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CARBON DIOXIDE FLUX AND ITS RELATIONSHIP TO WATER QUALITY IN THE TELUK AWUR - JEPARA, INDONESIA

Abstract: Anthropogenic activities on land will affect the carbon system in coastal waters. This condition will affect the role of coastal waters as a source or sink of carbon. This research will examine the distribution of carbonate systems and estimate CO₂ fluxes. Water samples were taken at 30 stations as well as measuring in situ water parameters including pH, temperature, salinity, and pressure. Alkalinity was analysed based on the titration method, chl-a using the fluorometer method, and carbonate system parameters ($p\text{CO}_{2(\text{sea})}$ and DIC) calculated using CO₂SYS.xlsm. The $p\text{CO}_{2(\text{atm})}$ value is calculated based on atmospheric data from satellite data, including the saturation vapour pressure of sea air in the atmosphere, fraction mol of CO₂, and sea level pressure. Pearson correlation analysis was used to see the correlation between the measured parameters and CO₂ flux. Carbon flux is determined based on the difference between atmospheric and oceanic $p\text{CO}_2$. The DIC calculation result was in the range of 1,946.09 $\mu\text{mol/kg}$ - 2,061.65 $\mu\text{mol/kg}$ and the total alkalinity was 2,156.86 $\mu\text{mol/kg}$ - 2,264.71 $\mu\text{mol/kg}$. Based on this value, Jepara coastal waters have $p\text{CO}_{2(\text{sea})}$ of 573,800 micro-atmospheric (μatm) which is higher than $p\text{CO}_{2(\text{atm})}$ (i.e., 386,772 μatm). The input of organic/inorganic carbon resulting from anthropogenic processes on land has influenced Jepara coastal waters which act as a source of CO₂ into the atmosphere amounting to 103,799 $\text{mmol/m}^2/\text{day}$. The results of this research can be used as a reference for managing coastal areas to achieve low carbon emissions.

Keywords: CO₂ flux, chlorophyll-a, carbonate, Teluk Awur Jepara

Introduction

Increasing human and industrial activities in coastal areas have contributed to global warming, causing a marked increase in air and seawater temperature [1]. As an effect, it will change the acidity level, dissolved oxygen (DO) content, nutrients and pollutant. Such changes will negatively impact the health and ecological quality of marine waters [2]. The carbon systems in coastal seas is highly complex, both temporally and spatially, with coastal systems being both heterotrophic (receiving large amounts of organic material from the mainland) or autotrophic (supplying large amounts of nutrients to the open oceans). Coastal areas are a small part of the marine seas, but have an important role in absorbing

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anthropogenic CO₂ [3, 4]. The absorption of CO₂ gas by the sea from the atmosphere can occur through solubility pumps (due to physical processes) and biological pumps (due to biological processes by aquatic organisms and the influence of water quality conditions itself).

However, not all seawater acts as a CO₂ sink, but also as a CO₂ source and even has a dual role as a sink and source of CO₂. Waters that have a dual role are found in Indonesian seas, especially around the Halmahera Sea and in the Makassar Strait [5]. The nature and characteristics of the water mass which is seasonally different will affect the solubility and flux pumping system of CO₂. The Java Sea (Indonesia) acts as a significant source to the atmosphere during El Nino and La Nina [5, 6]. Meanwhile, studies on the role of the Java coastal seas (whether as a source/sink of CO₂) in terms of biological pumps and their variations have not been extensively investigated. The high productivity in coastal areas can function as a CO₂ sink through the process of photosynthesis. On the other hand, it can also act as a source of carbon to the atmosphere, the effect of high input of organic matter produced by human activities on the coast or from land. Therefore, it is necessary to study the CO₂ flux in the coastal Java Sea. This study was carried out in the coastal waters of Teluk Awur, with the consideration that Teluk Awur has a fairly complex ecosystem, such as mangrove ecosystems, seagrass ecosystems, and coral reefs. In addition, ecosystem functions are also influenced by increasing human activities in the upstream area and around the bay waters. One of the activities being carried out is the intensification of aquaculture in the Marine Science Techno Park (MSTP), Jepara, which can affect the contribution of carbon into the coastal waters and will have an impact on the function of waters as a source or source of CO₂ sinks. Borges [3] explained that the condition of coastal waters affects the flux of CO₂ in the coastal seas.

Previous research related to CO₂ concentrations in Jepara waters has been carried out by [1], but this research has not examined the role of Jepara waters as a CO₂ source or sink. Thus, it is necessary to study the contribution role of the Jepara coastal waters, especially the waters of Teluk Awur, to determine whether it functions as a source or sinks of carbon for the Java Sea region. To achieve this goal, in this study measures and calculates carbon parameters in waters such as pH, Total Alkalinity (TA), Dissolved Inorganic Carbon (DIC), and the partial pressure of CO₂ (pCO₂) in air and atmosphere. Then calculate the water quality parameters (temperature, salinity, and DO) as physical pump parameters and biological pump parameters in the form of chlorophyll-a (chl-a) to see the spatial distribution of the parameters and see the supporting parameters for CO₂ flux fluctuations in the Teluk Awur coastal waters, Jepara.

