sciendo

DOI: 10.2478/eces-2022-0014 ECOL CHEM ENG S. 2022;29(2):183-197

Lilik MASLUKAH[1*], Anindya WIRASATRIYA[1,2], Sugeng WIDADA[1]
Dwi Haryo ISMUNARTI[1], Muh YUSUF[1], Ummu SALMA[3] and Muhammad ZAINURI[1,2]

FRACTIONATION AND BIOAVAILABILITY OF PHOSPHORUS AND ITS RELATION TO CHLOROPHYLL-*a* AT THE COASTAL AREA OF SEMARANG CITY

Abstract: We investigate the distribution of various fractions phosphorus (P) in sediments at the coastal area of Semarang City. Samples were collected from thirteen locations at the Banjir Kanal Barat, port and Banjir Kanal Timur. Sedimentary parameters such as sand, silt, clay, and organic carbon were analysed in order to find out their relation with various P fractions. The sediment types are predominantly sandy and silty with low clay content. Among all fractions (loosely bound/Ads-P), bound calcium/Ca-P), iron bound/Fe-P), and organic fraction/OP), Ca-P fractions constitute the largest portion (71.2 %) followed by iron-bound (17.0 %), organic fraction (10.4 %) and loosely bound (1.4 %). The bioavailable P fractions range from 20.2 % to 42.0 % of the total P (TP) content with average 28.8 %. Relatively high Ads-P content is observed in offshore locations with comparatively high mud percentage as compared with the near-shore locations. The order of abundance of the main forms of P in the Semarang coastal surface sediments is as follows: Ca-P > Fe-P > OP > Ads-P. The concentration of this fraction causes the abundance of chlorophyll-*a* from 9.09 to 21.09 mg/m^3.

Keywords: fractionation, phosphorus, surface coastal sediments, chlorophyll-*a*

Introduction

Estuary is a complex environment with strong interaction between rivers and the sea. This region is categorised as a highly productive ecosystem and functions as a nursery for several fishes, crustaceans, and molluscs species with commercial interest [1, 2]. Eutrophication has become a major environmental problem in most of this region due to large-scale alteration of N and P cycles [3]. Anthropogenic activities such as agriculture, industrialization, and urban development have been linked to increased nutrients and organic material input in estuarine and coastal waters, which can adversely affect water quality, productivity and trophic structures [4].

Primary production is usually limited by P in fresh water and N in seawater [5]. At the estuary, where mixing of fresh water and seawater occurs, spatial and seasonal variations in the availability of N and P causes nutrient limitations, which causes difficulties for

[1] Department of Oceanography, Faculty of Fisheries and Marine Science, Diponegoro University, 50275, Semarang, Indonesia, phone +62 24-7474698, fax +62 24-7474698, ORCID: LM 0000-0003-3794-9212, MY 0000-0002-4001-7099
[2] Center for Coastal Rehabilitation and Mitigation Studies, Diponegoro University, Semarang, Indonesia, ORCID: AW 0000-0003-1030-5126, MZ 0000-0001-8131-8448
[3] Marine Science Postgraduate, Faculty of Fisheries and Marine Science, Bogor Agricultural University, Bogor, Indonesia, ORCID: US 0000-0002-2108-6419
[*] Corresponding author: lilik_masluka@yahoo.com

prioritising the nutrient management [1, 6]. Phosphorus (P) is an essential nutrient that plays a main role in biogeochemical cycles of coastal environments [7, 8]. Sediments in the marine environment play as important buffering and reservoirs of P content and are important sources in the over laying water [9]. Fisher et al. [10] reported that sediments provide 28 % - 35 % P needed in primary productivity of coastal marine ecosystems. Numerous studies have shown that estuaries and adjacent areas are important sinks which can trap significant quantities of P [1, 2, 4].

The existence of P in marine sediments is in organic and inorganic forms. The fraction of inorganic P can be adsorbed by the surface minerals, or bound to aluminium, iron, or calcium [9, 11, 12]. The binding form P in sediments affects transportation, degradation and the ultimate of P in the marine environment. Desorption, dissolution and reduction by physical, chemical and biological processes determine their bio-availability which is influenced by certain P fractions [11]. After that, P will be released into the water column. This particular P fraction becomes important factors affecting the trophic status of water or causes eutrophication [13]. Therefore, research in the P geochemical fraction in the sediment can help the researchers to understand the dynamic cycle of P in seawater. Sediment is an important indicator of coastal environmental changes. The P cycle is an important scientific topic in the marine environment in several decades [7, 12, 14] and plays a main role in biogeochemical cycles of biogenic elements in the estuary and coastal environment [7, 8, 15] especially in areas that have large river flows.

Several studies on the geochemical characteristics of phosphorus, speciation and bioavailability have been carried out in several countries including China [4, 16, 17, 18] Arabia Sea [1], Brazil [2] and Japan [19]. Information about fractionation and availability for biological processes has not been exposed mainly in Indonesian waters, especially in the Semarang region. The previous studies of P fractionation in the Coastal area of Semarang have been conducted for the water column and suspended particle [20, 21]. Based on this background it is necessary to determine the concentration and forms of phosphorus (P) fractionation, distribution, bioavailability and its relation to chlorophyll-*a* in sediment in the coastal area of Semarang city. Therefore, this study aims to investigate the concentration and geochemical fractionations of P in the surface sediments of the Semarang coastal area, to analyze characteristics, distribution and find the effect of fractions on chlorophyll-*a* concentrations.

Materials and methods

Study area

Semarang estuary is on the north coast of Central Java (Fig. 1). The coastal length is around 105 km from the Bodri River estuary, Kendal Regency in the west to the Wulan River estuary, Demak Regency in the East. The coastal area of Semarang is an area where five rivers carry material from the land to enter the waters [22]. Coastal area of Semarang currently has experienced very rapid development because it becomes the main centre of economic growth in Central Java. The consequence of this development is that currently, the coast of Semarang Bay is experiencing various complex problems such as tidal floods, land subsidence, and coastal damage due to abrasion and sedimentation. River water input brings nutrients, especially phosphorus (P), from sewage and various human activities in its catchment area. The results of a previous study by Maslukah et al. [20] obtained concentrations of PO_4^{2-} in Semarang coastal waters in the range of 0.43 μM - 5.08 μM.

The sampling area divided into three areas; the first is near the Banjir Kanal Barat River (BKB), the second is near the port, and the third is near Banjir Kanal Timur river (BKT). Surface sediment samples and water samples collected at 13 stations (Fig. 1).

