Effects of suspended particular matters, excess PO_4^{3-} , and salinity on phosphorus speciation in coastal river sediments

Guoqiang Zhao^{1,2} · Yanqing Sheng¹ · Wenjing Wang¹ · Qunqun Liu^{1,2} · Ming Jiang^{1,2} · Zhaoran Li¹

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Abstract

Phosphorus (P) is an essential biogenic element in aquatic ecosystem, and its speciation in sediment may influence the water quality. The composition of P in suspended particular matters (SPM) and sediments were analyzed. Metal ions bonding PO_4^{3-} and chelating organic P (OP) were explored by Visual MINTEQ simulation and infrared spectroscopy. Inorganic P (IP) mainly comprises orthophosphate and pyrophosphate in SPM. OP mainly includes α -glycerol phosphate, β -Gly, monophosphate, and mononucleotides from aquatic plants in SPM. *Cyclotella*, *Nitzschia*, *Amphiprora*, and terrestrial C_3 plants are the main source of aquatic plants in JH, while they are from *Oscillatoria* and *Merismopedia* in JL. These aquatic plants directly determine whether OP or IP is taken to surface sediments during the setting of SPM. The bonding between PO_4^{3-} and Ca is more preferential than Al and Fe, so the excess PO_4^{3-} makes Ca compounds bonding IP (Ca-IP) and Al/Fe/Mn (hydr) oxides associated IP (Al/Fe/Mn-IP) dominant, but limited PO_4^{3-} preferentially contributes more Ca-IP. Metal ions in saline water can firmly cheat with OP via P-OH and/or P=O groups to promote the burial of OP.

Keywords Phosphorus · Salinity · Suspended particular matters · Sediments · Coastal rivers

Abbreviations

P	Phosphorus
OP	Organic P
IP	Inorganic P
TP	Total P
PIP	Particulate inorganic P
SRP	Soluble reactive PO_4^{3-}
POP	Particulate organic P
DOP	Dissolved organic P
SPM	Suspended particular matters

Al/Fe/Mn-IP	Al/Fe/Mn (hydr) oxides associated IP
Ca-IP	Ca compounds bonding IP

Introduction

Phosphorus (P) can directly regulate the growth of algae in aquatic ecosystems as a vital nutrition, which has been recognized as a limiting factor for eutrophication (Clarke et al. 2006). The uptake of P by aquatic algae is closely related to

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✉ Yanqing Sheng
yqsheng@yic.ac.cn

Guoqiang Zhao
gqzhao@yic.ac.cn

Wenjing Wang
wjwang@yic.ac.cn

Qunqun Liu
qunqliu@yic.ac.cn

Ming Jiang
jiangming17@mailsucas.edu.cn

Zhaoran Li
zrli@yic.ac.cn

¹ Research Center for Coastal Environment Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, China

² University of Chinese Academy of Sciences, Beijing, China

P speciation. Although soluble reactive PO_4^{3-} (SRP) can be preferentially absorbed, most complex P-containing compounds including labile organic P (OP) and pyrophosphate can be used by algae after hydrolysis by phosphatase (Cotner and Wetzel 1992; Zhu et al. 2013; Read et al. 2014; Huang et al. 2018).

Adsorption-desorption and settling process of suspended particular matters (SPM) are significant to regulate P speciation in surface sediments (Pan et al. 2013; Jin et al. 2018). Aquatic plants, including terrestrial plants, algae, and submerged plants are essential components in SPM (Jin et al. 2018). These plants wrapped SPM can significantly affect the adsorption-desorption of P. They usually have short life cycles (several weeks) in overlying water (Cleuvers and Ratte 2002). If these plants cannot be collected from waters, plant debris will sink to the sediment-water interface and contributes to loads of P in surface sediments (Zhang et al. 2018). However, previous studies did not give the information on the community of phytoplankton and the source of organic matters in SPM. In addition, there are many coastal rivers under the stresses of high P and salinity around the Bohai Sea (Shan et al. 2016; Yu et al. 2019). Previous studies reported that Al/Fe/Mn (hydr) oxide associated with inorganic P (Al/Fe/Mn-IP) was usually higher in heavily polluted rivers with high PO_4^{3-} , while the stable Ca compounds bound IP (Ca-IP) was always dominant in river sediments with less PO_4^{3-} load (Shan et al. 2016; Zhao et al. 2019). In the study of response of P speciation in lake sediments to anthropogenic activities, Ni et al. (2020) indicated that Al/Fe/Mn-IP was mainly controlled by industrial and domestic effluents, and there was high proportion of Al/Fe/Mn-IP in sediments just with high PO_4^{3-} . In addition to aquatic ecosystems, Al/Fe/Mn-IP was dominant P (even greater than that of Ca-IP) in sludge in wastewater treatment plants due to high PO_4^{3-} (Li et al. 2018a; Shi et al. 2019). However, the chemical priority by which excess PO_4^{3-} reacting with these metal ions (Al, Fe, and Ca) in sediments and/or sludge is still unclear. Salinity is also a key factor influencing P speciation in sediments. Salinity can promote the release of adsorbed PO_4^{3-} from sediments because SO_4^{2-} , Cl^- , and OH^- can compete ion-binding sites of some metal (hydr) oxides with PO_4^{3-} (Gardolinski et al. 2004; Bai et al. 2017; Zhao et al. 2019). For example, the proportions of Fe-bound P decreases but Ca-bound P increases in the transition from freshwater to saltwater because salinity can promote the release of PO_4^{3-} and fluoride from Fe (hydr) oxides into solution, leading to the formation of carbonate fluorapatite. The carbonate fluorapatite is a kind of Ca-bound P mineral accumulated in marine sediments. However, aluminum-bound P is less affected by salinity (Jordan et al. 2008; Hu et al. 2020). Although some studies had conducted the effect of salinity on OP cycle, these papers merely focused on the OP-related genes community, phosphatase, and adsorption efficiency (Gardolinski et al. 2004; Labry et al. 2016; Hu

