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An initial study on ocean acidification in Southern waters of Vietnam

Le Hung Phu*, Vo Tran Tuan Linh, Pham Hong Ngoc

Institute of Oceanography, VAST, Vietnam
*E-mail: hungphu219@gmail.com

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Abstract
Ocean acidification (OA) refers to the increase of dissolved CO_2 and the reduction in the pH of seawater as a consequence of the absorption of large amounts of carbon dioxide (CO_2) by the oceans. This process is the result of large quantities of CO_2, produced by vehicles and industrial and agricultural activities. Over the past decades there have been many worldwide studies focusing on potential impacts of OA. However, researches regarding this issue remain scarce in Vietnam. In this paper, data of pH, total alkalinity (TA), dissolved inorganic carbon (HCO_3^-, CO_3^{2-}, CO_2), partial pressure of CO_2 (pCO_2) and the state of aragonite saturation (Ω_{ar}) measured in Southern waters of Vietnam in 2018 were used to: (1) Provide the initial data of OA parameters in Southern waters of Vietnam; (2) Compare the current situation of OA in Southern waters of Vietnam with the situation of world oceans. The results showed that mean values of pH, TA and CO_3^{2-} concentrations were 8.04 (7.92–8.11), 2300.28 µmol/kgSW (2,144.10–2,523.15), 218.83 µmol/kgSW (151.32–262.83), respectively. These values were higher in offshore areas than in coastal areas, especially at the estuaries. The average value of pCO_2 was 414.47 µatm (327.93–568.59), higher when compared with that of other areas (370 µatm). On the other hand, the state of aragonite saturation of the studied area had the similar patterns of TA and CO_3^{2-} concentrations. Most of values were always greater than 3, with this saturation state, the marine calcifiers are more likely to survive and reproduce.

Keywords: Ocean acidification, Southern waters of Vietnam, aragonite, pH, CO_2, CO_3^{2-}, pCO_2.

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INTRODUCTION

The burning of fossil fuels and destruction of forests by humans have been mentioned as the main reasons to increase the partial pressure of CO_2 in the atmosphere. For example, the level of CO_2 in the atmosphere increased about 40%, from 280 ppm (pre-industrial period) to 384 ppm (2007) [1]. In addition, it is estimated that about 29% (170 ± 20 GtC) of atmospheric CO_2 emissions were absorbed by the oceans from 1750–2013. By the end of the century, the CO_2 levels in atmosphere and oceans are forecasted to exceed 800 ppm, the dissolved inorganic carbon (DIC) concentrations in surface water increase 12%, and the carbonate (CO_3^{2-}) concentrations decrease 60%. Thereby, pH values of the surface water will be decreased about 0.4 units [3]. Therefore, the ocean acidification is an inevitable consequence of the CO_2 emissions. When gaseous CO_2 is dissolved in seawater, it changes the carbonate system. The seawater carbonate system is governed by a series of chemical reactions:

$$CO_2\,(gas) \leftrightarrow CO_2\,(aqua) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

Once dissolved in water, gaseous CO_2 reacts with water to form carbonic acid H_2CO_3, which can dissociate by losing hydrogen ions, to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. At the equilibrium of seawater, pH values are about 8.1, approximately 90% of the inorganic carbon is bicarbonate ion, 9% is carbonate ion, and 1% is dissolved CO_2. Adding CO_2 in seawater will increase aqueous CO_2, bicarbonate and hydrogen ion concentrations, and reduce pH value and carbonate ion concentrations [4].