Materials and methods

Study site

This study was conducted in the coastal waters of Teluk Awur, Jepara Regency, Central Java, Indonesia with the coordinate boundaries of the area 110°35'00" - 110°39'10" E and 6°35'50" - 6°38'45" S (Fig. 1). Sampling was conducted in September 2022. There are several ecosystems including seagrasses, mangroves and coral reefs in these waters. The land area of the study area is very close to the Marine Science Techno Park (MSTP) Campus of Diponegoro University, which currently functions as a maritime-themed education and recreation area. The MSTP is built on 52 hectares of land, which currently has 8 box-shaped ponds, 18 circular ponds, one semi-indoor shrimp pond,

a laboratory, and a cool storage facility with a capacity of 200 metric tonnes (tonne = 10^6 g = Mg). Vaname shrimp farming has been intensively developed and in December 2021, 7 tonnes of vaname shrimp were harvested. As a potential area for recreation, several hotels such as Ocean View and Tilem Beach have been established in this area. Other human activities on land that can affect the waters of the study area are the presence of agricultural land and the presence of several hotels as well as recreational activities on the beach itself.

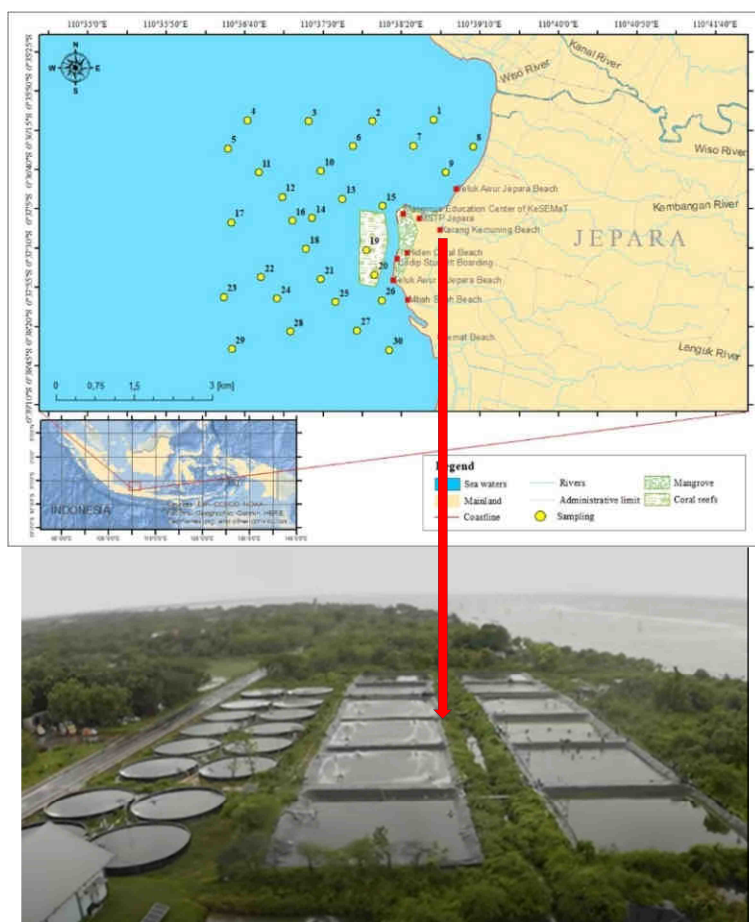


Fig. 1. Research sites

Physical-chemical analyses

Surface temperature data were measured using a Horiba U-53G Multi-parameter. Salinity is checked using a refractometer, pH with pH meter Lutron Pen pH-22, and dissolved oxygen (DO) using DO-meter H1 9146. Additionally, samples of seawater were collected using a Van Dorn Vertical Water Sampler at a depth of 0 m - 3 m for Total Alkalinity (TA) analysis, which is used to estimate Dissolved Inorganic Carbon (DIC) and

also for $p\text{CO}_{2(\text{sea})}$ parameters, and samples for chl-a as a representative of biological parameters. Water samples for carbonate analysis (Total Alkalinity) were put into a 1000 mL white HDPE bottle and dripped with HgCl_2 (200 μL) to kill biological activity in aquatic organisms [7], while samples for chl-a were stored in a 500 mL - 1000 mL black HDPE bottle to prevent sunlight from penetrating the bottles and stopping photosynthetic activity in aquatic organisms, then filtering water samples to obtain chl-a with the method referenced to [8].

Satellite and reanalysis data

Satellite and reanalysis data were used to calculate the CO_2 flux. Monthly wind speed data at 10 meters above sea level (U_{10}), Sea Level Pressure data, and Sea Surface Temperature (SST) data obtained from the ERA5-Copernicus page with a grid interval of $0.25^\circ \times 0.25^\circ$. Sea Surface Salinity (SSS) data used RSS SMAP (Remote Sensing System Soil Moisture Active Passive) Level-3 [6]. The atmospheric CO_2 mole fraction ($x\text{CO}_2$) data from Bukit Kototabang station, Sumatra, Indonesia (BKT) was obtained from NOAA (National Oceanic and Atmospheric Administration) in September 2017-2021 [5].

