



## Characteristics of Phosphate Sorption on Surface Sediments: A Study in Kendari Bay

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**Abstract:** Phosphate adsorption and desorption are significant processes that influence the presence of phosphate in aquatic ecosystems and regulate the concentration of phosphate at the water-sediment interface. This research aims to investigate the characteristics of phosphate adsorption and desorption in Kendari Bay sediments, study the relationship between adsorption capacity and sediment characteristics and its phosphorus fraction, and evaluate its potential contribution to the overlying water column. Physicochemical measurements of the water and sediments were performed in the sampling location and the laboratory. Two types of adsorption-desorption kinetics models and two types of isothermal adsorption models were used to estimate the adsorption rate and capacity of the surface sediments. Adsorption kinetics and desorption kinetics experiments produced pseudo-second-order kinetic model equations with regression coefficients ( $R^2$ ) of 0.865–0.936 and 0.886–0.947, respectively. The isothermal adsorption experiment follows the Langmuir equation model with  $R^2 = 0.964$ . The maximum adsorption capacity ( $Q_{\max}$ ) value was 156.3–227.3 mg/kg, and the phosphate concentration value at zero equilibrium ( $EPC_0$ ) was 0.0026–0.0047 mgP/L. Notably, the  $EPC_0$  value was higher than the SRP concentration, indicating that the resuspension of phosphate ions from sediment into the water column could occur. Furthermore, there was a correlation between  $Q_{\max}$  values with OP, Al-P, Fe-P, clay particles, and organic materials. Potential practical applications may include integrating sediment adsorption capacity data into ecosystem models to inform nutrient management strategies and promote sustainable coastal development in Kendari Bay and beyond.

**Keywords:** phosphate adsorption, desorption kinetics, water-sediment interface, coastal development, Kendari Bay

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### 1. Introduction

Phosphorus is one of the anthropogenic pollutants that causes eutrophication. Eutrophication can trigger the growth of algae, thereby reducing water quality, which has become a serious threat over the last few decades (Axinte *et al.*, 2015). This phenomenon can result in reduced biodiversity due to reduced dissolved oxygen content. Dissolved inorganic phosphorus (DIP) is a

phosphorus fraction that is easily utilized by algae and is a rate-limiting nutrient for phytoplankton primary productivity (Wang *et al.*, 2018). Particulate inorganic phosphorus is in the mineral phase, which is the result of DIP adsorption by particles in the water.

As a crucial element for life on earth, phosphorus regulates a variety of biogeochemical reactions in freshwater and marine systems. Phosphorus in water exists in

dissolved and particulate forms. Particulate phosphorus compounds can be found in the form of calcium salt (Ca-phosphate), iron (Fe-phosphate) or complex salts of aluminum (Al-phosphate), and organic phosphorus (OP) (Bramha *et al.*, 2014). Phosphorus dissolved or soluble reactive phosphorus (SRP) is commonly known as orthophosphate. Orthophosphate is a form of phosphate that can be used directly by phytoplankton. Loosely adsorbed P is often referred to as exchangeable P. Mobilization of particulate P in a form available to phytoplankton occurs through organic matter degradation, desorption, and mineral dissolution reactions.

In the water column, the phosphate ions will interact with the surrounding particles (Maslukah *et al.*, 2017). Naturally, the phosphate ions bind to particles by adsorption, leading to larger aggregates and deposition (Zhang *et al.*, 2015). The phosphate ions will be released into the water column below by a desorption process if the ambient conditions of the water change (pH, oxygen content, salinity). Therefore sediments can act as a source of internal phosphorus.

The hazardous potential of phosphorus in sediments is related not only to the total phosphorus (TP) content, but also to the presence of other fractional forms of phosphorus in the sediments. The adsorption-desorption characteristics of phosphate are mainly influenced by the physicochemical characteristics of the sediment, the phosphorus fraction, and the water column at the sediment-water interface. Sediments with different characteristics have different adsorption characteristics. The form of the phosphorus fraction plays a significant role as a cause of the eutrophication of water bodies (Gerard, 2016; Wang *et al.*, 2015). Other studies have reported that pH, macro elements, particle size, and organic matter have an impact on the adsorption of phosphate ions in soil and sediment (Zhu *et al.*, 2015; Cao *et al.*, 2016).

Kendari Bay which is located in Southeast Sulawesi, has significant potential as a habitat for various organisms that live in the aquatic. Around 13 rivers in the city of Kendari flow into the bay area, including the Wanggu River and the Kambu River. Various anthropogenic

pollutants resulting from activities along river basins are carried through river flows or urban drainage to the bay area. As a result, the waters of Kendari Bay have become a place for the accumulation of pollutants, including phosphorus and macro elements, especially iron (Armid *et al.*, 2017; Asriyana and Irawati, 2019).

Several studies in Kendari Bay have only studied the processes of sedimentation, trophic status, heavy metals pollution and water quality (Armid *et al.*, 2017; Asriyana and Irawati, 2019; Alfiani *et al.*, 2019; Makkawaru *et al.*, 2021). Adsorption and desorption are important processes and factors that influence the presence of phosphate in aquatic ecosystems and control their concentration at the water-sediment interface (Zhang *et al.*, 2015; Li *et al.*, 2017). Therefore, the study of phosphate adsorption-desorption is crucial to identifying the source phosphate in the sediment. The objectives of this study are to investigate the phosphate adsorption-desorption in Kendari Bay sediments, analyze the correlation between adsorption capacity with sediment characteristics alongside phosphorus fraction, and evaluate the potential for phosphate release into the overlying water column.

## 2. Materials and Methods

### 2.1. Time and Location of Research

The study was carried out from May 2022 to October 2022 and consisted of in situ observations, laboratory analysis, and laboratory experiments. Samples were taken in Kendari Bay, Southeast Sulawesi, using a purposive sampling method which considered that the sampling location was influenced by rivers, especially large rivers (Wanggu River and Kambu River) and the areas connected to the open sea. Therefore, five sampling points have been selected, three sampling points were located near the river mouth (TK.1, TK.2, and TK.3) and two sampling points were located near the bay's mouth or the open sea (TK.4 and TK.5). Geographically, Kendari Bay is located at 3°57'59.37" N, 3°59'32.39" S, and 122°31'38.07" E, 122°35'55.93" W (Figure 1). The experiment of adsorption-desorption and sample analysis was carried out at the Genomics Laboratory and Sedimentation

Laboratory, National Research and Innovation Agency (BRIN), Cibinong, Indonesia.

