



Vietnam Academy of Science and Technology

Vietnam Journal of Marine Science and Technology

journal homepage: vjs.ac.vn/index.php/jmst



Variation of carbonate buffer and air- water (CO₂) flux in Ha Long Bay

Pham Thi Kha*, Cao Thi Thu Trang, Le Van Nam, Dinh Hai Ngoc, Tran Anh Tu

Institute of Science and Technology for Energy and Environment, VAST, Vietnam

Received: 28 November 2024; Accepted: 16 March 2025

ABSTRACT

Investigations were carried out during the rainy and dry seasons of 2023–2024 in the Ha Long bay to evaluate composition of the carbonate buffer as well as the air-sea CO₂ flux. The results showed that in the dry season, pH, temperature and salinity was higher than in rainy season. pH were from 7.68–8.33, average 8.25 in the dry season, 8.10 in the rainy season. Temperature were from 17.6–34.6°C, average 20.1°C in the dry season, 32.12°C in the rainy season. Salinity were from 15–31‰, average 30.7‰ in the dry season, 25 ‰ in the rainy season. DIC were from 41.91–58.77 mg/kg. TA were from 868.29–1,148.9 μmol/kg, average 1,105.98 μmol/kg in the dry season, 966.42 μmol/kg in the rainy season. The carbonate buffer in rainy season composed of HCO₃⁻ occupied from 87.42 to 88.02%, CO₃²⁻ occupied from 11.67 to 12.20 %, CO₂ occupied from 0.31 to 0.38%, and in dry season HCO₃⁻ occupied from 85.97 to 88.02%, CO₃²⁻ occupied from 11.67 to 13.77 %, CO₂ occupied from 0.26 to 0.31%. The partial pressure of CO₂ (pCO₂) in water in dry season were lower and less fluctuation in the rainy season. In dry season, pCO₂ were from 81.75 to 169.84 μatm, average 99.16 μatm at day-night site and average 113.30 μatm at spatial sites. In rainy season, pCO₂ were from 60.47 to 430.96 μatm, average 164.78 μatm at day-night site and average 134.28 μatm at spatial sites. The flux of CO₂ exchange through the sea surface-air ranged from -13.0 to -7.4 mmol/m²/day, average -10.2 ± 1.0 mmol/m²/day at day-night site, average -11.6 ± 0.9 mmol/m²/day at spatial sites in rainy season; from -13.7 to -11.1 mmol/m²/day, average -12.9 ± 0.8 mmol/m²/day at day-night site and average 12.6 ± 0.6 mmol/m²/day at spatial sites in dry season. Thus, in the rainy season and dry season, Ha Long Bay acted as a sink for atmosphere CO₂ and the CO₂ flow rate in the dry season was higher than the rainy season.

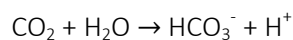
Keywords: CO₂ flux, pCO₂, carbonate, bicarbonate, Ha Long Bay.

*Corresponding author at: Institute of Science and Technology for Energy and Environment, 18 Hoang Quoc Viet Street, Nghia Do Ward, Hanoi, Vietnam. E-mail addresses: khapt@istee.vast.vn

INTRODUCTION

The concentration of CO₂ in the atmosphere continuously increases over time at a very rapid rate. According to NOAA in 1960, the concentration of CO₂ in the atmosphere was about 315 ppm. In July 2024, the concentration of CO₂ in the atmosphere will be 425.55 ppm [1]. The increase in atmospheric CO₂ compared to pre-industrial levels was primarily due to the release of carbon into the atmosphere from deforestation and land-use changes. Since the 1950s, strong industrial development has led to an increase in atmospheric CO₂ mainly from human activities in the process of burning fossil fuels. Anthropogenic CO₂ emissions occur on top of an active natural carbon cycle, which cycles carbon between atmospheric, oceanic and underground reservoirs over time, while exchanging changes with geological reservoirs occur on longer time scales [2]. Oceans are considered as atmospheric CO₂ sinks in the post-industrial era, pressure from human activities in coastal areas has an important impact on changes in ocean carbon stocks [3]. According to recent estimates, the ocean and land absorb about 23% and 32% of CO₂ emissions leaving 45% of the gas remaining in the atmosphere [4].

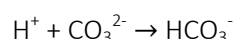
CO₂ entering the oceans changes the carbonate composition of seawater towards more acidity, lower pH and lower saturation of carbonate minerals used in the shells and skeletons of marine organisms. This process is called ocean acidification. This dissolved CO₂ reacts with seawater to form bicarbonate ions (HCO₃⁻) and hydrogen ions (H⁺) [4].



This reaction increases the concentration of hydrogen ions (H⁺) and reduces the pH of seawater.

$$\text{pH} = -\log [\text{H}^+]$$

Increased hydrogen ion concentration reduces the amount of carbonate ion (CO₃²⁻) by forming bicarbonate (HCO₃⁻).



Reducing carbonate ion concentration will reduce the saturation state of biological

calcium carbonate minerals, including calcite and aragonite, leading to a reduction in the ability of organisms to calcify to create shells.