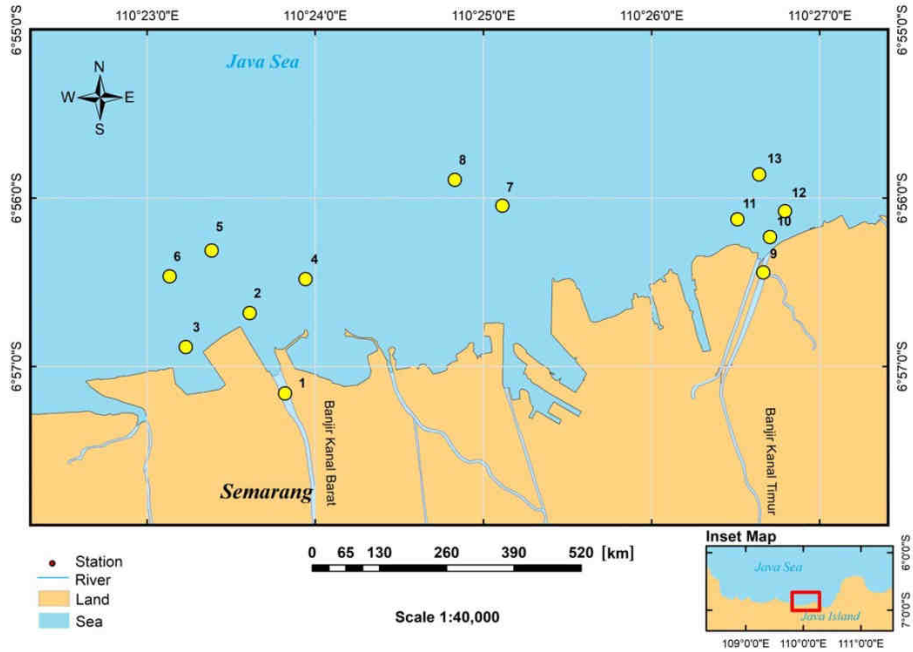


Fig. 1. Research location (map scale 1: 40,000)

Sampling and analysis

The study conducted in May 2017. The research locations are shown in Figure 1. Sediment samples were collected using a Van Veen grab (0.042 m^2) and water samples were collected using a Niskin sampler. Sediment samples are dried and homogenised. Analysis of sediment P fraction is carried out by chemical extraction. Sediments were grounded and sieved using a sieve shaker (< 150 mesh). Analysis of sediment P fraction is carried out by chemical extraction (Fig. 2). The geochemical characteristics of the sediments measured included grain size of sediments, concentration of organic carbon (OC), and sediment pH.

Water samples were taken 20 cm from the surface water and filtered with Millipore (0.45 µm pore size). The filtrate was analysed by the inorganic fraction P (here as DIP) and suspended was used for the analysis of chlorophyll-*a*. The analysing of dissolved inorganic phosphate (DIP) using phosphomolybdate blue method at wavelength λ = 885 nm using SP-3000 Plus spectrophotometer [23]. Chlorophyll-*a* was analysed by suspended extraction using 90 % acetone, incubated 24 hours, centrifuged and read using the trichromatic method with a spectrophotometer on 664 nm, 647 nm and 630 nm. Chlorophyll-*a* concentration, Chl-*a*, was determined based on the equation [24]:

$$\text{Chl-}a = \frac{11.85\ (\lambda 664)\ -1.54\ (\lambda 647)\ -\ 0.008\ (\lambda 630)}{V}\ .\upsilon \qquad (1)$$

where $\lambda 664$, $\lambda 647$ and $\lambda 630$ are the absorbance value of the sample at wavelengths of 664, 647 and 630 nm, υ - volume of extract [L], V - volume of sample [m^3].

The strength of correlation was analysed using Spearman's correlation analysis. The principal component analysis (PCA) in this study was used to interpret data from measurements of marine environmental parameters so that conclusions can be drawn precisely from a data matrix.

Sequencing extraction of phosphorus in sediment

We used the sequential extraction procedure reported in Ruttenberg [25] to determine different geochemical fractions of P. The four operationally defined forms of P obtained through this scheme were: (i) exchangeable or P was extracted by NH_4Cl (Ads-P); (ii) P bound to Al, Fe, and Mn oxides and oxyhydroxides was extracted by NaOH (Fe-P); (iii) P bound to calcium was extracted by H_2SO_4 (Ca-P); and (iv) organic P (OP). Determination of OP was based on differences in the results of extraction concentrations using 1 M HCl before and after ingestion [14, 26]. Inorganic P (IP) in sediments was calculated as the sum of the previous three form P (Ads-P, Fe-P and Ca-P) and total P (TP) was the sum of all forms of P. The extraction process can be seen in Figure 2.

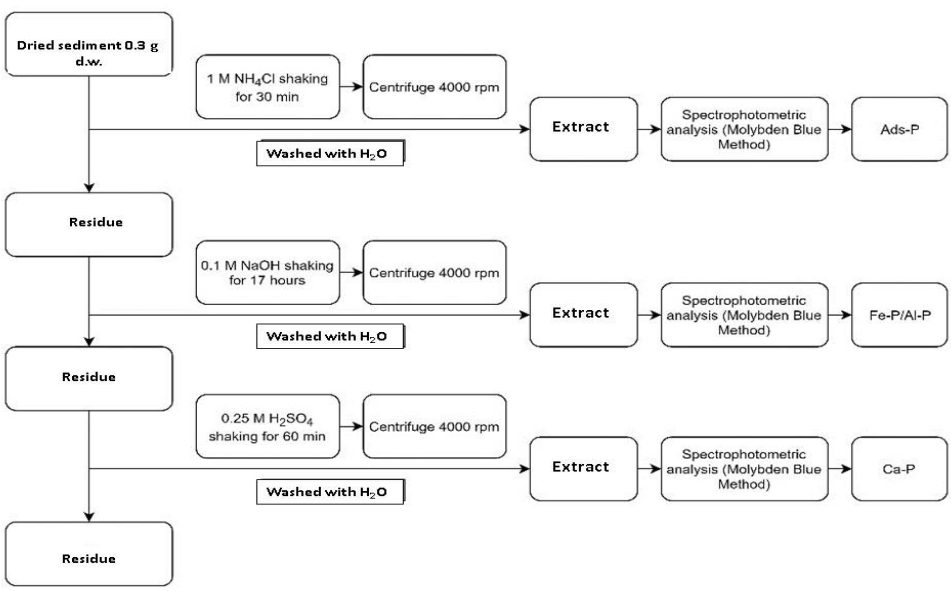


Fig. 2. Method for inorganic phosphorus forms determination in sediment

Quality control analysis method was conducted based on reagent blanks and repetition analysis. The accuracy of the analytical procedure is expressed as the relative standard deviation (*RSD*). All sample analyses were carried out in triplicate and *RSD* was less than 3 %. All analytical reagents or guaranteed grade; all lab wares (bottles, tubes, etc.) have

been cleaned by soaking in 10 % HNO_3 (v/v) for 1 day, followed by soaking and rinsing with non-ionised water. The detection limit for extracted P was 0.01 µmol/L, based on replicate blank sample measurements using 3 cm quartz cuvettes, with a precision better than 2 %. The concentrations of P [µmol/g d.w.] (d.w. - dry weight) were recorded.

