# Phosphorus Fractionation and Its Bioavailability in Panjang Island Jepara

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# Phosphorus Fractionation and Its Bioavailability in Panjang Island Jepara

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**Abstract.** Panjang Island waters located in Jepara Regency. It has rich diversities of aquatic ecosystems. Panjang Island close to the estuary of Wiso and Sampok River. Nutrient inputs from river to marine waters including phosphorus (P) affect primary productivity. A productive ecosystem is essential for nursery ground and coastal fisheries sustainability. The purposes of this research are to know the value of concentration and distribution of dissolved inorganic phosphate (DIP), the concentration of phosphorus fraction in sediment (Ads-P, Fe-P, Ca-P, TIP, Org-P, Total P) and their bioavailability. The concentration of dissolved inorganic phosphate in the water column shows different patterns where at 0.2 d; 0.6 d; 0.8 d the concentration value ranged between 0.010 µmol/l and 0.022 µmol/l; 0.005 µmol/l and 0.021 µmol/l; 0.010 µmol/l and 0.043 µmol/l. Inorganic phosphate concentrations in the sediment are larger than organic phosphates. The most abundant inorganic phosphate fraction of concentration is Ca-P. The relative abundance for inorganic phosphates follows the order of Ca-P> Fe-P> Ads-P. Concentrations of phosphate fraction in sediment for Ads-P, Fe-P, Ca-P, TIP, Org-P ranged between 0.05 and 0.30 µmol/g; 0.66 and 4.11 µmol/g; 2.9 µmol/g and 7.97 µmol/g; 3.69 and 12.48 µmol/g; 0.49 and 4.55 µmol/g. Total P (TP) has a concentration ranged between 5.13 µmol/g and 13.34 µmol/g. The potential of bioavailability of P (BAP) is 17.5 - 53.5% of TP. The concentration and the availability of P in the Panjang Island waters are influenced by various factors such as ocean current and sediment grain size.

## 1. Introduction

Panjang Island is one of the areas in the waters of Jepara Regency that has a diversity of aquatic ecosystems. These areas have a coral reef ecosystem. Coverage of coral reef at this location is between 9.45-39% [2], other than that there is a seagrass ecosystem with high seagrass cover [3] and various species that are important to the ecosystem. Panjang Island located close to the Wiso River and Sampok River where there are numerous human activities. Input from Wiso River reached 0.76 tons/month [4]. Nutrients in the ocean, especially phosphorus (P), affecting primary productivity [5][6] and has a significant impact on the biogeochemical cycle of other elements in the ocean

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ecosystem [7]. Productive ecosystems have a substantial effect on nursery ground and coastal fisheries sustainability. The impact of ocean currents resulted in phosphorus entering the waters of Jepara distributed to the Panjang Island Waters. Increasing the burden of nutrients unattended, especially P, will create ecological problems [8].

The phosphorus in the water column can be founded in dissolved and suspended form. Hydrodynamic conditions of calm waters will cause phosphorus to settle to the bottom of the sea. Sediment became the site of accumulation of phosphorus [9]. When the hydrodynamic conditions of the waters are more dynamic, the phosphorus is released back into the water column. In this condition, sediment has an essential role as the source and the loss of P in the waters [10]. Phosphorus in marine sediments in the form of organic and inorganic. The inorganic form of phosphorus is generally bound to aluminium, iron, and calcium [11]. The P bond in the sediment has a significant influence on transport, degradation, and deposition P in marine ecosystems that can be converted into bio-available after being affected by physical, chemical, and biological factors [12]. The P element in the sediment has the reactivity depending on the fraction [13][14].

Research on the concentration and distribution of dissolved inorganic phosphate (DIP) water was done by Maslukah et al. [4] while the investigation of DIP and total P in sediment in Panjang Island waters has been done before by Setiawan [16]. However, the measurement of P fraction in sediment has never been done. The analysis for phosphorus in sediments refers to the method used by modified Yamada and Kayama [17]. This method generally separated the sedimentary P into exchangeable or loosely sorbed P (Ads-P), iron-bound P (Fe-P), authigenic P (Ca-P; this includes authigenic carbonate fluorapatite, biogenic apatite and CaCO3-associated P). We also measured the amount of organic phosphorus (Org-P) dan phosphorus total (total P). Based on the samples obtained, the distribution of the P fraction, as well as the bioavailability, can be known at this location. This research is needed to support the activities in the waters of Panjang Island especially for the information about phosphorus bioavailability in sediment and water and its relation to other environmental parameters such as ocean currents, total organic carbon (TOC), and sediment grain size.