CO₂ reactions in water and carbonate mineral solubility are controlled by equilibrium thermodynamic relationships, characterized by temperature, salinity and pressure. The carbonate buffer system of seawater is characterized by 2 out of 4 chemical parameters: pCO₂, pH, DIC and alkalinity. In which, DIC is the total concentration of CO₂ gas and inorganic carbon forms created from the hydration process (HCO₃⁻ and CO₃²⁻). Alkalinity is the acid buffering capacity of seawater reflecting the formation of carbonates and borates as well as small trace species.

In this article, the carbonate buffer system in water and the correlation among its components in Ha Long Bay are studied and evaluated. The air–water CO₂ flux is also calculated to determine whether Ha Long Bay acts as a source or a sink of atmospheric CO₂. These are the initial results on the carbonate buffer system in the northern coastal waters of Vietnam.

MATERIALS AND METHODS

Study area and sampling stations

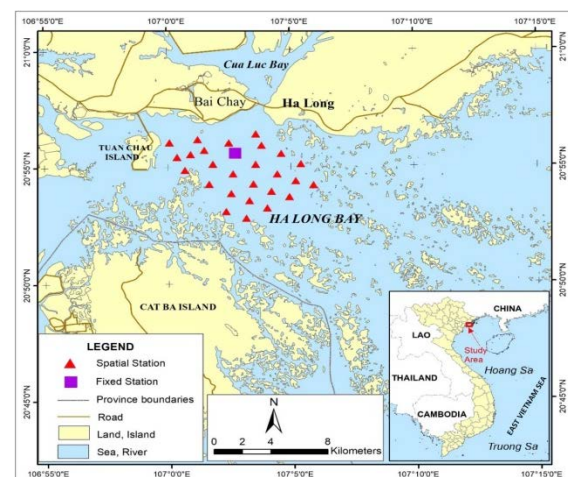


Figure 1. Sampling map of Ha Long bay (Purple point was the day-night site and Red point were spatial sites)

The samples were collected in Ha Long Bay and collected at the day-night site (24 hours) and spatial sites at both the surface and bottom layers to determine parameters of temperature, pH, salinity, and alkalinity. The sampling sites are shown in Figure 1. Sampling in March, 2024 (dry season) and July, 2023 (rainy season, 2023). To eliminate the tide effect, the sampling was taken on the days with less variation of tide. Totally, 27 samples at spatial sites and 13 samples at day - night site for each sample collection.

Study methods

Sampling sample: according to the regulations on marine research and investigation issued by the State Science and Technology Committee, 1982 and the Procedures for investigation and survey of marine resources and environment, 2014 of the Institute of Marine Resources and Environment.

Collect seawater samples according to TCVN 5998:1995 - Water quality - Sampling - Instructions for sampling seawater; TCVN 6663-1:2011: Water quality - Sampling - Part 1: Instructions for creating a sampling program and sampling techniques; TCVN 6663-3:2016: Water quality - Sampling - Part 3: Preserving and processing water samples.

Measuring parameters in the field:

Sanility: is determined by a Hand-Refractometer (Hand Refractometer), unit ‰;

pH: is measured with a pH meter, accurate to 0.01 pH;

Water temperature: is displayed on pH or DO meters with attached temperature probes.

Total alkalinity analysis (TA): Total alkalinity was determined by the titration method according to Standard method for Examination of water and wastewater 23rd edition. 2330 Alkalinity, 2320B Titration method [5]. Quality control: analyze CRM samples with alkaline titration of 1,000 mg/L. The results show that the difference in results with the CRM sample is in the range of 0.7–0.8%.

Calculating of carbonate buffer system: Calculating of carbonate buffer system follows Michael E. Q. Pilson (2013) [6]. Accordingly, we choose to accurately measure and analyze the pH

and total alkalinity of the buffer system and calculate other factor of system.

Calculate the concentration of CO₂ dissolved in water (CO₂aq):

$$[\text{CO}_2\text{aq}] = [\text{CA}] \frac{\{\text{H}^+\}^2}{K_1^* (\{\text{H}^+\} + 2K_2^*)}$$

Calculate the carbonate concentration (CO₃²⁻):

$$[\text{CO}_3^{2-}] = [\text{CA}] \left(\frac{K_2^*}{\{\text{H}^+\} + 2K_2^*} \right)$$

Calculate the bicarbonate concentration (HCO₃⁻):

$$[\text{HCO}_3^-] = [\text{CA}] \left(\frac{\{\text{H}^+\}}{\{\text{H}^+\} + 2K_2^*} \right)$$

in which: CA is carbonate alkalinity; [H⁺]: concentration of ion H⁺; K₁^{*} is the dissociation constant of carbonic acid; K₂^{*} is the dissociation constant of bicarbonate.

Carbonate buffer system factors was calculated using CO₂sys version 2.1 software of the U.S. Department of Energy, Office of Biological and Environmental Research. The constants K₁ and K₂ follow formular of Mehrbach, 1973 [7].

CO₂ flux enters the seawater through the air - water surface is calculated in the following of Wanninkhof, 1992 [8]:

$$F = k \times K_o \times (p_{\text{CO}_2\text{ water}} - p_{\text{CO}_2\text{ air}})$$

in there: F: CO₂ flux through the air - water surface (mol.m⁻².s⁻¹); k: gas transfer velocity (m/s); K_o: solubility of CO₂ in water (mol.atm⁻¹.m⁻³); p_{CO₂ water}: partialpressure of CO₂ in water (atm); p_{CO₂ air}: partial pressure of CO₂ in atmosphere (atm).