## 2.2. Water sampling and analysis

The water samples were the water collected from the sediment-water interface. Physicochemical parameters such as pH, Dissolved Oxygen (DO), salinity, and turbidity were measured in situ using a water quality checker. Water samples were collected using a water sampler and then filtered using 0.45  $\mu\text{m}$  pores filter paper to determine the concentration of orthophosphate or Soluble Reactive Phosphate (SRP) and as a material for adsorption-desorption examinations.

The sediment samples were taken using a Wildco Petite Ponar Grab with a capacity of 2.4 liters and stored in tightly closed bags at a cold temperature ( $\pm 4$  °C) during the trip to the laboratory. In the laboratory, the sediment sample was dried in the oven at 40 °C for two days, ground, and sieved until a dry sediment

of  $< 2$   $\mu\text{m}$  was obtained. The fine sediments were used for the analysis of particle composition (sand, silt, and clay), Organic Matter (OM), macro element content (iron (Fe), aluminum (Al), and calcium (Ca), Mangan (Mn)), phosphorus fractioning, and adsorption-desorption experiments. Sediment particles were analyzed using the hydrometry method in the technical guide for soil/sediment analysis (Eviati and Sulaeman, 2009).

The organic matter content was analyzed using the Gravimetry method (Mucha *et al.*, 2003). The macro elements composition was analyzed by the method of Atomic Adsorption Spectroscopy (AAS) with wet deconstruction (U.S. EPA, 1996). Phosphorus fractioning uses chemical extraction and sequential methods (Yilmaz *et al.*, 2012).

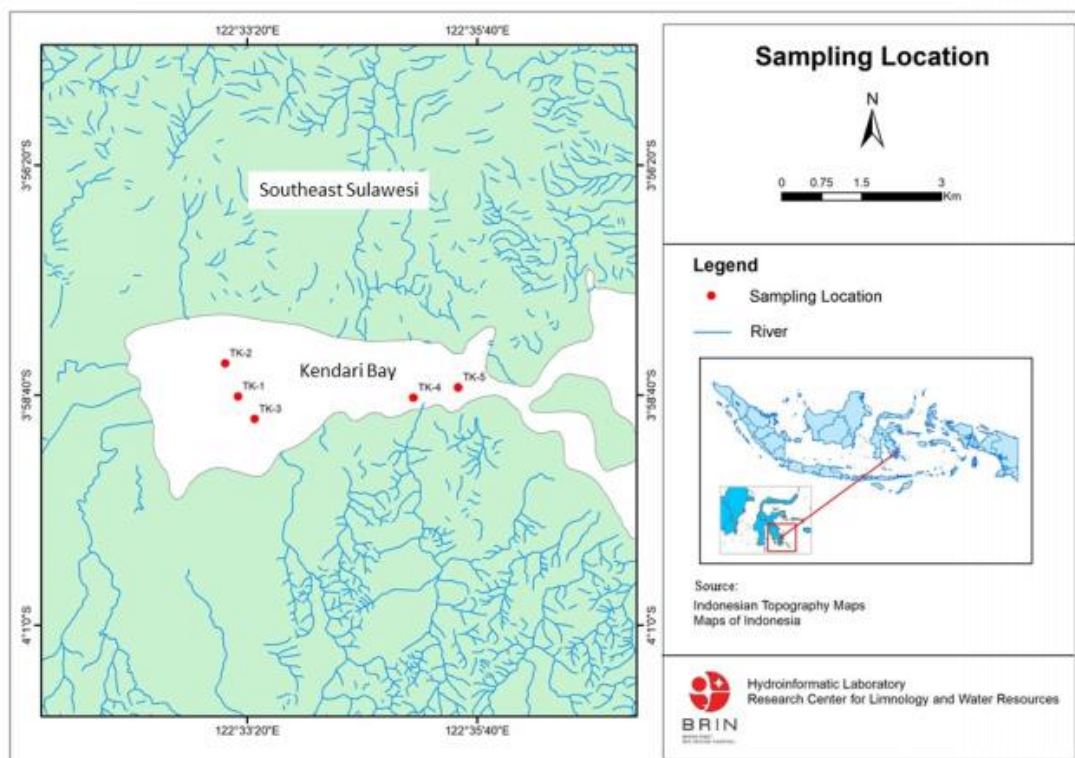


Figure 1. Map of sampling location in Kendari Bay, Sulawesi Island, Indonesia

### 2.2.1. Adsorption-desorption kinetics experiments

Adsorption-desorption kinetics experiments for all samples were carried out according to the method used by Wang *et al.*, (2018). 0.5 g of dry sediment samples and 25 ml of 1 mgP/L solution were placed in a series of 125 mL

conical flasks and mixed well using a shaker at  $25 \pm 1$  °C with a speed of 150 rpm for different time intervals (0; 0.25; 0.5; 1; 2; 4; 6; 10; 24; 36; 48; and 60 hours). As an inhibitor of bacterial activity, 1–2 drops of Chloroform were added to the sample solution. 15 ml of suspension solution was

separated using a centrifuge for 15 minutes at a speed of 5,000 rpm. The supernatant was filtered with 0.45  $\mu\text{m}$  pore filter paper and analyzed as SRP. The phosphate adsorption rate by sediment was obtained by entering the SRP concentration value into the *pseudo-first-order* and *pseudo-second-order* kinetic model equations.

The *pseudo-First-Order Model* assumes that in this model, the rate of adsorption at time  $t$  is proportional to the difference between the equilibrium amount adsorbed  $Q_e$  and the amount adsorbed at this instant  $Q_t$  and that the adsorption is reversible. The constant rate is given in the following Equation 1, by Lagergren (Ho and McKay, 1999):

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t, \quad \dots(1)$$

where  $Q_t$  is the amount of phosphorus adsorbed at the instant ( $t$ ) (mg/g),  $Q_e$  is the amount of phosphorus adsorbed at equilibrium (mg/g), and  $k_1$  is the pseudo-first-order rate constant of adsorption ( $\text{min}^{-1}$ ).

