang (Yangtze River). *Mar. Geol.* 139 (1–4), 95–108.
- Ruttenberg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* 37 (7), 1460–1482.
- Ruttenberg, K.C., 1993. Reassessment of the oceanic residence time of phosphorus. *Chem. Geol.* 107 (3), 405–409.
- Ruttenberg, K.C., Berner, R.A., 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochim. Cosmochim. Acta* 57 (5), 991–1007.
- Schroeder, K., Chiggiato, J., Haza, A.C., Griffa, A., özgökmen, T.M., Zanasca, P., Molcard, A., Borghini, M., Poulain, P.M., Gerin, R., 2012. Targeted Lagrangian sampling of submesoscale dispersion at a coastal frontal zone. *Geophys. Res. Lett.* 39 (11), 1–6.
- Sekula-Wood, E., Benitez Nelson, C.R., Bennett, M.A., Thunell, R., 2012. Magnitude and composition of sinking particulate phosphorus fluxes in Santa Barbara Basin, California. *Glob. Biogeochem. Cycles* 26 (2), 1–15.
- Shen, Z.L., Zhou, S.Q., Pei, S.F., 2008. Transfer and transport of phosphorus and silica in the turbidity maximum zone of the Changjiang estuary. *Estuar. Coast. Shelf Sci.* 78 (3), 481–492.
- Shim, M.J., Swarzenski, P.W., Shiller, A.M., 2012. Dissolved and colloidal trace elements in the Mississippi River delta outflow after Hurricanes Katrina and Rita. *Cont. Shelf Res.* 42 (1), 1–9.
- Sutula, M., Bianchi, T.S., McKee, B.A., 2004. Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico. *Limnol. Oceanogr.* 49 (6), 2223–2235.
- Tang, X.Q., Wu, M., Dai, X.C., Chai, P.H., 2014. Phosphorus storage dynamics and adsorption characteristics for sediment from a drinking water source reservoir and its relation with sediment compositions. *Ecol. Eng.* 64, 276–284.
- Tian, R.C., Chen, Y.Y., Zhou, J.Z., 1991. Dual filtration effect of geochemical and biogeochemical processes in the Changjiang Estuary. *Chin. J. Oceanol. Limnol.* 9 (1), 33–43.
- Turner, A., Millward, G.E., Tyler, A.O., 1994. The distribution and chemical composition of particles in a macrotidal estuary. *Estuar. Coast. Shelf Sci.* 38 (1), 1–17.
- Van der Zee, C., Slomp, C.P., van Raaphorst, W., 2002. Authigenic P formation and reactive P burial in sediments of the Nazare canyon on the Iberian margin (NE Atlantic). *Mar. Geol.* 185, 379–392.
- Van der Zee, C., Roevros, N., Chou, L., 2007. Phosphorus speciation, transformation and retention in the Scheldt estuary (Belgium/The Netherlands) from the freshwater tidal limits to the North Sea. *Mar. Chem.* 106 (1–2), 76–91.
- Vignati, D., Pardos, M., Diserens, J., Ugazio, G., Thomas, R., Dominik, J., 2003. Characterisation of bed sediments and suspension of the river Po (Italy) during normal and high flow conditions. *Water Res.* 37, 2847–2864.
- Vink, S., Chambers, R.M., Smith, S.V., 1997. Distribution of phosphorus in sediments from Tomales Bay, California. *Mar. Geol.* 139 (1–4), 157–179.
- Wakeham, S.G., Canuel, E.A., Lerberg, E.J., Mason, P., Sampere, T.P., Bianchi, T.S., 2009. Partitioning of organic matter in continental margin sediments among density fractions. *Mar. Chem.* 115 (3–4), 211–225.
- Walling, D.E., Woodward, J.C., 1993. Use of a field-based water elutriation system for monitoring the in situ particle size characteristics of fluvial suspended sediment. *Water Res.* 23 (9), 1413–1421.
