



Time Series Analysis of Chromophoric Dissolved Organic Matter (CDOM) at Perancak Estuary

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Abstrak

Penelitian ini bertujuan untuk mengetahui pengaruh pasang surut air laut terhadap perubahan CDOM, parameter in-situ dan nutrisi di Muara Perancak. Subyek penelitian ini adalah air muara yang diambil dari Muara Perancak dan disaring menggunakan GF/F 0,7 μm dengan bantuan injeksi. Objek penelitian ini adalah absorbansi CDOM, konsentrasi nutrisi dan parameter in-situ. Sampel dikumpulkan setiap 1 jam sekali selama 25 jam, diukur parameter in-situ. Air muara yang telah disaring dimasukkan ke dalam botol sampel dan diletakkan di dalam kotak yang dijauhkan dari cahaya. Absorbansi dan konsentrasi nutrisi diukur menggunakan Spektrofotometer UV-1800 Shimadzu UV-Vis. Kemiringan spektral absorbansi (S) dan $E_2:E_3$ dihitung dari absorbansi. Hasil menunjukkan bahwa $S_{275-295}$ dan $E_2:E_3$ berkorelasi negatif dengan ketinggian air, sedangkan S_R tidak menunjukkan korelasi positif dan negatif dengan ketinggian air. Selain itu sebagian besar parameter in-situ menunjukkan korelasi positif dengan ketinggian air dan beberapa unsur hara menunjukkan korelasi negatif dengan ketinggian air.

Kata kunci: Pasang surut, bahan organik terlarut kromoforik, kemiringan spektral, nutrisi, parameter in-situ dan muara.

Abstract

This study aimed at determining the effect of sea tides on changes of CDOM, in-situ parameters and nutrients on Perancak Estuary. The subject of this study was estuary water collected from Estuary Perancak and filtered using GF/F 0.7 μm with help of injection. The objects of this study were CDOM absorbance, nutrients concentration and parameters in-situ. Sampel collected every 1 hour once for 25 hours, were measured in-situ parameters. Filtered estuary water was placed into sample bottles and placed in a box was kept away from light. Absorbance and nutrients concentration were measured using UV-1800 Shimadzu UV-Vis Spectrophotometer. Absorbance spectral slope (S) and $E_2:E_3$ were calculated from the absorbance. Result shows that $S_{275-295}$ and $E_2:E_3$ had a negative correlation with water level, while S_R did not show any positive and negative correlation with water level. In addition most of in-situ parameters show a positive correlation with water level and some of nutrients show a negative correlation with water level.

Keywords: Tidal, chromophoric dissolved organic matter, spectral slope, nutrients, in-situ parameters and estuary.

1. INTRODUCTION

Organic substances in water can take the form of dissolved substances or substances that are difficult to dissolve. Organic matter that has been dissolved is one of the substances that dissolves easily (DOM). In the open ocean, DOM plays an important role in the absorption of ultraviolet (UV) and visible light (Nelson and Siegel, 2002). DOM is generally analyzed in one of its fractions, such as chromophoric dissolved organic matter, due to its complexity as a dissolved component (CDOM). Because CDOM is a colored fraction of DOM, it can absorb light, both ultraviolet and visible light. CDOM, in high concentrations, can protect aquatic organisms from ultraviolet (UV) light. Light-induced CDOM degradation can result in the production of NH_4 and PO_4 , both of which are required nutrients for phytoplankton growth (Bushaw et al., 1996). Furthermore, CDOM photolysis causes the release of low molecular weight compounds, which can serve as a source of labile substrates for microbes (Moran and Zeep, 1997). Estuaries serve as a link between marine and freshwater habitats. However, some of its physical and biological properties do not exhibit transitional characteristics from fresh water to seawater, but rather a water-specific

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characteristic (Rositasari & Rahayu, 1994). Estuaries play an important role in filtering organic and inorganic materials that are on their way to the sea, including heavy metals and nutrients. Estuaries are areas where fresh water and sea water mix due to tides (Fontes et al., 2016). Tides, or fluctuations in sea level at any time, occur in most places twice a day, for 24 hours. When described graphically, it is clear that the tide phenomenon is a periodic phenomenon. The difference between the lowest and highest water levels occurs over a 6-hour period.