In the above formula, the gas transfer velocity (k) is calculated according to the following formula of Sweeney, 2007 [9]:

$$k = \left[0.27 (U_{10})^2 (660/S_c)^{1/2} \right] / 360,000$$

with U_{10} : the wind speed at a height of 10 m (m/s); S_c : the Schmidt number; t : water temperature ($^{\circ}\text{C}$).

$$S_c = 2,073.1 - 125.62t + 3.6276t^2 - 0.043219t^3$$

Solubility (K_o) is calculated according to the formula of Weiss, 1974 [10]:

$$K_o = 1,000 * e^{(-58.0931 + 90.5069(100/T) + 22.2940 \ln(T/100) + S[0.0227766 - 0.025888(T/100) + 0.0050578(T/100)^2])}$$

where: T is the Kelvin temperature ($^{\circ}\text{K}$); S is the salinity (‰).

If $F < 0$: the water sinks CO_2 from the atmosphere; if $F > 0$: the water is source of CO_2 into the atmosphere.

RESULTS AND DISCUSSION

Daily variation in carbonate buffer system in the seawater

Results of measurement, analysis and calculation of carbonate buffer systems in seawater collected at the day-night site in 24 h shown that in the rainy season, the salinity in seawater changed according to the day-night cycle ranging from 25–30‰, pH ranged from 7.68–8.25, sea water temperature ranged from 30.7–32.0 $^{\circ}\text{C}$, alkalinity ranged from 905.77–

1,050.79 $\mu\text{mol/kg}$, dissolved inorganic carbon content ($\text{DIC} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2$) ranged from 41.91–52.10 mg/kg. The CO_2 component in water only accounts for 0.22 to 0.91%, the average partial pressure of CO_2 ($p\text{CO}_2$) reached 165 μatm .

In the dry season, water temperature ranged from 20.7 to 22.1 $^{\circ}\text{C}$, pH value ranged from 8.13 to 8.32, salinity from 30 to 31‰. Alkalinity ranged from 1,080–1,123.9 $\mu\text{mol/kg}$. Dissolved inorganic carbon content ($\text{DIC} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2$) ranged from 51.65–55.78 mg/kg. In the dry season, environment parameters as temperature, salinity, and pH showed little variation and remained stable throughout the day-night cycle. The pH value changed minimally, resulting in CO_2 content ranging only from 0.22 to 0.36%, with less fluctuation compared to the rainy season. The average partial pressure of CO_2 ($p\text{CO}_2$) reached 99.2 μatm (Table 1).

Table 1. Daily variation in physical and chemical variables and composition of Carbonate buffer in the seawater in Ha Long Bay

Parameters	Rainy season (July, 2023)			Dry season (March, 2024)		
	Average	Min	Max	Average	Min	Max
pH	8.07 $\pm$ 0.12	7.68	8.25	8.27 $\pm$ 0.06	8.13	8.32
Alkalinity ($\mu\text{mol/kg}$)	936.26 $\pm$ 40.76	905.77	1,050.79	1,105.77 $\pm$ 10.14	1,080.0	1,123.9
Sanility (‰)	28 $\pm$ 2	25	30	30 $\pm$ 1	30	31
Temperature ($^{\circ}\text{C}$)	31.5 $\pm$ 0.31	30.7	32.0	21.3 $\pm$ 0.36	20.7	22.1
DIC, mg/kg	47.18 $\pm$ 2.18	41.91	52.10	53.08 $\pm$ 1.15	51.65	55.78
CO_2 , mg/kg	0.18 $\pm$ 0.07	0.10	0.47	0.14 $\pm$ 0.02	0.12	0.20
HCO_3^- , mg/kg	41.32 $\pm$ 2.88	35.15	48.80	45.65 $\pm$ 1.72	43.76	49.76
CO_3^{2-} , mg/kg	5.72 $\pm$ 1.24	2.82	7.95	7.30 $\pm$ 0.64	5.82	8.01
CO_2 , %	0.38 $\pm$ 0.14	0.22	0.91	0.26 $\pm$ 0.04	0.22	0.36
HCO_3^- , %	87.42 $\pm$ 2.74	82.47	93.68	85.97 $\pm$ 1.41	84.43	89.21
CO_3^{2-} , %	12.20 $\pm$ 2.86	5.42	17.32	13.77 $\pm$ 1.45	10.43	15.34
$p\text{CO}_2$, μatm	164.8 $\pm$ 67.8	88.2	431.0	99.2 $\pm$ 18.2	83.1	147.7
Ω_{Ca}	2.48 $\pm$ 0.52	1.20	3.41	3.00 $\pm$ 0.26	2.41	3.30
Ω_{Ar}	1.64 $\pm$ 0.35	0.80	2.26	1.94 $\pm$ 0.17	1.56	2.13

In the rainy season, water temperature ranged from 30.7 to 32.0°C, pH value ranged from 7.68 to 8.25, salinity from 25 to 30‰. Alkalinity ranged from 905.77–1050.79 $\mu\text{mol/kg}$. Dissolved inorganic carbon content ($\text{DIC} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2$) ranged from 41.91–52.10 mg/kg. Water in the rainy season had more variable in pH, temperature, salinity than in the dry season. So the partial pressure of CO_2 in the rainy season had more variable, range form $164.8 \pm 67.8 \mu\text{atm}$.