Laboratory analysis

Carbonate parameters and chl-a parameters were analysed in a laboratory at the Biogeochemistry Laboratory, Oceanographic Research Center, National Research and Innovation Agency.

Total Alkalinity

In this study, a carbonate sample was carried out to measure the Total Alkalinity (TA) value using the titration method using a pH-meter and a magnetic stirrer. The titration's pH endpoint was determined using CRM Batch #156 (Certified Reference Material) standardisation solution in 50 mL with 0.1 N HCl 37 % is 3.00 - 4.00, where this solution has a TA value of $(2236.51 \pm 0.57) \mu\text{mol/kg}$ and a DIC value of $(2052.72 \pm 0.37) \mu\text{mol/kg}$ [5, 9]. Thus, the TA value can be calculated with the following equation [10]:

$$\text{TA}_{\text{as CaCO}_3} = \frac{1000 \cdot V_{\text{HCl}} \cdot N_{\text{HCl}} \cdot EW_{\text{CaCO}_3} \cdot 1000}{V_{\text{sample}}} \text{ [mg/L]} \quad (1)$$

where the value of V is the volume of HCl and the required sample volume [mL], N is the normality of the required HCl solution, and EW_{CaCO_3} is the equivalent weight of CaCO_3 (50.04).

Chlorophyll-a (chl-a)

Chl-a analysis using the method was carried out by [10] using the fluorometric method with Fluorometer Trilogy Turner Design PICES - ISSP 0068. To calculate the chl-a value, the following equation was used:

$$\text{chl-a} = \frac{y - b}{m} \cdot \frac{v}{V} \quad (2)$$

where y is the fluorescence value, b is the y -axis value that intersects the calibration curve, m is the slope of the regression line on the standard curve (calibration), v is the volume of extract (addition of 90 % acetone in mL), and V is the volume of filtered samples [mL].

The determination of CO₂ flux (FCO₂)

The FCO₂ value can be calculated with the following equation [6, 11]:

$$FCO_2 = k \cdot \alpha \cdot \Delta pCO_2 \quad (3)$$

$$k = 0.31 \cdot U_{10}^2 \cdot \left(\frac{660}{Sc}\right)^{0.5} \quad (4)$$

$$Sc = 2073.1000 - (125.6200 \cdot T) + (3.6276 \cdot (T)^2) - (0.0432 \cdot (T)^3) \quad (5)$$

$$\alpha = -58.0931 + \frac{90.5069}{\left(\frac{T}{100}\right)} + 22.2940 \cdot \ln\left(\frac{T}{100}\right) + S \left(0.0278 - 0.0259 \left(\frac{T}{100}\right) + 0.0051 \cdot \left(\frac{T}{100}\right)^2\right) \quad (6)$$

$$\Delta pCO_2 = pCO_{2(atm)} - pCO_{2(sea)} \quad (7)$$

where: k - CO₂ transfer speed, α - solubility of CO₂ with Sea Surface Temperature, [K] and Sea Surface Salinity, S [‰], ΔpCO_2 - the difference between the partial pressure of CO_{2(atm)} and the partial pressure of CO_{2(sea)}, U_{10} - wind speed 10 m above sea level, Sc - Schmidt number that represents a function of temperature [°C].

The calculation of $pCO_{2(sea)}$ was carried out with ex-situ data, according to [6, 11], where the calculation uses a function of the atmospheric CO₂ mole fraction parameter ($xCO_{2(atm)}$), Sea Level Pressure, SLP, p_b , and saturation vapour pressure of seawater in the atmosphere (pH_2O) with the following equation:

$$pCO_{2(atm)} = xCO_{2(atm)} \cdot (p_b - pH_2O) \quad (8)$$

$$pH_2O = \exp\left(24.4543 - 67.4509 \cdot \left(\frac{T}{100}\right) - 4.8489 \ln\left(\frac{T}{100}\right) - 0.0005 \cdot S\right) \quad (9)$$

where $xCO_{2(atm)}$ is mole fraction of CO₂, pH_2O is a function of temperature [K] and salinity [‰].

The calculation of ΔpCO_2 affects the results of positive or negative flux values. If the CO₂ flux value obtained is positive (negative), the result represents a net exchange of CO₂ from the air (water column) to the water column (air), so that the sea acts as a CO₂ source (sink) CO₂ to the atmosphere (water column) [11].

Data analysis

The analysis used in this study is Pearson correlation which is used to look at the parameters that play an important role in influencing the value of CO₂ flux by seeing the correlation between the parameters. The analysis in this study uses the IBM SPSS Statistics v.22 software.

Results and discussion

Measurements of CO₂ flux in coastal areas represent a value of 7 % of the total ocean surface area. However, in the process of marine biogeochemical cycles, coastal areas play an important role and are more vulnerable to climate change than the oceans, so that coastal

areas contribute to the open cycle of marine biogeochemistry. The marine biogeochemical cycles are connected to the air solubility pump process, which is influenced by the physical, biological, and carbonate properties of the water [12].