Tides are an important physical factor in the circulation of the estuary flow, which moves upstream during high tide and downstream during low tide. As the flow moves closer to the sea, the value of dissolved oxygen (DO) increases, because open areas allow oxygen to flow more easily (Sembiring & Agustriani, 2012). Tidal currents influence changes in salinity and turbidity along the estuary (Dharmawan, 2014), and changes in salinity influence changes in pH. When the salinity rises, the pH rises due to an increase in carbonate ions. An increase in salinity is the same as an increase in organic and inorganic substances, such as salt, so that as salinity rises, so will total anions and cations, which are calculated in the Total Dissolved Solid (TDS) value. According to the findings of Mustiawan et al. (2014), tides play a role in the distribution of dissolved inorganic nitrogen (nitrite and nitrate). Changes in the concentration of the dissolved nutrient nitrate are strongly influenced by physical and chemical factors; when DO levels are low, nitrate is reduced to nitrite, which is then reduced to ammonia.

DOM time series analysis has been performed in a number of studies. Many biogeochemical processes can be studied over time spans ranging from minutes to months (Downing et al., 2009). CDOM absorption decreases offshore to very low levels at distances greater than 100 km (Del Vecchio et al., 2009). The presence of a mixing process is the primary factor that governs the DOM characteristics along the estuary area (Asmala et al., 2016). Because studies on the CDOM time series mentioned above have not been conducted in Bali specifically, it is necessary to investigate the analysis of the CDOM absorbance time series based on tides to determine how the tidal effect affects CDOM absorbance, in-situ parameters, and dissolved nutrients. which is centered on the Perancak Estuary. A time series analysis is an example of a longitudinal design (Velicer & Joseph, 2003). Longitudinal design is a sampling technique that uses repeated observations accompanied by repeated measurements of each variable over a specific time period. Time series analysis is a sampling method that is performed continuously over a set period of time. Dissolved organic matter (DOM) will have a close relationship with several inorganic compounds and water quality parameters such as salinity, pH, and Total Dissolved Solids in time series analysis (TDS).

This time series analysis was carried out in the Perancak Estuary, which is heavily influenced by tides. The Perancak Estuary is located in Jembrana Regency, which is home to Bali's largest fishing industry unit. The activity of the fishing industry, which dumps waste into sea waters, as well as the traffic of fishing vessels and the movement of currents, causes disposed-of waste, particularly organic matter waste, to distribute nitrogen, particularly nitrate, nitrite, and ammonia, to other waters. Because the Perancak river and estuary (Perancak Estuary) are part of the mass circulation system of water in the Bali Strait as an equilibrium system between the Indian Ocean and the Java Sea, this distribution occurs (Mustiawan et al., 2014). The goal of this study was to look at how tides affect CDOM and nutrient absorption in the Perancak Estuary.

2. METHODS

The purpose of this descriptive study is to examine time series of Chromophoric Dissolved Organic Matter (CDOM) and Nutrients in the Perancak Estuary, Jembrana-Bali. The time series analysis in question involves continuous water sampling for at least one tidal cycle. The Perancak Estuary in Jembrana Regency, Bali, was chosen for sampling (Figure 1).

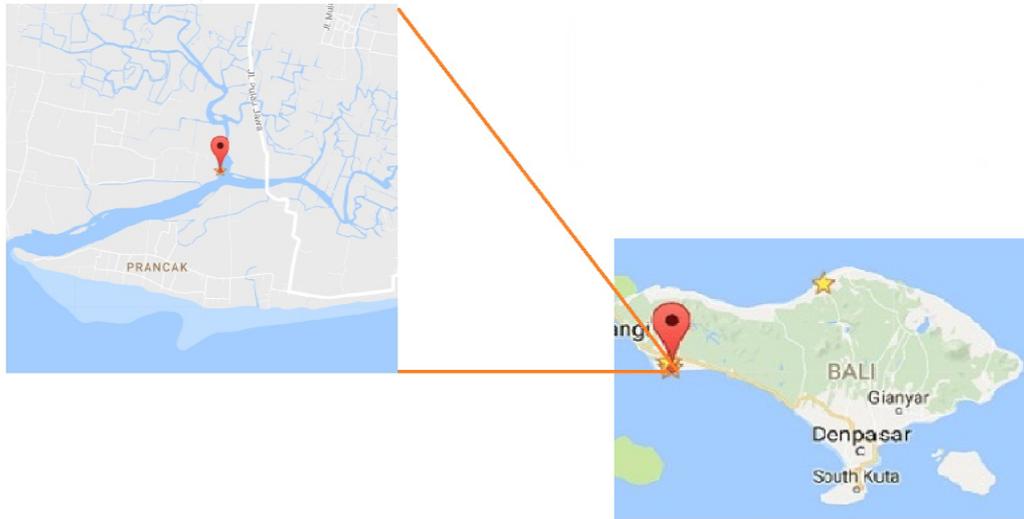


Figure 1. Sampling Area at Perancak Estuary.