## 2. Research Methods

### *2.1. Sample Collection*

The survey was conducted in October 2017 in Panjang Island Waters. The sample location is determined by purposive sampling method of 8 stations. Water samples were taken by using Nansen bottles. Water samples were taken at three depths, the water surface, the middle of the water column, and near the bottom of the water. Sediment samples were taken with Grab sediment. In addition, the environmental conditions such as pH water, salinity, temperature, DO (dissolved oxygen), sediment and pH were measured also.

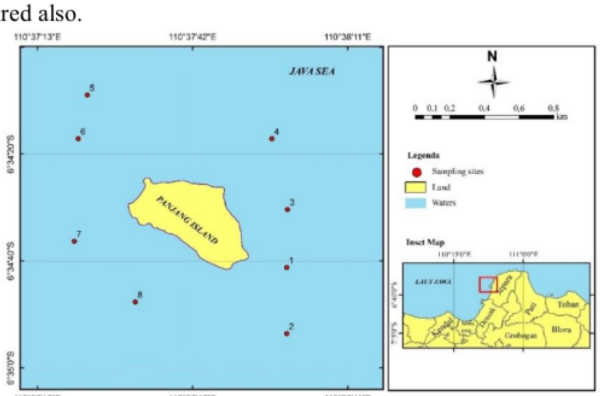


**Figure 1.** Study Area of Panjang Island Waters

### *2.2. Analysis of water and sediment sample*

Dissolved inorganic phosphate concentration was analysed by using spectrophotometric phosphomolybdate blue [18]. Ammonium molybdate and potassium antimony tartrate react in an acid medium with orthophosphate to form a heteropoly acid – phosphomolybdic acid – that is reduced to intensely colored molybdenum blue by ascorbic acid. Absorbance of the (blue) solution was measured at 880 nm. Samples of dried sediments were analysed by grain size. Dried sediments were analysed based on the sediment fraction. Sand and gravel fractions were determined solely by sieve analyses, and silt and clay fractions were determined by pipette methods.

The phosphorus fraction was analysed using sequential extraction modification method by Yamada and Kayama [19] to obtain the Ads-P, Fe-P, and Ca-P fractions. About 0.5 g of homogenized sediment was weighed and loaded into centrifuge tube, and Ads P extracted with 0.5 M $NH_4Cl$. The sediment residue was washed twice with high purity water and sediment residue was extracted with 0.1 M NaOH as Fe-P. After this process, the sediment residue was washed with high purity water. The sediment residue was extracted with 0.25 M $H_2SO_4$ as Ca-P. The detailed processes are shown in Figure. 2. TIP extracted with 1 M HCl for 24 hours. Concentration of Org-P was measured as the difference of between 1 M HCl extractable P (24 h) before and after high temperature combustion (550°C, 2 h) of the sediment [20]. The concentration of bioavailable P (BAP) in the sediment is the sum of Ads-P, Fe-P, and Org-P [21][22]. Total phosphorus (TP) content was the sum of OP and inorganic phosphorus (IP) contents [13][23]. All extracted P were determined directly using the spectrophotometric phosphomolybdate blue method [18]. The method used to measure TOC's in sediments using the Loss-On Ignition (LOI) method.

