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AIR-SEA FLUX OF CO_2 IN THE WATERS OF KARIMUNJAWA ISLAND, INDONESIA

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ABSTRACT

The purpose of this study was to determine the distribution of CO_2 flux in Karimunjawa in the east monsoon. The variables in this study were temperature; pH; salinity; DO; CO_2 atm was measured using a CO_2 meter; chlorophyll-a, phosphate, silicate were measured spectrophotometric method. Total Alkalinity / TA was measured using the titration method with the principle of changing pH; DIC (Dissolved Inorganic Carbon) was measured using CO_2sys software. The partial pressure of seawater carbon dioxide calculated using formula: $pCO_{2sea} = 6.31T^2 + 61,9\ Chla^2 - 365.85T - 94.41\ Chl\text{-}a + 5715.94$, the partial pressure of atmospheric carbon dioxide calculated using formula: $pCO_{2atm} = xCO_{2atm}\ (p_b - pH_2O)$. The calculation of the estimated CO_2 flux using the formula: Flux $CO_2 = K_h \times k_{wa} \times (\Delta pCO_2)$, if the CO_2 flux has a positive value water acts as a CO_2 source, and if it is negative, the waters act as a CO_2 sink.. CO_2 flux in Karimunjawa waters during east monsoon (represented by August 2018) showed that in Karimunjawa waters with normal pH 7.2-7.4 were dominated by bicarbonate ion $HCO^{3-}$with an average value of DIC 1847.24 µmol/kg dan TA 1912.51 µmol/kg. The partial pressure of seawater CO_2 is higher than the partial pressure of atmospheric CO_2 this indicates that the role of Karimunjawa waters as a source of CO_2 where there is release of carbon dioxide into the atmosphere with CO_2 flux values ranging from 8.549 – 13.272 mmol m^{-2} day^{-1}. The variables that affect the flux of CO_2 were the pCO_{2sea} and ΔpCO_2 with a very strong and positive correlation. These two variables were influenced by sea water temperature, salinity, chlorophyll-a, phosphate and silicate.

Keywords: CO_2 Flux; pCO_2; DIC; TA; Karimunjawa

INTRODUCTION

Naturally, the earth's surface consists of land, water, will absorb carbon dioxide gas in the atmosphere, but the rate of emission of CO_2 release into the atmosphere is greater than natural absorption with the result that increasing concentration of CO_2 in the atmosphere every year. The concentration of carbon dioxide in the atmosphere before the industrial revolution was 280 µatm and in 2005 380 µatm (Turley and Findlay 2015). This is supported by observations from NOAA-ESRL that from 2000; 2010 and 2018 there was an increase in CO_2 in the atmosphere, respectively 369.55 ppm; 389.90 ppm; and 409.68 ppm (Jackson et al. 2018). Increased CO_2 in the atmosphere is also influenced by human activities that are not environmentally friendly such as burning fossil fuels (petroleum, coal), deforestation, conversion of forests into settlements or ponds, and so on. These activities can increase greenhouse gases in the atmosphere. Greenhouse gases consisting of carbon dioxide (CO_2), methane (CH_4), di nitroxide (N_2O), methane (CH_4), sulfur Hexa Flouride (SF_6) with the largest gas composition in the atmosphere namely carbon gas dioxide (CO_2) by 75% of the total gases in the atmosphere (Darussalam, 2011). Increasing greenhouse gases in the atmosphere will have an impact on sunlight that cannot be transmitted outside the surface of the earth causing the temperature on the earth to get hotter (global warming). Human activities are estimated to have caused global warming of 0.8 - 1.2 ºC above pre-industrial levels (Hoegh-Guldberg O. et al. 2018).

The increase in the earth's temperature because global warming will be an impact on climate change and rising temperatures in the marine ecosystem (Pachauri 2014). Besides the increase in temperature, there is an increase in CO2 in the ocean because there is a lot of CO_2 gas in the atmosphere. Increased carbon dioxide CO_2 in the ocean will trigger a decrease in oxygen vertically and horizontally until hypoxia-anoxia occurs ((Oschlies et al. 2008) and (Engel et al. 2014)) Hypoxia-anoxia conditions in Indonesian waters especially in coastal areas can trigger the occurrence of toxic algal blooms, fish mortality, changes in stratification, reduction in the diversity of aquatic biota, decreased production of fish catches. Besides that, the increase of organic and inorganic carbon in the sea can stimulate the growth of phytoplankton which will utilize inorganic carbon through photosynthesis into dissolved inorganic carbon (Oschlies et al. 2008). An understanding of the existence of carbon systems in the ocean is essensial very important to estimate atmospheric CO2 concentrations in the future as well as the rate of global warming, especially in the context of changes in ocean circulation (Oschlies et al. 2008).