*Pseudo-Second-Order Model* characterizes the adsorption kinetics, by considering both the case of rapid solutes fixation on the most reactive sites and that of a slow fixation on the low-energy sites. This model suggests the existence of a chemisorption. The expression of the pseudo-second-order reaction model was obtained by the equation proposed by Ho and McKay (1999):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t, \quad \dots(2)$$

where  $k_2$  is the pseudo-second-order rate constant of adsorption ( $\text{g/mg/min}$ ). From Equation 2, the adsorbed quantity at equilibrium  $Q_e$  and the pseudo-second-order constant  $k_2$  can be determined experimentally from the slope and the ordinate at the origin of  $t/Q_t$  as a function of  $t$ .

Desorption kinetics experiments were carried out by serially mixing 0.5 g of dry sediment samples and 25 ml of 1 mg P/l solution into a 125 ml Erlenmeyer flask and 1–2 drops of chloroform as an inhibitor of bacterial activity. Next, the sample solution

was shaken using a rotary shaker at room temperature ( $25 \pm 1$  °C) at a speed of 150 rpm for 36 hours. The suspension solution was separated using a centrifuge at 5000 rpm for 15 minutes and filtered using filter paper with a 0.45  $\mu\text{m}$  pore. The residue was added with 25 ml of ion-free water and shaken again with a rotary shaker for different intervals (0, 0.25, 0.5, 1, 2, 4, 6, 10, 24, 36, 48, and 60 hours). A total of 15 ml of suspension solution was separated using a centrifuge for 15 minutes at a speed of 5000 rpm. The supernatant was filtered with 0.45  $\mu\text{m}$  pore filter paper and analyzed as SRP. The rate of phosphate adsorption by sediment was obtained by entering the SRP concentration value into the pseudo-first-order and pseudo-second-order kinetic model equations.

### 2.2.2. Isotherm phosphate adsorption

Isothermal adsorption experiments using a modified Wang *et al.* (2018). A sample of water from the study site was filtered using Millipore 0.2  $\mu\text{m}$  filter paper. A quantity of 0.5 g of dry sediment is weighed into Erlenmeyer 100 ml and 40 ml of water samples have been added to  $\text{KH}_2\text{PO}_4$  solution with concentration variations of 0; 0,1; 0,25; 0,5; 1,0; 2,0; 4,0; 6,0; 8,0 mg P/l. All suspension solutions are shaken using an orbital shaker at room temperature at a rate of 150 rpm for 24 hours. A total of 15 ml of the suspension is centrifugated for 15 minutes at a speed of 5000 rpm, filtered using Millipore 0.45  $\mu\text{m}$  filter paper, and analyzed as SRP. The sediment adsorption capacity was obtained by putting the SRP concentration values into the Freundlich and Langmuir isothermal equation model. The equations are described in Equations 3 and 4 respectively:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad \dots(3)$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m}, \quad \dots(4)$$

where  $K_F$  is the Freundlich adsorption constant ( $\text{mg/g}$ ) ( $\text{L/mg}$ ) $^{1/n}$ ,  $n$  is the intensity factor,  $Q_m$  is the maximum adsorption capacity ( $\text{mg/g}$ ), and  $K_L$  is the Langmuir adsorption constant ( $\text{l/mg}$ ).

### 2.3. Data analysis

The Pearson Correlation analysis was used to perform a quantitative assessment of the relationship between the adsorption-desorption phosphate parameters and sediment characteristics. Minitab version 16 software was utilized for further comprehensive data analysis on the potential dependencies and interactions within the studied variables, aiding in understanding the underlying patterns and dynamics governing phosphate behavior in the sediment system.

## 3. Results and discussion

### 3.1. Water physicochemical properties

The result of measurement for the physicochemical parameters in the water-sediment interface of Kendari Bay is shown in Table 1. The data revealed that the normal temperature values for tropical waters ranged from 30.0 °C to 30.9 °C, and the pH of water tends to be alkaline, ranging from 8.8 to 9.1 ( $8.97 \pm 0.12$ ). The concentration of dissolved oxygen was low even though it was still in

aerobic condition with a range of 2.6 mg/L to 4.0 mg/L, while the SRP concentration value was very low ( $<0.001$  mg/L). The values were lower than in the previous study in the same location (Asriyana and Irawati, 2019)

The pH parameter is significant in the adsorption process because it affects the bond between phosphate ions and the surface of the sediment. On the alkaline condition, the sediment surface will be dominated by negatively charged ions, consequently, it will tend to be more repellent to phosphate ions. The average pH value was in the range of 8.82 to 9.12. The relatively high pH value is thought to be due to the presence of  $\text{CaCO}_3$ , which originates from biogenic apatite and carbonate fluorapatite (CFA) compounds. These compounds come from the bones and teeth of dead marine organisms (Zhuang *et al.*, 2014). In the presence of carbonate compounds, a high pH value will cause phosphate adsorption or coprecipitation with carbonate (Omari *et al.*, 2019).

Table 1. The average value and standard deviation of the physicochemical characteristic of the water at Kendari Bay

Location	TK.1	TK.2	TK.3	TK.4	TK.5
Temperature (°C)	30.1±0.09	30.9±0.11	30.2±0.09	30.1±0.09	30.0±0.10
pH	8.9±0.08	8.8±0.09	8.9±0.09	9.0±0.08	9.1±0.09
Salinity (ppt)	16.3±1.54	17.7±1.87	16.5±2.01	16.6±1.98	16.5±2.41
DO (mg/L)	4.00±0.82	3.75±1.03	3.25±0.95	3.65±0.71	2.60±0.63
SRP (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001

The low SRP value is also supported by the salinity concentration value. Ca bonds with phosphate ions will be stable and easily released into the water column because Ca will not dissolve in environmental conditions with high salinity (Van Diggelen *et al.*, 2014). The DO values ranging from 2.6 to 4.0 mg/L indicated that it was still in an aerobic condition where it was allowing phosphate ions to bind to metal oxides.