The composition of the carbonate buffer at day-night site in Ha Long Bay indicated that the CO_2 component occupies only about 0.22–0.91%, with an average of 0.32%. The carbonate component occupies about 5.42–17.32%, average of 12.95%, while bicarbonate accounts for 82.47–93.68%, average of 86.70%.

The Calcium Saturation Index (Ω_{Ca}) and the Aragonite Saturation Index (Ω_{Ar}) are indicators of the calcium accumulation processes in corals and bivalves in marine. When this index is lower than 1 (indicating that seawater is not saturated with Aragonite), the calcium

synthesis processes in corals and the shell formation of organisms are limited and poorly developed. Conversely, when this index is higher than 1, the calcium accumulation processes in corals and other organisms favourably [11]. The Ω_{Ar} average index in the seawater of Ha Long Bay was 1.64 ± 0.35 in the rainy season, it was 1.94 ± 0.17 in the dry season at day night site, both of which were favorable for the growth of corals and organisms during the calcium accumulation process.

In the two survey of the rainy and dry seasons, pH, salinity, and alkalinity showed a strong correlation with the composition of carbonate buffer in the water. Specifically, there was a strong negative correlation with $[\text{CO}_2]$ and $[\text{HCO}_3^-]$ ($R^2 \text{ max} = -0.996$) and a strong positive correlation with $[\text{CO}_3^{2-}]$ ($R^2 \text{ max} = 0.996$). For in physical and chemical variables, the strongest correlation with the carbonate buffering system was observed with pH, followed by alkalinity and salinity.

Table 2. Correlation in daily variation between the composition of carbonate buffer and physical and chemical variables

	pH	Salinity, ‰	TA, $\mu\text{mol/kg}$	Temperature, °C	DO, mg/L	% CO_2	% HCO_3^-	% CO_3^{2-}
Rainy season (July, 2023)								
pH	1							
Salinity, ‰	0.276	1						
TA, $\mu\text{mol/kg}$	0.612	0.739	1					
Temperature, °C	0.233	0.551	0.430	1				
DO, mg/L	0.116	0.756	0.554	0.754	1			
% CO_2	-0.981	-0.222	-0.617	-0.264	-0.078	1		
% HCO_3^-	-0.925	-0.601	-0.756	-0.413	-0.402	0.872	1	
% CO_3^{2-}	0.933	0.588	0.754	0.409	0.390	-0.882	-1.000	1
Dry season (March, 2024)								
pH	1							
Salinity, ‰	0.845	1						
TA, $\mu\text{mol/kg}$	0.596	0.616	1					
Temperature, °C	-0.663	-0.346	-0.277	1				
DO, mg/l	0.537	0.494	0.232	-0.548	1			
% CO_2	-0.996	-0.884	-0.617	0.613	-0.525	1		
% HCO_3^-	-0.996	-0.868	-0.603	0.596	-0.519	0.997	1	
% CO_3^{2-}	0.996	0.868	0.603	-0.597	0.519	-0.997	-1.000	1

According to the daily cycle, the correlation coefficients between the partial pressure of CO_2 (pCO_2) in the water and pH, salinity, temperature,

and alkalinity (Fig. 2) indicated that pCO_2 in seawater was strong correlated with pH ($R^2 = 0.89$), followed by alkalinity, temperature, salinity.

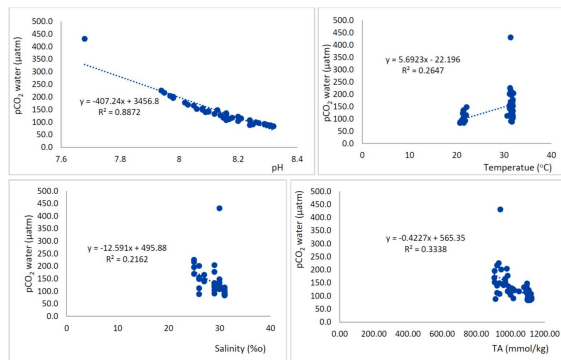


Figure 2. Relationship between pH, temperature, salinity and alkalinity with $p\text{CO}_2$

Spatial variation in the composition of the carbonate buffer

In the dry season of March 2024, water temperature ranged from 17.6 to 19.4 $^{\circ}\text{C}$, pH

varied from 8.09 to 8.33, and salinity was between 30 and 31‰. Alkalinity ranged from 988.1 to 1,148.9 $\mu\text{mol/kg}$. The concentration of dissolved inorganic carbon (DIC) ranged from 51.49 to 58.77 mg/kg (Table 3). The average partial pressure of CO_2 ($p\text{CO}_2$) reached 113.3 μatm .