The calcification plays an important role in the coral reef construction, as well as the growth of other calcareous organisms. The calcification depends on the aragonite saturation state (Ω_{ar}), defined as the ion product of calcium and carbonate ion concentrations: $\Omega = [Ca^{2+}]\ [CO_3^{2-}]/Ksp$, where Ksp is the solubility coefficient of aragonite. When $\Omega > 1$, shell and skeleton formation occurs, and dissolution occurs when $\Omega < 1$. The dissolved CO_2 concentrations increase to decrease pH value and aragonite saturation state, it can be expressed by the equation:

$$CO_2 + CaCO_3 + H_2O \leftrightarrow 2HCO_3^- + Ca^{2+}\ [6]$$

Ocean acidification can reduce calcification rate of coral reefs, as well as increase bioerosion and dissolution of $CaCO_3$ structures, impact the growth of calcareous organisms. Some studies analyzed the cores of Great Barrier reef and showed that the calcification rate decreased by 21% in the period 1988–2003 [4]. In addition, the study of Gazeau et al., (2007) [7] suggested that the calcification rate of *Mytilus edulis* and the Pacific oyster *Crassostrea gigas* decreased by 25% and 10%, respectively, with the CO_2 level ~ 740 ppmv. Therefore, research on ocean acidification is really necessary, to provide scientific evidences to contribute to the conservation of marine ecosystems.

Although there has been more and more attention, there are very few studies and publications on OA issue in Vietnam. Recently, a study presented an overview of acidification situation at coral reefs [8] but did not give widespread data of OA situation in Southern waters of Vietnam. Therefore, this paper tries (1) to provide the baseline data of the OA related parameters in Southern waters of Vietnam and (2) to estimate initially the OA situation of this area, by comparing to the situation of other oceans.

MATERIALS AND METHODS

Samples were collected at 20 stations from Khanh Hoa to Ca Mau, all stations are shown in figure 1. Water samples were collected at 2 layers, the upper layer was 5 m below the surface, the lower layer was at 20, 30, 40 or 60 m depending on the depth of stations. Totally, 40 samples were collected and analyzed.

Samples were collected and preserved, and analyzed following the WESTPAC Standard Operation Procedures (SOPs) for ocean acidification research and monitoring [9] and Dickson et al., (2007) [10]:

The pH of seawater was measured by a high accuracy method, using the indicator dye m-cresol purple;

TA determination used open-cell titration method;

Bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) ions, dissolved CO_2 concentrations, aragonite saturation values (Ω) were calculated by the use of CO_2sys software;

Temperature and salinity values were in situ measured by Seabird CTD (SBE 19+ V2).

For data analyzing, the spatial distribution of parameters at the East Sea was built by the interpolation process of QGIS 3-12 software.