Water quality parameters

The water quality parameters in this study were temperature, salinity, DO, and chl-a parameters. This is due to changes in temperature in the waters affecting the level of solubility of the waters; if the temperature increases (decreases), it causes a decrease (increase) in the solubility of CO₂ in the air, which is influenced by the wind factor on the surface [12]. In addition, changes in water temperature also contribute to aquatic biological activities, such as phytoplankton organisms, which contain chl-a which use CO₂, H₂O, and light to carry out photosynthesis. The abundance of phytoplankton helps in the production of oxygen (DO) in the waters. The existence of this phytoplankton is also influenced by the levels of nutrients in the water, which can come from weathering sediments or supplies from the land through rivers or run-off from the land when it rains.

The results of measurements of the physical-chemical (Table 1) conditions of the Teluk Awur Coastal Waters, Jepara waters are similar to several previous studies with temperature and salinity values of 27.0 °C - 31 °C and 28.7 ‰ - 32 ‰ [1, 13, 14]. However, the DO value is different from previous studies, where the DO value obtained was much higher than this study, which is around 11.44 mg/L - 11.75 mg/L [15]. Based on the standard from the Indonesian Government Decree No. 22 in 2021 [16], the water quality of Teluk Awur coastal waters, Jepara is still in normal condition.

Table 1
Results of measurement of physical, chemical, and biological conditions of Teluk Awur coastal waters, Jepara

No.	Parameter	Range value	Quality standards [16]
1.	Sea surface temperature [°C]	29.30 - 30.20	28 - 32
2.	Salinity [‰]	25.50 - 30.00	33 - 34
3.	Dissolved oxygen (DO) [mg/L]	5.31 - 8.24	> 5
4.	chl-a [µg/L]	0.52 - 8.44	±0.90 · 10 ⁻³

Seawater Quality Standards in Indonesian Seas

The value of chl-a in the Teluk Awur Coastal Waters, Jepara obtained a value of 0.52 µg/L - 8.44 µg/L (Table 1). chl-a measurements were carried out at 14 station points near coastal waters, it was found that the chl-a value at the station near the northern Marine Science Techno Park (MSTP) Jepara had a higher chl-a value (4.04 µg/L - 8.44 µg/L) than the chl-a value at the station near the southern of MSTP Jepara ranging from 0.52 µg/L - 2.47 µg/L. The results of the analysis carried out in this study were not much different from the research conducted by [13] in Teluk Awur waters, northern Jepara, close to stations 1, 7, 8, and 9, where the chl-a values were obtained at 3.77 µg/L - 7.76 µg/L. In addition, another study found that the coastal waters of Teluk Awur Jepara have relatively low chl-a (0.32 µg/L - 0.35 µg/L) [8].

The parameters of marine carbonate pump in Teluk Awur coastal waters, Jepara

The measurement of marine carbonate systems can be determined by parameters of pH, concentrations such as DIC, TA, and partial pressure of CO₂ (pCO₂) [7, 12]. The pH value plays an important role in the CO₂ system because it affects the carbonate balance in

seawater. When the pH value is low, the concentration of HCO_3^- ions and H_2CO_3 compounds is higher, whereas when the pH value is high, the concentration of free CO_3 ions is more formed in seawater. The pH measurements in the Teluk Awur coastal waters, Jepara tend to be uniform, ranging from 7.9495 to 8.1659, with an average of 8.052 (Fig. 2a). Thus, the pH characteristics in the Teluk Awur Coastal Waters, Jepara is a base condition. The pH values obtained were similar to those of previous studies, where the pH range in Teluk Awur Coastal Waters, Jepara was around 7.52 - 8.52 [1, 13, 15]. In a narrow seawater pH range (7.4 - 8.2), bicarbonate species (HCO_3^-) will be more dominant around 90 %, followed by carbonate (CO_3^{2-}) around 10 %, and CO_2 or H_2CO_3 around < 1 % [12]. Higher bicarbonate and carbonate species encourage the formation of more CaCO_3 . Complex processes in the biology, chemistry, and physics of the water, such as biological oxidation processes and CaCO_3 dissolution, as well as upwelling and internal mixing processes, can change the pH value of seawater. Human activities around coastal waters also lead to changes in pH values, because basa condition can encourage the process of decomposing organic matter into minerals. In addition, an increase in waste from human activities (anthropogenic) that is discharged into the waters can affect the pH value [9].