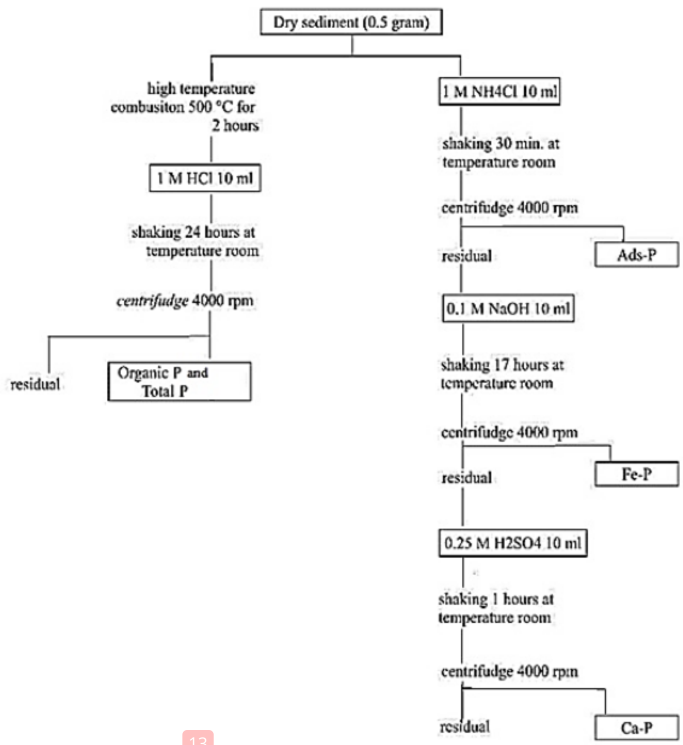


**Figure 2.** Flow diagram for the sequential extraction of various forms of phosphorus in sediments modified from Yamada and Kayama [19]

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## 3. Result and Discussion

Water quality parameters show the temperature in the survey area ranged from 29.8 °C to 30.8 °C, salinity between 30 ppt and 35 ppt, pH between 7.52 and 8.04, and DO between 4.32 and 5.16 ppm. Water depth ranges from 8 to 11.8 m. The results are shown in Table 1.

**Table 1**. Water Quality Parameters

| Station | Temperature (°C) | Salinity (ppt) | pH | DO (ppm) | Depth (m) |
|---|---|---|---|---|---|
| 1 | 30.5 | 30 | 7.98 | 5.16 | 9 |
| 2 | 30.7 | 31 | 7.52 | 4.62 | 9.4 |
| 3 | 29.8 | 33 | 7.54 | 4.4 | 8 |
| 4 | 30.6 | 35 | 8.03 | 4.53 | 9.1 |
| 5 | 30.7 | 34 | 7.92 | 4.96 | 11.8 |
| 6 | 30.8 | 33 | 8.02 | 4.32 | 10.7 |
| 7 | 30.7 | 35 | 7.65 | 4.87 | 11.1 |
| 8 | 30.6 | 35 | 8.04 | 4.36 | 10.3 |

**Table 2.** Characteristics of Surface Sediment from Panjang Island Waters

| Station | Percentage of Sediment Fraction | | | pH | TOC (%) |
|---|---|---|---|---|---|
| | *Sand (%)* | *Silt (%)* | *Clay (%)* | | |
| 1 | 0.2750 | 96.490 | 3.2349 | 6.9 | 17.34 |
| 2 | 3.7000 | 91.785 | 4.5147 | 6.7 | 10.84 |
| 3 | 97.6906 | 2.159 | 0.1504 | 6.6 | 6.87 |
| 4 | 99.7585 | 0.195 | 0.0466 | 6.9 | 10.37 |
| 5 | 1.1500 | 93.542 | 5.3084 | 6.8 | 14.86 |
| 6 | 99.4772 | 0.469 | 0.0539 | 6.9 | 8.06 |
| 7 | 0.9500 | 97.897 | 1.1531 | 6.7 | 12.58 |
| 8 | 1.9000 | 93.692 | 4.4075 | 6.8 | 10.22 |

The result of sediment grain size analysis showed that sediment fraction in Panjang Island is dominant of silt and sand. Stations 3, 4, and 5 are dominated by sand while stations 1, 2, 5, 6, 7, and 8 are dominated by silt. Sedimentary pH ranges from 6.5 to 6.9. The percentage of TOC levels ranged from 6.87% to 17.34%. The sediment quality parameters are shown in Table 2.

The distribution of sediments at the study sites is relatively variable because the result of a complex interaction between the hydrodynamic process and the geomorphological conditions. Silt sediment dominates the area to the south of the island. Geographically, this location is more protected from the influence of ocean currents coming from the open sea because it is behind the island. Ocean currents with higher speed will slowly decline and weaken. Sediment deposition of silt and clay fractions occurs due to a weak hydrodynamic process [24]. While, sand dominates stations 3, 4, and 6 because they are directly affected by offshore. This can be attributed to ocean currents and waves that cause continuous turbulence in the water column. This condition prevents the finer sedimentary particles from settling. A more dynamic hydrodynamic process leads to sand dominance at the research station [24][25]. However, at station 5 the dominance of sediment is silt when the location is directly opposite to offshore. This is because station 5 has the deepest bottom waters compared to other sites. The deeper the bottom of the seas, the dynamics of the water column on the bottom of the seas is not very significant.