### 3.2. Sediment physicochemical - properties

The results of sediment functional group analysis at five locations showed that TK.1, TK.2, TK.3, and TK.5 create nearly identical

spectrum profiles. However, TK.4 has a slightly different spectrum profile (Figure 2). The spectrum located between  $3600\text{ cm}^{-1}$  to  $3700\text{ cm}^{-1}$  is the O-H group, which indicates the presence of clay minerals (Veerasingam and Venkatachalapathy, 2014). The spectrum located at  $3393\text{ cm}^{-1}$  was thought to be the amine and amide groups of organic compounds containing nitrogen (N).

The appearance of the  $1634\text{ cm}^{-1}$  spectrum confirms the presence of C=C and C=O groups originating from biological materials (Veerasingam and Venkatachalapathy, 2014). The peak from  $900\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$  was thought to be related

to Al-OH bending and Si-O stretching vibrations of eroded silicate layers, particularly illite and kaolinite, whereas the spectral band from 693 cm<sup>-1</sup> to 776 cm<sup>-1</sup> is associated with the presence of quartz grains (Veerasingam and Venkatachalapathy, 2014).

The results of sediment particle size analysis showed the composition of sand, silt, and clay particles as shown in Figure 2. The silt fraction was the most dominant sediment particle, with an average percentage in the range of 74.8% to 79.25%. The distribution of silt particles is evenly distributed throughout all sampling locations.

The abundance of finer sediments at all sites reflects relatively weak hydrodynamic

energy (Vicente *et al.*, 2016). In research conducted by Putra *et al.* (2021), the current velocity value in the area of Kendari Bay is relatively lower compared to the outside area of the bay, with an average value of 5.26 cm/second. This showed that the hydrodynamic energy in Kendari Bay was relatively weak. This condition is supported by the morphometry of Kendari Bay, which resembles an estuary where processes such as flocculation occur more intensely due to reduced turbulence so that finer sediment is dominant (Vicente *et al.*, 2016), as shown in Table 2.

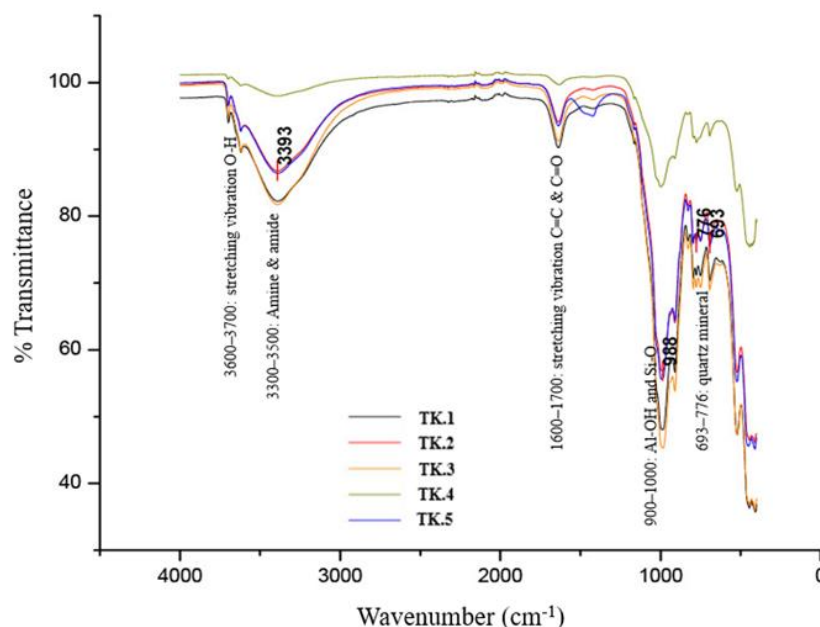


Figure 2. Collection of ATR-FTIR spectra from surface sediments at five sampling locations in the waters of Kendari Bay. Instrument conditions: nominal resolution of 4 cm<sup>-1</sup> and 16 accumulated scans per adsorption band. The color of the lines indicates the sampling points: TK.1 (black), TK.2 (red), TK.3 (orange), TK.4 (light green), and TK.5 (blue).

The differences in the particle compositions in the sediment will result in differences in the ratio of surface area to mass. Li *et al.* (2021) reported that sediment particles with a finer size (silt and clay) have a larger surface-to-mass ratio when compared to larger particles, thus providing a greater adsorption capacity.

The dominance of the fine particle size of Kendari Bay sediments supports the high concentration of organic matter at this research location, which ranges from 25.16%

to 68.44% (Table 2). This phenomenon was reported by Meng *et al.* (2014) and Simanjuntak *et al.* (2020), who found that sediments with a high proportion of fine particles tend to have a high organic material content. Figure 3. shows the relationship between organic matter and fine sediment particles, with a value of  $R^2 = 0.9068$ .

The results of macroelement analysis show that Fe is the element with the highest concentration compared to other macroelements, with values ranging from

5.496 to 9.077 mg/g (Table 2). This phenomenon was similar, as reported by Armid *et al.* (2017), at the same locations. The high Fe content in the waters of Kendari Bay is influenced by rivers entering the bay area, which carry anthropogenic pollutants, which originate from untreated mining and industrial

waste. According to the CBSSS (2015), as many as 136 ore mining companies is operating in North Konawe, Konawe, and South Konawe Regencies, where the entire district is crossed by the Wanggu River (Armid *et al.*, 2017).