The oceans absorb atmospheric CO2 through a transfer process called a solubility pump which functions as a solubility gas in seawater. In the sea, CO_2 will change its form to free aqueous CO_2, bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). The difference in the partial pressure of CO_2 in seawater and the atmosphere determines the direction of the flow of CO_2 gas between the ocean and the atmosphere. Thus the direction of CO_2 flux is controlled mainly by changes in ocean pCO_2 (Zeebe 2012). The partial pressure of CO_2 in seawater is determined by sea surface temperature and biological processes in the sea such as photosynthesis, so that the two parameters can determine between the sink CO_2 and source CO_2 (Feely et al. 2001). Research has been conducted to determine the distribution of CO_2 flux, the results of the study concluded that the high latitude sea which has 4 seasons and relatively cold temperatures has a function as a sink CO_2 ((Takahashi et al. 1997); (Takahashi et al. 2002); (Cai, Dai, and Wang 2006); (Yasunaka et al. 2016); (Arnone, González-Dávila, and Magdalena Santana-Casiano 2017); (Ito et al. 2018)). Whereas at low latitudes it has a function as a source CO_2 due to warm waters ((Fitranti et al. 2013); (Kartadikaria et al. 2015); (Afdal 2016); (Yan et al. 2018); (Wirasatriya et al. 2020)), however, in several studies, the waters in Indonesia can function as a sink CO_2 (Fachri et al. 2015) (Latifah, Endrawati, and Febrianto 2019). The investigation of CO_2 flux in the Java Sea during May 2016 – February 2017 has been conducted by Wirasatriya et al (2020) by using remote sensing approach. They show that Java Sea in mainly acts as carbon source. However, due to the limitation of the spatial resolution of the used satellite data, Karimunjawa area were left blank. In the present study we use field observation to reveal the CO2 flux in the Sea around Karimunjawa Island. Therefore, the purpose of this study was to determine the distribution of CO_2 flux in Karimunjawa in the east monsoon.

RESEARCH METHODS

The CO_2 flux research was performed at the waters of Karimunjawa Island, Indonesia, located in the middle of the Java Sea, during east monsoon (represented by August 2018). Samples were taken at 15 sampling points, all of which are at a depth of ± 3 meters close to the beach (Figure 1).

Figure 1. Research Location at Karimunjawa Waters

The variables in this study were temperature; pH; salinity; DO; atmospheric CO_2 was measured using a CO_2 meter; chlorophyll-a, phosphate, silicate were measured spectrophotometric method. Total Alkalinity / TA was measured by taking seawater samples and preserving it using $HgCl_2$ then the sample is taken to the laboratory for testing using the titration method with the principle of changing pH after the addition of NaOH and HCl; DIC (Dissolved Inorganic Carbon) was measured using CO_2sys software.

Partial Pressure of CO_2

Seawater CO_2 partial pressure was calculated using a formula (Zhu et al. 2009); (Wirasatriya et al. 2020):

$$pCO_{2sea} = 6.31T^2 + 61{,}9\ Chla^2 - 365.85T - 94.41\ Chl\text{-}a + 5715.94 \qquad (1)$$

where T is sea surface temperature (^oC); Chl-a is Chlorophyll-a

The partial pressure of atmospheric CO_2 can be calculated using a formula (Dickson, Sabine, and Christian 2007); (Zhu et al. 2009); (Kartadikaria et al. 2015):

$$pCO_2atm = xCO_2atm\ (pb - pH_2O) \qquad (2)$$

where pb = air pressure (atm); xCO_2atm (ppm) is the molar fraction of CO_2 air in the troposphere obtained from tropospheric mole fraction of CO_2 https://disc.gsfc.nasa.gov/datasets/AIRX3C2M_V005/summary, pH_2O is the water vapour pressure at the air boundary and observing the sea obtained from (Weiss et al. 1980):

$$pH_2O = \exp(24.4543 - 67.4509 \times (100/T)) - 4.8489 \times \ln(T / 100) - 0.000544 \times S \quad \text{.......... (3)}$$

where: T is sea surface temperature (ºC); S is salinity (‰).