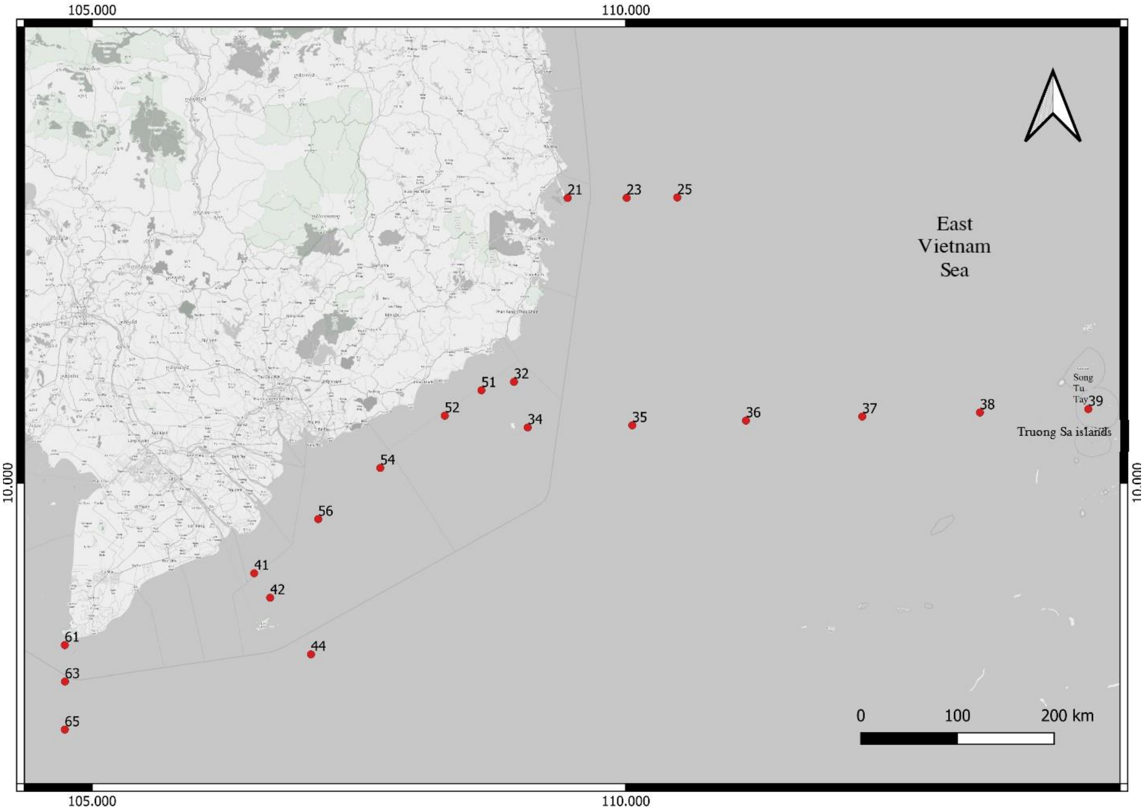

Figure 1. Sampling stations: Transection 2: 21–25; transection 3: 34–39; transection 4: 41–44; transection 5: 51–56; transection 6: 61–63

RESULTS AND DISCUSSIONS

The spatial distribution of observed parameters of Southern waters of Vietnam

The data showed that in transection 2, sea water temperature, total alkalinity (TA) and carbonate ion concentrations tended to decrease from the coast to offshore stations whereas salinity, HCO_3^- and CO_2 concentrations illustrated an opposite trend. In this transection, the highest values of pCO_2 and CO_2 concentration and the lowest value of CO_3^{2-} concentration were recorded at station 25. Besides, Ω_{ara} values were higher at the lower layer, at the offshore stations.

In transection 3, values of temperature, salinity, pH ranged slightly. Distributions of HCO_3^-, and CO_3^{2-} concentrations were similar, increased at the middle stations (35, 36, 37), and decreased at the offshore stations (38, 39). The trend of CO_2 concentration and pCO_2 had the same patterns. Those parameters had high levels at the onshore areas, decreased at the offshore areas. Most of CO_2 concentrations were greater than 10 µmol/kgSW, the smallest value (8.6 µmol/kgSW) was found at station 39. The Ω_{ar} values were always higher than 3, and increased at the offshore areas, the highest value was found at station 39.

In transection 4, trend of seawater temperature was not apparent, the lowest value was recorded at station 42. Salinity and TA had the similar distributions, increased from the coast to offshore stations. In this transection, pH values ranged slightly, the lowest pH value and highest values of CO_2, HCO_3^- and pCO_2 were found at station 44. All of Ω_{ara} values were greater than 3, except for station 44.