Table 2. The average and standard deviation of physicochemical characteristics of surface sediments at Kendari Bay

Location	TK.1	TK.2	TK.3	TK.4	TK.5
Sand (%)	3.8±1.93	2.8±1.74	2.9±1.54	7.8±2.71	4.5±2.32
Silt (%)	76.3±1.76	77.7±1.82	75.8±1.67	79.3±1.97	74.8±1.46
Clay (%)	20.0±3.43	19.4±3.17	21.3±3.95	12.9±2.56	20.7±3.73
Org. matter (%)	68.4±21.81	62.6±17.50	64.4±20.82	25.2±77.45	57.9±19.89
Al (mg/g)	0.268±0.12	0.125±0.06	0.210±0.07	0.088±0.02	0.230±0.10
Ca (mg/g)	2,408±0,98	1,737±0,31	2,422±1,21	2,182±0,52	4,100±1,37
Fe (mg/g)	9,077±2,50	5,498±1,90	5,570±2,21	4,520±1,18	5,100±1,41
Mn (mg/g)	0.292±0.18	0.166±0.13	0.320±0.21	0.066±0.01	0.480±0.28

Macroelements such as Fe, Mn, Al, and Ca play important roles in the cycle of phosphorus compounds in water. Additionally, these elements play a role in the adsorption and desorption of phosphate ions in sediments. The iron content in Kendari Bay sediments was significantly higher when compared to other oligotrophic coastal waters in Indonesia, such as Jepara coastal waters in Central Java (Maslukah *et al.*, 2019)

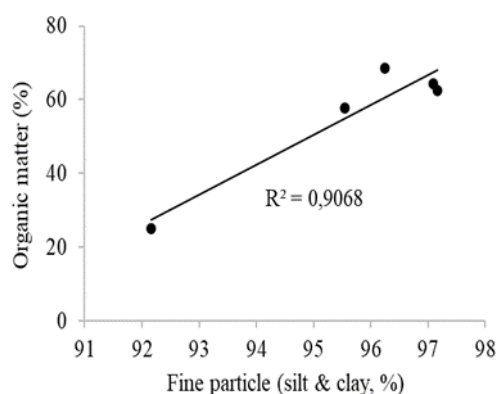


Figure 3. Relationship between fine sediment fraction and organic matter content

The concentrations of Mn and Al were in the range from 0.066 mg/g to 0.480 mg/g and 0.88 mg/g to 0.268 mg/g dry sediment, respectively. Meanwhile, the concentration of Ca was the second highest concentration after

Fe, in the ranges from 0.737 mg/g to 4.100 mg/g of dry sediment. Ca can bind phosphate ions to form apatite mineral deposits. Phosphate ions that bind to Ca will be more occluded and dissolved when the pH of water is lower. Meanwhile, the oxidized Fe, Mn, and Al will fall to the bottom of the bay in the solid form of sediment or minerals that have high adsorption capacity for phosphate ions. Therefore, these elements play an important role in the phosphorus cycle at the sediment-water interface.

### 3.3. Phosphorus fractions

The fractionation of phosphorus compounds in sediment is an important parameter to estimate the internal input of phosphorus compounds into the water column. Vicente *et al.* (2016) stated that phosphorus concentration is an important aspect in assessing the level of eutrophication in water. Phosphorus concentration in waters is mainly regulated by the release from sediment, which depends on the form of different phosphorus fractions because not all phosphorus compounds can be released from sediment. Barik *et al.* (2019) revealed that the composition of different P fractions affects the mobility of sediment phosphorus. The distribution of different P fractions in sediments needs to be known to assess the

risk of eutrophication in aquatic ecosystems (Aydin *et al.*, 2018).

The distribution of phosphate fraction concentrations in each sediment sample varies greatly (Figure 4). The total concentration of phosphorus (TP) in this study ranges from 0.300 to 0.410 mgP/g with an average of 0.360 mgP/g. The concentration of organic phosphorus (OP) was in the ranges from 0.026 to 0.133 mgP/g, contributing 21.5% to TP. Relatively low OP content was observed at the location of TK.4 and TK.5, where the area

is close to the open sea. Therefore, the accumulation of higher anthropogenic inputs occurred inside the bay, near the estuary (TK.1, TK.2, and TK.3). Organic P in marine sediments comes from the mineralization of organic materials containing phosphates, such as nucleic acids, lipids, and sugars bound to phosphorus (Li *et al.*, 2017; Tu *et al.*, 2019). Increased organic matter causing an increase in OP has been reported from several research sites (Vicente *et al.*, 2016; Yang *et al.*, 2019; Li *et al.*, 2017).