The water in the Perancak Estuary was filtered using 0.7 m GF/F filter paper with the help of an injection in this study. The Perancak Estuary was studied for CDOM absorbance, nutrient concentrations, salinity, DO, temperature, pH, and TDS. The sampling technique is a time series technique, which means that sampling is done on a regular basis for 25 hours based on a specific period of time. Samples were collected at the Perancak Estuary, Jembrana Bali, from 30 September 2016 at 10.55 WITA to 1 October 2016 at 11.55 WITA. Every 1 (one) hour, samples are taken, and salinity, pH, TDS, and DO are measured in-situ. After taking measurements and recording the results, the sample was immediately filtered using 0.7 m GF/F filter paper and collected into a bottle using an injection. The same treatment was used for 25 hours of sampling.

Dissolved Nutrients Analysis

a. Ammonium

A 25 mL sample was pipetted into a 50 mL volumetric flask. After adding 1 mL of phenol, 1 mL of sodium nitro prusside, and 2.5 mL of oxidizing agent (100 mL alkaline citrate with 25 mL sodium hypochlorite), the sample was homogenized. For one hour, the solution was placed in a dark room. The sample's absorbance was then measured with a UV-Vis spectrophotometer at a wavelength of 736 nm (SNI 3554: 2015).

b. Nitrate

A 25 mL sample was pipetted into a 50 mL Erlenmeyer tube, and 0.5 mL 1 N HCl was added. A UV-Vis spectrophotometer was used to measure the sample at 220 and 275 nm wavelengths (SNI 3554: 2015).

c. Nitrite

A 25 mL sample was pipetted into a 50 mL volumetric flask. Add 0.5 mL of sulfanilic acid and allow the solution to react for 2-8 minutes. The sample was treated with 0.5 mL of N-(1-naphthyl ethylenediamine dihydrochloride) solution, shaken, and allowed to stand for at least 10 minutes. A UV-Vis spectrophotometer was used to measure the

absorbance of the solution at wavelengths ranging from 190 nm to 900 nm (SNI 3554:2015).

d. Phosphate

A 25 mL sample was pipetted into an Erlenmeyer flask, then add 1 drop of phenolphthalein indicator. If a pink color appears in the sample, 5 N sulfuric acid is added drop by drop until the pink color disappears. A total of 8 mL of the mixed solution (50 mL of 5 N sulfuric acid, 5 mL of potassium antimonyl tartrate solution, 15 mL of ammonium molybdate solution, and 30 mL of ascorbic acid solution) was added and homogenized. A UV-Vis spectrophotometer set to 880 nm was used to measure the absorbance of the solution (SNI-06-6989.31-2005).

e. CDOM absorbance

Before measuring absorbance, the sample was allowed to cool to room temperature. The absorbance of the sample was then measured using a spectrophotometer while scanning at a wavelength of 200-800 nm. The spectral slope parameter, slope ratio (S_R), and $E_2:E_3$ will be used to analyze descriptively the CDOM absorbance measurement data in the Perancak Estuary. There are two methods for calculating Spectral Slope. The spectral slope is first calculated using non-linear regression and the Sigmaplot software. Second, according to research, the spectral slope was calculated using linear regression (Helms et.al., 2008). According to Helms et al (2008) the spectral slope is also calculated at wavelengths 275-295 nm and 350-400 nm using linear regression. The spectral slope at wavelengths of 275-295 nm and 350-400 nm is compared using S_R . In addition to the spectral slope, one should consider the absorbance ratio at 254 nm and 365 nm is the parameter used to describe CDOM ($E_2:E_3$). This parameter is frequently used to describe CDOM's molecular weight. The dissolved nutrient level in water and its relationship the descriptive relationship between dissolved nutrient levels and DOM was investigated.

3. RESULTS AND DISCUSSION

Result

Water samples for this study were collected at the Perancak Estuary in the Jembrana Regency of Bali, at coordinates 08.39361°S and 114.62321°E. The samples were collected on September 30, 2016 at 10.55 WITA and stored in the freezer at 0°C until October 1, 2016. The samples were measured between the 7th and 13th of February, 2017. Nutrient, pH, temperature, salinity, DO, and CDOM absorbance were all measured. Table 1 displays data from in-situ parameter measurements and Table 2 shows result of dissolved nutrients data.

