Distribution and speciation of phosphorus in surface sediments of the intertidal zone in the Yellow River Delta

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Abstract. For better understanding the phosphorus (P) cycle, it is essential to distinguish the contents of different P speciation in sediments. In the study, the content of total phosphorus (TP) in the sediments ranged from 88.80 to 227.56 μg·g⁻¹, with an average of 138.42 μg·g⁻¹. The content of inorganic phosphorus (IP) ranged from 84.21 to 224.26 μg·g⁻¹, accounting for 88.74%-98.55% of the TP content, which was the main occurrence form in the intertidal sediments of the Yellow River Delta. The contents of phosphorus fractions in surface sediments were 37.06 to 106.35 μg·g⁻¹ for detrital phosphorus (De-P), 2.99 to 34.39 μg·g⁻¹ for exchangeable phosphorus (Ex-P), 5.27-106.06 μg·g⁻¹ for iron bound phosphorus (Fe-P). On the whole, the existing forms of inorganic phosphorus could be ranked as follows: De-P > Fe-P > Ex-P > authigenic phosphorus (Au-P). The regression analysis between TOC content and various forms of phosphorus showed that TOC content was negatively correlated with De-P.

1. Introduction
Phosphorus is widely regarded as a major limiting nutrient and plays a very important role in regulating primary productivity [1]. The transport of phosphorus has important implications for the quality of marine systems. However, its excess supply can cause eutrophication leading to the deterioration of water quality and aquatic ecosystems [2]. Moreover, high-strength exploitation of coastal zones can cause the phosphate levels multiplied in the coastal waters.

Sediments have been recognized as sensitive indicators for monitoring contaminants [3]. Intertidal zones provide an environment for the inter-transformation of different phosphorus forms. Phosphorus species may dominate the nutrient cycle within the intertidal zone system, contributions to intertidal-zone P budgets will also be derived from the P stored within the system, including sediments.

As special zones, the characteristics of intertidal zones such as tides and hydrodynamics can vary along with time and space [4]. What's more, intertidal zones that closely link marine and terrestrial ecosystems have a great impact on the occurrence and fate of heavy metals. Therefore, the present study aims to analyze the distribution and speciation of phosphorus in surface sediments of the intertidal zone in the Yellow River Delta.
2 Materials and methods

2.1 Study area and sample collection

The study area is located in the intertidal zone of Yellow River Delta, China (Fig. 1), which is the fastest-growing wetland among the worldwide larger river deltas (Jiang et al., 2013). According to the surrounding land types, eight sampling sites was selected (Table 1). Sediment samples were collected in September 2013 at the sampling sites (Figure 1). Sediments with three replicates (0–5 cm) were collected using a stainless-steel box corer and stored in valve bags. All surface sediment samples were kept under 4 °C in a cooler and transported to laboratory for experimental analysis.

![Figure 1. Sampling sites in the Yellow River Delta and its geographical location](image)

### Table 1. Descriptions of the sampling sites

| Site | Location                  | Surrounding land type   |
|------|---------------------------|-------------------------|
| CK   | 38°15'59.5"E, 17°51'45.65"N | aquacultures            |
| YG   | 38°7'31.04"E, 118°40'0.04"N | roadbuilding            |
| HG   | 37°49'8.91"E, 119°6'51.91"N | nature reserve          |
| HH   | 37°49'7.33"E, 119°6'41.53"N | nature reserve          |
| HC   | 37°49'11.6"E, 119°6'30.97"N | nature reserve          |
| HL   | 37°49'14.2"E, 119°6'19.23"N | nature reserve          |
| GD   | 37°55'41.3"E, 119°3'45.46"N | causeway                |
| KD   | 37°41'33.40"E, 19°1'47.85"N | aquacultures            |

2.2 Sample preparation and analysis

Measurements of physicochemical properties were taken on the sediment samples which were thawed, air-dried, ground and sieved according to standard methods. The sediments were analyzed for particle size, pH, loss on ignition (LOI) and so on. The sediment particle size was determined by a laser particle size analyzer (Mastersizer, 2000, Malvern, UK). The pH was measured in a 1/2.5 (v/v) sediment/water suspension using a glass electrode. The conductivity was determined using a salinometer (Mettler Toledo, FE30, USA). The oxidation-reduction potential was measured by the Eh meter (Sartorius, PB-10, Germany). The LOI, widely used as a parameter to estimate organic matter (OM), was measured by ignition at 550°C for 16 h described by House and Denison (1998). The total contents of metals as Ca, Mg and Mn were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; ICAP-9000) after digestion. Dissolved phosphorus were measured colorimetrically with an
Autoanalyser-3 (Bran & Luebbe, France). In addition, the modified SEDEX procedure was employed to quantify the different forms of P in sediments, including exchangeable phosphorus (Ex-P), iron-bound phosphorus (Fe-P), authigenic phosphorus (Au-P), detrital phosphorus (De-P), organophosphorus (Or-P), total phosphorus (TP). All chemical reagents used in analysis were of analytical grade. The precision for sediments analysis was within 5% by relative standard deviation (RSD) of duplicates through repeated measurements. The physicochemical properties of sediments were provided in the Table 2.