et al. 2020). However, the mechanism of OP chelating metal ions in saline water has been poorly understood.

Chemical fractionation procedures for P, which use acid and alkaline extracts to separate various fractions based on the type and strength of P physicochemical interactions with other sediment components, such as the classical “SEDEX” and “SMT” methods (Bowman and Cole 1978; Ruttenberg 1992; Ruban et al. 2001). However, these fractionation procedures fail to give the information on molecular structure of complex P compounds because the P speciation is finally detected as the form of PO_4^{3-} using the standard molybdate blue method after the treatment of extraction and digestion (Murphy and Riley 1962; Read et al. 2014). The P-31 nuclear magnetic resonance spectroscopy (^{31}P -NMR) is a powerful approach for identifying and quantifying the complex P compounds (e.g., phytate, pyrophosphate, and DNA) in sediments (Cade-Menun 2005; Cade-Menun 2015). Thus, a combination of chemical fractionation method and ^{31}P -NMR can be used to interpret complementary information on the speciation, structure, and bioavailability of P.

Although we had published a preliminary work about effects of dredging and salinity on P characteristics, these work mainly focused on sediment disturbance and ecological effects of salinity. The composition of P in SPM, chemical priority of excess PO_4^{3-} reacting with metal ions among Al, Fe, Mn, and Ca, and OP chelating with metal ions in saline water were not mentioned (Zhao et al. 2019). Therefore, objectives of this paper were to (1) identify the source of organic matters and the community of phytoplankton in SPM; (2) study the composition of P in SPM affecting P speciation in sediments; (3) investigate the chemical priority of excess PO_4^{3-} bonding Al^{3+} , Fe^{3+} , Mn^{4+} , and Ca^{2+} ; and (4) explore the mechanism of OP chelating metal ions in saline water.

Materials and methods

Sampling

The Jiehe River (JH) and the Jiaolai River (JL) are two coastal rivers around the Bohai Sea. Sediments of JH are heavily polluted by P, while JL is a saline river with excessive waste brine inputs from many salt fields along the river (Zhao et al. 2019). Seven surface sediment samples (0–5 cm) were collected from the two rivers using a core sampler (HL-CN, Xihuay Technology, Beijing, China) in September 2018. Three sampling sites (J1, J2, and J3) were set in JH, while four sites (L1, L2, L3, and L4) were arranged in JL (Fig. S1). This season was selected because this was the period with the highest risk of algal bloom and water quality decline. Samples of the overlying water were also collected in each site simultaneously. Temperature, pH, dissolved oxygen, oxidation-reduction potential, and salinity in overlying water

were determined *in situ* using a portable multi-parameter probe (YSI Professional Plus, YSI Incorporated, USA). All samples were kept in sterile and sealable plastic bags or Niskin bottles, and then transported to laboratory in the dark at 4 °C. Sediment samples were freeze-dried and then ground and passed through a 100-mesh sieve for homogenization prior to analysis.

Chemical analysis

Total chlorophyll *a* (Chl *a*) in overlying water samples was filtrated by 0.45- μ m glass fiber filters (Pall®) and then extracted with 80% acetone for 16 h in the dark. The Chl *a* in the extract was analyzed by a colorimetric method (Holm-Hansen et al. 1965). Total nitrogen (TN) and total P (TP) in water samples were determined using the colorimetric method after potassium persulfate digestion (Chinese EPA 2002). Elemental maps of P, Al, Fe, and Ca on SPM from J2 and L3 were analyzed using a scanning electron microscope (SEM, S-4800, Hitachi, Japan) and an energy dispersive spectrometer (EDS EX-350, HORIBA, Japan).

