

# Analysis of Carbonate Chemistry Parameters and Impact of Anthropogenic CO<sub>2</sub> on Ocean Acidification in Selected Coastline Sites of Ghana

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## Abstract:

Anthropogenic carbon dioxide (CO<sub>2</sub>) dissolved into seawater at coastline has shown some effect on oceanic acidification after the preindustrial period. The coastline surrounded with human activities results to oceans acidity that has proven to affect the oceans' calcifying organisms. This study was conducted in three selected landing beach sites of Ghana coastline to determine the concentrations of CO<sub>2</sub>, carbonate ions (CO<sub>3</sub><sup>2-</sup>), partial pressures of carbon dioxide (pCO<sub>2</sub>) and pH for 12 months, and the impact of anthropogenic CO<sub>2</sub> on oceanic the oceanic acidification from the sampled sites within the year. The result from sampled sites showed that dissolved CO<sub>2</sub> concentration and other evaluated parameters were clearly different in each month and at every sampled site. High CO<sub>2</sub> concentration was determined in the months of January and February, and June from different sites. Total mean amount per a year for the sites showed a dissolved CO<sub>2</sub> concentration of  $16.19 \pm 1.73$ , CO<sub>3</sub><sup>2-</sup> concentration of  $143.21 \pm 21.12$   $\mu\text{mol/kg}$ , pCO<sub>2</sub> of  $600.36 \pm 131.92$  and pH of  $8.01 \pm 0.20$ . Correlation relationship showed an increase of anthropogenic CO<sub>2</sub> dissolved into seawater decreased pH at all the study sites, indicating that ocean acidification of seawater at the sites had increased from earlier projections. It was therefore concluded that the anthropogenic CO<sub>2</sub> at sites induces rise of ocean acidification, which could pose danger to marine organisms in the studied areas. Continue decrease of pH low harvest of fishes and the calcification rates of other sea organisms

## 1.0 Introduction

Carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere has oscillated between 200 to 280 ppm for over 400000 years during the preindustrial period (Feely et al., 2004). Currently, there is substantially increase of the atmospheric CO<sub>2</sub> above the 380 ppm which was estimated for 2018. This increased concentration due to the activities of industries and other human activities is higher than the natural reconstructed range of 172 to 300 ppm (Lüthi et al., 2008; Siegenthaler et al., 2005). In the year of 2017, the observational-based estimates indicated that the total anthropogenic CO<sub>2</sub> emission was  $660 \pm 95$  PgC (Sabine et al., 2004). This anthropogenic CO<sub>2</sub> among others is emitted from the burning of fossil fuels (Kawahata et al., 2019). Over the years, it is observed that the emitted CO<sub>2</sub> has irregularly been changed in the atmosphere after a century by a decreased of ~20% and <50% (Joos and Spahni, 2008). By the year 2018, about 42% of emitted  $407.44 \pm 0.10$  ppm CO<sub>2</sub> stayed in the atmosphere, 25 % and 33 % of the absorbed by both the

ocean and terrestrial biosphere, respectively (Le Quéré et al., 2018; H. Zhang and Wang, 2019). The increase rate of activities of industries and the faster depletion of our forest or vegetation suggest that higher concentration of atmospheric CO<sub>2</sub> would be available for ocean absorption.