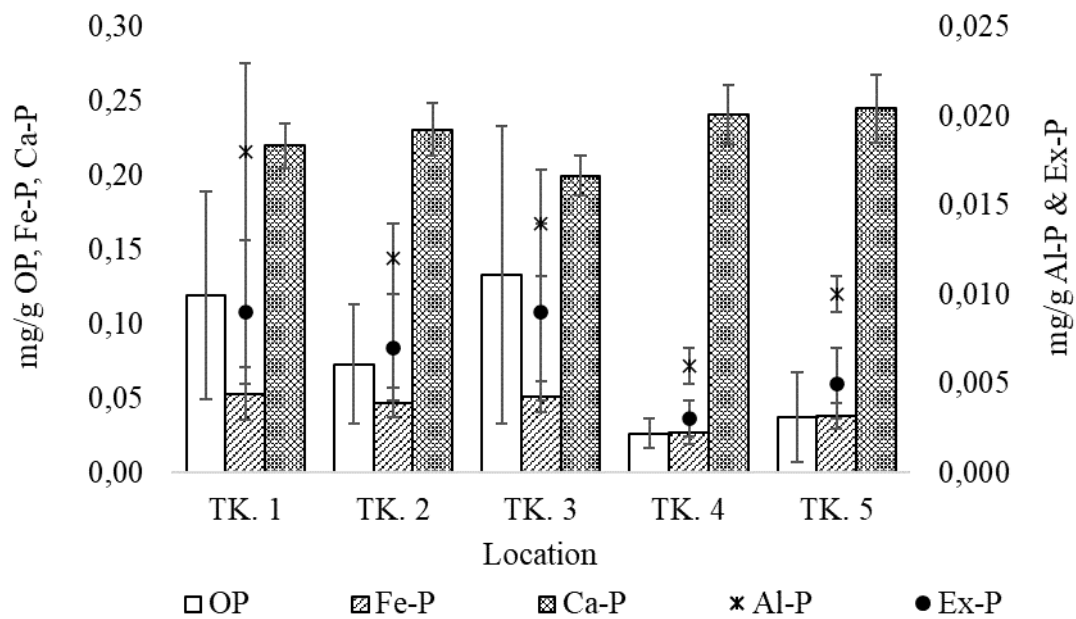


Figure 4. Distribution of phosphorus fraction

Inorganic phosphorus consists of Ca-P, Fe-P, Al-P, and Exchangeable Phosphates (Ex-P). Ca-P concentrations were in the range of 0.200 to 0.245 mgP/g, with an average contribution to TP of 63.13%. Ca-P is the main P fraction in Kendari Bay waters and generally comes from biogenic apatite (bones and teeth of dead marine organisms) (Zhuang *et al.*, 2014) and carbonate fluorapatite (CFA) (Hou *et al.*, 2009). Based on research by Zulham *et al.* (2017), the waters of Kendari Bay and its surrounding areas have a high production of fish and shellfish. Biogenic apatite and fluorapatite are almost insoluble in the physicochemical conditions of marine waters and remain stable both under oxidizing and reducing conditions, thereby rendering it impossible for them to be released from the sediment and enter the water column above it. Therefore, the P form in the Ca-P fraction

will not be bioavailable, so it is not easily utilized by algae.

The high Ca-P concentrations are also associated mainly with excessive calcite saturation and coprecipitation of phosphates. In addition, the high carbonate adsorption capacity also contributed to the phosphorus fraction. It is known that calcite is produced at high salinity through precipitation reactions and biological activity. Therefore, calcite production in waters far from the coast will be higher than in waters near the coast. This can be seen in this study, where locations TK.4 and TK.5 have higher Ca-P values than locations TK.1, TK.2, and TK.3.

Fe-P concentrations were in the range of 0.027 to 0.053 mgP/g, with an average contribution to TP of 12%. Al-P and Ex-P concentrations have the same relative value of 0.003–0.009 mgP/g, with the smallest



contribution to TP being an average of 2%. The concentration of Fe-P tends to decrease from the location in the bay to the location at the mouth of the bay. Previous studies revealed that Fe-P concentrations decreased from brackish waters to waters with higher salinity due to the trapping of large amounts of phosphorus by Fe hydroxide/oxides in brackish water sediments (Kang *et al.*, 2017). Phosphorus that binds to Fe and Al is used to determine the availability of P for algae growth in waters (Ghaisas *et al.*, 2019).

The presence of Fe/Al-P in Kendari Bay sediments is important to understand eutrophication in the waters of this bay. This P fraction will release phosphate ions in anoxic environmental conditions due to the oxidation-reduction process (Yan *et al.*, 2017; Barik *et al.*, 2019; El Semary, 2022). The presence of the Fe/Al-P fraction in the waters of Kendari Bay is closely related to the content of Fe and Al, which can be seen from the values of the Pearson correlation coefficient, respectively, with  $r = 0.717$  and  $r = 0.802$  ( $P < 0.05$ ) as shown in Table 3.

Table 3. Correlation between phosphorus fraction and macro elements content in Sediment of Kendari Bay

	TP	IP	OP	Ex-P	Fe-P	Al-P	Ca-P	Al	Ca	Fe
<b>TP</b>	1									
<b>IP</b>	0,940*	1								
<b>OP</b>	0,656*	0,359	1							
<b>Ex-P</b>	0,953*	0,991*	0,414	1						
<b>Fe-P</b>	0,967*	0,986*	0,464	0,988*	1					
<b>Al-P</b>	0,762*	0,806*	0,301	0,735*	0,757*	1				
<b>Ca-P</b>	0,915*	0,997*	0,299	0,988*	0,973*	0,788*	1			
<b>Al</b>	0,590*	0,697*	0,073	0,654*	0,582*	0,802*	0,719*	1		
<b>Ca</b>	-0,260	-0,184	-0,305	-0,203	-0,322	0,051	-0,140	0,554	1	
<b>Fe</b>	0,559*	0,805*	-0,251	0,772*	0,717*	0,612*	0,845*	0,716*	0,088	1

\* $P < 0.05$

Ex-P is the fraction of sedimentary P that is loosely adsorbed Phosphorus so that it is easily released into the sediment-water interface. Therefore, this phosphorus fraction is often called the exchangeable phosphorus fraction (Ex-P). Its concentration in Kendari Bay sediments is relatively low, ranging from 0.003–0.009 mgP/g, with a contribution of 1.8% to TP.

Together with the OP, Fe-P, and Al-P fractions, Ex-P is the P compound in sediments that is biologically available (Bioavailability Phosphorus, BAP), which means it can be used directly for algae growth (Yang *et al.*, 2018). The availability of phosphorus in sediments is directly related to the amount of phosphorus that can be easily released. By knowing the various P fractions, the potentially available phosphorus can be determined. Calcium-phosphorus (Ca-P) is not expected to be a bioavailable fraction due to its insolubility in the brine environment, while Fe/Al-P cannot be released if the environmental conditions at the sediment-

water interface are still aerobic. However, Ex-P and OP are considered potentially available fractions. Ex-P can be released gradually when the phosphate concentration in the water column is lower than in the pore water, and OP can be bioavailable through the demineralization process (Zheng *et al.*, 2022). In this study, Ex-P and OP contributed 10% to 35% of TP.

### 3.4. Kinetics of Phosphate Adsorption and Desorption

According to the experiment in the laboratory, the phosphate adsorption into sediment samples from all sampling locations indicated high and quick adsorption from the initial time until the sixth-hour experiment; however, after the sixth-hour experiment, the phosphate adsorption was getting slow (Figure 5). An average of 79% adsorption occurred during 6 to 36 hours, and an equilibrium process occurred after 36 hours. The adsorption progressed slowly because of the reduced active adsorption sites; almost no further adsorption could be found after 36

hours, indicating either that adsorption equilibrium had been reached or that desorption occurred as the consequence of the less active sites being available to P (Guo *et al.*, 2018). This pattern also occurs in the results of phosphate desorption kinetics experiments, which show the desorption rate

in the first 0–6 hours. In the first few hours, the concentration in the surface water is lower, P is adsorbed quickly, and then the concentration of the overlying water increases, and the P desorption rate decreases. After 36 h, equilibrium desorption had been reached or adsorption might occur.

