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Distribution Patterns of Chlorophyll-a and its Relationship with Phosphate, Nitrate in Banjir Kanal Barat and Banjir Kanal Timur, Semarang, Indonesia

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ABSTRACT

Banjir Kanal Barat (BKB) and Banjir Kanal Timur (BKT) are widely used for various community activities such as residential areas, industry, fish cultivation, and auction. Community activity around BKB and BKT will affect N and P nutrient inputs, which further affects phytoplankton abundance. In this study, phytoplankton biomass was estimated through chlorophyll-a (chl-a) measurements. The purpose of this study was to determine the distribution of the chl-a and determine the influence of phosphate and nitrate in front of the estuary from BKB and BKT. Sampling was carried out at 8 stations from each estuary and was carried out in the dry season. The concentration of chl-a, phosphate, and nitrate is further described in the form of a distribution pattern based on the interpolation method with ArcGIS 10.2 software. The results showed that the average ± sd of chl-a, respectively was 15,781 ± 16.90 mg/m^3 and 17,710 ± 15.31 mg/m^3, phosphate was 0.0174 ± 0.0057 ppm and 0.0096 ± 0.0164 ppm, nitrate was 2.9086 ± 1.1824 ppm and 1.6919 ± 1.6316 ppm. The distribution pattern of chlorophyll-a and phosphate decreases in concentration towards the sea, while nitrate forms an irregular pattern and has a different pattern in each estuary. Nutrient phosphate has a positive correlation with chlorophyll-a.

Keywords: chlorophyll-a, phosphate, nitrate, BKT, BKB.

INTRODUCTION

The 10th annual program of LOICZ (Land Ocean in the Coastal Zone), describes the apparent impact of human activity on coastal systems (Siregar & Koropitan, 2016), which affects increasing pollutant input into estuarine waters (William et al., 2010). Anthropogenic activities such as agriculture, industrialization, and urban development have been linked to increased nutrient and organic matter inputs in estuarine and coastal waters, which can adversely affect water quality, productivity, and trophic structure (Zhou et al., 2016; Maslukah et al 2019). Organic pollutants contribute 50-70% of the total wastewater produced by anthropogenic activity (Putnam et al., 2010). Organic pollutants from land entering the mouth of the river will have an impact on fertility as a result of an increase in N and P nutrients (Maslukah et al., 2018). These nutrients are necessary for the process and development of living organisms such as phytoplankton (Wisha and Maslukah, 2017). The presence of phytoplankton in the estuary can be determined through the measurement of chlorophyll-a concentrations (Damar et al., 2020; Maslukah et al., 2020). The high and low Chl-a in estuaries will vary due to nutritional variations (Bucci et al., 2012; Maslukah et al., 2020). The N and P inputs of the estuary have influenced the values of chlorophyll-a, which is the main pigment of phytoplankton (Magumba et al., 2013; Trommer et al., 2013; Maslukah et al.,

2016) and affect the level of primary productivity of waters. The results of the research of Maslukah et al. (2019) in estuarine waters explain that chlorophyll-a has a positive response to the rise of phosphate nutrients.

High water fertility has a positive impact, but if conditions are too fertile, it will have a negative impact. The positive impact is that plankton becomes abundant and is followed by an abundance of fish. Meanwhile, the negative impact can cause mass death of fish due to reduced dissolved oxygen (DO) and the emergence of toxic substances such as ammonia and hydrogen sulfide (H2S). This toxic substance results from the process of aerobic decomposition (Maslukah et al., 2014).

The Banjir Kanal Barat and the Banjir Kanal Timur are two river estuaries that are part of Semarang Bay. The area around the BKB and BKT is used for various human activities such as settlements, moorings, ports, and fish auction sites. These activities will contribute to pollutants such as domestic waste and other organic and inorganic materials. This will affect the process of eutrophication of water, which can lead to a decrease in water quality. Previous research in BKB and BKT on chlorophyll-a concentrations has been conducted by Maslukah et al. (2019) on its relationship to phosphate but has not been linked to nitrate (N). Thus the pattern of its distribution in front of the estuary has never been done. Based on this background, it is necessary to conduct research on the distribution pattern of nutrients (N, P) related to chlorophyll-a. It is hoped that this study can provide the latest information on the condition of primary productivity in BKB and BKT waters, which can be used as a reference to see the development of primary productivity conditions of waters and their fluctuations.