Total organic carbon (TOC) and TN in sediments were determined by a TOC analyzer (TOC-VCPH, Shimadzu, Japan). TOC was determined after the acidification with 1 mol L⁻¹ HCl for 16 h, whereas samples for TN determination were not acidified (Kao et al. 2003). Carbon and nitrogen isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) in sediments were analyzed using a Delta^{plus} XL mass spectrometer connecting to a Flash EA elemental analyzer (Thermo Fisher, USA) (Zhu et al. 2018).

Identification and counting of phytoplankton

Phytoplankton in overlying water samples were fixed with neutral Lugol's solution and concentrated through 48 h of sedimentation. The concentrated phytoplankton samples (30 mL) were used for the identification and quantification of phytoplankton species (Dai et al. 2017). After mixing, phytoplankton was counted and identified in a counting chamber using a light microscope (Ergaval Carl Zeiss, Germany) with a magnification of 400 times. Every phytoplankton species with more than 100 random fields was observed. Phytoplankton phyla and genus were identified based on cell sized and morphology (Hu and Wei 2006).

Determination of P in overlying water

Total dissolved P in the filtered waters was determined by the molybdenum blue method after potassium persulfate digestion. SRP was directly measured without digestion. Dissolved organic P (DOP) was obtained by subtracting DIP from total dissolved P (Chinese EPA 2002). SPM were obtained by filtration of water samples on 0.45- μ m glass fiber filters (Pall®), and then were lyophilized. Total particular P,

particular inorganic P (PIP), and particulate OP (POP) in SPM were determined by the standard method from Solorzano and Sharp (1980). Detailed determination procedures are given in *supporting information*.

The P compounds in SPM were further characterized using ³¹P-NMR. Specifically, the lyophilized SPM was extracted in 50-mL acid-washed centrifuge tubes with 15 mL of 0.5 M NaOH and 0.1 M EDTA by shaking at 250 rpm for 16 h (Read et al. 2014). Then, the supernatant was lyophilized for 24–48 h to obtain dry powders. Approximately 250 mg of dried powder was dissolved in 0.6-mL D₂O and 0.1 mL 10 M NaOH. Finally, the supernatant was transformed to 5-mm nuclear magnetic tubes to analyze P compounds by a 500 MHz nuclear magnetic resonance spectrometer at 202.47 MHz (Advance III Bruker, Germany). Parameters were set according to the published paper with a pulse of 45°, an acquisition time of 0.68 s, a pulse delay of 4.32, a temperature of 20 °C, and ~ 10,000 scans. Detailed analysis procedures were consistent with report of Zhao et al. (2019).

Determination of P in sediments

The P speciation in sediments was analyzed by the standards, measurements, and testing method (SMT) (Ruban et al. 2001). The P speciation was divided into TP, IP, OP, NaOH-IP, and HCl-IP. The NaOH-IP is Al/Fe/Mn (hydr) oxides associated IP. And the HCl-IP is IP bound to Ca minerals. The P compounds in sediments were analyzed using ³¹P-NMR. The determination procedure for ³¹P-NMR is consistence with section “[Determination of P in overlying water](#).”

Stimulation of excess PO₄³⁻ reacting with metal ions

The chemical priority of excess PO₄³⁻ bonging Al, Fe, Mn, and Ca was analyzed by Visual MINTEQ 3.0. Thermodynamic states of the reacting systems were set as pH 8.0 and 25 °C because the reaction conditions are kept as closed as possible to the *in situ* natural conditions. Concentrations of Al³⁺, Fe³⁺, Mn²⁺, and Ca²⁺ were set as 1 mM, while the concentration of PO₄³⁻ was set as 10 mM to stimulate the excess PO₄³⁻.

Analysis of OP chelating metal ions in saline water

The lyophilized and sieved sediment samples from JL were washed with Milli-Q water three times to remove salts because the complex salts can interfere with the subsequent experiment. If the salts in sediment were not removed, the final salinity in the incubation would be not inaccurate. And then the desalinated sediments were baked at 550 °C for 3 h to remove background OP. The β -glycerophosphate (β -Gly, Sigma G9422) and phytate (*myo*-IHP, Sigma 68388) were purchased from Sigma-Aldrich as two model OP compounds

Fig. 1 Relative abundance of phytoplankton community **a**: phyla level, **b** genus level in two rivers

to conduct the OP sorption experiment. Sea salts (Sigma S9883) was also obtained from Sigma-Aldrich to prepare the simulated seawater with different salinities. A series of 100-mL centrifugal tubes were added with 1.0-g pretreated sediments and 50 mL β -Gly or *myo*-IHP solutions. The above β -Gly and *myo*-IHP solutions (2 mM P, pH 7.0 ± 0.5) were prepared using the simulated seawater with the salinity of 0‰, 5‰, 10‰, 30‰. These tubes were then shaken for 24 h at 25 °C. After shaking, supernatants were collected to determine the remaining OP by the molybdenum blue method after potassium persulfate digestion (Chinese EPA 2002). The OP adsorbed by sediments was calculated from the difference between the added amount of OP and the remaining OP in the solution after the adsorption.