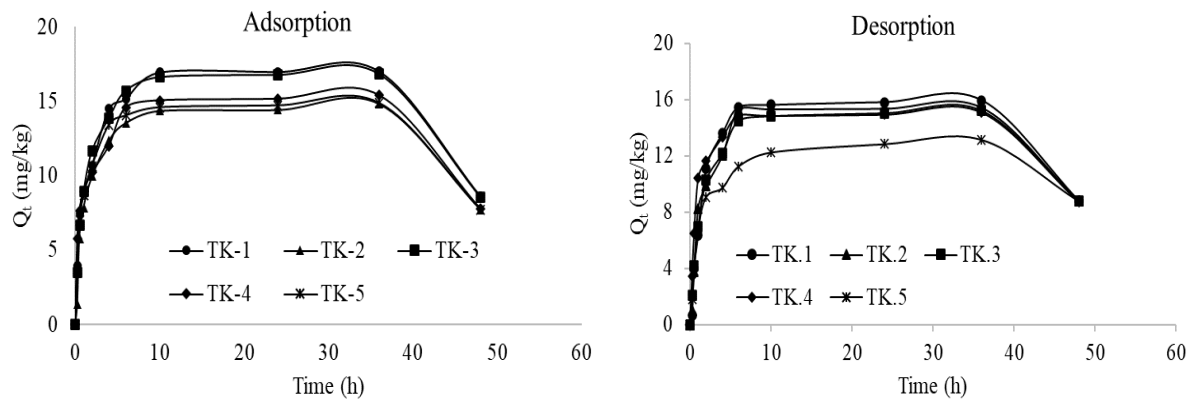


Figure 5. Adsorption and desorption rates of phosphate in sediments of Kendari Bay

The experimental results of the kinetic model showed that for both adsorption and desorption processes of phosphate by Kendari Bay sediments, the pseudo-second-order kinetic model gave a higher regression coefficient ( $R^2$ ) value. The high value of the regression coefficient also shows that the adsorption capacity is proportional to the number of active sites contained in the adsorbent (Dim *et al.*, 2021). This indicated that adsorption and desorption in Kendari Bay

sediments are controlled by chemisorption (Khamizov, 2020). The parameters of adsorption and desorption constants ( $k$ ) and the amount of phosphate adsorbed ( $Q_e$ ) are presented in Table 3. The adsorption and desorption rate constant values ( $k$ ) have an average of 1.074 kg/mg/min and 0.878 kg/mg/min, respectively. Both  $k$  values are relatively the same as study results in Semarang coastal waters and higher than in Jepara coastal waters (Maslukah *et al.*, 2020).

Table 4. Adsorption and desorption kinetic parameters of pseudo-second-order

Location	Adsorption			Desorption		
	$K_a$ Kg/mg/min	$Q_e$ mg/kg	$R^2$	$K_d$ Kg/mg/min	$Q_e$ mg/kg	$R^2$
TK.1	0.476	25.417	0.876	1.171	15.935	0.886
TK.2	0.674	24.699	0.896	1.015	15.423	0.898
TK.3	0.712	24.362	0.893	0.871	15.200	0.907
TK.4	1.157	20.924	0.936	0.675	15.084	0.910
TK.5	2.349	17.447	0.865	0.660	13.139	0.947
Average	1.074	22.570	0.893	0.878	14.956	0.910

K: adsorption and desorption constants,  $Q_e$ : adsorption and desorption capacity,  $R^2$ : regression coefficient

### 3.5. Isothermal adsorption

To describe the adsorption capacity at several different phosphate concentrations, isothermal adsorption experiment was carried out using the Langmuir and Freundlich isothermal adsorption models. The results

showed that the adsorption rate tends to increase as the equilibrium concentration of phosphate increases and then reaches equilibrium after saturation conditions are reached (Figure 6).

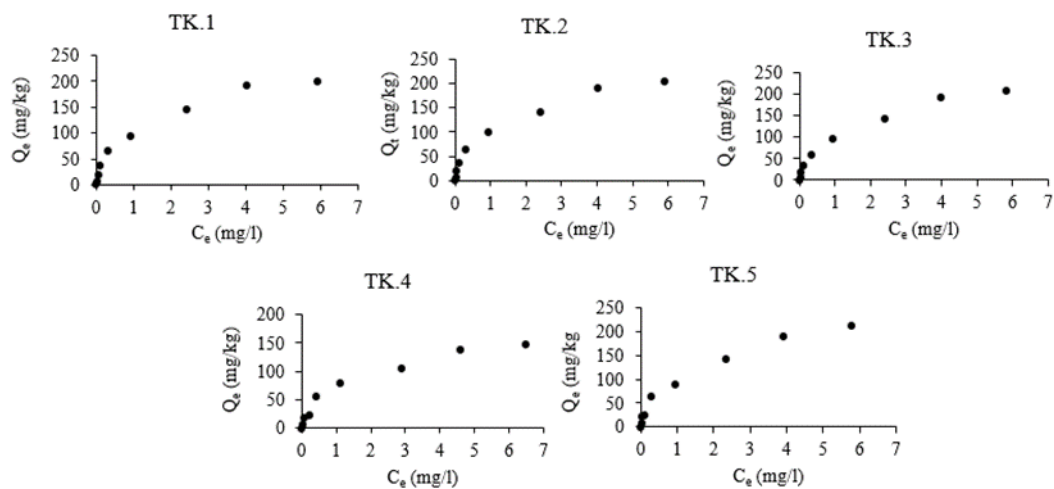


Figure 6 Phosphate isothermal adsorption of Kendari Bay sediments

Table 5. Isothermal adsorption parameters of Freundlich and Langmuir

Loca-tion	R <sup>2</sup> Freundlich	R <sup>2</sup> Langmuir	Q <sub>max</sub> (mg/kg)	EPC <sub>0</sub> (mgP/L)
Tk.1	0.948	0.974	212.8	0.0029
Tk.2	0.939	0.968	212.8	0.0026
Tk.3	0.947	0.961	227.3	0.0033
Tk.4	0.950	0.968	156.3	0.0047
Tk.5	0.935	0.950	222.2	0.0028

R<sup>2</sup>: regression coefficient, Q<sub>max</sub>: maximum capacity of adsorption, EPC<sub>0</sub>: zero equilibrium phosphate concentration.