Flux CO_2

Calculation of CO_2 flux or CO_2 gas flow exchange is calculated using a formula (Takahashi et al. 2002); (Du et al. 2015); (Fachri et al. 2015); (Kartadikaria et al. 2015); (Takahashi and Sutherland 2017); (Yan et al. 2018); (Wirasatriya et al. 2020):

$$\text{Flux } CO_2 = K_h \times k_{wa} \times (\Delta pCO_2)$$
$$\Delta pCO_2 = pCO_{2sea} - pCO_{2atm} \quad \text{........................ (4)}$$

Where: Flux CO_2 is a carbon dioxide flux (mmol/m^2/day); Kh = solubility of CO_2 in mol/l/atm; k_{wa} = CO_2 gas transfer velocity in m/s; ΔpCO_2 sea+atm = the partial pressure difference of CO_2 in the seawater and the atmosphere.

Calculate K_h solubility of CO_2 is derived from (R. F. Weiss 1974); (Wirasatriya et al. 2020):

$$\ln K_h = -58.0931 + 90.5069/(Tk/100) + 22.2940 \times \ln(Tk/100) + S \times (0.02776 - 0.02588 \times (Tk/100) + 0.0050578 \times (Tk/100)^2) \quad \text{... (5)}$$

Where Tk is sea surface temperature (Kelvin) and S is sea surface salinity (‰).

Calculate the k_{wa} value using the WM99 formula to parameterize the gas transfer rate ((Zhu et al. 2009); (Robbins et al. 2010); (Kartadikaria et al. 2015)):

$$k_{wa} = f \times U_{10}^2 \times (Sc/660)^{-1/2} \quad \text{........................... (6)}$$

Where K is in cm/day; U_{10} is the wind speed at an altitude of 10 m (m/s); U_{10} data is obtained from the ECMWF website (European Centre for Medium-Range Weather Forecasts) https://apps.ecmwf.int/datasets/data/interim-full-daily/; f is the proportional coefficient, when the average wind speed is long-term, the value is f = 0.39 and if the wind speed is instantaneous the value is f = 0.31.

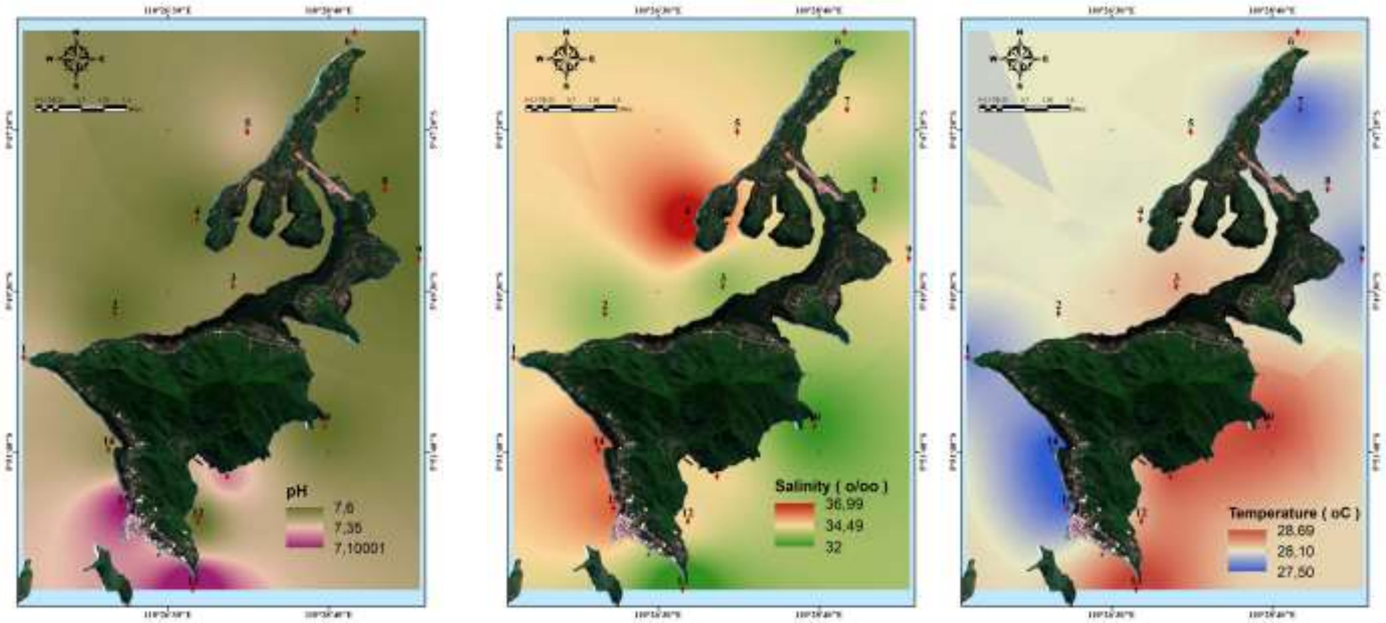
Sc is a dimensionless Schmidt number calculated from (Wanninkhof, 1992):