Results and discussion

The quantification of total phosphorus concentration is considered as the crucial factor for determining the eutrophication levels in water ecosystems [13]. Although information from the total phosphorus concentration itself, it is not sufficient to determine the risks associated with its natural existence [2]. The study of fractions is essential for better monitoring of the availability of different forms of P fraction in the water. Forms of phosphorus fractionation in sediments are related to sedimentary geochemical characteristics, including grain size, organic carbon and physical-chemical factors.

The fraction of the sediments and carbon organic content

Spatial variability of the character size of sediment particles in Semarang waters is the interaction of complex hydrodynamic and geomorphological processes. The grain size distribution location near the estuary consists mainly of sand while fine grain sizes are found on the offshore (at deeper depths). The presence of sand reflects stronger hydrodynamic energy [2]. The grain size distribution of Semarang waters sediments show variation in each study location. Silt and clay fractions are more dominant than the sand fraction (sand). Sediments near the river mouth (stations 1 and 10) have the dominant fraction of sand and reach > 90 %. The confluence region between the river flow and tidal currents occurs in the process of fine sediment deposition, as a result of the more intensive process of flocculation. It conditions likely to occur at stations 2, 3, 6 (BKB region) and 11 (BKT). The process also causes high levels of organic carbon (OC) found in the same area. Then the organic contents are 9 % to 29 % with an average value of (18 ±6) % (Fig. 3).

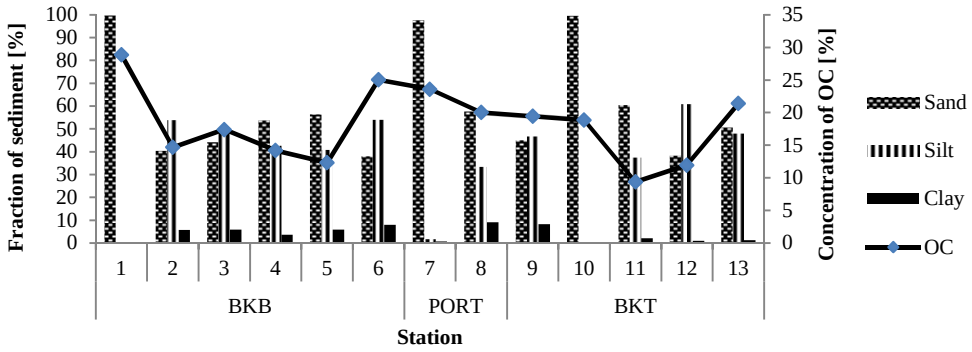


Fig. 3. Percentage of grain size and organic carbon distribution in sediments

Physicochemical characteristics of Semarang coastal area

Physical and chemical parameters of the environment affect the shape of the P fraction in the sediment and the release of P from the sediment into the overlying water. Table 1 illustrates the physical-chemical factors of the study area.

Table 1

Physical-chemical characteristics in Semarang coastal area

Station	pH [-]	Dissolved oxygen [mg/L]	Temperature [°C]	Transparency [cm]	Depth [cm]
1	6.8	6.9	30.3	30	110
2	7.3	8.8	31.2	80	180
3	7.3	8.3	30.8	220	220
4	7.4	9.5	31.3	60	280
5	7.4	9.7	31.1	120	320
6	7.2	9.4	31.2	30	340
7	6.5	6.5	29.7	80	250
8	7.7	7.9	31.8	130	360
9	6.9	3.2	28.8	40	100
10	6.8	2.8	29.6	50	160
11	6.9	6.9	30.1	50	180
12	7.4	7.8	30.1	70	140
13	7.5	7.4	30.1	90	250

Phosphorus sediment fraction

The sediment phosphorus fraction in this study included the NH_4Cl-P (Ads-P) or exchangeable P fraction, a fraction with NaOH extract (NaOH-P/Fe-P) or fraction which is an organic fraction which is easily released and binds to iron and aluminium oxide, and extraction using sulfuric acid (H_2SO_4-P/Ca-P). Inorganic phosphate (IP) is calculated from the number of fractions of Ads-P, Fe-P, and Ca-P. Then, total phosphorus (TP) is the sum-up of organic-P (OP) and IP [19].

Table 2

The concentration of P-fraction in sediments [µmol/g d.w.] and Chl-*a* in Semarang coastal area

Station	Value	Ads-P	Fe-P	Ca-P	OP	IP	TP	BAP	Chl-*a*
BKB	Min.	0.03	1.04	5.47	0.42	7.53	7.94	2.39	9.09
	Max.	0.30	2.60	8.12	1.89	10.53	11.57	3.79	20.40
	Mean	0.14	1.78	7.34	1.03	9.26	10.29	2.95	15.71
	RSD	0.09	0.52	1.00	0.58	1.05	1.28	0.54	4.04
Port	Min.	0.04	1.45	7.37	1.73	9.15	11.79	3.22	14.90
	Max.	0.18	1.61	8.57	3.42	10.05	12.57	5.20	17.70
	Mean	0.11	1.53	7.97	2.58	9.60	12.18	4.21	16.30
	RSD	0.10	0.11	0.85	1.19	0.64	0.55	1.40	1.98
BKT	Min.	0.09	1.12	5.77	0.53	8.19	8.79	1.83	7.13
	Max.	0.28	3.10	8.90	0.79	10.37	11.15	4.17	21.09
	Mean	0.17	1.83	7.39	0.70	9.39	10.08	2.69	12.71
	RSD	0.08	0.52	0.60	0.95	0.82	1.21	1.04	5.16

RSD - relative standard deviation; Ads-P - exchangeable-P; Fe-P - iron-bound P; Ca-P - authigenic P; IP - inorganic phosphate; OP - organic P; TP - the sum-up of OP and IP

In Table 2, the Ads-P concentration is low compared to other fractions with variation range is 0.03 µmol/g to 0.30 µmol/g. This fraction reaches a total percentage of 1.1 % of

TP. Ads-P presents P uptake that is quickly released and easily trapped in the sediment [8] where Ads-P is part of porewater. Ads-P in the sediment is reactive phosphorus. Factors that affect its existence are the presence of oxides, particle hydroxides in clay minerals in the sediment [2]. Physical, chemical factors (such as temperature and pH), dynamic conditions of water and redox potential (Eh) can cause the release of Ads-P to the overlying water [27]. The Ads-P concentration at the port location results in a high DIP in the water column (Fig. 6). This location has fine sediment due to deep waters compared to other locations Station 5 has the highest Ads-P because it is related to a high percentage of silt and clay fraction. Sediments with smaller particles will have the strongest adsorption capacity because they have a large particle surface [28]. This condition explains that Ads-P is higher in fine sediments [1] (Figs. 2 and 5). The sand sediment fraction at station 1 is 99.7 %. Therefore, Ads-P has the lowest concentration (0.03 µmol/g).