Increase of this atmospheric CO<sub>2</sub> concentration causes global warming through greenhouse effect (Lin, Gettelman, Fu, and Xu, 2018; Ren, Ding, and Tang, 2017; Sarmiento, 2013; Wolff, 2007; Zhiwei, 2018). This phenomenon of global warming has severe effects on the physical, biological and chemical processes in the seawater (Cao and Zhang, 2017; Yuan et al., 2014; Zhou et al., 2005). One key effect of the increased in absorption of anthropogenic CO<sub>2</sub> from the atmosphere into the ocean is that it disturbs the ocean chemistry, which consequently among others leads to ocean acidification (Caldeira and Wickett, 2003; Le Quéré et al., 2018; H. Zhang and Wang, 2019). For instance, the over 30 % absorption of CO<sub>2</sub> into the oceans in the 21st century is currently a global concern because of its greater negative impact on human and aquatic organisms (Feely et al., 2004; Steinacher, Joos, Frölicher, Plattner, and Doney, 2009). Ocean acidification which is caused by ocean chemistry could also be promoted as a result of uptake of CO<sub>2</sub> from the atmosphere into the ocean. Also, other factors such as the introduction of the anthropogenic nitrogen into the ocean and the resultant changes in organic matter production, oxidation, and deoxygenation cause the acidifying of seawater at the coastal sea (Strong, Kroecker, Teneva, Mease, and Kelly, 2014). Some current studies reported that although anthropogenic nitrogen could result to the seawater acidification, it is however negligible compared to the effect of CO<sub>2</sub> absorption in the ocean (Koweek et al., 2018; Mongin et al., 2016).

The introduction of industrial revolution is report to have contributed greatly to about 30 % increase in hydrogen ion concentrations [H<sup>+</sup>] in sea surface (Caldeira and Wickett, 2003; Orr et al., 2005; Page, 2005). This hydrogen ion concentration in seawater comes from the rise in global emission of anthropogenic activities due to the increasing of atmospheric CO<sub>2</sub> (Bates et al., 2012; Doney, Fabry, Feely, and Kleypas, 2009; Society, 2005). The large amount of hydrogen ion in seawater has serious consequences on the marine carbonate system where Ghana coastal water is not excluded. Ocean carbonate system is essential factor for the control of pH in global oceans and that could account of oscillation of CO<sub>2</sub> between the ocean and the atmosphere (Sigman and Boyle, 2000; Yu et al., 2010). In addition, carbonates from rivers flown into the ocean also alter the seawater acidity in coastal areas, creating instability of specified seawater acidification in such areas (Raymond and Hamilton, 2018). The ocean CaCO<sub>3</sub> chemistry cycle of calcification and ballast effects produce reactions that results to formation of ocean acidification (Han Zhang and Cao, 2016, 2018). For instances, when the reaction of CaCO<sub>3</sub> occur in the ocean, its acidification is mostly decrease down the pH scale, away from alkalinity and toward acidity” (Barnard and Grekin, 2010). Carbon dioxide-carbonate is also noted to be largely responsible for the control of pH of the seawater, which affects a balance state of many chemicals in the sea.

Carbon dioxide is far more soluble than many other gases, like nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>) or argon (Ar) because (CO<sub>2</sub> rapidly combines with water (in milliseconds) to produce a weak carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Once CO<sub>2</sub> is hydrated, it results in a series of rapid proton transfer steps to form bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. Carbonate ion in the seawater acts as antacid that neutralize hydrogen ion (H<sup>+</sup>) to form more bicarbonate (Hilmi et al., 2013).

Dissolved CO<sub>2</sub> in the sea increases the carbonic acid which thereby lowers the pH because of increase in hydrogen ion concentration and thereby decreasing the carbonate ion concentration of the sea as given in the scheme 1A. In equation 1. The reaction process is reversible, which suggests that H<sub>2</sub>CO<sub>3</sub> can dissociate to form back CO<sub>2</sub> and water. However, the equilibrium favours the left due to more carbon dioxide

continue to dissolve and react with seawater. Increase in the hydrogen ion concentration in seawater is due to increase in global CO<sub>2</sub> emission from anthropogenic activities and it has daring consequences on the marine carbonate system (Bates et al., 2012)