To investigate the complex reaction between OP and sea salts, β -Gly and *myo*-IHP solutions (concentration 2‰) were prepared with the 30‰ simulated seawater. The control was β -Gly and *myo*-IHP solutions (concentration 2‰) were prepared with Milli-Q water. The concentration of β -Gly and *myo*-IHP was adjusted to 2‰ rather than the incubation concentration because of the low detection limit of Fourier transform infrared spectrometer (FTIR). The pH of all solutions was adjusted to pH 7.0 ± 0.5 . Functional groups of β -Gly

and *myo*-IHP in solutions were analyzed by FTIR (Nicolet iS10, Thermo Fisher, USA) after shaking for 24 h.

Statistical analysis

One-way analysis of variance (ANOVA) and Pearson correlation analysis were performed with the SPSS 19 software package. Student-Newman-Keuls multiple range test was selected in ANOVA. Significance levels were $p < 0.05$.

Results

Properties of overlying water and sediments

Parameters of overlying water in two rivers were listed in Table S1. Temperature ranged from 22.6 to 26.8 °C. The pH and salinity in JH ranged 7.0 to 7.5 and 1.2‰ to 2.3‰, respectively. However, in JL, the pH and salinity varied from 6.3 to 6.9 and 2.2‰ to 24.9‰, respectively. Both dissolved oxygen and oxidation-reduction potential in two rivers were higher than 7 mg L⁻¹ and 240 mV. The average Chl *a* was 83.9 $\mu\text{g L}^{-1}$ in JL, which was ~ 1.4 times higher than that in

Fig. 2 Distributions of different P species in water samples in JH and JL. TPP, total particulate P; TDP, total dissolved P; PPI, particulate inorganic P; SRP, soluble reactive P; POP, particulate organic P; DOP, dissolved organic P

Fig. 3 ^{31}P -NMR spectra of water samples from JH and JL. **a–b** Full spectra were initially processed with 10 Hz line broadening (LB). **c–d**, The region of orthophosphate monoester was subsequently processed with 2 Hz LB adding a series of phosphorus standards. G6P, D-glucose 6-phosphate; α -Gly, DL- α -glycerol phosphate; β -Gly, β -glycerol phosphate; AM, adenosine 5' monophosphate; PC, phosphocholine chloride calcium salt tetrahydrate; GIP, α -D-glucose-1-phosphate

JH ($60.1 \mu\text{g L}^{-1}$). The averages of TN and TP in JH and JL were 10.8 mg L^{-1} and $394 \mu\text{g L}^{-1}$, 3.1 mg L^{-1} , and $264 \mu\text{g L}^{-1}$, respectively. Average phytoplankton density in JL was $4.6 \times 10^7 \text{ cells L}^{-1}$, which was ~ 5.3 times higher than that in JH. Sediment parameters were given in Table S2. Mean values of TOC and TN were 1.2% and 0.1% in JH, 1.5% and 0.2% in JL. Weight ratios of TOC/TN ranged from 12 to 13.5 in JH, while they were between 6 and 8.6 in JL. The $\delta^{13}\text{C}$ (‰) varied from -24 to -27 ‰ in JH; -21 to -23 ‰ in JL. The $\delta^{15}\text{N}$ (‰) ranged from 1.2 to 3.0‰ in JH, 3.7‰ to 6.0‰ in JL.

Plankton community in overlying water

Phytoplankton communities at phyla and genus levels in overlying water were illustrated in Fig. 1. A total of eleven dominant genera of phytoplankton were identified, belonging to Bacillariophyta, Cyanophyta, and Chlorophyta (three phyla). Among these genera, three genera belonged to Bacillariophyta, six genera belonged to Cyanophyta, and two genera were classified as Chlorophyta. Bacillariophyta dominated the total phytoplankton abundances ($\sim 70\%$) in JH, while Cyanophyta was the dominant phyla in JL with an average relative abundance of 70%. Bacillariophyta in JH was further identified at the genera levels with dominant algal *Cyclotella*, *Nitzschia*, and *Amphiprora*. The genera *Oscillatoria* and *Merismopedia* belonged to Cyanophyta in JL, accounting for 61% of total phytoplankton.

The P in overlying water and SPM

The P speciation in overlying water and SPM were displayed in Fig. 2. Compared with total dissolved P, total particular P in SPM was the dominant P speciation in two rivers. Total particular P was significantly higher than total dissolved P in all sampling sites. Averages of total particular P and total dissolved P were $300 \mu\text{g L}^{-1}$ and $143 \mu\text{g L}^{-1}$ in JH, while they were $215 \mu\text{g L}^{-1}$ and $56 \mu\text{g L}^{-1}$ in JL. The means of PIP were $177 \mu\text{g L}^{-1}$ (JH) and $103 \mu\text{g L}^{-1}$ (JL), accounting for 56% (JH) and 77% (JL) of total IP. POP in SPM was the main fraction of OP in two rivers. The average POP in JH was $58 \mu\text{g L}^{-1}$ accounting for 73% of total OP, while higher POP was found in JL with the mean of $98 \mu\text{g L}^{-1}$. The averages of SRP in JH and JL were $133 \mu\text{g L}^{-1}$ and $32 \mu\text{g L}^{-1}$. However, the mean DOP was $30 \mu\text{g L}^{-1}$ in JL, which was 1.5 times greater than that in JH with the mean of $20 \mu\text{g L}^{-1}$. Generally, PIP and SRP were the dominant P fraction in JH, while POP and DOP were the main P fraction in JL.