MATERIALS AND METHODS

The study was conducted on May 25 and May 26, 2019, in the BKT and the BKB estuary, Semarang city, Indonesia. The measured environmental parameters include temperature, salinity, pH, dissolved oxygen (DO), and brightness. chlorophyll-a, nitrate (N), and phosphate (P) concentrations were analyzed at the Chemical Oceanography Laboratory, Faculty of Fisheries and Marine Sciences, Diponegoro University, Semarang. Coordinates of the location at BKB at 110°23'51.40"E - 6°57'15.88"S to 110°23'21.17"E - 6°55'51.47"S and at BKT at 110°26'38.36"E - 6°56'29.00"S to 110°26'46.99"E - 6°55'7.49"S.

Nitrate and phosphate analysis: determination of nitrate concentration was carried out using the HACH Cadmium Reduction Method 8039 method (Hach, 1999). In this method, Nitraver 5 Nitrate Reagent Powder Pillow reagent is used. Cadmium metal reduces nitrates in the sample to nitrites. Nitrite ions react on acidic media with sulfanilic acid to form milk salts, namely intermediate diazonium. Samples that have been reagent were analyzed using a UV-Vis spectrophotometer with a wavelength of 500 nm. The sensitivity of this method can be analyzed at concentrations of 0–30 mg/L NO_3^-N. Phosphate concentration is measured by a method based on the reaction of phosphate ions with molybdate reagents which are acidified with ascorbate acid and potassium antimony tartrate. This method uses the principle of ammonium molybdate acid and potassium antimony tartrate reacting with orthophosphate to form phosphomolybdate then reduced by ascorbate acid becomes molybdenum blue. The sensitivity of this method analyzes at a concentration of 0.03–5 µg-atP/L.

Chlorophyll-a analysis: chlorophyll-a was measured following the standard method from APHA. The sample water was taken and filtered using millipore filter paper 0.45 µm. The concentration of chlorophyll-a is calculated using the formula (APHA, 2012).

$$\begin{gathered} C = 11.85^*(\text{abs } a - \text{abs } b) - \\ 1.54^*(\text{abs } c - \text{abs } b) - 0.08^*(\text{abs } d - \text{abs } b) \end{gathered} \tag{1}$$

Correction factors:

$$mg\,\frac{chlorophyll}{m3} = \frac{C \times v}{V \times 10} \tag{2}$$

where: C – chlorophyll-a concentration (µg/ml); abs a – light absorbance at λ 644 nm; abs b – light absorbance λ 750 nm: abs c – light absorbance at λ 647 nm; abs d – light absorbance at λ 630 nm; V – volume of water sample (m^3); v – volume of extract (acetone) (mL).

Data analysis

The Kruskal-Wallis test was performed to determine the difference ($p < 0.05$) of nutrient N (nitrate), P (phosphate), and chlorophyll-a from different locations. Meanwhile, to see the correlation between variables, we used Spearman correlations and model regression N and P analyzed with the software SPSS 16.0. Spatial distribution patterns of N, P, and chlorophyll a were mapped using ArcGIS 10.0. The map results are in the form of a visualization of the level of color differences. The dark color indicates that the station has a high concentration. Meanwhile, stations that have a low concentration will be characterized by bright color changes.

RESULTS

Chlorophyll-a concentration

Based on the results of research from two estuaries, namely BKT and BKB. The concentration of chlorophyll-a ranges from 3.746–44.298 mg/m^3. Complete chlorophyll-a data is presented in Table 1. Based on Table 1, the following patterns of chlorophyll-a distribution on the two estuaries are presented in Figure 1.

Phosphate and nitrate

The phosphate concentration of BKB is between 0.0013–0.0665 ppm and BKT is 0.0013–0.0485 ppm. The phosphate concentration is lower than nitrate with a concentration of 1.21–4.934 ppm in BKB and 0.13–3.486 ppm in BKT. More detailed values are presented in Table 2 and the distribution pattern in each estuary is depicted in Figures 2 and 3.