Oceans' carbonate system is rapidly depleting due to an influx of anthropogenic CO<sub>2</sub> (Caldeira and Wickett, 2003; Orr et al., 2005). Carbonate ions are reported more currently less abundant in our oceans than they were in the past (Feely et al., 2004), because of the reduction of calcium carbonate (CaCO<sub>3</sub>) through the interaction with dissolved CO<sub>2</sub> (Hönisch et al., 2012). Generally, ocean acidification is not equal to the ocean becoming acid, but instead, the sliding of the oceanic pH from the base range to the acid range (Hardt and Safina, 2008). It therefore obvious when atmospheric CO<sub>2</sub> dissolves into the sea, it can influence the acidity by increasing the carbonic acid, and also decreasing the seawater pH. This ocean chemistry takes place in seawater that are highly explore large amount of anthropogenic CO<sub>2</sub> which the ocean of Ghana is not an exception. Considering the effects of the CO<sub>2</sub> on the acidification of ocean Chemistry, there is the need to assess the variants of dissolved CO<sub>2</sub>, pH and carbonate ions in the coastal sea in Ghana.

The outcome could lead to the understanding of the possible impact of the seawater acidification to ocean organisms in the study areas. According to Vezina and Hoegh-Guldberg (2008), the uptake of CO<sub>2</sub> in ocean waters point to more corrosive conditions for calcifying organisms, resulting to the inability of them to build and maintain their carbonate skeletons. Coralline algae, crustose, some phytoplankton, warm and cold-water corals are all organisms that use carbonate minerals to form shells and skeletons (Barnard and Grekin, 2010; Kroeker et al., 2010). Due to varying sensitivity, biological organisms will react to ocean acidification differently (Cooley and Doney, 2009). Calcifying organisms play a crucial role in marine food chains and food webs, and any effects to them would have food security and nutrition consequences on human. Reduction of sea fisheries which are particularly crucial as a source of protein and income in low latitudinal regions such as West Africa may be affected by acidification of ocean (Cheung et al., 2010). About 54.8 million people depend on fisheries worldwide with Africa being the second largest employer of fisher folks after Asia (FAO, 2012). In Ghana, fish accounts for about 16.6% of the global population's intake of animal protein and 6.5 percent of all protein consumed (FAO, 2012) with 2.2 million people employed in the sector (Aseidu and Nunoo 2013). Therefore, it is important to evaluate the ongoing change in the ocean chemistry that result in the occurrences of ocean acidification. The increase of dissolved CO<sub>2</sub> could be factors responsible for global decline in fish catch across the world (Honisch et al. 2012).

This study was to determine the impact of the dissolved anthropogenic CO<sub>2</sub> on the ocean acidification in the selected coastlines of Ghana. It focuses on the assessment of the variant of dissolved CO<sub>2</sub>, pH and carbonate ions and the individual effect of oceanic CO<sub>2</sub> uptake on ocean acidification, which is generally considered a key process affecting seawater acidity, in the study area in Ghana.