Spatial distribution of the parameters pH, TA, DIC, and $p\text{CO}_{2(\text{sea})}$ indicates that a decrease (increase) in pH causes an increase (decrease) in the values of TA, DIC, and $p\text{CO}_{2(\text{sea})}$. Other marine carbonate parameters are DIC concentration and Total Alkalinity (TA), where both DIC and TA concentrations describe the total concentration of seawater CO_2 consisting of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and dissolved free CO_2 [9]. The distribution of TA and DIC values in the Coastal Waters of Teluk Awur, Jepara can be seen in Figure 2b and 2c, where the results of TA and DIC analysis in this study ranged from 2,156.86 $\mu\text{mol/kg}$ - 2,264.71 $\mu\text{mol/kg}$ and 1,946.09 $\mu\text{mol/kg}$ - 2,061.65 $\mu\text{mol/kg}$. The DIC results in Teluk Awur Coastal Waters, Jepara were higher than the DIC values in other nearby coastal waters, namely Karimun Jawa Island, at around 1,113.83 mol/kg - 1,726.65 mol/kg, as well as the TA value, which was higher than other studies conducted by [17]. Likewise with other waters in the northern region of the Java Seawater, Banten Bay is around 1,280.44 $\mu\text{mol/kg}$ - 1,720.04 $\mu\text{mol/kg}$ [18]. The high DIC and TA values in the Teluk Awur Coastal Waters, Jepara are caused by the position of the observation station, which is close to the coast and is included in the euphotic zone, where the euphotic zone tends to have high DIC/TA values due to the influence of the land which causes high water productivity, different with waters that lead to the open sea [17]. The concentration of DIC is also influenced by the presence of organic matter in the waters and the introduction of inorganic materials from the land through rivers/water runoff from land near the coastal waters of Teluk Awur, Jepara. In addition, there is the influence of the extensive seagrass ecosystem in the Teluk Awur Coastal Waters, Jepara which contributes to carbon in the waters, where seagrass has the ability to store carbon under the substrate/sediment even though the shoots on the seagrass die, while the carbon on the substrate will only be stored if the seagrass shoots are still alive [19]. The existence of this can be interpreted as changes in DIC/TA values being influenced by changes in the partial pressure gradient of CO_2 or CO_2 concentrations in the waters.

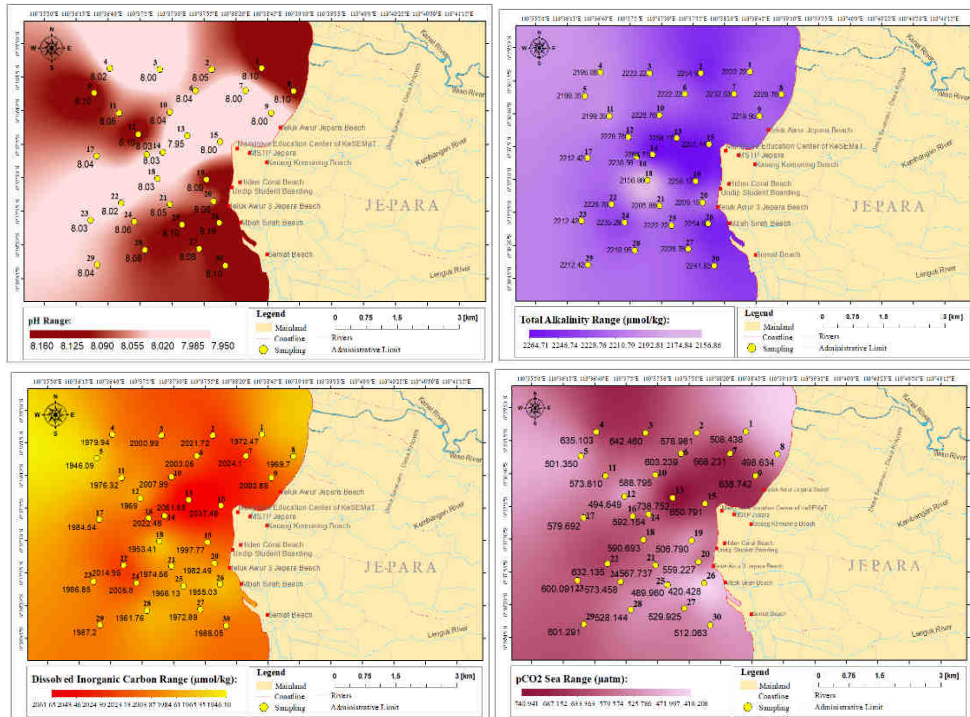


Fig. 2. Map of the spatial distribution of carbonate parameters in the Teluk Awur Coastal Waters, Jepara: a) pH, b) Total Alkalinity (TA), c) Dissolved Inorganic Carbon (DIC), d) $p\text{CO}_{2(\text{sea})}$

The high concentration of DIC in marine waters will be accompanied by an increase in the compressive strength gradient of $p\text{CO}_{2(\text{sea})}$. This is because $p\text{CO}_{2(\text{sea})}$ is a function derived from the parameters of the marine carbon system (pH, DIC and TA), physical-chemical-biological waters (temperature, salinity, and nutrients), and wind speed at 10 meters above sea level [20]. The results of the calculation of $p\text{CO}_{2(\text{sea})}$ can be seen on the spatial distribution map (Fig. 2d) which shows that the value of $p\text{CO}_{2(\text{sea})}$ in the Teluk Awur coastal waters, Jepara ranges from 420.428 μatm - 738.752 μatm (average 573.800 μatm), where the value of $p\text{CO}_{2(\text{sea})}$ is greater than the calculated average $p\text{CO}_{2(\text{sea})}$ of 573.800 μatm . Meanwhile, the results of calculating $p\text{CO}_{2(\text{air})}$ show that the average for 5 years is 386.772 μatm . The difference in CO_2 pressure between the two reservoirs greatly effect on the CO_2 flow (Fig. 3, blue line). The flow is supported by the CO_2 transfer rate in the area and changes the concentration of CO_2 carried. The high value of $p\text{CO}_{2(\text{sea})}$ is caused by the influence of aquatic ecosystems, such as mangroves, seas, and corals, where these ecosystems store a lot of organic CO_2 in their roots and/or sediments, so coastal ecosystems play an important role in carbonate balance. In seagrass beds in the Teluk Awur Coastal Waters, Jepara, they tend to be larger [14] compared to other ecosystems, so the carbon stores in seagrass contribute much more to the marine carbonate system.