$$Sc = 2073.1 - 125.62\,T + 3.628\,T^2 - 0.0432\,T^3 \quad \text{.... (7)}$$

Where: Sc = Schmidt number (Schmidt number) radon gas CO2 seawater and T is sea surface temperature (ºC).

RESULTS AND DISCUSSION

Figure 2 showed that the seawater quality results in pH, salinity, and temperature. The pH of the seawaters in east monsoon 2018 is alkaline with a pH value> 7, small pH changes so that the pH range is between 7.1-7.6. Changes in seawater pH are minimal very small because the marine carbonate system acts as a buffer so that if there are an addition of acid (H^+) or alkaline (OH^-) ions, the aquatic carbonate system will change the proportion of bicarbonate HCO_3^- and carbonate CO_3^{2-} ions (National Research Council 2010).



(a) (b) (c)

Figure 2. Spatial Distribution of (a) pH, (b) salinity, (c) temperature in the Waters of Karimunjawa Island During East Monsoon

Changes in seawater pH will cause changes in the composition of carbon dioxide in the water. According to (Effendi 2003); (National Research Council 2010) states that the composition of carbon dioxide in waters with a normal pH of 7-8 will be dominated by bicarbonate ions (HCO_3^-). Acidic pH will be dominated by carbon dioxide ions (CO_2) and in alkaline conditions will be dominated by carbonate ions (CO_3^2). The theory was the same as the results in this study where the composition of carbon dioxide can be seen from the analysis of DIC (Dissolved Inorganic Carbon) which is the sum of HCO_3^-, CO_3^{2-} and CO_2 (Figure 3). DIC (Dissolved Inorganic Carbon) is the addition of CO_2 dissolved in water. Carbon dioxide in water was present in several forms, carbon dioxide-free (CO_2 (aq)); carbonic acid ions (H_2CO_3); bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}) which form some equilibrium:

$CO_2(gas) \rightleftarrows CO_2(aq)$ (free carbon dioxide)
$CO_2 + H_2O \rightleftarrows H_2CO_3$ (carbonic acid)
$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$ (bicarbonate)
$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$ (carbonate)

Figure 3. showed that in Karimunjawa waters with normal pH 7.2-7.4 were dominated by bicarbonate ion HCO_3^- was 94.09%, while the ion CO_3^{2-} was 3.71% and the ion CO_2 was 2.20. Ion bicarbonate HCO_3^- was favoured by phytoplankton and other algae to carry out the photosynthesis process. Carbon dioxide and pH play an important role as mediators of physiological functions in marine organisms such as phytoplankton, seagrass, algae, and other photosynthetic organisms by converting CO_2 into organic C through photosynthesis. (King et al. 2015).

Figure 3. Composition of carbon dioxide in the Waters of Karimunjawa Island during east monsoon

Alkalinity is the capacity of water to neutralize acids, as a buffering capacity against changes in water pH. According to (Gerardi 2003), total alkalinity is the amount of acid needed to lower the pH to a point where all carbonate (CO_3^-) and bicarbonate (HCO_3^-) can be converted into carbonic acid (H_2CO_3). High alkalinity has a sound buffer system. Total alkalinity is the amount of acid needed to lower the pH of the sample water to a point where all carbonates and bicarbonates turn into carbonic acid (Yang, Byrne, and Lindemuth 2015). The range of alkalinity values in this study ranged from 1311.91 to 2746.80 µmol kg^{-1} with a mean of 1912.51 (Figure 4), most of which have lower amounts than other studies. Research by (Fachri et al. 2015), the alkalinity value of 2097.30 - 2343.92 µmol kg^{-1}, while the study of (Yan et al. 2018) the alkalinity value is 2682 - 2776 µmol kg^{-1}.