In the rainy season of July 2023, water temperature ranged from 30.6 to 34.6 $^{\circ}\text{C}$, pH ranged from 7.83 to 8.38, and salinity varied from 15 to 30‰. Alkalinity ranged from 868.3 to 1,062.7 $\mu\text{mol/kg}$. The concentration of dissolved inorganic carbon ($\text{DIC} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2$) was between 42.07 and 55.07 mg/kg of seawater.

Water in the rainy season had more variable in pH, temperature, salinity than in the dry season. So the partial pressure of CO_2 in the rainy season at the spatial had more variable, range from 134.3 ± 48.9 μatm .

Table 3. The composition of carbonate buffer in the seawater in Ha Long Bay at the spatial variation

Parameters	Rainy season (July, 2023)			Dry season (March, 2024)		
	Average	Min	Max	Average	Min	Max
pH	8.16 ± 0.11	7.83	8.38	8.23 ± 0.05	8.09	8.33
Alkalinity ($\mu\text{mol/kg}$)	969.57 ± 48.05	868.29	1,062.74	$1,106.2 \pm 19.39$	988.1	1148.9
Sanility (‰)	23 ± 3	15	30	31 ± 1	30	31
Temperature ($^{\circ}\text{C}$)	32.7 ± 0.76	30.6	34.6	18.9 ± 0.37	17.6	19.4
DIC, mg/kg	47.38 ± 3.02	42.07	55.07	54.95 ± 1.32	51.49	58.77
CO_2 , mg/kg	0.15 ± 0.05	0.07	0.35	0.17 ± 0.03	0.12	0.26
HCO_3^- , mg/kg	40.98 ± 3.65	34.43	49.72	48.37 ± 1.37	44.78	53.62
CO_3^{2-} , mg/kg	6.26 ± 1.19	3.61	9.77	6.40 ± 0.59	4.33	7.58
CO_2 , %	0.31 ± 0.10	0.15	0.66	0.31 ± 0.04	0.23	0.45
HCO_3^- , %	86.37 ± 2.88	77.77	92.50	88.02 ± 1.21	85.32	91.24
CO_3^{2-} , %	13.33 ± 2.97	6.84	22.07	11.67 ± 1.25	8.31	14.45
$p\text{CO}_2$, μatm	134.3 ± 48.9	60.5	318.5	113.3 ± 16.5	81.8	169.8
Ω_{Ca}	2.85 ± 0.51	1.61	4.15	2.63 ± 0.24	1.78	3.11
Ω_{Ar}	1.84 ± 0.34	1.05	2.75	1.69 ± 0.16	1.14	1.69

The composition of the carbonate buffering at spatial in Ha Long Bay indicated that the CO_2 component occupies only about 0.15–0.66%, with an average of 0.31%. The carbonate component occupies about 6.84–22.07%, average of 11.67%, while bicarbonate accounts for 77.77–92.50%, average of 88.02%. The partial pressure of CO_2 in seawater in the rainy season averaged 134.28 μatm (ppm), while in the dry season it averaged 113.30 μatm (ppm).

The average saturation index Ω_{Ar} was 1.84 in the rainy season and 1.69 in the dry season, both of which were favorable for the calcium accumulation processes of corals and bivalves in the region.

The results shown a strong correlation of pH, salinity, and alkalinity with the carbonate composition in the sea water. There was a strong negative correlation with $[\text{CO}_2]$ and $[\text{HCO}_3^-]$, with the correlation being stronger in

the dry season (R^2 max = -0.989) compared to the rainy season (R^2 max = -0.932). Additionally, there was a strong positive correlation with

$[\text{CO}_3^{2-}]$, where the correlation coefficient in the dry season was R^2 max = 0.989 and in the rainy season R^2 max = 0.935 (Table 4).

Table 4. Correlation between the composition of carbonate buffer in physical and chemical variables at spatial variation

	pH	Salinity, ‰	TA, mol/kg	Temperature, °C	DO, mg/L	%CO ₂	%HCO ₃ ⁻	%CO ₃ ²⁻
Rainy season (July, 2023)								
pH	1							
Salinity, ‰	0.158	1						
TA	0.345	0.588	1					
Temperature, °C	-0.176	-0.498	-0.690	1				
DO, mg/L	0.085	-0.434	-0.273	0.614	1			
%CO ₂	-0.984	-0.239	-0.379	0.170	-0.109	1		
%HCO ₃ ⁻	-0.932	-0.476	-0.456	0.247	0.062	0.934	1	
%CO ₃ ²⁻	0.935	0.470	0.455	-0.246	-0.057	-0.937	-1.000	1
Dry season (March, 2024)								
pH	1							
Salinity, ‰	0.548	1						
TA	0.464	0.274	1					
Temperature, °C	0.506	0.571	0.687	1				
DO mg/l	-0.015	0.391	-0.468	-0.263	1			
%CO ₂	-0.989	-0.606	-0.549	-0.600	0.053	1		
%HCO ₃ ⁻	-0.989	-0.637	-0.467	-0.591	-0.027	0.987	1	
%CO ₃ ²⁻	0.989	0.637	0.470	0.592	0.024	-0.988	-1.000	1

According to the spatial sampling sites in Ha Long Bay, the correlation coefficients between the partial pressure of CO₂ (pCO₂) in the water and pH, salinity, temperature, and alkalinity indicated that pCO₂ in seawater was closely correlated with pH (R^2 = 0.9398), followed by alkalinity, temperature, and salinity (Fig. 3).