Table 1. In-situ Measurement

| Sample | Temperature (°C) | Salinity | TDS | DO, mg/L | pH |
|--------|------------------|----------|-------|----------|------|
| TSA 1 | 30.4 | 30.9 | 30.98 | 6.8 | 7.77 |
| TSA 2 | 30.7 | 32.2 | 32.16 | 7.31 | 8.08 |
| TSA 3 | 31.8 | 31.9 | 31.92 | 7.46 | 8.04 |
| TSA 4 | 33.2 | 31.2 | 31.33 | 7.25 | 8.02 |
| TSA 5 | 34.3 | 31.1 | 31.28 | 6.96 | 7.95 |
| TSA 6 | 33.5 | 28.2 | 28.65 | 6.36 | 7.87 |
| TSA 7 | 33.3 | 12.6 | 13.82 | 6.42 | 7.86 |
| TSA 8 | 33.2 | 11.6 | 12.79 | 6.45 | 7.88 |
| TSA 9 | 33.1 | 25.3 | 26.04 | 6.04 | 7.83 |
| TSA 10 | 32.4 | 28 | 28.45 | 6.31 | 7.88 |
| TSA 11 | 30.3 | 32.1 | 32.07 | 9.76 | 8.15 |
| TSA 12 | 29.8 | 32.5 | 32.4 | 9.68 | 8.17 |
| TSA 13 | 29.4 | 32.5 | 32.38 | 9.29 | 8.17 |

| Sample | Temperature (°C) | Salinity | TDS | DO, mg/L | pH |
|--------|------------------|----------|-------|----------|------|
| TSA 14 | 29.4 | 32.6 | 32.47 | 9.21 | 8.16 |
| TSA 15 | 29.5 | 32.1 | 32.07 | 8.78 | 8.1 |
| TSA 16 | 29.4 | 31.6 | 31.67 | 7.69 | 8.04 |
| TSA 17 | 29.2 | 31.4 | 31.38 | 6.61 | 7.92 |
| TSA 18 | 29.8 | 29.8 | 30.08 | 5.89 | 7.85 |
| TSA 19 | 29.7 | 28.6 | 28.99 | 5.85 | 7.85 |
| TSA 20 | 28.9 | 27.8 | 28.15 | 6.04 | 7.73 |
| TSA 21 | 29.8 | 25.6 | 26.25 | 5.88 | 7.68 |
| TSA 22 | 30.2 | 27.2 | 27.66 | 6 | 7.78 |
| TSA 23 | 29.8 | 31.6 | 31.6 | 8.16 | 7.96 |
| TSA 24 | 30.2 | 32.3 | 32.33 | 7.14 | 8.13 |
| TSA 25 | 29.8 | 32.8 | 32.63 | 8.54 | 8.13 |
| TSA 26 | 30.1 | 33 | 32.5 | 8.9 | 8.2 |

Table 2. Dissolved nutrients data.

| Sample | Parameter | | | |
|--------|-----------|---------|---------|-----------|
| | Amonium | Nitrate | Nitrite | Phosphate |
| TSA 1 | 0.001 | 0.039 | 0.001 | 0.0535 |
| TSA 2 | 0 | 0.044 | 0.003 | 0.0525 |
| TSA 3 | 0.006 | 0.041 | 0.003 | 0.059 |
| TSA 4 | 0 | 0.042 | 0.003 | 0.202 |
| TSA 5 | 0.001 | 0.068 | 0.004 | 0.0735 |
| TSA 6 | 0.074 | 0.036 | 0.001 | 0.093 |
| TSA 7 | 0.005 | 0.069 | 0.008 | 0.1145 |
| TSA 8 | 0.004 | 0.077 | 0.011 | 0.142 |
| TSA 9 | 0.005 | 0.066 | 0.01 | 0.1625 |
| TSA 10 | 0.011 | 0.069 | 0.008 | 0.121 |
| TSA 11 | 0.012 | 0.039 | 0.002 | 0.0645 |
| TSA 12 | 0.002 | 0.048 | 0.001 | 0.059 |
| TSA 13 | 0.003 | 0.04 | 0.001 | 0.043 |
| TSA 14 | 0.006 | 0.043 | 0.001 | 0.0425 |
| TSA 15 | 0.002 | 0.045 | 0.002 | 0.0485 |
| TSA 16 | 0.012 | 0.045 | 0.002 | 0.063 |
| TSA 17 | 0.02 | 0.068 | 0.006 | 0.0925 |
| TSA 18 | 0.005 | 0.051 | 0.006 | 0.0885 |
| TSA 19 | 0.003 | 0.054 | 0.008 | 0.101 |
| TSA 20 | 0.005 | 0.072 | 0.01 | 0.0955 |
| TSA 21 | 0.024 | 0.066 | 0.011 | 0.091 |
| TSA 22 | 0.006 | 0.069 | 0.009 | 0.104 |
| TSA 23 | 0.008 | 0.043 | 0.004 | 0.057 |
| TSA 24 | 0.015 | 0.029 | 0.002 | 0.05 |
| TSA 25 | 0.007 | 0.035 | 0.004 | 0.057 |
| TSA 26 | 0.006 | 0.04 | 0.002 | 0.051 |