Table 1. Statistical values of observed parameters at upper layer

	Values	Transection				
		2	3	4	5	6
Temperature (^oC)	mean	**28.7**	**28.3**	**29.0**	**28.4**	**29.5**
	Sd	0.24	0.7	0.1	1.0	0.2
	min	28.59	27.04	28.91	26.87	29.34
	max	29.00	29.08	29.09	29.04	29.64
Salinity (‰)	mean	**33.6**	**32.9**	**31.9**	**31.6**	**32.3**
	Sd	0.14	0.4	0.7	1.3	0.2
	min	33.5	32.29	31.09	30.31	32.08
	max	33.8	33.32	32.54	33.23	32.46
pH	mean	**8.092**	**8.098**	**8.033**	**8.070**	**8.103**
	Sd	0.03	0.02	0.05	0.02	0.00
	min	8.059	8.056	7.975	8.046	8.100
	max	8.109	8.121	8.076	8.103	8.105
TA (µmol kg^{-1})	mean	**2204.2**	**2288.5**	**2214.1**	**2271.6**	**2311.7**
	Sd	36.83	75.7	39.0	48.3	37.6
	min	2161.7	2153.8	2183.1	2225.0	2269.9
	max	2226.2	2363.1	2258.0	2338.0	2342.7
pCO_2 (µatm)	mean	**391.2**	**396.1**	**481.3**	**433.1**	**416.7**
	Sd	23.91	20.3	78.1	21.1	7.5
	min	374.3	377.8	418.0	402.5	408.4
	max	418.6	436.6	568.6	450.7	422.9
HCO_3^- (µmol kg^{-1})	mean	**1665.0**	**1734.6**	**1744.7**	**1763.1**	**1756.0**
	Sd	2.48	61.5	68.4	45.6	28.3
	min	1662.2	1641.7	1695.3	1710.2	1724.1
	max	1667.0	1831.2	1822.8	1821.5	1778.4
CO_3^{2-} (µmol kg^{-1})	mean	**217.4**	**225.6**	**191.0**	**208.0**	**227.5**
	Sd	14.49	12.1	14.0	4.7	4.4
	min	200.7	206.1	177.4	201.0	222.8
	max	226.2	240.3	205.4	210.9	231.6
CO_2 (µmol kg^{-1})	mean	**10.2**	**10.5**	**12.6**	**11.5**	**10.7**
	Sd	0.65	0.6	1.99	0.6	0.2
	min	9.8	9.96	10.9	10.6	10.5
	max	10.9	11.9	14.8	12.1	10.8
Ω_{ara}	mean	**3.5**	**3.7**	**3.15**	**3.43**	**3.76**
	Sd	0.24	0.2	0.23	0.1	0.1
	min	3.3	3.37	2.92	3.34	3.69
	max	3.7	3.93	3.39	3.51	3.83

Transection 5 was located at the coastal areas, parallel to the shoreline from Phan Thiet to Dinh An estuary. Seawater temperature tended to increase gradually from north to south, but salinity values illustrated the opposite trend, decreased at the estuaries. pH values ranged slightly, fluctuated around 8.00. Total alkalinity levels were concentrated in the northern stations. The maximum values of pCO_2, CO_2, and HCO_3^- ion concentrations were found at station 52. Besides, Ω_{ar} and CO_3^{2-} concentration had the minimum values at this station. All of Ω_{ara} values were greater than 3, except for station 52.

In transection 6, seawater temperature and pH values fluctuated slightly, while salinity tended to increase from the coast to the offshore stations. The lowest values of pCO_2, TA, HCO_3^-, and CO_2 ion concentrations were recorded at station 61 - onshore station. Meanwhile, Ω_{ar} and CO_3^{2-} concentration had maximum values at the offshore station - 63. Ω_{ara} values were always greater than 3 and tended to increase from station 61 to station 65.

The statistical results of salinity, temperature, pH, total alkalinity (TA), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), CO_2 ions concentration, spatial pressure (pCO_2) and saturation aragonite (Ω_{ar}) were presented in tables 1 and 2.