The results of the statistical test (Table 3) show that Ads-P is positively correlated with clay and silt (r = 0.50 and r = 0.50 for clay, silt, respectively, $p < 0.05$) and negatively correlated with sand (r = –0.48) [1]. This indicates that the particle size is a significant factor that controls the concentration and distribution of Ads-P in the sediment [8]. This result is similar to the previous results which stated that fine particles have a wider surface and provide a strong bond to phosphate adsorption (especially HPO_4^{2-}) [7]. These results supported by the results of the correlations shown in Table 4. The percentage of Ads-P concentrations in the study ranged from 0.30 % to 2.9 % of the TP and were the lowest P fraction. This result is the same as the results of the study by Yang et al. [8] in Hainan Coastal, China, Vicente et al. [2] in Guapirimim, Brazil, and Yang et al. [29] in Northern South China Sea.

The concentration of Fe-P ranged from 1.04 µmol/g to 3.10 µmol/g with a mean of (1.76 ±0.59) µmol/g, the percentage reaches 17.02 % of TP. Fe-P is an important indicator in the transfer of P and Fe [2]. This fraction is often used as an indicator of sediment quality and the level of environmental pollution [2, 30]. Fe is formed through co-precipitation phosphate with Fe oxide and hydroxides [19]. It is very related to anthropogenic activity and mainly comes from domestic waste and industrial waste [2]. This fraction may be vulnerable to change due to changes in the redox condition [2, 12]. When the redox potential is low, P will be released, and the concentration of dissolved P water will increase and vice versa [2, 4, 30]. The percentage of Fe-P concentration is the second most abundant after Ca-P (Fig. 5). Fe-P has a strong correlation with clay sediments (r = 0.53, $p < 0.05$) and strongly correlates with DIP in the water column. This indicates that the dissolved fraction in the water column is strongly influenced by the fraction of Fe-P in the sediment (Table 3). This same trend appears in research in Changjiang estuary [7] and the eastern coast of Hainan, the South China Sea [8].

The Ca-P fraction is the most dominant fraction and ranges from 5.47 µmol/g to 8.90 µmol/g, which represents 71.2 % of the TP. The highest Ca-P found in Banjir Kanal Timur (BKT), and the lowest was in Banjir Kanal Barat (BKB) at station 2. Ca-P reaches 79.6 % from IP in sediments and has the highest percentage compared to other fractions [13, 19] (Fig. 5). The highest Ca-P found at station 12 located in BKT. The possibility comes from the biological deposit and terrigenous inputs. The mangrove ecosystems in this region supports biological sources. From this terrigenous source, it can be seen that the Ca-P correlation tends to be high in the BKB and BKT rivers.

A similar distribution occurs in the OP, with a range of (0.42, 3.42) µmol/g, with an average value of (1.14 ±0.83) µmol/g. The highest value in BKT at station 9 and the

lowest in BKB at station 2. Organic phosphorus (OP) reached (5.2, 27.2) % of TP in the waters of Semarang Bay. The OP mainly comes from the terrestrial and biological process inputs [8, 12, 17]. The highest OP concentration at the BKT River location at station 9, which is located at the mouth of the river with silt-clay fraction dominates. Throughout the river estuary, there are mangrove ecosystems. The high OP at this location is also closely related to domestic, agricultural and aquaculture waste inputs [4, 8, 31]. Areas with high productivity in the estuary and the coast can produce organic matter and are deposited in the sediment in that location [8, 32, 33].

The amount of concentration from Ads-P, Fe-P, and OP is the bioavailable estimated value in the sediment. It refers to the results of Meng et al. [19]; Kang et al. [16], and Zhou et al. [4]. Bioavailable is a P element that is available either in the pore water or directly released into the water column and is ready to be used by phytoplankton through physical, chemical and biological processes [1]. Bioavailable concentrations are 1.83 µmol/g - 5.20 µmol/g µmol/g(Table 2). The high bioavailable phosphorus values in the area around the port indicate that the region has a high dissolved phosphate concentration (DIP) compared to other regions. It also followed high chlorophyll-*a* concentrations compared to the BKT and BKB regions (Fig. 6).

The inorganic form of P (IP) has the highest concentration of total phosphate (TP) concentration. This research is the same as what was done by Cao et al. [13]. High values are found at stations near the river. It reflects the source of input from the mainland [4, 8]. Inorganic fraction (IP) is the sum of the Ads-P, Fe-P and Ca-P fractions. The IP fraction is more dominant than organic phosphorus (OP). This is because the research location is in the coastal area and hydrodynamic condition at the bottom of the water due to high current and wave factors. The same results also occurred in the study by Zhuang et al. [12] in Laizhou Bay and the coastal waters of Zhangzi Island.

Based on the average value of each station, the differences in sequential fractions from the largest are Ca-P > Fe-P > OP > Ads-P. The distribution pattern of each station is shown in Figure 4. To see the percentage of each P fraction against total P, presented in Figure 5.