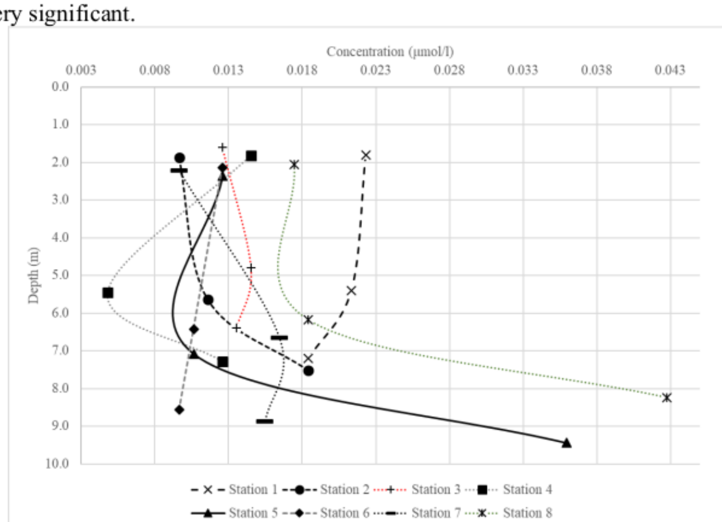
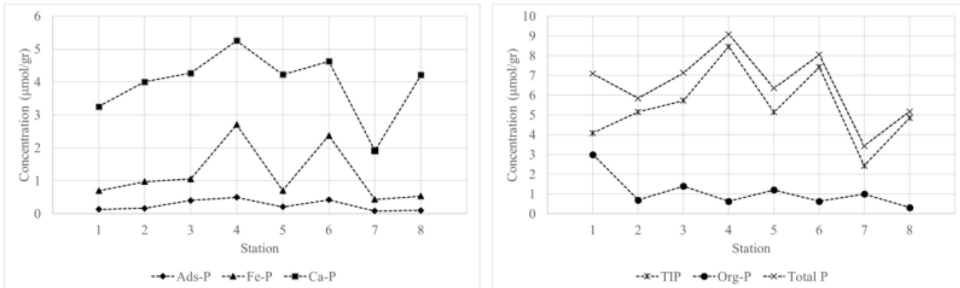



**Figure 3.** Fluctuation of DIP Concentration in Panjang Island Waters, Jepara

The DIP concentration analysis results are shown in Figure. 3. Concentrations ranged from 0.010 µmol / l - 0.022 µmol / l at depths of 1.6 m - 1.3 m; 0.005 µmol / l - 0.021 µmol / l at a depth of 4.8 m - 7.1 m; and 0.010 µmol / l - 0.043 µmol / l at a depth of 6.4 m - 9.4 m. In general, the highest DIP concentration is at a depth of 0.8 d. High DIP concentration is due to close to the bottom of the sea. Sediment is one of the P contributors to the ocean [25]. When turbulence occurs in the water column, the P bound in the sediment will be released into the water column. The closer to the bottom of the water, the concentration of P in the water column will be higher. DIP concentrations at depths of 0.6 d and 0.2 d show at every depth relatively high at station 1. The position of station 1 is closest to the Wiso River. Wiso River is one of the major rivers in Jepara that carry many nutrients. This causes the P concentration in Panjang Island to obtain much nutrient input from Jepara that brings domestic waste from agriculture, industry and fisheries

The concentration obtained from the analysis of P fraction in sediment for Ads-P is between 0.05 and 0.30 µmol / gr with the highest concentration in station 4 and the lowest at station 7. The concentration of Fe-P fraction between 0.66 and 4.11 µmol / g with the highest level at station 4 and the lowest at station 7. The Ca-P fraction has the highest concentration value of 7.97 µmol / gr at station 4, and the lowest is 2.90 µmol / gr at station 7. TIP has a range of concentration values between 3.69 and 12.48 µmol / g with the highest concentration at station 4 and the lowest at station 7. The concentration of Org-P is between 0.49 and 4.55 µmol / g with the highest concentration at station 1 and lowest in station 8. Total P has the highest concentration range of 13.34 µmol / g at station 4 to lowest 5.13 µmol / g at station 7 (see **Figure** 4 and 5).