Table 2. Statistical values of observed parameters at lower layer

	Values	Transection				
		2	3	4	5	6
Temperature (^oC)	mean	**22.1**	**26.6**	**28.7**	**27.4**	**28.6**
	Sd	5.35	2.5	0.12	1.2	0.1
	min	18.66	21.55	28.60	26.22	28.42
	max	28.28	28.58	28.83	28.74	28.67
Salinity (‰)	mean	**34.2**	**33.5**	**32.4**	**33.0**	**32.6**
	Sd	0.8	0.5	0.1	0.7	0.2
	min	33.3	32.9	32.3	31.9	32.4
	max	34.7	34.4	32.5	33.4	32.7
pH	mean	**7.983**	**8.095**	**8.073**	**8.042**	**8.086**
	Sd	0.10	0.05	0.02	0.06	0.01
	min	7.882	8.016	8.061	7.947	8.073
	max	8.083	8.146	8.096	8.086	8.101
TA (µmol kg^{-1})	mean	**2263.1**	**2400.0**	**2286.1**	**2326.1**	**2293.2**
	Sd	32.95	125.7	27.1	52.7	21.6
	min	2228.4	2144.1	2263.2	2258.1	2273.1
	max	2294.0	2523.2	2316.0	2369.4	2316.0
pCO_2 (µatm)	mean	**417.3**	**390.5**	**434.0**	**458.5**	**417.2**
	Sd	54.01	36.6	17.8	70.0	12.8
	min	374.4	360.0	413.5	403.6	404.8
	max	478.0	464.4	445.4	557.7	430.4
HCO_3^- (µmol kg^{-1})	mean	**1805.0**	**1820.1**	**1762.4**	**1816.2**	**1753.8**
	Sd	98.57	107.9	5.6	62.4	2.7
	min	1696.8	1626.3	1756.4	1733.9	1752.2
	max	1889.6	1932.8	1767.6	1883.2	1756.9
CO_3^{2-} (µmol kg^{-1})	mean	**184.5**	**237.5**	**213.8**	**208.3**	**220.1**
	Sd	31.94	23.5	10.7	23.3	8.1
	min	151.3	208.2	206.6	174.2	212.3
	max	215.0	262.8	226.0	226.7	228.4
CO_2 (µmol kg^{-1})	mean	**13.0**	**10.7**	**11.4**	**12.4**	**10.9**
	Sd	2.82	1.3	0.5	2.1	0.3
	min	10.5	9.6	10.8	10.9	10.6
	max	16.1	13.2	11.7	15.4	11.3
Ω_{ara}	mean	**2.92**	**3.8**	**3.5**	**3.39**	**3.61**
	Sd	0.6	0.4	0.2	0.4	0.1
	min	2.34	3.38	3.39	2.81	3.49
	max	3.51	4.27	3.71	3.66	3.75

In general, trends of salinity, pH, TA and CO_3^{2-} ion concentration were similar. In vertical distribution, these parameters tended to increase at the lower layer. In addition, these factors were highly concentrated in offshore areas, and decreased in onshore areas, especially the estuaries. This result was similar to the study by Lee et al., (2006) which reported that total alkalinity had the positive correlation with salinity values [11]. Meanwhile, pCO_2 levels tended to decrease in the offshore stations, and increase in the onshore stations. In the Truong Sa archipelago, TA concentrations (2,144.10–2,595.33 µmol/kgSW) and CO_3^{2-} (206.1–263.0 µmol/kgSW) were smaller than the values of the offshore areas, but pH values (8.03–8.11) were similar to those of these areas. The distributions of salinity, TA, pH, pCO_2, CO_3^{2-} and Ω_{ar} were shown in figures 2–3.