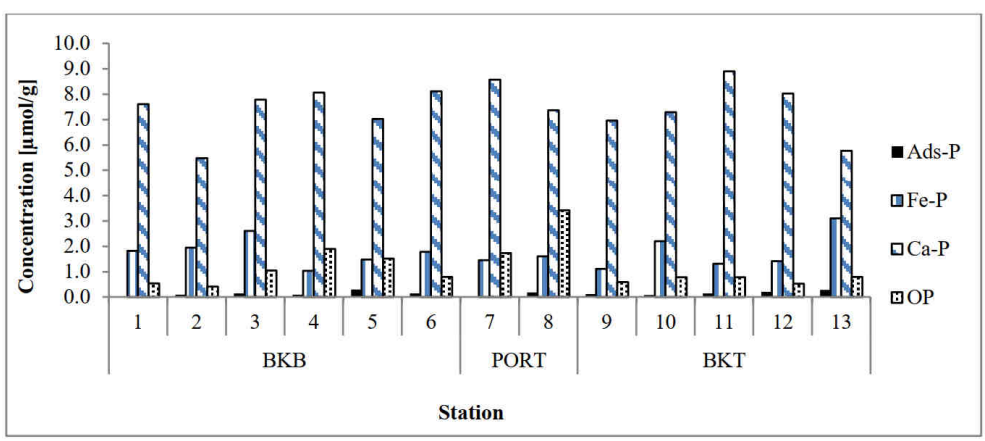


Fig. 4. Distribution of P fractions in each study location

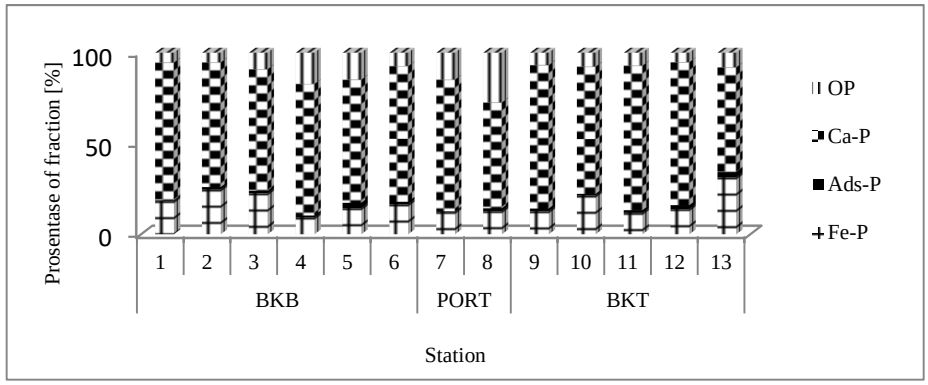


Fig. 5. Percentage of fractions to total P

The spatial variations of inorganic phosphorus (IP) and total phosphorus (TP) sediments in Semarang coastal waters are shown in Table 2. The TP concentration ranges from 7.94 µmol/g to 12.57 µmol/g. The highest concentration found in the Banjir Kanal Timur (BKT) river mouth, station 9 and the minimum concentration at the Banjir Kanal Barat (BKB) river mouth at station 2. The IP concentration in Semarang coastal sediments reaches 89.6 % of TP. The inorganic form of P (IP) reaches the highest of the total phosphate (TP) concentration. The high concentration found at stations close to the river. This reflects input sources from the mainland [17]. Inorganic fraction (IP) is the sum of the Ads-P, Fe-P and Ca-P fractions. The IP fraction is more dominant than organic phosphorus (OP). It is because the research location is in the coastal area where the dynamics of the bottom of the water due to current and wave factors are quite high. Similar results also occur in the study of Zhuang et al. [10] in Laizhou Bay and the coastal waters of Zhuangzi Island.

Based on the results of this study, the port area has a higher concentration of fractions for Ads-P, Fe-P, OP, IP, and TP (Table 2). It is related to water depth and grain size. Depth is a factor that has a significant influence. Deeper depth causes water hydrodynamic processes tend to be weaker, so that interference with sediments that is deposited is small. The resuspension process is not intensive compared to coastal waters with shallow depths. Evidence of small resuspension in this study can be observed with high brightness values reaching 80 cm - 130 cm (Table 1). This causes the deposited chemical elements tend to be high, including some P fractions, except for the Ca-P fraction. The Ca-P fraction is higher near both the Banjir Kanal Barat (BKB) river mouth and in the Banjir Kanal Timur (BKT). This situation illustrates that Ca-P is high due to the water input of the river Banjir Kanal Barat and Banjir Kanal Timur which contain minerals.

The distribution of P fraction in sediments to dissolved inorganic phosphate (DIP) and chlorophyll-*a* in Banjir Kanal Barat (BKB), Port and Banjir Kanal Timur (BKT)

The P fraction in the sediment can affect the dissolved inorganic phosphate (DIP) concentration in the water column. The dissolved inorganic phosphate in waters ranged from 0.43 µmol/L to 0.69 µmol/L. Locations near the port have a higher DIP than BKB and BKT. The presence of this DIP causes a high chlorophyll-*a* concentration measured at the port location (Fig. 6). This is also supported by the presence of heavy metal Fe from

the addition of sediment. The results of the study [34] explained that heavy metals can affect the content of chlorophyll-*a* in organisms

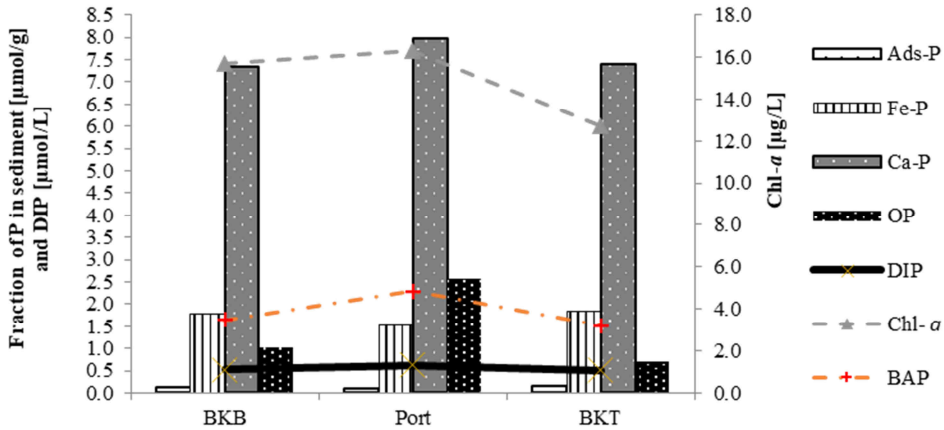


Fig. 6. Response DIP and chlorophyll-*a* with fractionation of P

The relationship between grain size, fraction of sediments, DIP and chlorophyll-*a*

The relationship between fractions and sediment characteristics can be seen through the correlation between variables (Table 3). Clay fraction has a positive correlation with Fe-P, Ads-P, bioavailable (BAP), and DIP. This correlation indicates an association with the correlation value > 0.5, while the sand fraction has a negative correlation with the fraction P [17, 19].