- Wang, A.P., Yang, S.Y., Zhou, Q., 2006. Phosphorus adsorption characteristics of sediments in Congming Dongtan wetland, the entrance of Yangtze River. *Chin. J. Ecol.* 25 (8), 926–930 (in Chinese with English abstract).
- Waterson, E.J., Canuel, E.A., 2008. Sources of sedimentary organic matter in the Mississippi River and adjacent Gulf of Mexico as revealed by lipid biomarker and $\delta^{13}\text{C}_{\text{OC}}$ analyses. *Org. Geochem.* 39 (4), 422–439.
- Yao, Q.Z., Yu, Z.G., Li, L.L., Chen, H.T., Mi, T.Z., 2014a. Transformation and source of nutrients in the Changjiang Estuary. *Sci. China Chem.* 57 (5), 779–790.
- Yao, P., Zhao, B., Bianchi, T.S., Guo, Z.G., Zhao, M.X., Li, D., Pan, H.H., Wang, J.P., Zhang, T.T., Yu, Z.G., 2014b. Remineralization of sedimentary organic carbon in mud deposits of the Changjiang Estuary and adjacent shelf: implications for carbon preservation and authigenic mineral formation. *Cont. Shelf Res.* <http://dx.doi.org/10.1016/j.csr.2014.08.010>.
- Yu, Y., Song, J.M., Li, X.G., Yuan, H.M., Li, N., 2012. Distribution, sources and budgets of particulate phosphorus and nitrogen in the East China Sea. *Cont. Shelf Res.* 43 (15), 142–155.
- Zhang, J.Z., Chi, J., 2002. Automated analysis of nanomolar concentrations of phosphate in natural waters with liquid waveguide. *Environ. Sci. Technol.* 36 (5), 1048–1053.
- Zhang, J.Z., Huang, X.L., 2007. Relative importance of solid-phase phosphorus and iron on the sorption behavior of sediments. *Environ. Sci. Technol.* 41 (8), 2789–2795.
- Zhang, J.Z., Huang, X.L., 2011. Effect of temperature and salinity on phosphate sorption on marine sediments. *Environ. Sci. Technol.* 45 (16), 6831–6837.
- Zhang, J., Zhang, Z.F., Liu, S.M., Wu, Y., Xiong, H., Chen, H.T., 1999. Human impacts on the large world rivers: would the Changjiang (Yangtze River) be an illustration? *Glob. Biogeochem. Cycles* 13 (4), 1099–1106.
- Zhang, S., Ji, H.B., Yan, W.J., Duan, S.W., 2003. Composition and flux of nutrients transport to the Changjiang Estuary. *J. Geogr. Sci.* 13 (1), 3–12.
- Zhang, J.Z., Fischer, C.J., Ortner, P.B., 2004. Potential availability of sedimentary phosphorus to sediment resuspension in Florida Bay. *Glob. Biogeochem. Cycles* 18 (4), GB4008.
- Zhang, J., Liu, S.M., Ren, J.L., Wu, Y., Zhang, G.L., 2007. Nutrient gradients from the eutrophic Changjiang (Yangtze River) Estuary to the oligotrophic Kuroshio waters and re-evaluation of budgets for the East China Sea Shelf. *Prog. Oceanogr.* 74 (4), 449–478.
- Zhang, J.Z., Guo, L.D., Fischer, C.J., 2010. Abundance and chemical speciation of phosphorus in sediments of the Mackenzie River Delta, the Chukchi Sea and the Bering Sea: importance of detrital apatite. *Aquat. Geochem.* 16 (3), 353–371.
- Zhang, B., Fang, F., Guo, J.S., Chen, Y.P., Li, Z., Guo, S.S., 2012. Phosphorus fractions and phosphate sorption-release characteristics relevant to the soil composition of water-level-fluctuating zone of Three Gorges Reservoir. *Ecol. Eng.* 40, 153–159.
- Zhou, M.J., Shen, Z.L., Yu, R.C., 2008. Responses of a coastal phytoplankton community to increased nutrient input from the Changjiang (Yangtze) River. *Cont. Shelf Res.* 28 (12), 1483–1489.