(a) (b)

**Figure 4.** (a) Fluctuations in the Fractions of Ads-P, Fe-P, and Ca-P in Sediments (b) Fluctuations in TIP, Org-P, and Total P Fractions in Sediment

The percentage of Ca-P fraction is most dominant compared to the other P fraction whereas the Ads-P fraction is the fraction of P with the lowest rate. Inorganic P in sediment has more concentration than organic P. Station 4 has an inorganic percentage of P higher than other stations, while station 1 is the lowest (**Figure** 6).

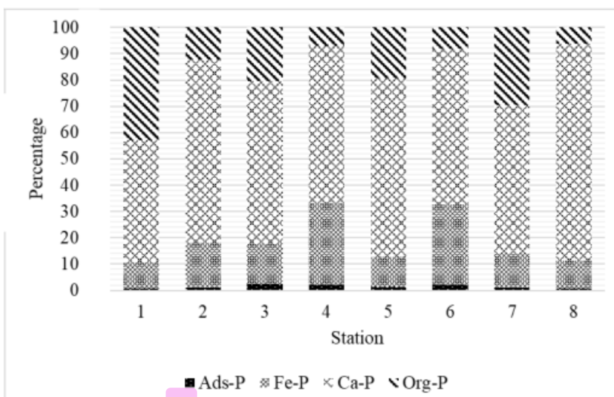
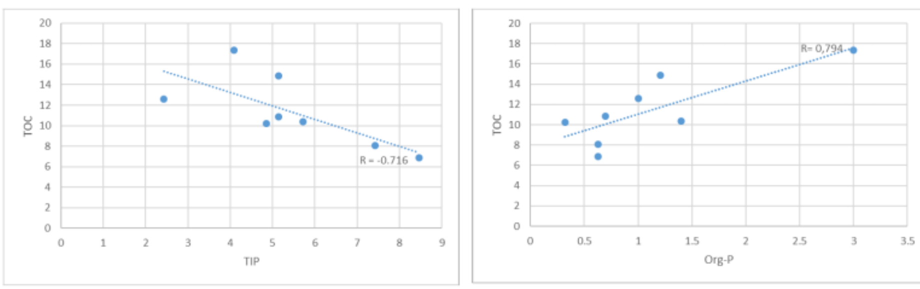



**Figure 5.** Relative Percentage of Al-P, Fe-P, Ca-P, and Org-P Fractions on Sediments in Panjang Island Waters, Jepara

The results of this study indicate that the most abundant fraction of concentration is Ca-P. Its relative abundance for inorganic P follows the order of Ca-P> Fe-P> Ads-P (Figure 5). The previous study by Saravi et al. [10] in the Caspian Sea Sea, Bramha et al. [25] in the Kalpakkam Coast and Yamada and Kayama [19] in Seto Inland Sea Japan showed the tendency of Ca-P concentrations in the most abundant sediments compared to the other P fractions. Ca-P is generally derived from residual bones and teeth of dead marine organisms [23]. P that binds to $CaCO_3$ and autothermal carbonate fluorapatite (CFA) settles in sediment [26] where fluorapatite is the strongest mineral binding to other compounds so the concentration is found to be the most abundant of the different fractions. The waters of Panjang Island, Jepara, and surrounding areas are areas with high fisheries and shellfish production. The remains of these marine organisms contain the large amounts of apatite detrital that are likely to bind to P and settle in the sediments. The highest concentration of Ca-P is in station 4 then followed by station 6. This is because on sediment samples taken in the field for stations 4 and 6 are many remaining shells that are degraded and cause bond with P.