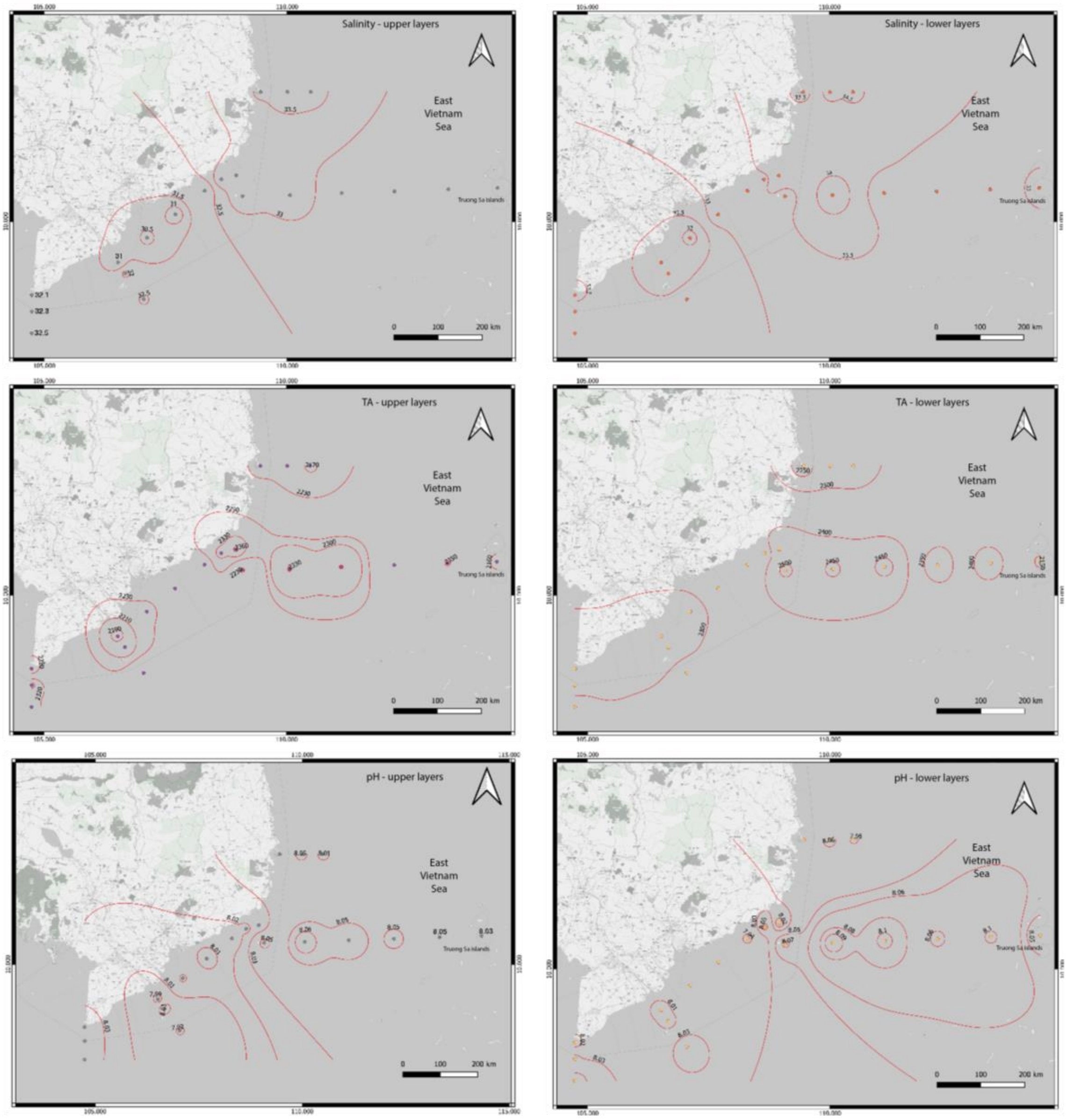

Figure 2. Spatial patterns of observed parameters of salinity, TA, pH at upper layer (left side) and lower layer (right side)