The CO₂ flux in the Teluk Awur coastal waters of Jepara

CO₂ flux or CO₂ gas flow between the atmosphere and the sea occurs due to differences in properties between the two reservoirs, which are influenced by CO₂ pressure ($p\text{CO}_2$), solubility, and transfer rate of CO₂ gas at sea level. The results of CO₂ flux calculations in the Teluk Awur coastal waters, Jepara show that the waters act as a source of CO₂ into the atmosphere. This can be seen based on the difference in partial pressure of CO₂ between the atmosphere and the sea ($\Delta p\text{CO}_{2(\text{sea-atm})}$), where the result is positive, which means that the partial pressure of CO₂ in the sea is greater than the atmosphere (CO₂ flows from the sea into the atmosphere). The results of the calculation of $\Delta p\text{CO}_{2(\text{sea-atm})}$ in this study were 33.656 μatm - 351.981 μatm (average 187.029 μatm). CO₂ flux in the Teluk Awur Coastal Waters, Jepara spread over 30 station points is 18.573 $\text{mmol}\cdot\text{m}^{-2}/\text{day}$ - 195.525 $\text{mmol}\cdot\text{m}^{-2}/\text{day}$ (average 103.799 $\text{mmol}\cdot\text{m}^{-2}/\text{day}$) (Figs. 3 and 4, red line). The spatial distribution of the results of CO₂ flux is similar to the spatial distribution of the results of the analysis of TA, DIC, and $p\text{CO}_{2(\text{sea})}$ parameters. So, the $p\text{CO}_2$ describes the total pressure of carbon dioxide gas in the atmosphere and in seawater. In marine waters, changes in pH and DIC/TA (carbonate parameters) have significant impact on $p\text{CO}_2$. The pH value of the water is strongly influenced by changes in temperature, while DIC and TA do not depend on changes in these water quality parameters [11, 20].

The results of the correlation analysis in this study found that the $p\text{CO}_{2(\text{sea})}$ value has a perfect correlation ($r = 1$) and is closely related to CO₂ flux (Table 2). The pH and DIC parameters have a very strong inverse and strong correlation with CO₂ flux. That is, any change in pH will affect the CO₂ flux value, when there is a decrease (increase) in pH, the CO₂ flux will increase (decrease), so the relationship is inversely proportional. DIC with CO₂ flux shows that when there is an increase (decrease) in DIC, the value of CO₂ flux will increase (decrease), so the relationship is directly proportional. Other parameters, such as chl-a have a fairly strong correlation with DO, meaning that DO in the Teluk Awur Coastal Waters, Jepara comes from the photosynthetic activity of chl-a in aquatic organisms. Aquatic organisms, such as phytoplankton, are influenced by aquatic nutrients [21] which can come from coastal ecosystems, such as coral reefs, water sedimentation processes, and the supply of terrestrial nutrients as a result of human activities on land. However, this happens indirectly and requires a long process because the results of the correlation DO values also have a relationship with the temperature of the waters. The temperature in the waters controls the solubility of CO₂ in the waters [12], so that the diffusion process between water and free air also affects DO levels in the waters [22]. Parameters pH, DIC and $p\text{CO}_{2(\text{sea})}$ are carbonate pump parameters in the marine carbon cycle, while temperature, salinity, DO parameters are physical pump parameters of waters, and chl-a parameters are aquatic biological pump parameters. Based on the results of the correlation in this study, it shows that the CO₂ flux in the Teluk Awur coastal waters, Jepara is more influenced by the presence of a carbonate pump.

The Teluk Awur coastal waters, Jepara still have complete coastal ecosystems, such as coral reefs, seagrasses, and mangroves, although the existing coastal ecosystems tend to be few and the coastal ecosystems near the Teluk Awur coastal area are threatened by their health conditions due to the influence of excessive nutrient supply from the land through groundwater runoff, as well as the influence of the supply of remaining shrimp feed waste originating from the MSTP, Jepara ponds [14]. The study found that the average amounts of nutrients N (nitrate) and P (phosphate) in the nearshore areas (9, 15, 27) were

0.165 ppm (N) and 0.048 ppm (P). In contrast, the mean concentrations of N and P in the open seas [5, 12, 18] were 0.126 ppm and 0.048 ppm, respectively.