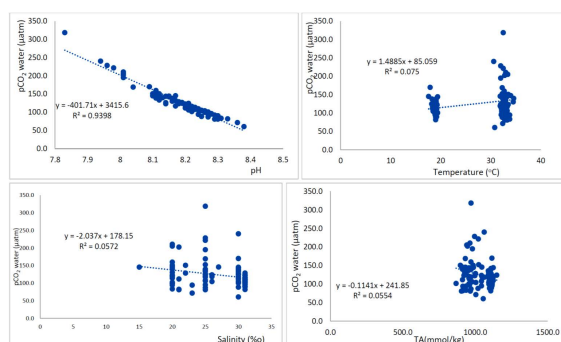


Figure 3. Relationship between pH, temperature, salinity and alkalinity with pCO₂ at spatial stations

Fluxes CO₂ air - water at Ha Long bay

The pCO₂ in the atmosphere during the rainy season in July 2023 was 422.31 µatm, while in the dry season in March 2024, it was 425.38 µatm [12]. The wind speed (U10) was measured during the sampling process. The gas transfer velocity (k) was calculated based on wind speed and temperature. The results of k in rainy season were greater than in dry season. The solubility coefficient (K₀) depended on temperature and salinity and was greater in dry season.

The average calculated gas flux (FCO₂) in daily-night site was -10.2 ± 1.0 mmol/m²/day in the rainy season, and was -12.9 ± 0.8 mmol/m²/day in the dry season. For spatial stations, the average gas flux (FCO₂) was -11.6 ± 0.9 mmol/m²/day in the rainy season, and was -12.6 ± 0.6 mmol/m²/day in the dry season (Tables 5). Thus, Ha Long Bay acted as a reservoir for atmospheric CO₂ during both the rainy and dry seasons. In the dry season, Ha Long bay sink more CO₂ than rainy season.

Table 5. Fluxes CO₂ air - water at Ha Long bay

	Δ (CO ₂ water - air) (atm)	U ₁₀ (m/s)	k (m/s)	K ₀ (mol/atm/m ³)	F _{CO2} (mmol/m ² /day)
Rainy season					
Daily site	-0.0003–(-0.0002) (-0.00028)	3.50–4.31 (4.00)	1.57×10^{-5} – 1.64×10^{-5} (1.62×10^{-5})	25.3–26.3 (25.6)	-11.4–(-7.4) (-10.2 ± 1.0)
Spatial sites	-0.0003–(-0.0002) (-0.00031)	3.56–4.42 (4.00)	1.64×10^{-5} – 1.84×10^{-5} (1.70×10^{-5})	24.7–26.7 (25.5)	-13.0–(-9.3) (-11.6 ± 0.9)
Dry season					
Daily site	-0.0003–(-0.0002) (-0.00032)	3.44–4.72 (4.28)	1.40×10^{-5} – 1.44×10^{-5} (1.42×10^{-5})	32.1–33.0 (32.6)	-13.6–(-11.1) (-12.9 ± 0.8)
Spatial sites	-0.0003–(-0.0002) (-0.00031)	3.53–5.00 (4.26)	1.28×10^{-5} – 1.34×10^{-5} (1.32×10^{-5})	34.6–36.4 (35.0)	-13.7–(-11.3) (-12.6 ± 0.6)

Compared to other studies, the J-Parana River and Karimunjawa Island, Indonesia were identified as a source of CO₂ emissions, while the Chesapeake Bay, specifically the upper and lower bay areas, is also a source of CO₂, although the middle bay acts as a reservoir for atmospheric CO₂ and the delta of the Paraíba do Sul river (Southeastern Brazil) is a source of CO₂ in high river flow and a reservoir for atmospheric in low river flow. The East China Sea functions as a CO₂ reservoir in all seasons—winter, spring, summer, and autumn. Similarly,

the Sudanese Red Sea is considered a CO₂ reservoir. In the southern North Sea, CO₂ absorption occurs with a maximum absorption rate of -0.95 ± 0.90 mmol/m²/day in April 2018, and the annual average rate is -130.19 ± 149.93 mmol C/m²/year (Table 6).

Thus, in Ha Long Bay the results agreed with previous studies with pH levels ranging from 7.78 to 8.38, salinity from 15 to 31‰, and temperatures from 20.7 to 34.6°C, indicated characteristics that suggest it acts as a sink for atmospheric CO₂.