Table 3

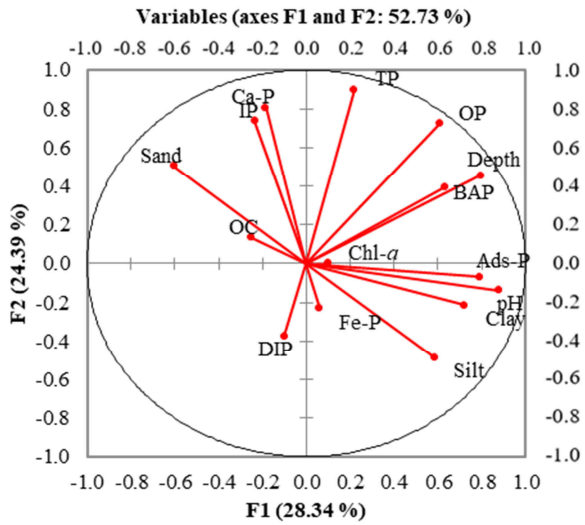
Correlation of grain size and form of fractionation in sediments

Variables	Sand	Silt	Clay	Ads-P	Fe-P	Ca-P	OP	IP	TP	BAP	DIP	Chl-*a*	Depth	pH	OC
Sand	**1.00***	**–0.99**	–0.47	–0.48	0.02	0.30	0.30	0.25	0.38	0.15	0.08	0.04	0.07	–0.51	0.44
Silt	**–0.99**	**1.00**	0.39	0.50	0.02	–0.27	–0.33	–0.20	–0.40	–0.14	–0.16	–0.10	–0.06	0.51	–0.48
Clay	–0.47	0.39	**1.00**	0.50	–0.16	–0.29	0.33	–0.40	0.11	0.23	0.44	0.11	0.39	0.49	–0.29
Ads-P	–0.48	0.50	0.50	**1.00**	0.04	–0.21	0.16	–0.18	–0.02	0.28	–0.14	–0.40	0.40	**0.75**	–0.49
Fe-P	0.02	0.02	–0.16	0.04	**1.00**	–0.50	–0.11	0.00	–0.11	**0.59**	0.06	0.39	0.07	0.05	0.42
Ca-P	0.03	–0.27	–0.29	–0.21	–0.50	**1.00**	0.31	**0.83**	**0.69**	–0.17	–0.28	–0.24	0.08	–0.23	–0.21
OP	0.03	–0.33	0.33	0.16	–0.11	0.31	**1.00**	0.16	**0.76**	**0.71**	–0.20	0.13	**0.85**	0.28	0.13
IP	0.23	–0.20	–0.40	–0.18	0.00	**0.83**	0.16	**1.00**	**0.66**	0.01	–0.23	–0.21	–0.07	–0.33	–0.08
TP	0.38	–0.40	0.11	–0.02	–0.11	**0.69**	**0.76**	**0.66**	**1.00**	0.48	0.01	0.07	0.56	0.01	0.01
BAP	0.15	–0.14	0.23	0.28	**0.59**	–0.17	**0.71**	0.01	0.48	**1.00**	–0.11	0.40	**0.80**	0.40	0.33
DIP	0.08	–0.16	0.44	–0.14	0.06	–0.28	–0.20	–0.23	0.01	–0.11	**1.00**	0.28	–0.19	–0.15	0.01
Chl-*a*	0.04	–0.10	0.11	–0.40	0.39	–0.24	0.13	–0.21	0.07	0.40	0.28	**1.00**	0.19	0.05	**0.69**
Depth	0.07	–0.06	0.39	0.40	0.07	0.08	0.85	–0.07	0.56	**0.80**	–0.19	0.19	**1.00**	0.55	–0.06
pH	–0.51	0.51	0.49	**0.75**	0.05	–0.23	0.28	–0.33	0.01	0.40	–0.15	0.05	0.55	**1.00**	–0.31
OC	0.44	–0.48	–0.29	–0.49	0.42	–0.21	0.13	–0.08	0.01	0.33	0.01	**0.69**	–0.06	–0.31	**1.00**

* Values in bold are different from 0 with a significance level α = 0.05; Ads-P - exchangeable-P; Fe-P - iron-bound P; Ca-P - authigenic P; IP - inorganic phosphate; OP - organic P; TP - the sum-up of OP and IP

In this study we used the principal component analysis (PCA) to see the relationship between the physicochemical parameters of the environment to each fraction to make a cognitive decision process that affects the form of the P fraction in this study region. PCA is a multivariate analysis tool that can reduce data. Based on the eigen values of the component, three axes are extracted and differentiated by the height of the load. The loading for three variance PCs is shown in Figure 7.

a)



b)

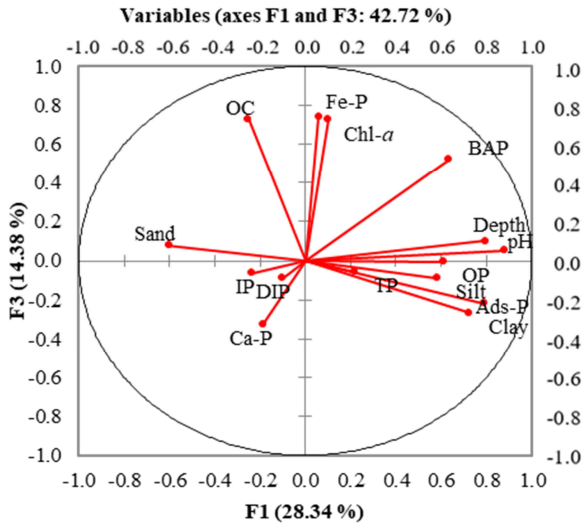


Fig. 7. PCA loadings for various P fractions and relevant parameters in surface sediments from PCA analysis: a) Factor principal component analysis (F) 1 vs 2; b) Factor principal component analysis (F) 1 vs 3

The total variance can reach 67.11 %. PC1 is accounted for 28.34 % of the data variance, and is distinguished by the high positive loadings for the variables Ads-P, BAP and clay fractions, pH and depth (Fig. 7). This suggests that the Ads-P and BAP in sediments mainly consist of Ads-P, and the concentrations and distributions of Ads-P and BAP are dominated mainly by the fine sediment fractions (clay), pH and depth. A negatively correlated contribution to PC1 is evident for sand, indicating that this sediment type was associated with a lack of accumulation of various P fractions. Negative correlation to PC1 explained the sand fraction. PC2 explains 24.39 % of the total variances and on the positive axis is characterised by the Ca, IP and TP fractions and their existence is related to the sand fraction [8]. The presence of chlorophyll-*a* is related to the fraction of Fe-P and organic carbon in sediments (PC3). This indicates the importance of organic carbon in influencing the bonding fraction of Fe-P and both of these affect the concentration of chlorophyll-*a*.