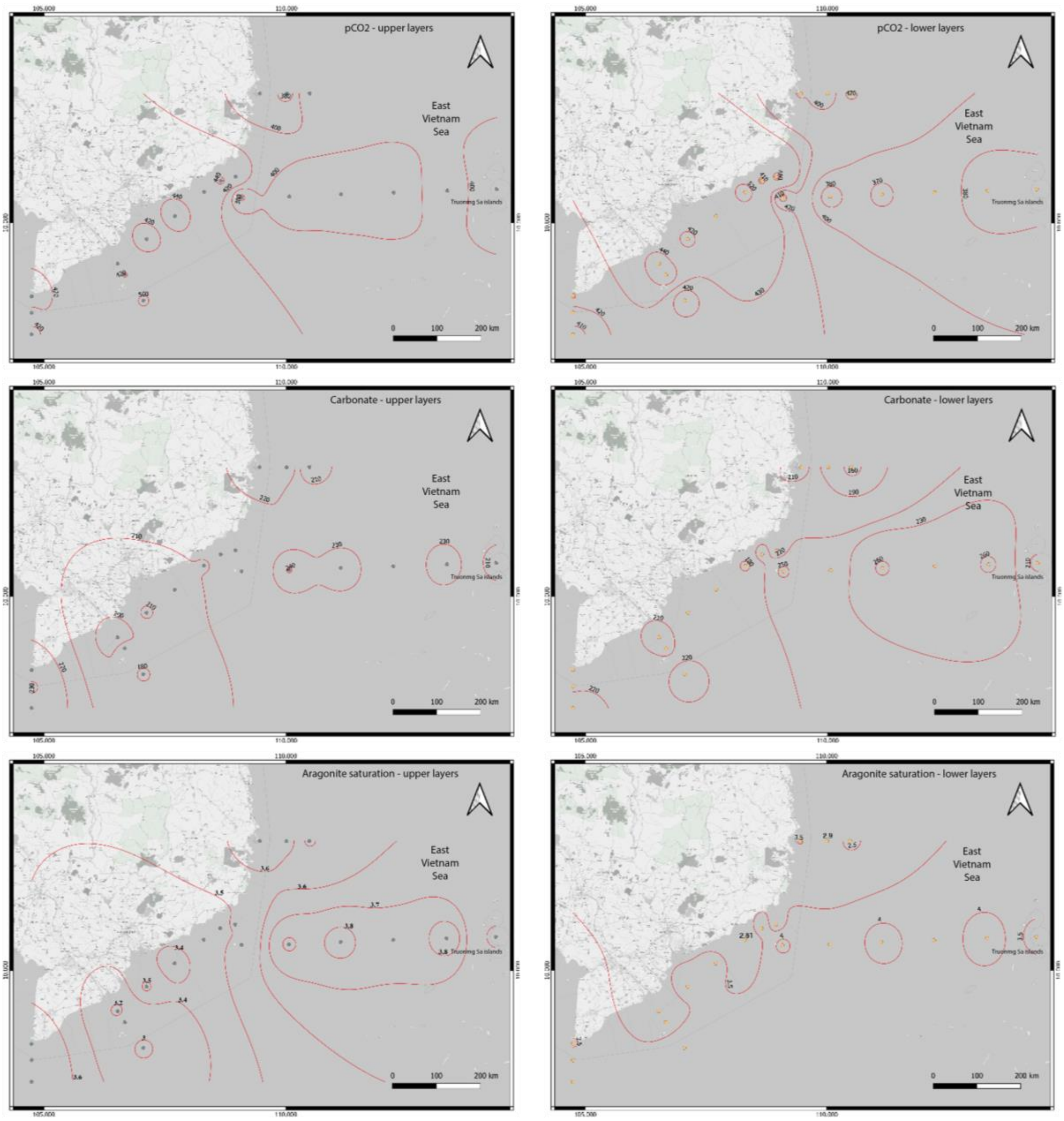

Figure 3. Spatial patterns of observed parameters of pCO_2, CO_3^{2-} and Ω_{ar} at upper layer (left side) and lower layer (right side)

Assessing the ocean acidification state of Southern waters of Vietnam

It can be said that 7 parameters in this paper have not been observed in Southern waters of Vietnam, especially pCO_2, Ω_{ar}, CO_2 concentration parameters. Therefore, it is difficult to assess the ocean acidification state of this area.