Table 6. Comparison of pCO₂ and air-sea CO₂ flux of Ha Long bay and other areas

Areas	Physical and chemical characteristics	pCO ₂	F _{CO₂}	References
Ji- Parana River	Dry season: Temp: $27.97 \pm 1.65^\circ\text{C}$; DO: 6.31 ± 0.29 mgO ₂ /L; alkalinity: 19.53 ± 5.27 ppm CaCO ₃ ; pH 5.88		711.20 ± 131.51 mgC/m ² /day	[13]
	Rainy season: Temp: $26.70 \pm 1.11^\circ\text{C}$; DO: 4.50 ± 0.57 mgO ₂ /L; alkalinity: 13.17 ± 2.29 ppm CaCO ₃ ; pH: 5.46		$4,869.20 \pm 779.95$ mgC/m ² / day	
Chesapeake Bay	Salinity: upper bay: 0–3‰; middle bay: 3–12‰; lower bay: 12–33‰	Range: 43–3,408 μatm , mean: 493 ± 304 μatm	Upper bay: 31.2 ± 5.6 ; middle bay: -5.8 ± 1.3 ; lower bay: 1.0 ± 1.6 ; whole bay: 2.0 ± 1.7 mmolC/m ² /day	[14]
East China Sea	In winter: temp $17.8 \pm 2.2^\circ\text{C}$, salinity 33.2 ± 2.5 ; In spring: temp $19.7 \pm 2.9^\circ\text{C}$, salinity 33.3 ± 4.7 ; in summer: temp $26.2 \pm 1.8^\circ\text{C}$, salinity 33.0 ± 1.6 ; In autumn: temp $23.2 \pm 1.2^\circ\text{C}$, salinity 33.8 ± 1.3	330 ± 360 μatm	In winter: -10.0 ± 2.0 ; in spring: -11.7 ± 3.6 ; in summer: -3.5 ± 4.6 ; In autumn: -2.3 ± 3.1 ; annual: -6.9 ± 4.0 mmol/m ² /day	[15]
Sudanese Red Sea	Temp: 26–31°C; sanility: 38.9–39.9; TA: 2,435–2,485 $\mu\text{mol/kg}$; DIC: 2,035–2,115 $\mu\text{mol/kg}$	370–440 μatm	-3 – 4.7 mmol/m ² /day	[16]

Areas	Physical and chemical characteristics	pCO ₂	F _{CO₂}	References
In the southern North Sea	Salinity: 32.1–34.7, mean: 33.4 ± 0.58; temp: 3.3 ÷ 22.2°C, mean 13.4°C; wind speed: 0.3–17.9 m/s; mean 6.8 m/s	126.9–525.6 µatm	April 2018: -0.95 ± (-0.90); August 2018: 0.08 ± 0.13; annual: -130.19 ± (-149.93) mmolC/m ² /year	[17]
Karimunjawa Island, Indonesia	pH 7.2–7.4; DIC: mean: 1,847.24 µmol/kg; TA: 1,311.91–2,746.80 µmol/kg, mean: 1,912.51 µmol/kg	ΔpCO ₂ : 33.205–46.123 µatm	8.549–13.272 mmol/m ² /day	[18]
The delta of the Paraíba do Sul river (Southeastern Brazil)	Salinity: 0–5; TA: 363 ± 16 µmol/kg	pCO ₂ : 1,800 to 390 ppm	Low river flow: -1.34–(-5.26); high river flow: 5.71–19.37 mmol/m ² /day	[4]
In the Southern marine water of Vietnam	pH 7.92–8.11; TA: 2,300.28 µmol/kgSW (2144.10–2523.15); salinity: 30.31–34.7‰	327.93–568.59 µatm (414.47 µatm)		[19]
Ha Long Bay	pH 7.68–8.33; DIC: 41.91–58.77 mg/kg; TA: 868.29–1,148.9 µmol/kg; temp: 17.6–34.6; salinity: 15–31‰	60.47–430.96 µatm	Rainy season: range: -13.0–(-7.4) mmol/m ² /day, average: -11.6 ± 0.9 mmol/m ² /day; Dry season: range: -13.6–(-11.3) mmol/m ² /day; average: -12.6 ± 0.6 mmol/m ² /day	This study

CONCLUSION

The carbonate buffer and the partial pressure of CO₂ in seawater in Ha Long bay fluctuated greatly with season and spatial and the carbonate buffer had stronger correlation with pH and total alkalinity. In rainy season, the variation of pCO₂ was stronger than dry season. Conversely, CO₂ flux in dry season was higher than rainy season. The results of gas flux (FCO₂) in day-night site was -10.2 ± 1.0 mmol/m²/day in the rainy season, and was -12.9 ± 0.8 mmol/m²/day in the dry season. For spatial stations, the average gas flux (FCO₂) was -11.6 ± 0.9 mmol/m²/day in the rainy season, and was -12.6 ± 0.6 mmol/m²/day in the dry season. Ha Long Bay acted as a sink for atmospheric CO₂ during both the rainy and dry seasons.

Acknowledgements: The authors would like to thank the project VAST06.04/23–24 and VAST 07.05/24–25 sponsored by Vietnam Academy of Science and Technology for giving permission to publish the data of the project.