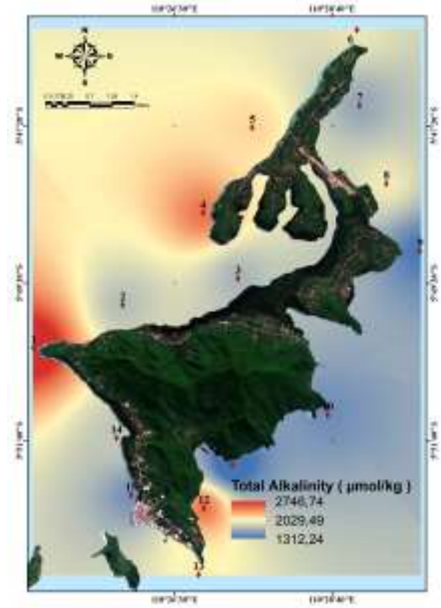
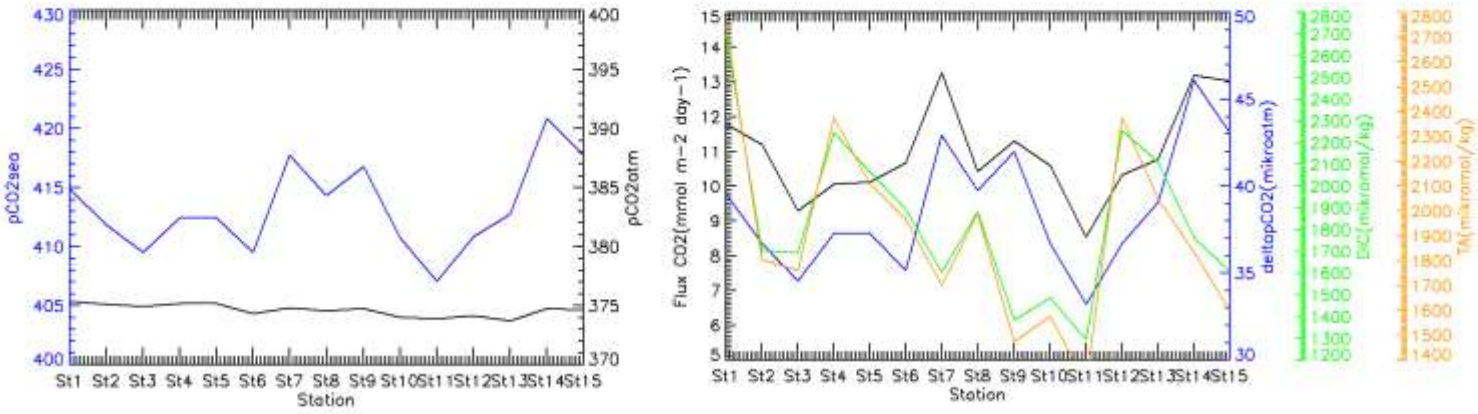


Figure 4. Spatial Distribution Total Alkalinity (TA) in the Waters of Karimunjawa Island During East Monsoon

The results of the partial pressure of carbon dioxide and CO_2 flux at 15 stations were different. The difference in CO_2 flux and partial pressure of CO_2 in each water is due to the interaction of the oceans and the atmosphere in each water, because the earth rotates and evolves with respect to the sun and moon. The form of interaction between the oceans and the atmosphere is the atmosphere will transfer gases including carbon dioxide gas and transfer rainfall to the waters. In contrast the oceans will transfer water vapour and return the gases to the atmosphere. This interaction causes differences in carbonate systems in the sea, differences in the partial pressure of carbon dioxide and CO_2 flux spatially ((Song et al. 2016); (Yasunaka et al. 2016)).

Karimunjawa act as a source of CO_2, meaning that the partial pressure of seawater CO_2 is higher than the partial pressure of atmospheric CO_2 (Figure 5a) so that the transfer of gases including carbon dioxide gas from the oceans is returned to the atmosphere. This pattern is indicated by a positive ΔpCO_2 value in the range of 33.205 – 46.123 µatm followed by a positive CO_2 flux value in the range of 8.549 – 13.272 mmol/m^2/day (Figure 5b and Figure 6). The results of this study are the same as previous research by (Wirasatriya et al. 2020)in the Java Sea during the summer monsoon 2015 that the Java Sea acts as a source of CO_2 where the CO_2 flux value is more than 10 mmol m^{-2} day^{-1}. The seawater pCO_2 depends on the dissolved inorganic carbon (DIC); the temperature dan the pH of seawater (Takahashi and Sutherland 2017). According to the research results of (Kartadikaria et al. 2015), showed that temperature has a limited effect in controlling the CO_2 sink or the source of CO_2. It added that the change in sea surface temperature during La Nina effectively reduced the pCO_2 difference between the oceans and the atmosphere by 50% compared to a normal year.