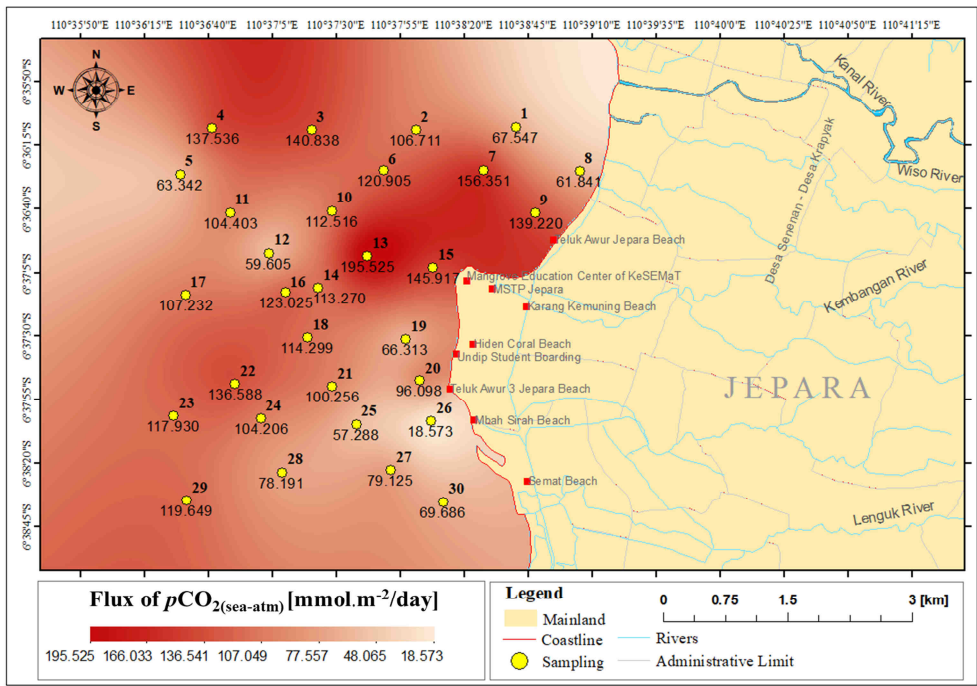


Fig. 3. The distribution map of CO₂ flux in the Teluk Awur coastal waters, Jepara

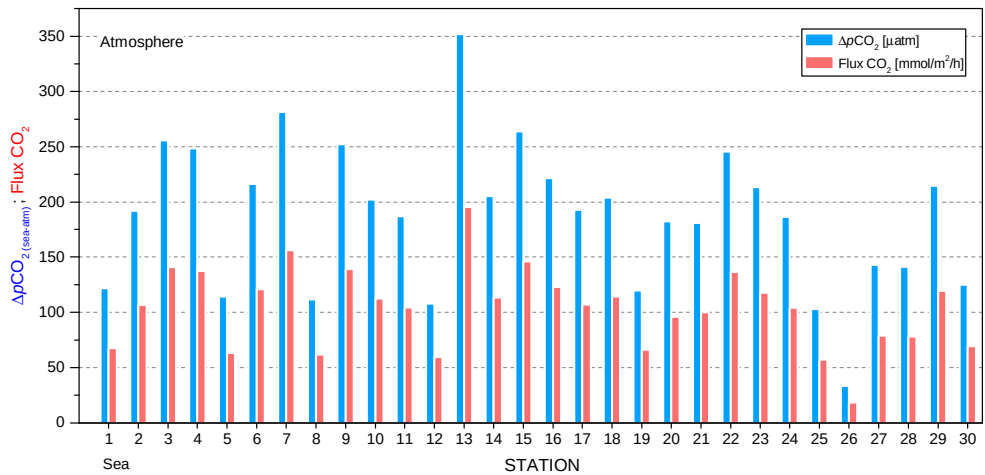


Fig. 4. The CO₂ partial pressure ($\Delta p\text{CO}_2$) (blue line) and CO₂ flux (red line) in the Teluk Awur coastal waters, Jepara

Coastal ecosystems are believed to play a role as sinks of CO_2 stored in their leaves, stems, roots, and sediments, so DIC, TA and $p\text{CO}_{2(\text{sea})}$ in their waters are very high. According to [23], the sediment where seagrass grows is the best carbon storage place, even though seagrass shoots have died, the substrate still stores carbon, whereas shoots will still store carbon if the shoots are still alive. However, this does not occur in the Teluk Awur Coastal Waters, Jepara, where the waters act as a source of CO_2 , this is related to the supply of organic/inorganic carbon originating from the waters themselves (autochthonous) or from rivers or other ecosystems (allochthonous) [24]. The results showed that the values of DIC, TA and $p\text{CO}_{2(\text{sea})}$ in the coastal waters of Teluk Awur Jepara were very high, as was obtained by research conducted by [17]. This is influenced by the presence of organisms in the Teluk Awur Coastal Waters, Jepara near its coastal ecosystems, where many organisms, such as shellfish and other organisms that produce calcium and form calcium carbonate, live [22]. Carbonate formation helps control aquatic carbonate systems because it releases or requires CO_2 in the water and controls the pH in waters to keep it balanced. This is shown in the results of the correlation analysis, where the pH of the Teluk Awur Coastal Waters, Jepara has a strong and very strong correlation to DIC and $p\text{CO}_{2(\text{sea})}$. Another factor is the supply of fresh water, which carries organic or inorganic carbon as a result of increased anthropogenic activities in its coastal areas, such as industrial activities, settlements, tourism, and trade. Fresh water from land or rivers also carries the major element bicarbonate, which comes from the reaction between rock weathering and soil erosion with CO_2 concentrations, so the carried carbonate concentration will precipitate in coastal waters [24, 25].