Table 4

Comparison of the concentrations of different geochemical forms of P in sediments of the present study and for some coastal sediments that reported in the literature [μg/g]. It should be noticed that the sequential extraction methods used in the cited literature are not exactly the same as in our research; assuming 1 μmol/g ~ 31 μg/g

Location	Sampling date	TP	IP	Ads-P	Fe-P	Ca-P	OP	Bio-P	Refe-rence
East China Sea shelf	May-June, 2014	(324.0, 499.6) μg/g	(222.8, 423.2) μg/g	(20.8, 21.9) μg/g	(7.7, 36.5) μg/g	(28.0, 250.7) μg/g	(39.6, 131.4) μg/g	(72.4, 187.1) μg/g	[4]
	Oct.-Nov., 2014	(345.1, 810.4) μg/g	(293.9, 732.1) μg/g	(5.4, 20.4) μg/g	(7.6, 42.2) μg/g	(60.0, 332.1) μg/g	(39.6, 144.5) μg/g	(57.6, 203.2) μg/g	[4]
Rushan Bay	2014-2015	(10.9, 29.5) μmol/g	na*	(0.10, 0.34) μmol/g	(0.61, 5.48) μmol/g	(0.66, 4.72) μmol/g	(1.39, 5.29) μmol/g	na*	[17]
Zhangzi Island	November 2011	(81.3, 401.3) μg/g	na*	(2.3, 9.5) μg/g	(9.1, 27.9) μg/g	(3.1, 24.1) μg/g	(22.8, 85.8) μg/g	na*	[12]
Eastern coastal of Hainand Island, South China Sea	August 2008	(7.96, 22.34) μmol/g	(6.39, 14.24) μmol/g	(0.63, 1.29) μmol/g	(0.67, 1.85) μmol/g	(2.27, 5.96) μmol/g	(1.14, 9.39) μmol/g	na*	[8]
Guapi-mirim estuary	July 2010	na*	(3.18, 7.13) μmol/g	(0.03, 0.93) μmol/g	(0.79, 1.71) μmol/g	(0.85, 1.91) μmol/g	na*	na*	[2]
Jobokuto Bay, Jepara, Indonesia	May 2017	(7.968, 12.822) μmol/g	(4.259, 11.403) μmol/g	(0.038, 0.713) μmol/g	(0.409, 4.818) μmol/g	(3.670, 6.461) μmol/g	(0.437, 4.101) μmol/g	na*	[35]
Semarang Coastal Waters	May 2017	(7.94, 12.570) μmol/g or (~246.1-389.7) μg/g[b]	(7.53, 10.53) μmol/g	(0.03, 0.30) μmol/g	(1.04, 3.10) μmol/g	(5.47, 8.90) μmol/g	(0.42, 3.42) μmol/g (~13.02-106.42 μg/g)	na*	This study

* na - not available; Ads-P - exchangeable-P; Fe-P - iron-bound P; Ca-P - authigenic P; IP - inorganic phosphate; OP - organic P; TP - the sum-up of OP and IP

This is explained by the positive charge on PC3 (Fig. 7). Comparison of the results of the concentration of several fractions conducted in several countries, can be seen in Table 4. Coastal water of Semarang has the little lower TP than Rushan Bay (10.9, 29.5) µmol/g, and Eastern coastal of Hainand Island (7.96, 22.34) µmol/g, but a little higher than Zhangzi Island (2.62, 12.94) µmol/g. The concentration of Ads-P in the coastal water of Semarang is little lower than the estuaries and coastal seas of China (Eastern coastal of Hainand Island, Rushan Bay, Zhangzi Island) and Guapimirim estuary, SE Brasil. In contrast, Fe-P in the coastal water of Semarang is little higher than those waters (Table 4). This indicate that the results of the present study are comparable with other estuaries and coastal seas of China (Eastern coastal of Hainand Island, Rushan Bay, Zhangzi Island) and Guapimirim estuary, SE Brasil.

Conclusion

We have presented data here concerning the various fractions of P in sediments of the Semarang coastal area. The concentrations ranges for Ads-P, Fe-P, Ca-P and OP are (0.03, 0.30) µmol/g, (1.04, 3.10) µmol/g, (5.47, 8.90) µmol/g and (0.42, 3.42) µmol/g, respectively. Ca-P was the main fraction of sedimentary P; it mainly originates from terrigenous inputs, and generally accounts for more than 71 % of TP in the sediments that we analysed. Fe-P in this study is also higher than the value of several other estuaries in the world. This Fe-P causes the BAP fraction to reach (1.83, 5.20) µmol/g (with average 3.04 µmol/g). The high concentration of BAP causes dissolved inorganic phosphat (DIP) to be higher in the waters and causes high chlorophyll-*a*. PCA shows the level of Ads-P associated with the presence of fine sediment, depth, and pH. The presence of a fraction of Fe-P also controls the concentration of chlorophyll-*a*.

Acknowledgements

We would like to thank to the Faculty of Fisheries and Marine Science, Diponegoro University for the research funding with the contract 233/UN7.5.10.2/PP/2022 and 013/UN7.5.10.2/PP/2020.

References

[1] Gireeshkumar TR, Deepulal PM, Chandramohanakumar N. Phosphorous speciation in surface sediments of the Cochin estuary. Environ Monitoring Assess. 2013;185(3):2535-52. DOI: 10.1007/s10661-012-2729-3.

[2] Vicente MAF, de Melo G, Neto JAB, de Oliveira AS. Phosphorus fractionation distribution in Guapimirim estuary: SE Brazil. SpringerPlus. 2016;5(1). DOI: 10.1186/s40064-016-3065-9.

[3] Martin GD, Muraleedharan KR, Vijay JG, Rejomon G, Madhu NV, Shivaprasad A, et al. Formation of anoxia and denitrification in the bottom waters of a tropical estuary, southwest coast of India. Biogeosci Discuss. 2010;7:1751-82. DOI: 10.5194/bgd-7-1751-2010.

[4] Zhou F, Gao X, Yuan H, Song J, Tung C, Chen A, et al. Geochemical forms and seasonal variations of phosphorus in surface sediments of the East China Sea shelf. J Marine Systems. 2016;159:41-54. DOI: 10.1016/j.jmarsys.2016.03.005.

[5] Riley JP, Chester R. Introduction to Marine Chemistry. London: Academic Press; 1971. p. 465. ISBN: 9780125887502

[6] Conley DJ. Biogeochemical nutrient cycles and nutrient management strategies. Hydrobiologia. 2000;410:87-96. DOI: 10.1023/A:1003784504005.

[7] Meng J, Yu Z, Yao Q, Bianchi TS, Paytan A, Zhao B, et al. Distribution, mixing behavior, and transformation of dissolved inorganic phosphorus and suspended particulate phosphorus along a salinity gradient in the Changjiang Estuary. Marine Chem. 2015;168:124-34. DOI: 10.1016/j.marchem.2014.09.016.