(a) (b)

Figure 5. a) Graph pCO_{2sea} and pCO_{2atm} b). Graph CO_2 Flux, ΔpCO_2, DIC and TA in the Waters of Karimunjawa Island During East Monsoon

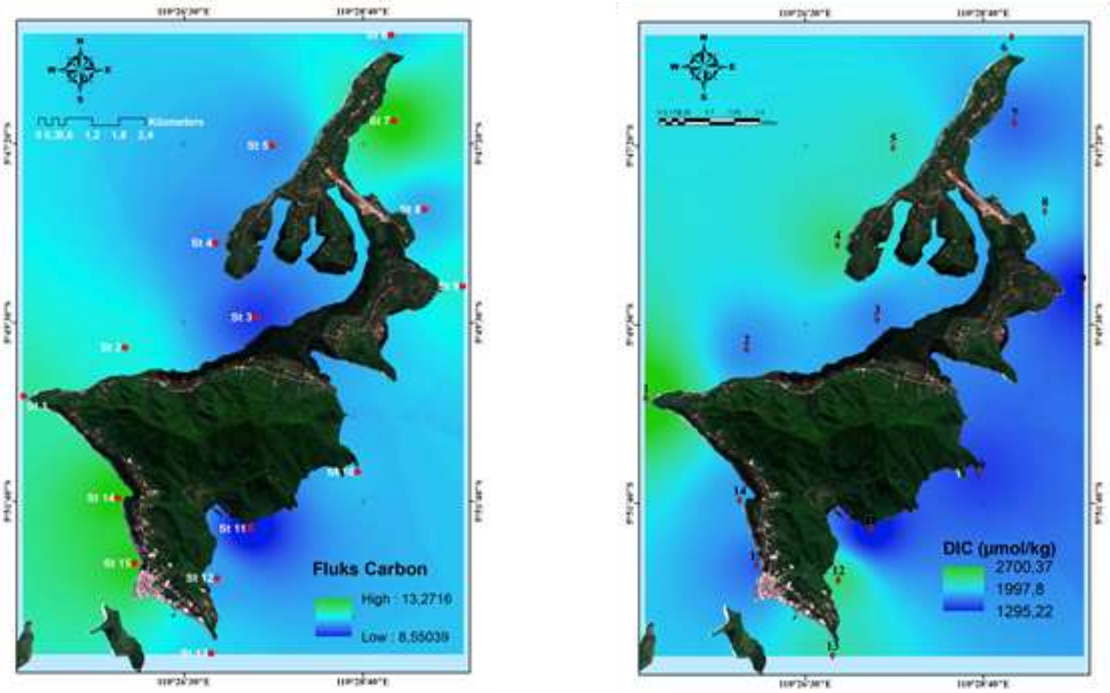


Figure 6. a) Spatial distribution of (a) DIC, (b) Flux of CO_2 in the Waters of Karimunjawa Island During East Monsoon

Principal Component Analysis is a statistical analysis method that aims to determine the relationship between two variables to be observed without having to reduce the number of these variables. In the PCA analysis, new variables called the principal component, whose number is the same as the original variables. The results of the PCA analysis on the east monsoon 2018 (Table 1 and Figure 7) show that the first principal component (PC1) has a variance of 4.173403 or the same as a proportion of 34.778% of the total variance of the overall data. The second principal component (PC2) has a variance of 2.540 or equal to a proportion of 21.1686% of the total variance of data and so on until the last component 11. The first component and two component called PC1 and PC2, account for 55.947% of the total variance. So with two main components to explain the variance of data. This shows that the degree of inter-correlation between several variables and PCA analysis is valid.