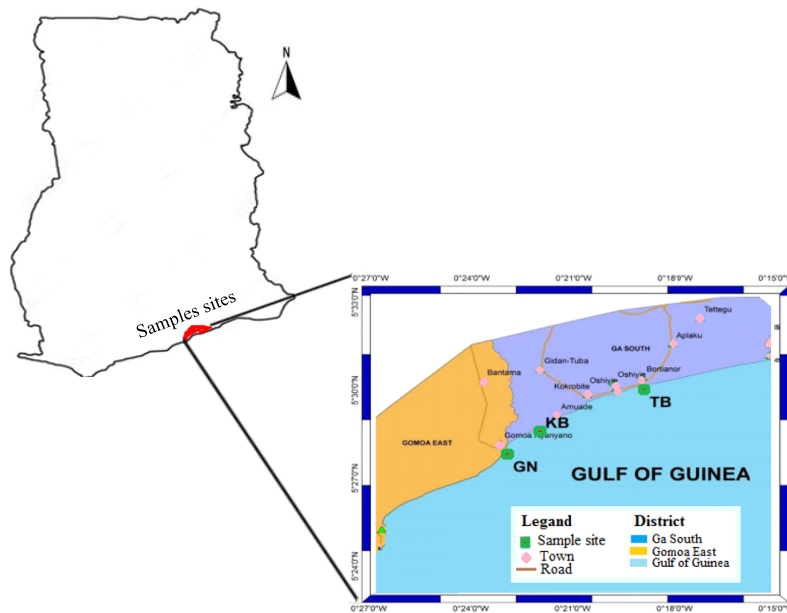
## 2.0 Materials and Methods

### 2.1 Study Area

The study area comprises the Tsokomey (TK), Bortianor (TB) and Gomoa Nyanyano (GN) Fish Landing Beaches. The Tsokomey/Bortianor fish landing beach is found within in the Ga South municipality of the Greater Accra region of Ghana. As shows in the Figure1, the Tsokomey/Bortianor fish landing beach is situated between coordinates; Latitude 05°28.354" N, Longitude 000° 20.157" W and Latitude 05° 34.327" N, Longitude 000° 20.136" W. The beach is located between Bojo Beach Resort Hotel and

Muston Beach Resort. It serves the landing base for fishing where most Fishmongers come to buy their fish in large quantities for household consumption or to trade with. The fishing storage facility is provided at the place by the Ministry of Fisheries and Aquaculture for storing fish.

The GN fish landing beach is located in the Gomoa East municipal of the Central region of Ghana (Figure 1). The GN fish landing beach is located between GPS coordinates of latitude  $05^{\circ} 28.295''N$ , Longitude  $000^{\circ} 24.474''W$  and Latitude  $05^{\circ} 28.264''N$ , Longitude  $000^{\circ} 24.409''W$ . Majority of the people in the locality are fishers. There are many vessels used for fishing such as dugout canoes with the motorized ones being the majority in these study areas.



**Figure 1: Map of sample sites (three landing beaches) for the study in Ghana**

## 2.2 Collection of Seawater Samples

Samples from the three sites were always collected in the same day into a well labeled and clean 500 mL High Density Polyethylene (HDP) sampling bottles. The samples were then stored in thermally insulated containers for easy handling and transportation for analysis. Seawater samples were collected by using a motorized marine vessel in each site. The samples of the seawater were collected about 100 m from the offshore into the labeled HDP bottles. The HDP sampling bottles were always rinsed with the same seawater at each sampling point before collecting the actual surface seawater into it. The sampling bottles were rinsed three (3) times with the seawater prior to the collecting of samples as recommended by literature (Serfo-Armah et al., 2004; Donkor et al., 2006). The samples from all the sites were then same for analysis.

## 2.3 Calibration of Hanna HI 9829 and measurement of study sites' parameters.

Prior to the parameters' measurement, the Hanna HI 9829 Multi-parameter Meter Probe was calibrated. The pH meter calibration was done with two standard buffer solutions of pH 4.02 and 7.02. Parameters such as pH and temperature were measured in all the sampling sites using Hanna HI 9829 multi-parameter probe with the help of a motorized vessel. The measurements were taken three replicates. Before the readings of the measurement was taken, the Hanna HI 9829 multi-parameter probe was rinsed thrice with the seawater to be measured before finally immersing the probe into the seawater sampled. Three seawater

samples were collected from each sampling sites using the rinsed water sampling bottles for each parameter for the analysis.

## 2.4 Determination of Carbonate Chemistry Parameters

Determination of interested ocean chemistry parameters was done by using the United States Geological Survey (USGS) computer software programme known as the USGS CO<sub>2</sub>calc V4.0.9 based on measured pH, total alkalinity, temperature, and salinity (Robbins et al., 2010), which are calculated based on Wallace (1998) report and carbonate acid dissociation constants proposed by Dickson and Millero (1987). The computed parameters for the study were partial pressure of carbon dioxide ( $p\text{CO}_2$ ); total carbon dioxide (TCO<sub>2</sub>), carbonate ion concentration (CO<sub>3</sub><sup>2-</sup>); dissolved carbon dioxide (CO<sub>2</sub>aq); and bicarbonate (HCO<sub>3</sub><sup>-</sup>).