Data on the average value of Spectral Slope measurements from the time series results are presented in Table 3.

Table 3. CDOM measurement data.

| Sample | S ₂₇₅₋₂₉₅ | S ₃₅₀₋₄₀₀ | S _R | E ₂ :E ₃ |
|--------|----------------------|----------------------|----------------|--------------------------------|
| TSA 1 | 0.000292 | 7.13E-05 | 4.088356 | 1.538462 |
| TSA 2 | 0.000219 | 5.92E-05 | 3.697893 | 1.459459 |
| TSA 3 | 0.000363 | 9.40E-05 | 3.860445 | 1.658537 |
| TSA 4 | 0.000411 | 0.000106 | 3.862793 | 1.731707 |
| TSA 5 | 0.000518 | 0.000133 | 3.90305 | 1.906977 |
| TSA 6 | 0.000524 | 0.00013 | 4.030036 | 1.826087 |
| TSA 7 | 0.000706 | 0.000171 | 4.138107 | 2.155556 |

| | | | | |
|--------|----------|----------|----------|----------|
| TSA 8 | 0.000901 | 0.000291 | 3.098609 | 2.214286 |
| TSA 9 | 0.000743 | 0.000195 | 3.809239 | 2.191489 |
| TSA 10 | 0.000588 | 0.000168 | 3.499518 | 1.977778 |
| TSA 11 | 0.000332 | 8.29E-05 | 4.010244 | 1.609756 |
| TSA 12 | 0.000232 | 7.44E-05 | 3.122363 | 1.475 |
| TSA 13 | 0.000223 | 5.24E-05 | 4.264716 | 1.421053 |
| TSA 14 | 0.000253 | 6.56E-05 | 3.85853 | 1.487179 |
| TSA 15 | 0.000348 | 8.61E-05 | 4.037472 | 1.619048 |
| TSA 16 | 0.000407 | 0.000112 | 3.647761 | 1.697674 |
| TSA 17 | 0.000581 | 0.000167 | 3.47311 | 1.957447 |
| TSA 18 | 0.000556 | 0.00015 | 3.710631 | 1.911111 |
| TSA 19 | 0.000583 | 0.00016 | 3.652384 | 1.977778 |
| TSA 20 | 0.000655 | 0.000175 | 3.736628 | 2.086957 |
| TSA 21 | 0.000685 | 0.000184 | 3.714068 | 2.106383 |
| TSA 22 | 0.000667 | 0.000181 | 3.686122 | 2.0625 |
| TSA 23 | 0.000334 | 9.34E-05 | 3.576866 | 1.65 |
| TSA 24 | 0.000254 | 8.42E-05 | 3.016113 | 1.5 |
| TSA 25 | 0.000212 | 5.57E-05 | 3.803228 | 1.421053 |
| TSA 26 | 0.000234 | 5.67E-05 | 4.121468 | 1.473684 |