**Table 2. The physicochemical properties of sediments**

| Sample site | Sal  | OM (%) | Eh (mV) | pH | size distribution (%) | Ca   | Mg  | Mn |
|-------------|------|--------|---------|----|-----------------------|------|-----|----|
|             |      | Clay   | Silt    | Sand | Al          | Fe    |     |    |
| CK          | 9.37 | 3.28   | 297.50  | 8.41 | 2.58        | 71.42 | 26.00 |    |
| YG          | 12.62| 2.25   | 521.07  | 8.66 | 1.85        | 91.53 | 6.62  |    |
| HG          | 11.14| 2.46   | 458.73  | 8.51 | 0.00        | 40.08 | 59.92 |    |
| HH          | 11.37| 2.10   | 426.57  | 8.50 | 0.00        | 35.03 | 64.97 |    |
| HC          | 21.42| 4.38   | 490.37  | 8.82 | 0.00        | 60.57 | 39.43 |    |
| HL          | 24.52| 4.44   | 446.17  | 8.52 | 0.00        | 59.82 | 40.18 |    |
| GD          | 16.01| 5.20   | 331.77  | 8.45 | 0.00        | 81.57 | 18.43 |    |
| KD          | 12.45| 1.75   | 90.72   | 7.53 | 8.03        | 93.02 | 6.98  |    |

Note: Sal means the salinity; OM means the organic matter; Eh means the redox potential; the range of clay particle size was <3.9 µm, the particle size of silt ranged from 3.9 to 62.5 µm, the particle size of sand ranged from 62.5 to 2000 µm; the unit for metals was mg·L⁻¹.

3 Results and discussion

3.1 The content and the spatial distribution of TP in surface sediments

The determination results of phosphorus with different forms in surface sediments at each sampling point are shown in Table 3. The contents of total phosphorus are shown in Figure 3.

**Table 3. The contents of phosphorus with different forms at different sampling points (µg·g⁻¹)**

| Sampling Point | Ex-P | Fe-P | Au-P | De-P | Or-P | IP | TP |
|----------------|------|------|------|------|------|----|----|
| CK             | 3.35 | 38.59| 5.21 | 37.06| 10.69| 84.21| 94.90|
| YQE            | 3.32 | 10.15| 4.68 | 87.40| 4.37 | 105.53| 109.91|
| GD             | 3.17 | 41.04| 7.46 | 40.71| 3.07 | 92.38 | 95.45|
| HG             | 34.39| 63.27| 4.30 | 106.35| 3.56 | 208.31| 211.86|
| HH             | 3.49 | 22.46| 3.72 | 88.84| 3.86 | 118.51| 122.36|
| HC             | 2.99 | 5.27 | 6.32 | 71.06| 3.16 | 85.64 | 88.80|
| HCL            | 13.31| 106.06| 5.47 | 99.42| 3.30 | 224.26| 227.56|
| KD             | 9.37 | 67.40| 7.14 | 66.52| 6.14 | 150.44| 156.58|
Figure 2. The distribution of TP in surface sediments of the intertidal zone

The results showed that the content of total phosphorus in the sediments ranged from 88.80 to 227.56 μg·g⁻¹, with an average of 138.42 μg·g⁻¹. It could be seen from figure 1 that the maximum value of total phosphorus appeared at the site of HCL. Because the site of HCL was the uncultivated area and had little interference from human activities, the sediment might be used as a "sink" of phosphorus. The larger value appeared at the site of KD, which might be related to human activities such as the oilfield development.

3.2 The content distribution of the organic and inorganic phosphorus

The content of inorganic phosphorus ranged from 84.21 to 224.26 μg·g⁻¹, accounting for 88.74%-98.55% of the total phosphorus content, which was the main occurrence form in the intertidal sediments of the Yellow River Delta. The content of organic phosphorus ranged from 3.07 to 10.69 μg·g⁻¹, accounting for 1.45%-11.26% of the total phosphorus content. Among them, the site of CK accounted for the highest proportion (11.26%), which was related to the change of the sediment environment caused by large-scale reclamation in this area. The field investigation showed that there were more fish culture in the mudflat of CK, and a large amount of aquaculture wastewater might be one of the important reasons for the high content of organic phosphorus in the intertidal sediments.