Experimental results show that the Langmuir model equation provides slightly higher regression coefficient values compared to the Freundlich model equation (Table 5). But generally, both equations produce strong regression coefficients. This phenomenon showed that the phosphate adsorption process in Kendari Bay sediments occurs due to the presence of a monolayer and multilayer. From the Langmuir isothermal adsorption model, the maximum adsorption capacity (Q<sub>max</sub>) value of Kendari Bay sediments was 156.3 mg/kg to 227.3 mg/kg. This value is lower than the results of research in the waters of Semarang Bay (347.2 mg/kg) and Jepara Bay (358.7 mg/kg) (Maslukah *et al.*, 2020). Yang *et al.* (2019) even found that the Q<sub>max</sub> value of phosphate ions in sediment enriched with organic material in the concentration of 611.2 mg/kg.

There was a positive correlation between the Q<sub>max</sub> values and the inorganic P fraction, specifically Fe-P ( $r = 0.797$ ) and Al-P ( $r = 0.502$ ) (Table 5). The Q<sub>max</sub> value with the organic P fraction also produces a positive correlation coefficient value with  $r = 0.610$ . The high content of macro element-bound phosphorus in the sediment shows the great ability of the Kendari Bay sediment to adsorb phosphate ions.

Particle size and organic matter content are also important factors in sediment adsorption capacity. Sediment with fine particle size has a stronger adsorption capacity because of its larger specific surface area (Zhuang *et al.*, 2014). This can be seen from the research results, which obtained a positive correlation coefficient value between the Q<sub>max</sub> value and clay particles ( $r = 0.998$ ). Due to the large surface area, sediments with finer particles have stronger adsorption capacity (Vicente *et al.*, 2016; Kang *et al.*, 2017). Meng *et al.* (2015) also reported that the higher the composition of fine particles, the higher the specific surface area, and the stronger the surface energy in the adsorbed particles, the more phosphorus is absorbed. A positive correlation with organic matter content indicated a strong correlation coefficient value ( $r = 0.934$ ). Yang *et al.* (2019) reported the maximum adsorption capacity value for sediment enriched with organic material (611.2 mg/kg).

Table 5. Correlation between maximum adsorption capacity ( $Q_{\max}$ ) with physicochemical characteristics and phosphorus fraction of Kendari Bay sediments

	OP	Ex-P	Fe-P	Al-P	Ca-P	Sand	Silt	Clay	OM	$Q_{\max}$
OP	1									
Ex-P	0,966	1								
Fe-P	0,911	0,986	1							
Al-P	0,643	0,735	0,761	1						
Ca-P	-0,941	-0,842	-0,751	-0,358	1					
Sand	-0,717	-0,849	-0,905	-0,521	0,588	1				
Silt	-0,391	-0,498	-0,523	-0,451	0,274	0,612	1			
Clay	0,632	0,766	0,813	0,544	-0,494	-0,915	-0,879	1		
OM	0,740	0,882	0,937	0,732	-0,543	-0,952	-0,725	0,944	1	
$Q_{\max}$	0,610	0,747	0,797	0,502	-0,482	-0,920	-0,869	0,998	0,934	1

Significant level ( $P$ ) = 0,05

### 3.6. Equilibrium Phosphate - Concentration in Kendari Bay

Phosphate concentration at zero equilibrium ( $EPC_0$ ) is an important parameter in determining the role of sediment resuspension in the phosphate adsorption-desorption process. When the phosphate concentration in the water is less than the  $EPC_0$  value, sediment is expected to release phosphate from the sediment into the water column. On the other hand, if the phosphate concentration is greater than the  $EPC_0$  value, the sediment will tend to adsorb phosphate (Wang *et al.*, 2018).

The waters of Kendari Bay are classified as an oligotrophic bay because the results of the SRP analysis in the Kendari Bay water body show a relatively low average value (0.001 mg/L), while the  $EPC_0$  value resulting from isothermal adsorption experiments using the Langmuir equation is around 0.0026 mg/L to 0.0047 mg/L (Table 4). This indicated that Kendari Bay sediment potentially resuspends phosphate ions into the water column.

Although Kendari Bay sediments have the potential to release phosphate ions into water bodies based on the  $EPC_0$  value, the phosphate equilibrium mechanism in the environment is highly dependent on environmental conditions. Jiang *et al.* (2022) revealed that temperature and pH influence the concentration of phosphate. The low concentration of Ex-P in this study was less supportive of phosphate release. Furthermore,

turbulence in the bay waters will disperse and dilute the released phosphate ions in seawater.

### 4. Conclusion

The adsorption-desorption kinetics of the Kendari Bay sediments were investigated using the pseudo-second-order rate equation, which indicated that the adsorption capacity is proportional to the number of active sites filled by P ions, with chemisorption being the rate limitation.

The maximum adsorption capacity ( $Q_{\max}$ ) value is influenced by particle size and phosphorus fraction. This is evident from the significant positive correlation between  $Q_{\max}$  and the clay fraction, iron, Fe-P, and Al-P. Consequently, sediment in Kendari Bay exhibits a high adsorption capacity for phosphate ions due to its fine particle size and high Fe content. Despite the SRP value being smaller than the  $EPC_0$  value, resulting in the resuspension of adsorbed phosphate ions, this process is limited by the very low Ex-P content. Therefore, Kendari Bay sediments have little potential to serve as a source of P input into Kendari Bay.

Furthermore, practical applications may involve incorporating sediment adsorption capacity data into ecosystem modeling frameworks to guide nutrient management practices and support sustainable coastal development initiatives in Kendari Bay and beyond.

39(5):193-197.

<http://doi.org/10.46770/AS.2018.05.003>.**Data availability statement**

The data included and used in this study is not confidential and available upon request.

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**Conflict of interests**

The authors declare no conflicts of interest.

**Author contribution**

**SA** designed the topic and research method, data collection and analysis, wrote the manuscript, **ARB** designed the topic and research supervision, **ER** and **MR** contributed to research supervision.

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