Discussion

In-situ Parameter

The highest tide occurred 11 hours and 23 hours after the sampling began. The lowest ebb occurred 5 hours and 17 hours after sampling began. In-situ measurements for the parameters measured, including salinity, DO, pH, TDS, and temperature, were also performed at the sampling point. Salinity has a tendency to have maximum and minimum values that are nearly equal to sea level. However, there was a significant decrease in salinity at 7 hours after sampling, which was close to 9. This meant that fresh water had made its way into the estuary system. TDS exhibits a trend of maximum and minimum values that are nearly identical to sea level. There was a change in pattern 7 hours after sampling that resembled the salinity pattern. This indicates a positive relationship between salinity and TDS, which is related to the amount of dissolved salts, which increases as salinity increases. The pH does not have a tendency for the maximum and minimum values to be nearly the same; in theory, the pH will rise during a tide because the dominant seawater is alkaline (Spellman, 2010). DO exhibits a tendency for maximum and minimum values to invert with sea level, indicating a negative correlation. DO rises as the water flows towards the sea, because open areas allow oxygen to diffuse more easily into the water (Sembiring and Agustriani, 2012). Temperature does not have a tendency for maximum and minimum values to be nearly the same, indicating that tides have no effect on temperature because sea surface temperature is affected by rainfall, air humidity, and the intensity of solar radiation.

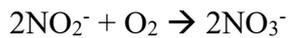
Effect of Tides to the CDOM Absorbance

The highest tide occurred 11 hours and 23 hours after the sampling began. The lowest ebb occurred 5 hours and 17 hours after sampling began. In addition to in-situ measurements, the samples were analyzed for CDOM parameters such as Spectral Slope ($S_{275-295}$), Slope Ratio (S_R), and $E_2:E_3$. The value of $S_{275-295}$ demonstrates the tendency of maximum and minimum values to invert with sea level. This implies that when it recedes, the majority of the CDOM comes from the mainland (territorial). $E_2:E_3$ values show an inverted trend of maximum and minimum values with sea level. $E_2:E_3$ values decrease as CDOM molecule size increases due to stronger light absorption by CDOM with a higher molecular weight

(Helms et al. 2008). This is significant. This means that when the water level is high (tide), the $E_2:E_3$ value decreases because of the presence of CDOM with a high molecular weight (HMW). The lack of a negative or positive correlation in the SR results indicated that the wavelength range was too wide to provide sufficient information about the relative molecular weight of DOM.

4.3. Dissolved Nutrients

The highest tide occurred 11 hours and 23 hours after the sampling began. The lowest ebb occurred 5 hours and 17 hours after sampling began. In addition to obtaining in-situ measurement data, nutrient levels (NO_3^- , NO_2^- , NH_4^+ , and PO_4^{3-}) were measured to analyze several CDOM parameters. The ammonia parameter has no tendency for maximum and minimum values to be nearly equal to sea level. This indicates that the concentration of ammonia is not affected by tides. This can be explained by the fact that ammonia is a component of nitrogen compounds that are unstable because they are easily oxidized to nitrite compounds through the nitrification process, and nitrite compounds are also easily oxidized to nitrate compounds, and in low dissolved oxygen conditions, nitrate will be reduced to nitrite, which will be further reduced to ammonia and nitrogen gas. The following is the reaction equation.



The nitrate parameter demonstrates the tendency of maximum and minimum values to invert with sea level. This indicates that the concentration of nitrate increases as the tide recedes because at high tide, there is a mass mixing of water from the sea and river water, which causes salinity to increase and a dilution of the concentration of nitrate around the mouth of the river (Mustiawan et al., 2014), as well as the nitrite parameter showing a trend in which maximum and minimum values are reversed with sea level. This means that as the water mass recedes upstream, it will carry nitrite, a transitional compound between nitrate and ammonia formed by ammonia oxidation and the reduction of nitrate compounds from organic matter as a result of waste from human activities and natural processes. The phosphate parameter exhibits an inverse relationship between maximum and minimum values and sea level. This indicates that phosphate, nitrate, and nitrite have the same tendency, which can be explained by the fact that the source of phosphate can be natural or the result of human activity, which is the same as the source of nitrite and nitrate compounds, so that when it recedes, the source of phosphate is from the mainland.

4. CONCLUSION

The tides can affect CDOM absorbance; spectral slope analysis ($S_{275-295}$) can provide information that when the tide recedes, the CDOM that dominates comes from terrestrial (land); the slope ratio (S_R) value is not accurate enough when used to determine the average molecular weight of CDOM and $E_2:E_3$ can provide information on changes in the size of the molecular weight of CDOM; therefore, the value of $E_2:E_3$ will decrease in the presence of CDOM with a high molecular weight (HMW). Nitrate, nitrite, and phosphate nutrients have a negative correlation with sea tides, whereas ammonia does not. Because ammonia is an unstable compound, this can happen. In-situ parameters (salinity, TDS, pH, and DO) have a positive correlation with sea tides, whereas temperature does not.

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