Correlation between chlorophyll-a to nitrate and phosphate in BKB and BKT

The presence of nutrients affects the concentration of chlorophyll-a in waters (Maslukah et al, 2018). Thus, to see the effect, it is necessary to conduct a correlation test. The correlation results in this study are presented in Table 3. Table 3 shows that phosphate has a positive relationship, but nitrate shows an unequal relationship in both estuaries. Muslim and Jones (1993) in Nelly bay, Australia found the correlation of chlorophyll-a to phosphate was 0.47. While research by Maslukah et al (2019), in the Java Sea obtained a correlation coefficient of 0.74.

Furthermore, the regression model between the two nutrients (N, P) to the chlorophyll value can be described following the equation $y = -0.785 + 561.634[P] + 2.329[N]$ for BKB estuary waters with the value of the coefficient of determination (R^2) is 0.609 and $y = 20.402 + 440.656[P] - 4.101[N]$ with the coefficient of determination (R^2) being 0.521. To see the significant value can be seen in Table 4. Based on Table 1, shows that the concentration of chlorophyll-a in the BKB estuary based on the average value shows a slightly higher value, compared to BKT. This is closely related to the concentration of nutrients, both nitrates, and phosphate which show high in BKB compared to BKT. However, based on the real difference test using Kruskal-Wallis, the three water

Table 1. Chlorophyll-a (Chl-a) in the waters of the BKB and BKT

Location	Station	Depth (m)	Chl-a (mg/m^3)	Average ± SD (mg/m^3)
BKB	1	0.08	41.688	15.781 ± 16.90
	2	0.17	5.389	
	3	0.40	8.287	
	4	0.42	44.298	
	5	0.52	9.544	
	6	0.59	7.355	
	7	0.68	5.945	
	8	0.61	3.746	
BKT	1	0.30	41.343	17.710 ± 15.31
	2	0.35	43.018	
	3	0.38	7.238	
	4	0.34	7.495	
	5	0.4	9.305	
	6	0.42	8.179	
	7	0.55	15.154	
	8	0.55	9.954	

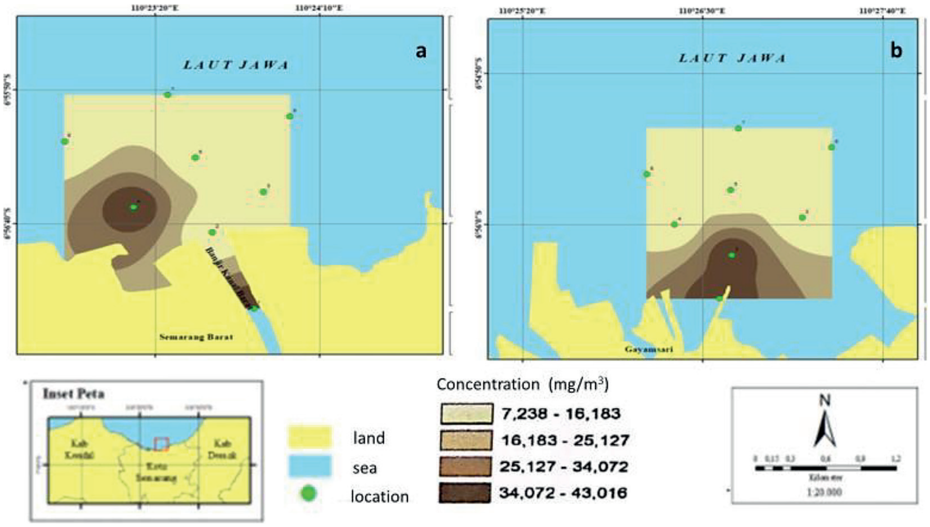

Figure 1. Distribution of Chlorophyll-a Banjir Kanal Barat (a) and Banjir Kanal Timur (b)