Sea-air exchange flux of CO<sub>2</sub> was calculated from the following equation 1;

$$F = KS (p\text{CO}_{2w} - p\text{CO}_{2a}) \quad 1$$

Where: K = gas transfer velocity of CO<sub>2</sub> S = solubility of CO<sub>2</sub> in seawater (calculated as a function of temperature and salinity) and  $p\text{CO}_{2w}$  and  $p\text{CO}_{2a}$  are the Partial pressures of CO<sub>2</sub> in seawater and air respectively. The USGS CO<sub>2</sub>calc V4.0.9 developed by the U.S. Geological Survey Florida Shelf Ecosystems in reaction to its Ocean Acidification is used for the calculation of carbonate system parameters.

## 2.5 Quality Control/Quality Assurance (QC/QA)

To ensure quality control, a set of procedures were employed in the laboratory for continues monitoring of the analysis processes that made sure that the results attained during the course of analysis was accurate. there was arithmetical sum of all the activities conducted during the analysis to ensure that the data gathered met the quality desire from the study. All the sampling glassware were soaked in the solution of 10 % HNO<sub>3</sub> for two days and later rinsed with deionized water to avoid contamination before used to collect samples from various sampling sites and during analysis. All the cleaned samples' bottles were each marked with unique identification codes. Sampling bottles were rinsed with the seawater at the sampling sites and followed sample collection which were kept on ice packs and transported for analysis. all the reagents used throughout the study were of analytical grade and procured from Merek Chemicals Ltd. The instruments were calibrated before used. Sample matrixes were analysed in triplicate to ensure efficiency. The procedures for sampling and analysis were done according to the internationally recommended protocols.

## 2.6 Data Analysis

Statistical analyses were designed to access the correlation and effect of the carbon dioxide that contribute to ocean carbonate chemistry and acidification. All obtained from the sampling sites and in the laboratory were recorded in Microsoft excel 2010 and used for analysis. Using origin software (Origin 8.9 version), the graphic and statistically analysis were designed. All structures of compounds and their reaction mechanisms were designed in ChemBioDraw Ultra 11.0 software. In addition, the correlation among the carbonate chemistry parameters was assessed and the effect of dissolved CO<sub>2</sub> on the carbonate chemistry parameters estimated through simple correlation analysis.

### 3.0 RESULT AND DISCUSSION

Data was analyzed through basic statistics and charts for CO<sub>2</sub>, pCO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup> and pH to help determine the effects of increasing anthropogenic CO<sub>2</sub> on the ocean acidification in the study areas. There several reports of the influences of dissolved CO<sub>2</sub> in seawater on the oceans acidification [Strong et al, 2014: Mongin et al, 2016: Koweek et al, 2018: Kawahata et al, 2019], which have negative effect on the some living organisms in the sea (Kroeker et al. 2010: Manno et al. 2012: Iguchi et al. 2014; Sekizawa et al. 2017). The ocean chemistry parameters and reactions are illustrated as shown in Figure 2, depicting their possible relationships with respect to CO<sub>2</sub> that result from the human activities The correlation between the carbonate chemistry parameters was evaluated. The results from the data gathered from the twelve (12) months for the three study sites are presented in graphs and table with the findings and discussion on it.

#### 3.1 Presence of CO<sub>2</sub>

The concentration of dissolved anthropogenic CO<sub>2</sub> was determined in the three sample sites in Ghana from November to October. The result shown in Figure 2 indicates that the sample from the landing beach site of KB had highest concentration of CO<sub>2</sub> in November and from June to October among the three sites. However, CO<sub>2</sub> concentration was most high in the GN sampling site for the months of January and February, whiles highest CO<sub>2</sub> concentration was recorded at TB site from March to May, 2021. Dissolved CO<sub>2</sub> concentration was recorded and varying for different months and different samples sites. The CO<sub>2</sub> concentration was low in December and relatively increases from January to October for the sites. The variation of air–sea CO<sub>2</sub> fluxes can vary in different season (Takahashi, Sutherland. and Kozyr., 2009; Wesslander et al., 2010). The key factors contributing to this is as a result of is mainly due to human activities of fossil fuel burning and land use that destroy plants by Humankind (Feely et al., 2004; Zhang and Wang, 2019). The decrease of CO<sub>2</sub> absorption by the terrestrial biosphere due to inadequate plants contributes to availability high volume of anthropogenic CO<sub>2</sub> for the increase of its dissolving in sea water [Le Quéré et al., 2018]. The sample sites have relatively different human activities and diverse vegetation covers, which could have accounted for the difference in the availably CO<sub>2</sub> concentrations.