REFERENCES

- [1] NOAA, *Trends in CO₂, CH₄, N₂O, SF₆*, 2024. [Online]. Available: <https://gml.noaa.gov/ccgg/trends> [accessed December 26, 2024].
- [2] D. Archer, M. Eby, V. Brovkin, A. Ridgwell, L. Cao, U. Mikolajewicz, K. Caldeira, K. Matsumoto, G. Munhoven, A. Montenegro, and K. Tokos, “Atmospheric lifetime of fossil fuel carbon dioxide,” *Annual Review of Earth and Planetary Sciences*, vol. 37, no. 1, pp. 117–134, 2009. DOI: 10.1146/annurev.earth.031208.100206.
- [3] J. E. Bauer, W. J. Cai, P. A. Raymond, T. S. Bianchi, C. S. Hopkinson, and P. A. Regnier, “The changing carbon cycle of the coastal ocean,” *Nature*, vol. 504, no. 7478, pp. 61–70, 2013. DOI: 10.1038/nature12857.
- [4] L. C. Cotovicz Jr, L. O. Vidal, C. E. de Rezende, M. C. Bernardes, B. A. Knoppers, R. L. Sobrinho, R. P. Cardoso, M. Muniz, R. M. dos Anjos, A. Biehler, and G. Abril, “Carbon dioxide sources and sinks in the delta of the Paraíba do Sul River

- (Southeastern Brazil) modulated by carbonate thermodynamics, gas exchange and ecosystem metabolism during estuarine mixing,” *Marine Chemistry*, vol. 226, 103869, 2020. DOI: 10.1016/j.marchem.2020.103869.
- [5] A. Solutions, A. Solutions, and I. Solutions, “Standard methods: for the examination of water and waste water,” *Analytical Biochemistry*, vol. 186, no. 1, 183, 1990.
- [6] M. E. Pilson, *An Introduction to the Chemistry of the Sea*. Cambridge, U.K.: Cambridge University Press, 2013.
- [7] C. Mehrbach, C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz, “Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure 1,” *Limnology and Oceanography*, vol. 18, no. 6, pp. 897–907, 1973. DOI: 10.4319/lo.1973.18.6.0897.
- [8] R. Wanninkhof, “Relationship between wind speed and gas exchange over the ocean,” *Journal of Geophysical Research: Oceans*, vol. 97, no. C5, pp. 7373–7382, 1992. DOI: 10.1029/92JC00188.
- [9] C. Sweeney, E. Gloor, A. R. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof, “Constraining global air-sea gas exchange for CO₂ with recent bomb ¹⁴C measurements,” *Global Biogeochemical Cycles*, vol. 21, no. 2, 2007. DOI: 10.1029/2006GB002784.
- [10] R. F. Weiss, “Carbon dioxide in water and seawater: the solubility of a non-ideal gas,” *Marine Chemistry*, vol. 2, no. 3, pp. 203–215, 1974. DOI: 10.1016/0304-4203(74)90015-2.
- [11] K. Rangesh, M. Anand, and B. Rajeswari, “Carbonate parameters—an indicator of ocean acidification and climate change,” in *Proc. National Conference on Recent Trends and Prospects in Energy, Environment & Natural Resources*, 2019.
- [12] Pro Oxygen, *Daily CO₂*, 2024. [Online]. Available: <https://www.co2.earth/daily-co2> [accessed December 26, 2024].
- [13] T. J. D. S. Pinto and B. M. Gomes, “CO₂ flux and its relationship with water parameters and biological activity in the Ji-Paraná River (Rondônia State–Western Amazon),” *Biogeosciences Discussions*, pp. 1–14, 2017. DOI: 10.5194/bg-2017-407.
- [14] B. Chen, W. J. Cai, J. R. Brodeur, N. Hussain, J. M. Testa, W. Ni, and Q. Li, “Seasonal and spatial variability in surface pCO₂ and air–water CO₂ flux in the Chesapeake Bay,” *Limnology and Oceanography*, vol. 65, no. 12, pp. 3046–3065, 2020. DOI: 10.1002/lno.11573.
- [15] X. H. Guo, W. D. Zhai, M. H. Dai, C. Zhang, Y. Bai, Y. Xu, Q. Li, and G. Z. Wang, “Air–sea CO₂ fluxes in the East China Sea based on multiple-year underway observations,” *Biogeosciences*, vol. 12, no. 18, pp. 5495–5514, 2015. DOI: 10.5194/bg-12-5495-2015.
- [16] E. B. Ali, I. Skjelvan, A. M. Omar, A. Olsen, T. E. De Lange, T. Johannessen, and S. Elageed, “Sea surface pCO₂ variability and air–sea CO₂ exchange in the coastal Sudanese Red Sea,” *Regional Studies in Marine Science*, vol. 44, 101796, 2021. DOI: 10.1016/j.rsma.2021.101796.
- [17] S. Pint, G. Everaert, H. Theetaert, M. B. Vandeghechuchte, and T. Gkritzalis, “Air–sea carbon flux from high-temporal-resolution data of in situ CO₂ measurements in the southern North Sea,” *Biogeosciences Discussions*, pp. 1–17, 2020. DOI: 10.5194/bg-2020-442.
- [18] N. Latifah, S. Febrianto, A. Wirasatriya, H. Endrawati, M. Zainuri, S. Suryanti, and A. N. Hidayat, “Air–sea flux of CO₂ in the waters of Karimunjawa Island, Indonesia,” *Indonesian Journal of Fisheries Science and Technology*, vol. 16, no. 3, pp. 171–178, 2020. DOI: 10.14710/ijfst.16.3.171-178.
- [19] P. Le Hung, T. L. V. Tran, and N. P. Hong, “An initial study on ocean acidification in southern waters of Vietnam,” *Vietnam Journal of Marine Science and Technology*, vol. 21, no. 1, pp. 47–55, 2021. DOI: 10.15625/1859-3097/16051.