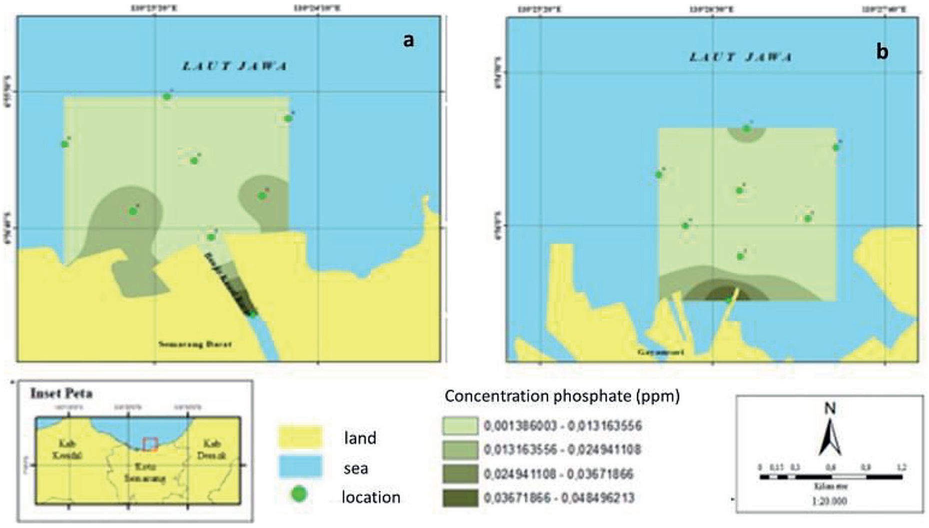

Figure 2. Phosphate distribution in BKB(a) and BKT(b)

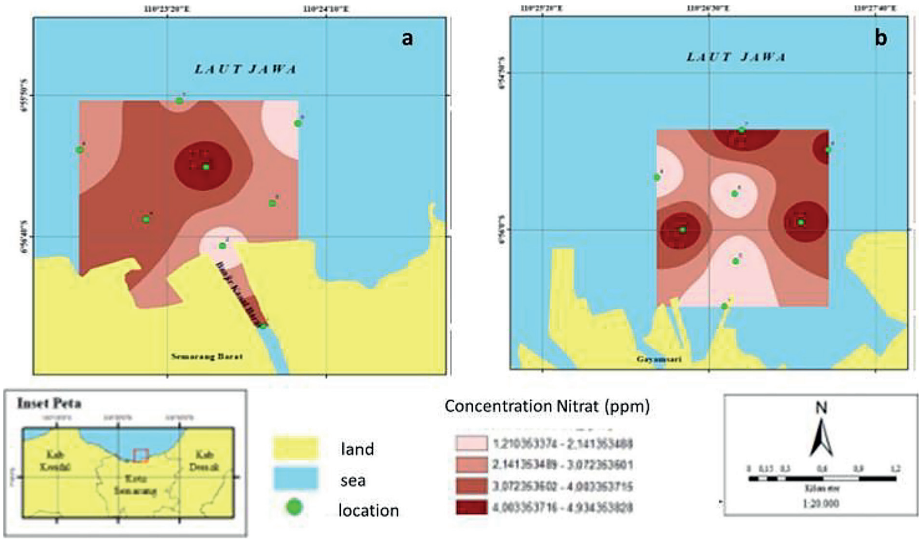

Figure 3. Nitrate distribution in the BKB (a) and the BKT (b)

Table 2. Phosphate concentrations in the waters of the BKB and the BKT

Location	Station	Phosphate (ppm)	Average phosphate ± SD (ppm)	Nitrate (ppm)	Average nitrate ± SD (ppm)
	1	0.0665		3.521	
	2	0.0055		1.659	
	3	0.0207		2.452	
BKB	4	0.0221	0.0174 ± 0.0057	3.693	2.9086 ± 1.1824
	5	0.0097		4.934	
	6	0.0013		1.21	
	7	0.0124		3.038	
	8	0.0013		2.762	
	1	0.0485		0.130	
	2	0.0013		0.200	
BKT	3	0.0013		3.106	
	4	0.0027	0.0096 ± 0.0164	3.486	1.6919 ± 1.6316
	5	0.0041		0.130	
	6	0.0027		2.727	
	7	0.0152		3.486	
	8	0.0013		0.270	

Table 3. The correlation coefficient of nutrient (N, P) with chlorophyll-a

Location	Parameters		Phosphate	Nitrate
BKB	Chlorophyll-a	Pearson correlation	0.765^{*}	0.406
		Sig. (2-tailed)	0.027	0.318
		N	8	8
BKT		Pearson correlation	0.586	-0.561
		Sig. (2-tailed)	0.127	0.148
		N	8	8

quality parameters (chlorophyll-a, nitrate, and phosphate) showed values that did not differ markedly ($p > 0.05$) with signification values (p) for chlorophyll-a, nitrate and phosphate respectively are 0.345, 0.141 and 0.345. In addition to nutrients N and P, the presence of chlorophyll-a as an indicator of phytoplankton in waters is also influenced by other environmental parameters, such as temperature, salinity, pH, brightness, water depth, and current speed (Table 5). The results of the correlation test between chlorophyll-a to these parameters are presented in Table 6. Table 6 shows that the distribution of chl-a, in both estuaries is more affected by salinity. The correlation negatively describes the chl-a near the estuary higher and slowly descending towards the sea. Other water quality parameters also have the same relationship in both estuaries, except for temperature.