The partial pressure of CO_2 presents the potential absorption of gaseous CO_2 into seawater. The average value of pCO_2 in the studied area was 414 µatm, ranging from 328 µatm to 569 µatm. On the global scale, pCO_2 fluctuated with the large range (from 150 µatm to 750 µatm) depending on the geographic regions and seasons, and mean value was 370 µatm, lower than that of the studied area [12]. However, pCO_2 value of the studied area was similar to that of Canary islands and Hawaii

(400 µatm), and lower compared to that of Bermuda (450 µatm) (from https://www.epa.gov/climate-indicators/climate-change-indicators-ocean-acidity).

The CO_2 emission level has been increasing more and more, reducing pH value, carbonate concentration, and saturation aragonite Ω_{ar}. For this reason, saturation aragonite Ω_{ar} is useful parameter to assess the state of seawater acidification. Corals and other calcifiers can survive and reproduce when the saturation state is greater than 3. When aragonite saturation state decreases below 3, these organisms become stressed, and when saturation state is less than 1, shells and other structures begin to dissolve. The results showed that most of Ω_{ar} values of Southern waters of Vietnam were greater than 3, the average value was 3.57, ranging from 2.34 to 4.27. Ω_{ar} values less than 3 were found at 4 locations, including station 23 (2.91 at 60 m layer), station 25 (2.34 at 60 m layer), station 52 (2.81 at the 20 m layer), and station 44 (2.92 at the 5 m layer).

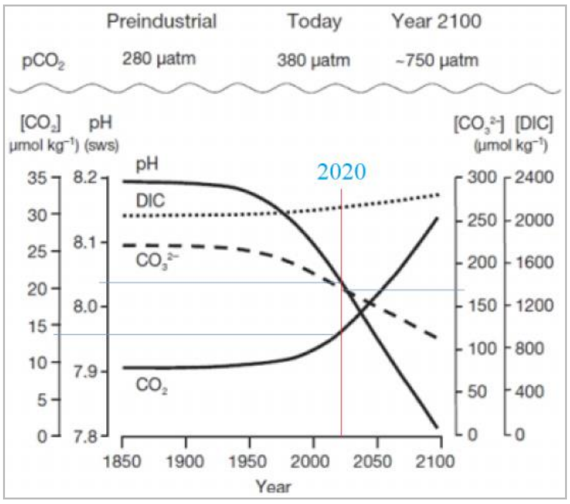

Figure 4. Variation of pCO2, pH, CO_2, CO_3 and DIC from 1850 to 2100 (www.marine.ie/Home/site-area/areas-activity/)

Evaluating the state of seawater acidification of Southern waters of Vietnam, pH value, CO_2 and CO_3^{2-} concentration of the studied area were compared with those which have been forecasted in 2020 (fig. 4). The results show that the mean value of CO_3^{2-} in the studied area (219 mol/kgSW) was higher than that of the same period in the figure (170 µmol/kgSW). The mean value of CO_2 in the Southern waters (11 µmol/kgSW) was lower than that of the same period in the figure (14 µmol/kgSW). The mean value of the pH in the Southern waters (8.04) was equal to that for the same period in the figure. Thereby, it can be proved that the seawater acidification in the Southern waters of Vietnam has been similar to the other areas.

CONCLUSION

In the studied area, the variations of pH values, TA and CO_3^{2-} concentration were similar: Their presence was higher at the offshore areas, in comparison with those at coastal stations, especially at the estuaries. In Truong Sa archipelago, TA and CO_3^{2-} concentration were lower than those at the offshore stations, but pH value was quite similar. Meanwhile, pCO_2 fluctuated in the opposite pattern, increasing in the coastal areas and decreasing in the offshore areas.

When 7 typical parameters for ocean acidification of Southern waters of Vietnam were compared with the values which have been forecasted on the global scale, it showed that the seawater acidification in the Southern waters of Vietnam has been similar to the other areas. In addition, most of the aragonite saturation values of the studied area were greater than 3, creating favorable conditions for the growth of the calcifiers.

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