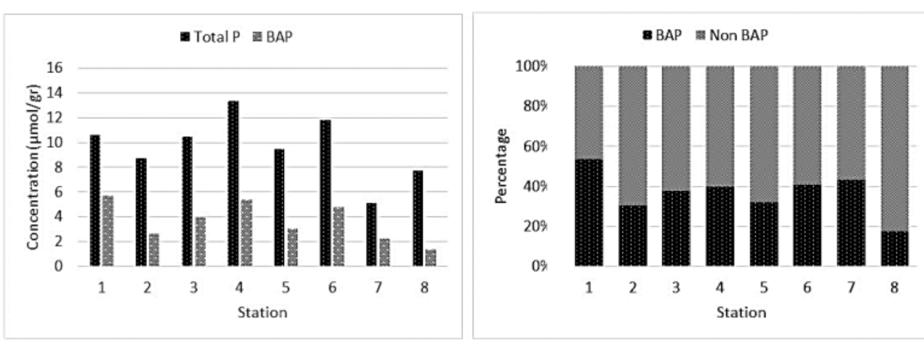
Ads-P is a fraction of P that can be used directly by phytoplankton. Physical-chemical factors in the waters including pH, temperature, and hydrodynamic conditions that may encourage the release of Ads-P into the water column [27]. This study shows the fraction of Ads-P percentage is smallest compared to the other fraction of total inorganic P. A study by Yang et al. [26], Zhuang et al [23], and Saravi et al. [10] showed the relative percentage of Ads-P is smallest compared to other inorganic phosphate fractions. The Ads-P concentration was found to be high at stations 4 and 6 with the dominance of grain size of sand sediments. This is not in accordance with the research that has been done by Meng et al. [13] which states that the high concentrations of the Ads-P fraction in sediments are affected by grain size in the increasingly fine. However, sampling conducted at high tide conditions where ocean currents are at the highest speed causes turbulence at the bottom of the waters causing the release of Ads-P into larger water columns. This is in accordance with Vicente et al. [28] which stated the hydrodynamic conditions in the waters will affect the release of phosphate from sediment into the water column The Fe-P fraction has a concentration fluctuation similar to the Ca-P fraction. The high concentration of Fe-P fraction followed by high Ca-P. According to Zhang et al. [29]. Fe-P is an important indicator of P displacement in the waters. Inorganic P unstable in waters will become stable when associated with iron oxyhydroxide. In the associated sediment between P and iron occurs with a large amount in which iron absorbs P strongly [30].




(a) (b)

**Figure** 6. (a) Correlation between TOC and TIP (b) Correlation between TOC and Org-P

The correlation between Org-P and TOC is relatively high compared to other P fractions with r = 0.631 (Figure 6), suggesting that organic matter plays important role in shaping the concentration of P fractions in sediments. So, in Panjang Island Waters, it is assumed that the tendency of high Org-P concentration will be followed by high TOC proportion.




(a) (b)

**Figure** 7. (a) The Comparison between The Concentration of BAP and P total, (b) The Relative Percentage of BAP to The P Total

In this study, the concentration of BAP ranged between 1.36 and 5.7 µmol/g. The BAP accounted about 17.5 - 53.5% of TP (Figure 7). Compared with the proportion of BAP in TP surface sediments in the South China Sea [26] showed the percentage ranged from 20.3% to 54.2% and Southern Caspian Sea [19] ranged from 32.57% to 42.65%. This result indicated a similar rate with other studies. However, in general, the concentration of BAP in the waters of Panjang Island is lower than in other research areas. This condition happens because the phosphate source in this region is not as high as in other areas. One of the factors is the level of phosphate pollution in this region is still within safe limits. The BAP indicates that the upper threshold of the removable P into the water column under appropriate environment of physical and chemical conditions including Ads-P, Fe-P and Org-P in sediments [13]. When BAP is released into the water column, the primary productivity will simultaneously increase [21]. The concentration of BAP in the east of the island is higher than in the west of the island. It can be indicated that the input of rivers from Jepara is a source of important P for the ecosystems [26].

## 4. Conclusion

The concentration of dissolved inorganic phosphate in the water column shows the different patterns where at 0.2 d; 0.6 d; 0.8 d the concentration value ranged between 0.010 µmol/l and 0.022 µmol/l; 0.005 µmol/l and 0.021 µmol/l; 0.010 µmol/l and 0.043 µmol/l. DIP concentration found higher near the bottom of the water. Inorganic P concentrations in the sediment are larger than organic P. The most abundant inorganic P fraction of concentration is Ca-P. The relative abundance for inorganic P follows the order of Ca-P> Fe-P> Ads-P. Concentrations of P fraction in sediment for Ads-P, Fe-P, Ca-P, TIP, Org-P ranged between 0.05 and 0.30 µmol/g; 0.66 and 4.11 µmol/g; 2.9 µmol/g and 7.97 µmol/g; 3.69 and 12.48 µmol/g; 0.49 and 4.55 µmol/g. Total P (TP) has a concentration ranged between 5.13 µmol/gr and 13.34 µmol/gr. The concentration of BAP ranged between 1.36 and 5.7 µmol/gr. The BAP accounted about 17.5 - 53.5% of TP.

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