[8] Yang B, Kang Z, Lu D, Felix S, Ning Z, Lan W, et al. Spatial variations in the abundance and chemical speciation of phosphorus across the river-sea interface in the Northern Beibu Gulf. Water. 2018;10(8):1103. DOI: 10.3390/w10081103.
[9] Soliman NF, El-Zokm GM, Okbah MA. Evaluation of phosphorus bioavailability in El Mex Bay and Lake Mariut sediments. Int J Sediment Res. 2017;32:432-41. DOI: 10.1016/j.ijsrc.2017.05.006.
[10] Fisher TR, Carlson PR, Barber RT. Sediment nutrient regeneration in three North Carolina estuaries. Estuarine Coastal Shelf Sci. 1982;14:101-16. DOI: 10.1016/S0302-3524(82)80069-8.
[11] Song JM. Biogeochemical Processes of Biogenic Elements in China Marginal Seas. Berlin Heidelberg: Springer; 2010, 676 pp. DOI: 10.1007/978-3-642-04060-3.
[12] Zhuang W, Gao X, Zhang Y, Xing Q, Tosi L, Qin S. Geochemical characteristics of phosphorus in surface sediments of two major Chinese mariculture areas: The Laizhou Bay and the coastal waters of the Zhangzi Island. Marine Pollution Bull. 2014;83(1):343-51. DOI: 10.1016/j.marpolbul.2014.03.040.
[13] Cao X, Liu X, Zhu J, Wang L, Liu S, Yang G. Characterization of phosphorus sorption on the sediments of Yangtze River Estuary and its adjacent areas. Marine Pollut Bull. 2017;114(1):277-84. DOI: 10.1016/j.marpolbul.2016.09.026.
[14] Aydin I, Aydin F, Saydut A, Hamamci C. A sequential extraction to determine the distribution of phosphorus in the seawater and marine surface sediment. J Hazard Materials. 2009;168(2-3):664-9. DOI: 10.1016/j.jhazmat.2009.02.095.
[15] Slomp CP. Phosphorus cycling in the estuarine and coastal zones. Estuarine Coastal Sci. 2011;5:201-29. DOI: 10.1016/B978-0-12-374711-2.00506-4.
[16] Kang X, Song J, Yuan H, Shi X, Yang W, Li X, et al. Phosphorus speciation and its bioavailability in sediments of the Jiaozhou Bay. Estuarine Coastal Shelf Sci. 2017;188:127-36. DOI: 10.1016/j.ecss.2017.02.029.
[17] Liu J, Zang J, Zhao C, Yu Z, Xu B, Li J, et al. Phosphorus speciation, transformation, and preservation in the coastal area of Rushan Bay. Sci Total Environ. 2016;565:258-70. DOI: 10.1016/j.scitotenv.2016.04.177.
[18] Meng J, Yao P, Yu Z, Bianchi TS, Zhao B, Pan H, et al. Speciation, bioavailability and preservation of phosphorus in surface sediments of the Changjiang Estuary and adjacent East China Sea inner shelf. Estuarine Coastal Shelf Sci. 2014;144:27-38. DOI: 10.1016/j.ecss.2014.04.015.
[19] Yamada H, Kayama M. Distribution and dissolution of several forms of phosphorus in coastal marine sediments. Oceanologica Acta. 1987;10:311-21. DOI: 10.1007/s10661-012-2729-3.
[20] Maslukah L, Zainuri M, Wirasatriya A, Salma U. Spatial distribution of chlorophyll-a and its relationship with dissolved inorganic phosphate influenced by rivers in the north coast of Java. J Ecol Eng. 2019;20(7):18-25. DOI: 10.12911/22998993/108700.
[21] Maslukah L, Zainuri M, Wirasatriya A, Maisyarah S. The relationship among dissolved inorganic phosphate, particulate inorganic phosphate, and chlorophyll-a in different seasons in the coastal seas of Semarang and Jepara. J Ecol Eng. 2020;21(3):135-42. DOI. 10.12911/22998993/118287.
[22] Setyowati DL, Wilaksono SA, Aji A, Amin M. Assessment of watershed carrying capacity and land use change on flood vulnerability areas in Semarang City. Forum Geografi. 2021;35(2):15542. DOI: 10.23917/forgeo.v35i2.15542.
[23] Murphy J, Riley JP. Anal Chim Acta. 1962;27(C):31-6. DOI: 10.1016/S0003-2670(00)88444-5.
[24] Jeffrey SW, Humphrey GF. New spectrophotometric equations for determining chlorophylls a, b, c1 and c2 in higher plants, algae and natural phytoplankton. Biochem Physiol Pflanz. 1975;167(2):191-4. DOI: 10.1016/S0015-3796(17)30778-3.
[25] Ruttenberg KC. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol Oceanogr. 1992;37:1460-82. DOI: 10.4319/lo.1992.37.7.1460C.
[26] Aspila KI, Agemian H, Chau ASY. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst. 1976;101:187-97. DOI: 10.1039/AN9760100187.
[27] Chen J, Lu S, Zhao Y, Wang W, Huang M. Effects of overlying water aeration on phosphorus fractions and alkaline phosphatase activity in surface sediment. J Environ Sci. 2011;23(2):206-11. DOI: 10.1016/S1001-0742(10)60394-4.
[28] Yang B, Liu SM, Zhang GL. Geochemical characteristics of phosphorus in surface sediments from the continental shelf region of the northern South China Sea. Marine Chem. 2018;198:44-55. DOI: 10.1016/j.marchem.2017.11.001.
[29] Hezhong Y, An S, Liu E, Pan W, Zhu Z. J Soil Water Conservation. 2015;70(5):313-21. DOI: 10.2489/jswc.70.5.313.
[30] Santos IR, Bryan KR, Pilditch CA, Tait DR. Influence of porewater exchange on nutrient dynamic in two New Zealand estuarine intertidal flats. Marine Chem. 2014;167:57-70. DOI: 10.1016/j.marchem.2014.04.006.

[31] Lukkari K, Leivuori M. Fractionation of sediment phosphorus revisited: II. Changes in phosphorus fractions during sampling and storing in the presence or absence of oxygen. Limnol Oceanogr Methods. 2007;5:445-56. DOI: 10.4319/lom.2007.5.445.
[32] Liu S, Zhang J, Li DJ. Phosphorus cycling in sediments of the Bohai and Yellow Seas. Estuarine Coastal Shelf Sci. 2004;59(2):209-18. DOI: 10.1016/j.ecss.2003.08.009.
[33] Li RH, Liu SM, Li YW, Zhang GL, Ren JL, Zhang, J. Nutrient dynamics in tropical rivers, lagoons, and coastal ecosystems of eastern Hainan Island, South China Sea. Biogeosciences. 2014;11(2):481-506. DOI: 10.5194/bg-11-481-2014.
[34] Świsłowski P, Rajfur M, Wacławek M. Influence of heavy metal concentration on chlorophyll content in Pleurozium schreberi mosses. Ecol Chem Eng S. 2020;27(4):591-601. DOI: 10.2478/eces-2020-0037.
[35] Maslukah L, Wirasatriya A, Yusuf M, Sari RS, Salma U, Zainuri M. Distribution of phosphorus fraction in surface sediments of the Jobokuto Bay. Molekul. 2021;16(2):100-9. DOI: 10.20884/1.jm.2021.16.2.572.