Table 1. Eigenvalues of correlation matrix and related statistics in the Waters of Karimunjawa Island during east monsoon

	Eigenvalue	% Total	Cumulative	Cumulative
1	4.173403	34.77836	4.17340	34.7784
2	2.540237	21.16864	6.71364	55.9470
3	2.194194	18.28495	8.90783	74.2319
4	1.373965	11.44971	10.28180	85.6817
5	0.643899	5.36582	10.92570	91.0475
6	0.385986	3.21655	11.31168	94.2640
7	0.271682	2.26401	11.58336	96.5280
8	0.239557	1.99631	11.82292	98.5244
9	0.174587	1.45489	11.99751	99.9792
10	0.002487	0.02073	12.00000	100.0000
11	0.000004	0.00003	12.00000	100.0000

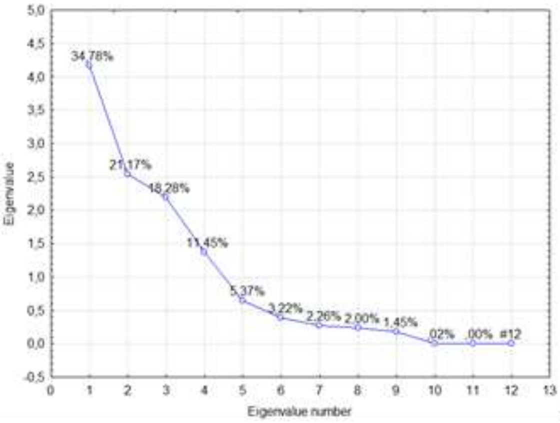


Figure 7. Eigenvalues of Correlation Matrix in the Waters of Karimunjawa Island During East Monsoon

In Figure 8, shown that the fluxes of CO_2, pCO_2sea and ΔpCO_2 were positive and stong correlation. Where the CO_2 flux was positively correlated by ΔpCO_2 of 0.99 (very strong correlation) and partial pressure CO_2 seawater with a correlation value of 0.98 (very strong correlation).

ΔpCO_2 was influenced by phytoplankton, the abundance of different phytoplankton in the waters will cause a difference in the partial pressure of ocean carbon dioxide. According to (Moreau et al. 2013)and (Takao et al. 2020) there was a significant negative correlation between chlorophyll-a and ΔpCO_2 concentrations at stations that were dominated by diatomic phytoplankton, but not at stations dominated by phytoflagellates. In this study, the phytoplankton variable was approached using the chlorophyll-a variable, the results showed that the relationship between chlorophyll-a, and ΔpCO_2 was very strong correlation with a value of 0.8133 using polynomial regression (Figure 9).

Result study of (Takao et al. 2020) shows that ΔpCO_2 has a strong correlation with productivity primary. In this study, productivity primary was approached using chlorophyll-a, phosphate and silicate variables (Figure 10). Increased nutrients can increase phytoplankton growth, increase chlorophyll-a concentration and increase the consumption of carbon dioxide by phytoplankton for photosynthesis so that it can change the partial pressure of carbon dioxide to low. pCO_2sea is also influenced by sea water temperature where the higher the sea water temperature will make it difficult for CO_2 to dissolve in water so that it will be released into the atmosphere and cause high pCO_{2sea}..

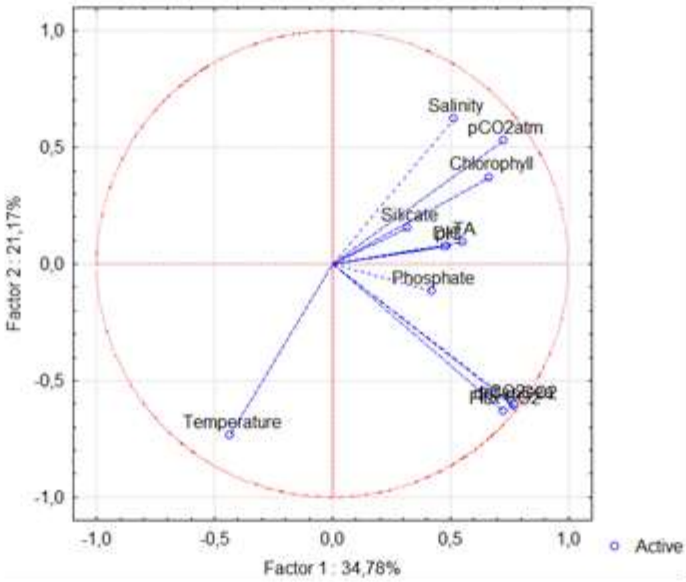


Figure 8. Projection of the Variables in this Study in the Waters of Karimunjawa Island During East Monsoon