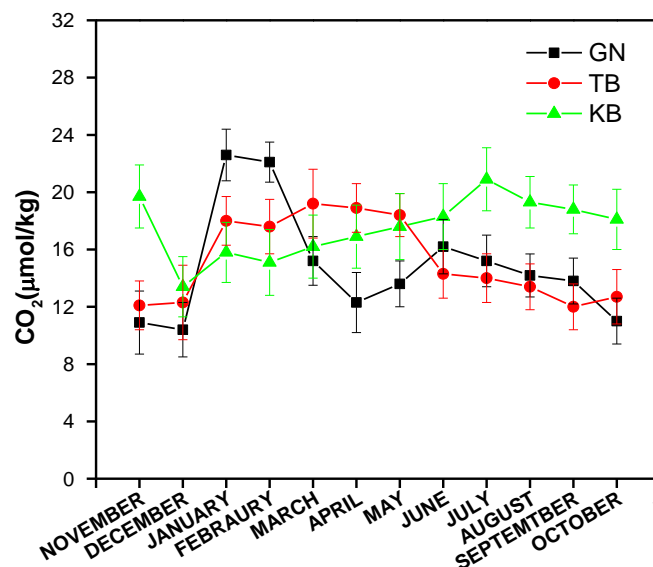


Figure 2. The dissolved CO<sub>2</sub> concentration at the sample sites

### 3.2 Observed Variability in pCO<sub>2</sub>

Earth’s surface has previously experienced a high pCO<sub>2</sub> environment, which was generally associated with “hot house” conditions. The high pCO<sub>2</sub> has also been identified as an influencing factor that results to seawater acidification (Kawahata et al., 2019). The riverine flux of carbon to the ocean estimated be 1.06 PgC year<sup>-1</sup> is predicted to increase pCO<sub>2</sub> in coastal regions (Li et al. 2017), This warming is predicted to cause extreme rainfall and further increase pCO<sub>2</sub> of river water (Goswami et al. 2006). High pCO<sub>2</sub> around surface sea would induce intensified hydrological cycles on the Earth’s surface (Jenkyns, 2010). In seawater, the simple ocean carbon cycle model was used to understand the relationship between carbonate dissolution and pCO<sub>2</sub> in the oceans.

From the result indicated in Figure 3, pCO<sub>2</sub> concentration is high in the months of January and February for GN and TB sampling sites respectively. There was observed decrease in pCO<sub>2</sub> concentration during the May to December for the sampling sites of TB. The pCO<sub>2</sub> concentration was lower in March, April and May but slightly increase June but again decrease between the month of July to November for the sites of GN. In December, pCO<sub>2</sub> concentration for sampling site of KB was relatively low but continues to increase from January to November. However, for all study sites experienced an increase in partial pressure of pCO<sub>2</sub> as compared to the in 2007 which was 384 μatm and expected to by the year 2100 to get to 793 μatm (Gattuso et al., 2009). The fluctuation of pCO<sub>2</sub> concentration could be attributed to the fluctuations in temperature for the months. Therefore “high level” pCO<sub>2</sub> is factors, which has relationship between carbonate dissolution in ocean, lead to acidification in the seawater.