The P compounds in SPM were further characterized by ^{31}P -NMR (Fig. 3 and Table 1). Recovery of TP and OP was all greater than 60% (Table S3). Based on the spiking experiments, P compounds in orthophosphate monoesters region were identified and quantified. Results indicated that orthophosphate, orthophosphate monoesters and diesters, DNA, and pyrophosphate were the dominant P compounds in SPM (Fig. 3a and b). For the orthophosphate monoesters, α -glycerol phosphate, β -glycerol phosphate, monophosphate, and mononucleotides were further identified (Fig. 3c and d). According to the quantitative result of integration, orthophosphate was the most primary compounds in SPM in two rivers, accounting for $\sim 78\%$ of PIP. Pyrophosphate was the second dominant P compounds with the average of ~ 12 of PIP. POP mainly comprised α -glycerol phosphate, β -glycerol phosphate, monophosphate, and mononucleotides with the mean percentages of 12%, 32%, 26%, and 31%, respectively.

Table 1 The relative distribution of P species determined by ^{31}P -NMR spectroscopy in water samples. Ortho-P, orthophosphate; α -Gly, DL- α -glycerol phosphate; β -Gly, β -glycerol phosphate; AM, adenosine 5' monophosphate

Samples	Integral area (%)							
	Ortho-P	α -Gly	β -Gly	AM	Mononucleotides	DNA	Pyrophosphate	Teichoic acids
J1	76.1	2.50	4.67	3.53	2.02	n.d.	9.29	n.d.
J2	54.4	4.67	10.2	8.53	7.47	1.85	14.8	n.d.
J3	61.1	2.57	8.69	7.08	5.56	n.d.	15.2	n.d.
L1	50.3	2.70	8.72	8.05	10.7	n.d.	18.8	n.d.
L2	37.0	4.4	14.4	11.6	16.6	1.66	14.4	0.55
L3	31.3	6.25	17.8	14.1	18.8	3.65	7.29	1.04
L4	29.4	6.93	16.0	13.4	17.2	7.4	16.0	n.d.

n.d., not detected or below the limits of quantification

The P in surface sediments

The P speciation determined by the SMT protocol was shown in Fig. 4a. TP ranged from 800 mg kg⁻¹ to 1800 mg kg⁻¹ in JH, while it kept a narrow range with 400 mg kg⁻¹ in JL. Both Al/Fe/Mn-IP and Ca-IP were dominant fractions in JH, accounting for 47.6% and 41% of TP. However, in JL, Ca-IP was the primary P fraction with the average percentage of 70% of TP. The content of Al/Fe/Mn-IP in JL was only 12%. The percentage of OP (18%) in JL was 1.6 times greater than that in JH (11.4%). As shown in Fig. 4b, 99% of Al in solution was precipitated as diaspore (AlOOH), 98% of Fe³⁺ was solid hematite (Fe₂O₃) without bonding with PO₄³⁻. However, Mn²⁺ and Ca²⁺ reacted with PO₄³⁻ as precipitation of MnHPO₄ and hydroxyapatite [Ca₅(PO₄)₃OH]. And 84.2% of PO₄³⁻ was still presented as ionic state (HPO₄²⁻ and H₂PO₄⁻) in the presence of above ions under the lab condition.

The P compounds in surface sediments characterized using ^{31}P -NMR were demonstrated in Fig. 5 and Table 2. Recovery of TP and OP in JH was obviously higher than that of JL (Table S4). Comparing to P compounds in SPM,

orthophosphate was the most dominant compound in two rivers. Orthophosphate monoesters in JH were mainly comprised of α -glycerol phosphate, β -glycerol phosphate, and *myo*-inositol hexaphosphate, while it mainly contained α -glycerol phosphate and β -glycerol phosphate in JL. Pyrophosphate was found in JH with the percentage of only 0.26%, no pyrophosphate was detected in JL.

Effects of salinity on OP sorption

Results of Fig. 6a displayed that β -Gly and *myo*-IHP could be both adsorbed by sediments under the stress of salinity, but the adsorption capacity of *myo*-IHP was much higher than that of β -Gly. The *myo*-IHP sorption obviously increased with salinity; however, β -Gly sorption kept a narrow range with salinity. Fig. S2 showed that white precipitate was formed at tube bottom with *myo*-IHP addition, but no white precipitate was found with β -Gly addition after the sorption experiments. Figure 6b showed that in the FTIR of β -Gly, two peaks appeared at 1090 cm⁻¹ and 975 cm⁻¹. The intensity of the peak located at 1090 cm⁻¹ decreased after sea salt addition.