DISCUSSION

The existence of these two nutrients affects the measured chlorophyll-a concentration. Thus, the pattern of distribution of chlorophyll-a has a relationship with the distribution of nutrients. Table 3 shows that there is a positive relationship between phosphate and chlorophyll-a. The same research was also found by Maslukah et al. (2018) in Jepara waters and Kadim et al. (2019) in Gorontalo Bay. Based on the research by Maslukah et al. (2018) distribution of chlorophyll-a is more similar to phosphate than to nitrate. The correlation of phosphate to phosphate is 0.7. Likewise by Kadim et al. (2019) in Gorontalo Bay, a significant positive relationship between chlorophyll-a was in phosphate ($p < 0.01$) with a correlation of 0.94, but not with nitrate (the correlation was negative and not significant ($p > 0.01$). Table 2 shows that the concentration of nitrate has a higher value than phosphate. This is consistent

Table 4. Regression model coefficients in BKB and BKT

Model		Unstandardized coefficients		Standardized coefficients	t	sig.
		B	Std. error	Beta		
BKB	(Constant)	-.785	12.448		-0.063	0.952
	Phosphate	561.634	235.924	.709	2.381	0.063
	Nitrate	2.329	4.258	.163	0.547	0.608
BKT	(Constant)	20.402	7.853		2.598	0.048
	Phosphate	440.656	299.906	.471	1.469	0.202
	Nitrate	-4.101	3.010	-.437	-1.363	.0231

Note: a. Dependent variable: Chl-a.

Table 5. Water quality values (temperature, salinity, DO, pH, brightness, current speed)

Location	Station	Temperature	Salinity	DO'S	pH	Brightness	Current speed
		(ºC)	$(^0/_{00})$	(ppm)		(m)	(m/s)
BKB	1	29.5	8	4.18	7.68	0.5	0.34
	2	30.2	24	4.57	7.94	0.7	0.01
	3	30.6	26	7.28	8.14	1.3	0.35
	4	30.4	20	5.05	7.99	1.35	0.04
	5	30.5	22	6.97	8.12	1.6	0.29
	6	30.4	22	7.27	8.13	1.6	0.02
	7	30.4	26	6.67	8.13	2	0.30
	8	30.3	24	6.2	8.11	1.7	0.02
BKT	1	30.3	300	4.34	7.87	0.5	0.002
	2	30.4	350	5.25	7.89	0.35	0.13
	3	30.3	375	6.01	8.06	0.8	0.004
	4	30.7	340	7.41	8.13	1.1	0.11
	5	30.3	400	6.45	8.1	1.5	0.03
	6	30.3	420	6.14	8.05	1.1	0.09
	7	29.3	550	6.8	8.07	1.8	0.05
	8	30.4	550	6.92	8.11	1.5	0.08

Table 6. The correlation chlorophyll-a (chl-a) with water quality

Model		Temperature	Salinity	DO	pH	Brightness	Depth	Current speed
Chl-a BKB	Correlation coefficient	0.220	-0.667	-0.095	-0.180	-0.431	-0.452	0.548
	Sig. (2-tailed)	0.601	0.071	0.823	0.670	0.286	0.260	0.160
	N	8	8	8	8	8	8	8
Chl-a BKT	Correlation coefficient	-0.077	-0.405	-0.405	-0.500	-0.193	-0.193	0.095
	Sig. (2-tailed)	0.857	0.319	0.320	0.207	0.647	0.647	0.823
	N	8	8	8	8	8	8	8