Table 2

Pearson correlation water quality, carbonate system and flux

Variable	Temp. [°C]	Salinity [‰]	pH [-]	DO [mg/L]	TA [μmol/kg]	DIC [μmol/kg]	$p\text{CO}_{2(\text{sea})}$ [μatm]	chl-a [μg/L]
Temp.	1							
Salinity	0.353	1						
pH	0.011	0.151	1					
DO	0.506**	0.218	0.1	1				
TA	0.139	0.434*	0.012	0.208	1			
DIC	0.012	-0.043	-0.739**	0.045	0.618	1		
$p\text{CO}_{2(\text{sea})}$	0.042	-0.182	-0.989**	-0.05	0.012	0.763**	1	
chl-a	0.021	0.194	-0.267	0.584	0.207	0.32	0.331	1
Flux	0.041	-0.194	-0.988**	-0.051	0.007	0.763**	1,000**	0.328

* Correlation is significant at the 0.05 level (2-tailed), ** Correlation is significant at the 0.01 level (2-tailed)

According to [17], the DIC and TA values tend to be very high due to the position of the observation station, which is close to the coast and included in the euphotic zone, where the euphotic zone tends to have high DIC/TA values due to influence from the land, which causes high water productivity. This statement is in accordance with the DIC/TA distribution map, where DIC/TA values tend to be higher in coastal waters than offshore waters. In this study, DIC was strongly correlated with TA. The DIC and TA values have similarities related to the amounts of bicarbonate and carbonate concentrations in the waters. However, the DIC value is affected by changes in the dynamics of sea air CO_2 pressure [11], while the TA value is influenced by the amount of minerals present in the waters.

The temperature of the water column that produce water minerals directly influences their storage capacity and thus impacts the salinity of the water. Increases in temperature leads to an increase in salinity [5]. Factors that affect the value of salinity in the Teluk Awur Coastal Waters, Jepara are the supply of fresh water from rivers in the territorial waters and the presence of air runoff from land to sea when the rainy season is close to MSTP, Jepara. However, based on the correlation results, the salinity value in the Teluk Awur Coastal Waters, Jepara does not have a weak relationship/correlation with the water temperature value, so it can be interpreted that the salinity value in the Teluk Awur Coastal Waters, Jepara tends to come from the weathering of rocks in the waters as well as the supply of river or runoff from the mainland, which is near the Teluk Awur coastal.

The results of the study as a whole show that the value of CO_2 flux in the Teluk Awur Coastal Waters, Jepara is strongly influenced by changes in pH and DIC values (Table 2). Changes in pH and DIC values in the water will have an impact on the pressure of some of the CO_2 in the water. Metabolic processes like photosynthesis, respiration, precipitation, and CaCO_3 dissolution have an impact on $p\text{CO}_2$ in water and alter the mass balance in the carbonate system [9]. In addition, the existence of coastal ecosystems in the Teluk Awur Coastal Waters, Jepara also controls $p\text{CO}_2$ in the waters and the presence of anthropogenic activities in coastal areas contributes to the supply of organic/inorganic materials through rivers/land runoff and increases anthropogenic CO_2 absorption in coastal ecosystems, so the $p\text{CO}_2$ of the sea in Teluk Awur Coastal Waters, Jepara is very high compared to the $p\text{CO}_2$ value of the atmosphere. This causes the flow of CO_2 to move from the sea to the atmosphere, and the Teluk Awur Coastal Waters, Jepara act as a source of CO_2 to the atmosphere. This study is similar to research in other coastal areas of the Java Sea, such as Banten Bay, where the pH factor is more strongly correlated with changes in CO_2 flux [18]. Meanwhile, a research conducted in the Bintan Coastal Waters [26] discovered that temperature variations had an impact on the carbon flux.

Conclusion

The coastal waters of Teluk Awur, Jepara act as a releaser or source of CO_2 into the atmosphere with an average transfer value of CO_2 gas to the atmosphere of $103.799 \text{ mmol} \cdot \text{m}^{-2} / \text{day}$ due to a sea-atmosphere $p\text{CO}_2$ difference of $187.029 \text{ } \mu\text{atm}$. The transfer rate of CO_2 released into the atmosphere is very high in all parts of the Teluk Awur Coastal area, Jepara due to the high concentration of DIC ($1,991.451 \text{ } \mu\text{mol/kg}$) and $p\text{CO}_{2(\text{sea})}$ ($573.800 \text{ } \mu\text{atm}$) as a result of an increase in waste resulting from the activities of the surrounding population (anthropogenic waste), such as industrial/agriculture/household waste/tourism waste, which enters seawaters, either directly via land or river transport, near the Teluk Awur Coast and the presence of coastal ecosystems such as sea grasses, mangroves, and corals, which also store more carbon, and there is a process of weathering rocks/sediments originating from aquatic organisms close to coastal ecosystems.

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