Fig. 4 **a** The component of P fractions in surface sediments by the SMT protocol; **b** thermodynamic states of 1 mM of Al³⁺, Fe³⁺, Mn²⁺, and Ca²⁺ with the addition of 10 mM PO₄³⁻ at pH 8 and 25 °C

Fig. 5 ^{31}P -NMR spectra of sediment samples from JH and JL. **a–b** Full spectra were initially processed with 10 Hz line broadening (LB). **c–e** The region of orthophosphate monoester was subsequently processed with 2 Hz LB adding a series of phosphorus standards. α -Gly, DL- α -glycerol phosphate; β -Gly, β -glycerol phosphate; myo-inositol hexaphosphate

Figure 6c illustrated that the intensities of two peaks at 1194 cm^{-1} and 1074 cm^{-1} in the FTIR of myo-IHP solution decreased in the presence of sea salts.

Discussion

Potential sources of organic matter in sediments

The C/N ratio can interpret sources of organic matters in aquatic ecosystems. TOC/TN weight ratio of aquatic algae is between 5 and 7, which is greater than 15 for terrestrial C3 vascular plants (Meyers 1997). In this study, TOC/TN ratios varied from 12 to 13.5 in JH, which were close to the range for typical terrestrial C3 sources rather than for aquatic algae sources, indicating that external inputs had already posed a significant impact on JH. A previous study demonstrated that PO_4^{3-} was mainly from anthropogenic inputs in JH based on the source analysis of P (Zhao et al. 2019). Therefore, high P load in JH was mainly related to the external P inputs. However, this ratio was between 6 and 8.6 in JL, which was close to the range for aquatic algae, suggesting internal algae deposition was the main source for organic matters in JL. In contrast to C/N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values can be more accurate to identify sources of organic matters because they cannot be obviously influenced by sediment particle size and the decomposition of organic matters (Meyers 1997). Previous studies indicated that C3 plants derived from terrestrial tree leaves and humic acid in soils. The $\delta^{13}\text{C}$ value of these terrestrial organic matters usually ranges from -25 to -33‰ (Hamilton and Lewis 1992; Zhu et al. 2018). The $\delta^{15}\text{N}$ value is $\sim 0.5\text{‰}$, which is always recognized as land plants in soils (Xiong et al. 2010). Aquatic algae usually have $\delta^{13}\text{C}$ ranging from -18 to -22‰ , and the $\delta^{15}\text{N}$ in dissolved NO_3^- were from 7 to 10‰ (Fry and Sherr 1984; Zhu et al. 2018). In this work, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediments in JH varied from -24 to -27‰ and 1.2 to 3.0‰, respectively, which were close to the range of terrestrial C3 plants. This further confirmed that JH had received abundant organic matters from terrestrial inputs. However, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ranged from -21 to -23‰ , and 3.7 to 6.0‰ in JL, which were near to the values of aquatic algae. This suggested internal algae deposition was the main source of organic matters in JL.

Effects of SPM on P speciation in surface sediments

SPM is usually composed of four standard components, including inorganic particles, biotic/bioorganic components, water and pore (Droppo 2001). The inorganic components represent mineral particles, accounting for most weight of SPM (Qafoku et al. 2004). The biotic/bioorganic components mainly include aquatic algae and microbial excreta, which act as organic coated layer that wrap up the inorganic particle (Jia et al. 2016; Jin et al. 2018). Fig. 2 showed that PIP and POP were the dominant P fractions in SPM. Results of ^{31}P -NMR indicated that these PIP mainly consisted of orthophosphate ($\sim 78\%$) and pyrophosphate ($\sim 22\%$). Al, Fe, and Ca are major ions in the mineral particles in SPM, which can closely