with the existence in nature, that P sources are more limited. Trommer et al. (2013) state that the P element has a role as a nutrient boundary when chlorophyll-a is high. Furthermore, Stelzer and Lamberti (2001) suggest that an increase in N concentration will affect an increase in chlorophyll-a concentration. The high concentrations of N and P nutrients at BKB and BKT in the Semarang estuary are closely related to their location in the urban centers of the Semarang Regency. Throughout the flow of the river area, many household activities dispose of household waste into these waters. Just like in other cities, along this river, many residents live and directly throw the residual of household activity into the waters. Based on Figure 1, the distribution of chlorophyll-a concentrations in the waters of the BKB has a pattern of convergent distribution. Abigail et al. (2015) explained that convergent distribution patterns are patterns whose sources experience distribution because they are influenced by several factors to produce a specific form. Nutrients are needed for the process of photosynthesis (Wisha and Maslukah, 2017). This is related to the concentration of N and P nutrients found in the area. Rosyid (2011) explained the low concentration of chlorophyll-a in open sea waters due to the lack of supply of nutrients in this water.

Based on Figure 1(b), the distribution of chlorophyll-a concentrations in the BKT waters has gradually decreased from the mouth of the river to the open sea area. Station 2 has a high concentration because of its location near the mouth of the river. The highest concentration is found at the front side of the estuary indicating that the land is a nutrient input (Maslukah et al., 2018; Rahmawati 2016). Shaari et al. (2013) and Cong et al., (2006) suggest that the presence of terrestrial influences through the runoff stream causes high nutrient inputs to coastal waters. This high nutrient causes chlorophyll-a in front of the estuary to be high. This high value is also related to the depth of the station (Maslukah et al., 2018). River estuaries receive nutrient inputs from existing activities in the river through river water runoff. In addition, estuary often occurs stirring process due to the confluence between the seawater period and the freshwater period. Rigitta et al. (2015) state that the presence of turbulence processes can cause sediment resuspension. The resuspension process can cause sediments on the seabed to rise into the water column and is one of the processes that have the potential to contribute to the inclusion of nutrients such as important nitrate in the water column (Dzialowki et al., 2008). Compared to the previous study in 2017, BKB and BKT waters have a slightly smaller concentration of chlorophyll-a, which is 12.67 mg/m^3 in BKT and 15.28 mg/m^3 in BKB (Maslukah et al., 2019). With a concentration of more than 10 mg /m^3, the two estuary areas are included in the mesotrophic category but have not yet entered the eutrophic category (<40 mg/m^3). Figures 2 and 3, illustrate the different chlorophyll-a concentrations against phosphate distribution patterns. The highest phosphate concentration is found at station 1, which is due to the location of station 1 near residential areas, industry, and fishing activities. While station 8, due to its location far from the estuary, has a smaller phosphate concentration. The river is one of the carriers of waste drift and phosphate sources from the mainland (Ulqodry et al*.,* 2010; Maslukah et al., 2014; Maslukah et al., 2019). Household waste activities such as detergents can also increase phosphate concentrations in water. Tungka et al (2016) explained that the results of household waste disposal in the form of detergents can increase phosphate concentrations in water. Figure 2, shows that the phosphate dispersal in the waters of the BKB is gradually decreasing towards the open sea. This pattern is the same as the results of the research of Rahmawati et al. (2014) and Megawati et al. (2014), where phosphate concentrations have decreased towards the sea. The confluence of water flows from land and seawater causes a stirring process, which can increase the phosphate concentration at station 1. The intensive stirring process will be noticeable at locations with low depth and this resuspension process seen that the brightness value is low compared to other stations (Table 5). The resuspension process can lead to the detachment of the organic material in the water column. Muslim and Jones (2003) explain that the process of stirring sediments can lead to the release of nutrients from bottom sediments into the waters.

CONCLUSION

The concentration of chlorophyll-a in the Banjir Kanal Barat (BKB) ranged from 3.7465 – 44.298 mg/m^3 and in the Banjir Kanal Timur (BKT) between 7.238–43.018 mg/m^3. The distribution of chlorophyll-a has decreased towards the open sea. This chlorophyll concentration is related to the presence of phosphate and nitrate nutrients. Phosphate and nitrate concentrations in BKB (BKT), respectively between 0.0013–0.0665 ppm (0.0013–0.0485 ppm) and 1.210–4.934 ppm (0.13–3.486 ppm). The distribution of chlorophyll-a has a positive correlation with phosphate for both estuaries, but not for nitrate. The results of statistical tests using Kruskal Wallis showed that the concentrations of chlorophyll-a, nitrate, and phosphate in the BKB and BKT estuaries did not show any difference ($p > 0.05$).

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