3.3 The chemical speciation of inorganic phosphorus

The results about the fractionated extraction of inorganic phosphorus showed that the content of detrital phosphorus in sediments ranged from 37.06 to 106.35 μg·g⁻¹, accounting for 44.00%-82.98% of the total phosphorus content, with an average value of 58.55%. It was the main form of inorganic phosphorus, and it belonged to calcium bound phosphorus as authigenic phosphorus, which was consistent with the fact that marine sediments were dominated by calcium phosphorus. As the percentage of calcium phosphorus can reflect the strength of land-sea interaction to a certain extent, it showed that the environmental chemical behavior of phosphorus in the coastal sediments of the Yellow River Delta was greatly affected by the marine action.

In addition, exchangeable phosphorus was the most easily released into the overlying water and was easily absorbed by organisms. The results showed that the content of exchangeable phosphorus was low, ranging from 2.99 to 34.39 μg·g⁻¹, accounting for 2.94%-16.51% of the total phosphorus content, and it indicated that the resuspension of intertidal sediments had little effect on the release of phosphorus. Moreover, the maximum content of exchangeable phosphorus appeared at the site of HG, which was less affected by human activities.
The range of the content about iron bound phosphorus was 5.27-106.06 μg·g⁻¹, accounting for 6.15%-47.29% of the total phosphorus content. Some research showed that the content of Fe-P in the surface sediments could indicate the source of land phosphorus and the degree of environmental pollution [5]. The higher Fe-P content was at the reclaimed sites (CK, GD and KD) which were highly affected by human activities. And it indicated that the pollution degree of these areas was higher. On the whole, the existing forms of inorganic phosphorus could be ranked as follows: detrital phosphorus > iron bound phosphorus > exchangeable phosphorus > authigenic phosphorus.

![Chemical speciation of inorganic phosphorus in the intertidal sediments](image)

**Figure 3.** Chemical speciation of inorganic phosphorus in the intertidal sediments

The contents of total phosphorus and various forms of phosphorus were analyzed by regression analysis. The results showed that there was a good linear relationship between total phosphorus and inorganic phosphorus (Figure 4), and the correlation coefficient R² was 0.998. The results indicated that the distribution characteristics of inorganic phosphorus content controlled the change of total phosphorus. However, the correlation coefficient between total phosphorus and organic phosphorus or Fe bound phosphorus was small, which reflected the complexity of pollution at each sampling point to a certain extent.

![The relationship between TP and IP in the surface sediments of intertidal zones](image)

**Figure 4.** The relationship between TP and IP in the surface sediments of intertidal zones
3.4 Correlation analysis between various forms of phosphorus and TOC
The TOC content in the surface sediments ranged from 2.37% to 25.32%. The overall performance was as follows: enclosed area>unclosed area. And the highest content was in the enclosed area (GD), which might be related to the surrounding oilfield development, fishery and aquaculture. The regression analysis between TOC content and various forms of phosphorus showed that TOC content was negatively correlated with detrital phosphorus. Because calcium phosphorus (including detrital phosphorus and authigenic phosphorus) was closely related to the intensity of land-sea interaction, the trend was opposite to the TOC content. In addition, the correlation between other phosphorus forms and TOC was not obvious dueing to the small number of sampling sites.

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References
[1] Pant, H.K., Reddy, K.R. (2001) Phosphorus sorption characteristics of estuarine sediments under different redox conditions. J. Environ. Qual., 30, 1474–1480.
[2] Liang, B.C., Qian, X., Liu, X.H., et al. (2018) Quantitative prediction and typical factor effects of phosphorus adsorption on the surface sediments from the intertidal zones of the Yellow River Delta, China. Mar. Freshwater Res., 69: 648-657.
[3] Huang, Y., Zhu, W., Le, M., Lu, X. (2012) Temporal and spatial variations of heavy metals in urban riverine sediment: an example of Shenzhen river, pearl river delta, China. Quatern. Int., 282, 145-151.
[4] Metaxas, A., Scheibling, R.E. (1993) Community structure and organization of tidepools. Mar. Ecol. Prog., 98: 187-198.
[5] Hisashi J. (1983) Fractionation of phosphorus and releasable traction in sediment mud of osaka Bay. B. Jpn. Soc. Sci. Fisheries, 49:447-454.