combine with PO_4^{3-} (Zhu et al. 2018). Pyrophosphate is a natural excellent complexing agents for Al, Fe and Ca ions, which associates with metal ions in the form of M^{n+} -Pyrophosphate (M^{n+} : Al, Fe, and Ca) (Zhu et al. 2015). Therefore, PIP mainly presented as PO_4^{3-} (~ 78%) and pyrophosphate (~ 22%) bounded to these mineral particles in SPM. Elemental mapping of P, Al, Fe, and Ca of SPM confirmed this coupling relationship between P and these metal ions (Fig. S3). POP had a significantly positive correlation with phytoplankton density ($p < 0.01$, $r = 0.983$) and Chl *a* ($p < 0.01$, $r = 0.947$), which indicated these terrestrial plants and aquatic algae probably contributed to the most of OP. Results of ^{31}P -NMR showed that these POP mainly consisted of α -glycerol phosphate (~ 12), β -Gly (~ 31), monophosphate (~ 26%) and mononucleotides (~ 31%). Previous studies revealed that these OP compounds mainly derived from macrophytes and phytoplankton (Cade-Menun 2017; Feng et al. 2018). Based on the identification of phytoplankton community and organic matters source, bacillariophyta (*Cyclotella*, *Nitzschia*, and *Amphipore*) and terrestrial C_3 plants were the main aquatic plants in JH, while, for JL, it was cyanophyta (*Oscillatoria* and *Merismopedia*). Therefore, POP was mainly composed of α -glycerol phosphate (~ 12), β -Gly (~ 31), monophosphate (~ 26%), and mononucleotides (~ 31%), which came from the bacillariophyta and C_3 plants in JH, and the cyanophyta algae in JL. And, there was more POP in JL than that in JH mainly because of the amount of aquatic plants in JL was higher than that in JH. SPM in JL wrapped more aquatic plants than that in JH. The concentration of Chl *a* could confirm this conclusion. The less aquatic plants in JH could result in more naked mineral particles of SPM with less organic coated layer. The exposed mineral particles of SPM with less wrapped organic matters in JH could continuously adsorb SRP from water to transform into PIP. Therefore, the setting of SPM could contribute more OP to the surface sediments of JL, while it took more IP to the surface sediments in JH. Results of Fig. 4a

confirmed IP was indeed higher in surface sediments of JH than that of JL, while OP in JL sediments was greater than that of JH.

Effects of high PO_4^{3-} and salinity on P speciation in surface sediments

JH is a freshwater river with high P load in overlying water (average TP, $400 \mu\text{g L}^{-1}$) and sediments (average TP, 1200 mg kg^{-1}). Figure 4a displayed Al/Fe/Mn-IP and Ca-IP were dominant P fractions in sediments in JH. The ^{31}P -NMR further showed that these IP in sediments mainly comprised of orthophosphate (Table 2). As Al, Fe, Mn, and Ca coexist, high PO_4^{3-} reacts with Mn^{2+} and Ca^{2+} to form MnHPO_4 and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), respectively. Al and Fe mainly present as diaspor and hematite, which are difficult to directly form ions and covalent bonds with PO_4^{3-} (Fig. 4b). However, diaspor and hematite can adsorb PO_4^{3-} through van der Waal forces and inner-sphere complexation because there are abundant PO_4^{3-} adsorption sites on surfaces of Al and Fe (hydr) oxides (Zamparas and Zacharias 2014; Xu et al. 2017). Therefore, PO_4^{3-} can preferentially combine with Ca and Mn because of the high stability of Ca-PO_4^{3-} and Mn-PO_4^{3-} . Then, excess and/or surplus PO_4^{3-} is adsorbed by Al/Fe (hydr) oxides after reacting with Ca and Mn due to this electrostatic adsorption and complexation are much weaker than the direct chemical bonds. In addition, the solubility product constant ($\text{p}K_{\text{sp}}$) can reflect the solubility and stability of compounds in solution. A higher $\text{p}K_{\text{sp}}$ value indicates that the compound is more difficult to be dissolved, and its chemical structural is extraordinarily stable. Wu et al. (2020) summarized the $\text{p}K_{\text{sp}}$ sequence of various “metal-phosphate” compounds: $\text{Ca} (28.68) > \text{Mg} (23.98) > \text{Al} (20.01) > \text{Fe} (15.00)$, and concluded the affinity between Ca and PO_4^{3-} was the strongest among Al, Fe, and Ca. This conclusion further confirmed the result of MINTEQ simulation in this

Table 2 The relative distribution of P species determined by ^{31}P -NMR spectroscopy in sediment samples. Ortho-P, orthophosphate; α -Gly, DL- α -glycerol phosphate; β -Gly, β -glycerol phosphate; AM, adenosine 5' monophosphate; *myo*-IHP, *myo*-inositol hexaphosphate

Samples	Integral area (%)								
	Ortho-P	α -Gly	β -Gly	AM	Mononucleotides	DNA	Pyrophosphate	<i>myo</i> -IHP	Phosphonate
J1	91.9	0.5	0.95	n.d.	n.d.	n.d.	0.23	0.69	n.d.
J2	85.4	0.6	0.95	n.d.	n.d.	n.d.	0.41	2.1	0.40
J3	88.3	0.5	0.8	n.d.	n.d.	n.d.	0.15	1.8	0.62
L1	98	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L2	97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L3	95	0	0.02	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
L4	95	0.01	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	0.05

n.d., not detected or below the limits of quantification

Fig. 6 **a** Effects of salinity on the OP sorption for sediments; **b** FTIR spectra of solutions of β -Gly with or without the addition of sea salts, **c** *myo*-IHP with or without sea salts