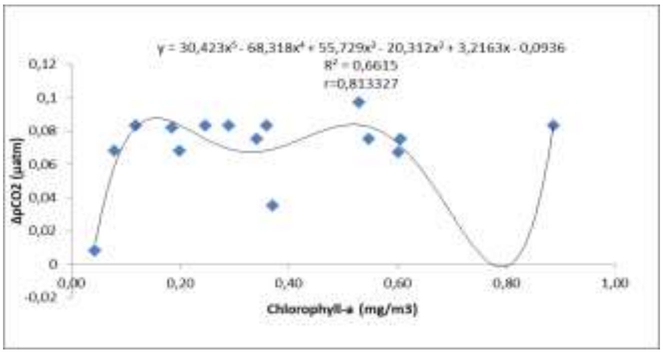
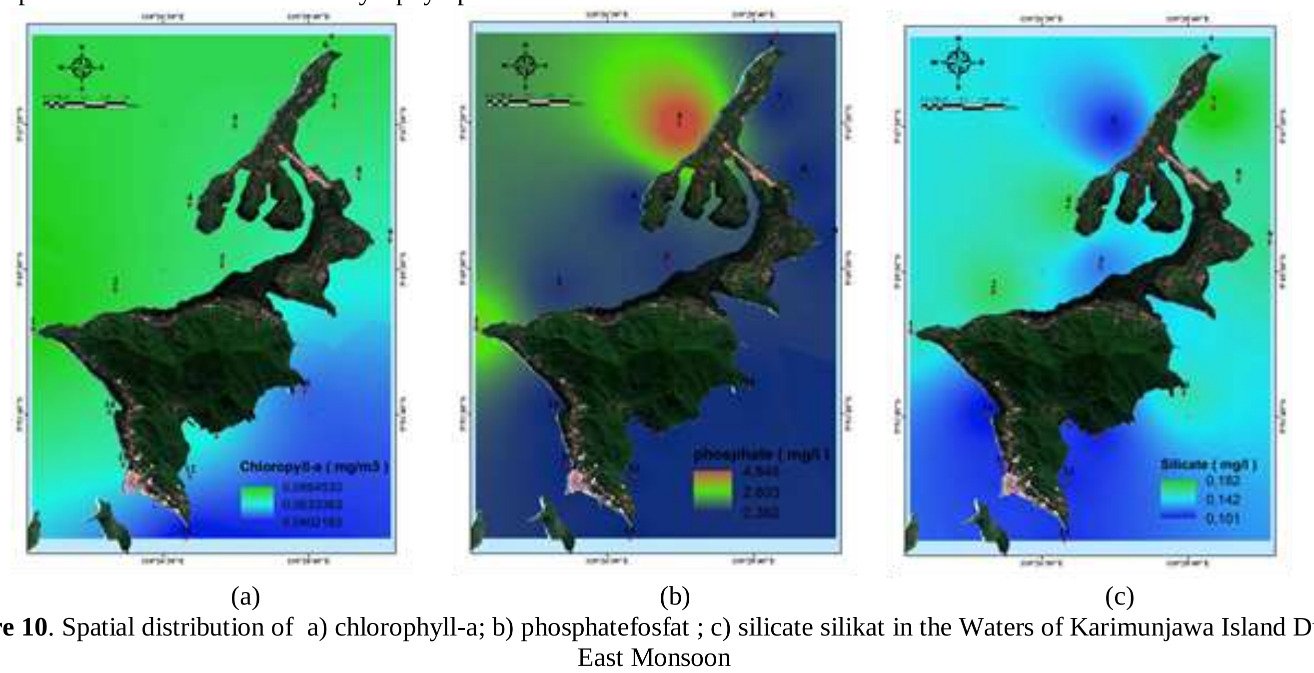


Figure 9. Polynomial regression Chlorophyll-a wit ΔpCO_2



(a) (b) (c)

Figure 10. Spatial distribution of a) chlorophyll-a; b) phosphatefosfat ; c) silicate silikat in the Waters of Karimunjawa Island During East Monsoon

CONCLUSION

CO_2 flux in Karimunjawa waters during east monsoon (represented by August 2018) showed that in Karimunjawa waters with normal pH 7.2-7.4 were dominated by bicarbonate ion $HCO^{3-}$with an average value of DIC 1847.24µmol/kg dan TA 1912.51 µmol/kg. The partial pressure of seawater CO_2 is higher than the partial pressure of atmospheric CO_2 this indicates that the role of Karimunjawa waters as a source of CO_2 where there is release of carbon dioxide into the atmosphere with CO_2 flux values ranging from 8.549 – 13.272 mmol $m^{-2}day^{-1}$. The variables that affect the flux of CO_2 were the pCO_{2sea} and ΔpCO_2 with a very strong and positive correlation. These two variables were influenced by sea water temperature, salinity, chlorophyll-a, phosphate and silicate.

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