study. Moreover, the distribution of various speciation of P in sediments is also closely related to the earth abundance and redox sensitivity of related metal elements (Zamparas and Zacharias 2014; Wu et al. 2020). The content of Mn in sediments is much lower than that of Al, Fe, and Ca, so the content of Mn-bonding PO_4^{3-} is the lowest (Table S5). And Mn (IV) is easily changed into Mn (III) and/or Mn (II) under reductive conditions resulting in the disintegration of MnHPO_4 and the regeneration of PO_4^{3-} (Dijkstra et al. 2017). Although PO_4^{3-} can preferentially combine with Ca and Mn according to the analysis of their affinities, Mn-bonding PO_4^{3-} should be classified as reactive P speciation just like Al/Fe-IP, and its amount can be negligible because of its redox sensitive and earth abundance. Therefore, excess PO_4^{3-} can promote the generation of both Ca-IP and Al/Fe-IP, while limited PO_4^{3-} preferentially contributes more Ca-IP. And the ratio of Al/Fe-IP to Ca-IP can be probably used as an indicator for the degree of P contamination in aquatic ecosystems.

JL is a saline river with average salinity of 11‰. The average TP in overlying water and sediments was 264 $\mu\text{g L}^{-1}$

and 388 mg kg^{-1} , respectively, which were both lower than those in JH. Figure 4a showed the stable Ca-IP was the primary P speciation in JL sediments, which could attribute to the adequate Ca^{2+} in river water with high salinity in JL. Previous studies reported that salinity could enhance the Al/Fe/Mn-IP release because anions (e.g., Cl^- , SO_4^{2-} , and OH^-) may capture accessible sorption sites for PO_4^{3-} (Jordan et al. 2008; Bai et al. 2017). However, in JL, adequate Ca^{2+} preferentially reacted with limited PO_4^{3-} , resulting in the dominant Ca-IP rather than Al/Fe/Mn-IP. For OP, it always has stronger adsorption capability than IP because many organic functional groups can strongly stick to sediments (Jia et al. 2016). In this study, this strong adsorption capability was verified by the result of Fig. 6. Figure 6a indicated that labile micro-molecular OP (β -Gly) and stable macro-molecular OP (*myo*-IHP) could be both adsorbed by sediments under high salinity. It indicated that salinity could promote the adsorption of OP by sediment through chelation between functional groups in OP and metal ions on sediment surface (Zhu et al. 2015; Zhu et al. 2018). According to the FTIR of β -Gly, the two peaks at

Fig. 7 Schematic overview of SPM, high salinity, and PO_4^{3-} affecting P cycling in coastal river sediments

1090 cm^{-1} and 975 cm^{-1} were the vibration of P-OH and P-O-C bonds in phosphate groups of β -Gly (Li et al. 2018b; Liu et al. 2019). The intensities of the P-OH peaks declined with sea salt addition, indicating complex generation between β -Gly and metal ions from sea salt via P-OH bond (Zhao et al. 2020). However, this complexation was unstable because the complex compound of β -Gly and metal ions could be easily hydrolyzed by phosphatase (Zhao et al. 2020). The 1193 cm^{-1} and 1073 cm^{-1} peaks in Fig. 6c could be assigned to the vibration of P=O bonds and P-OH bonds in *myo*-IHP, respectively (Liu et al. 2019). The intensity of the two peaks both significantly decreased after the addition of sea salt, indicating that *myo*-IHP could chelate with metal ions from sea salts via P=O and P-OH bonds (Zhao et al. 2020). Previous studies confirmed this complex compound of *myo*-IHP and metal ions was very stable that could be stably buried in sediments (Turner et al. 2012; Zhu et al. 2018). And these chelates (OP and metal ions) presented more stable than free OP, and some of them could be resistant to hydrolysis by phosphatase (Zhu et al. 2015; Zhao et al. 2020). Therefore, salinity could enhance fixation or stabilization of OP by sediments, resulting in higher OP in JL than that in JH.

Conclusions

The composition of P in SPM, chemical priority of Al, Fe, Mn, and Ca reacting with PO_4^{3-} , and mechanism of OP chelating metal ions in saline sediments were studied. As Fig. 7 shown, PIP is present mainly in form of orthophosphate or pyrophosphate binding Al, Fe, and Ca minerals in SPM. POP is mainly composed of α -glycerol phosphate, β -Gly, monophosphate, and mononucleotides, which derives from terrestrial C3 plants and aquatic algae. The setting of SPM wrapped more plants contributes more OP to surface sediments, while SPM with less plants takes more IP to surface sediments because naked minerals in SPM tend to absorb more SRP from water. Excess PO_4^{3-} makes both Ca-IP and Al/Fe-IP dominant, but limited PO_4^{3-} preferentially contributes more Ca-IP. Salinity promotes the release of reactive Al/Fe/Mn-IP, but improves the adsorption of OP in sediments. Metal ions in saline water can cheat with OP via P-OH and/or P=O groups to promote the burial of OP. Further studies need to identify the contribution of bacterial community in SPM and sediments to P cycle by seasonal and/or monthly repeated sampling.

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Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

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