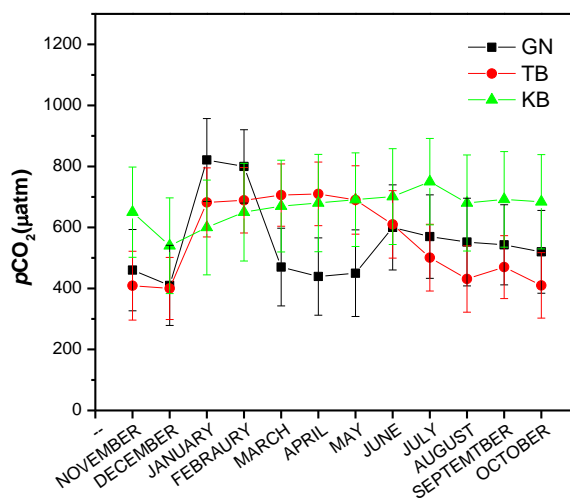
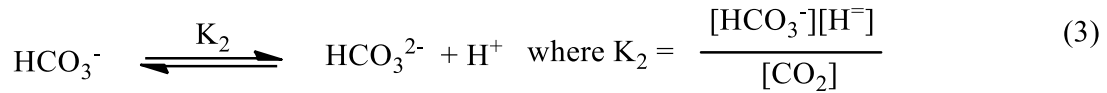
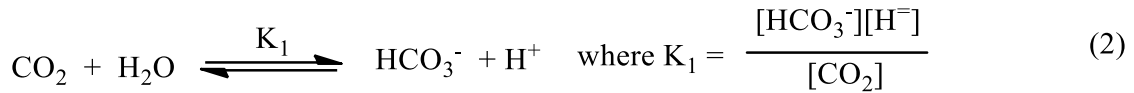


Figure 3. Availability of the pCO<sub>2</sub> in different months for sample sites

### 3.3 Variability of Carbonate Ion Observed in the Five Study Sites across the Year

Carbonate ions are one of the key ocean chemistry parameters that is evaluated from the anthropogenic CO<sub>2</sub> emission. When CO<sub>2</sub> is dissolved in seawater, there is chemical reactions that occur with the resultant effect on the CO<sub>3</sub><sup>2-</sup> and pH, and the saturation states of biogenic carbonate minerals. The explanation of the chemistry of carbon dioxide in the ocean illustrated the equations below as suggest by Koffi et al, 2015.



The  $K_1$  and  $K_2$ , which are the stoichiometric equilibrium constants, describe the carbonate process and the resultant  $\text{H}^+$  ion in the seawater. These reactions process systems account for different sums of the formation of the dissolved compounds such as  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  to give the dissolved carbon. The formation of  $\text{CO}_3^{2-}$  in the ocean of the sampling sites in Ghana was measured for 12 months to determine their availability over time. From Figure 4., there was a significant presence of carbonate ion in the study sites for all the months. However, the carbonate ions in the sea water from TK were in a higher concentration than the other study sites for the months of December, January and February. There an increase in the carbonate ion concentration at the GN sampling site, which higher than the TB sample site and a decreased concentration of it at TK sample site for the months of march, April and May. There was also a higher concentration of carbonate ions for the months of May and June at the TB site compared to the other study sites. The difference of carbonate ions concentration at the three sampling sites and in different months of the year was due to the  $\text{CO}_2$ -induced warming acts which mitigated the reductions in the seawater  $\text{CO}_3^{2-}$  and the individual effect of oceanic  $\text{CO}_2$  uptake at the various time and study (Zhang and Wang, 2019). In addition, the increase of hydrogen ion concentration also tended to reduce carbonate ion concentration, which account for the low concentration of  $\text{CO}_3^{2-}$  in some of the months in the study areas. The anthropogenic  $\text{CO}_2$  emission contributes to the variability of  $\text{CO}_2$  for its uptake in the sea that accounts for the resulting to carbonate ion formation as indicated in equation (2) in the study areas. Carbonate ion concentrations increases the saturation horizon closer to the surface of the seawater (Bates *et al.*, 2014).

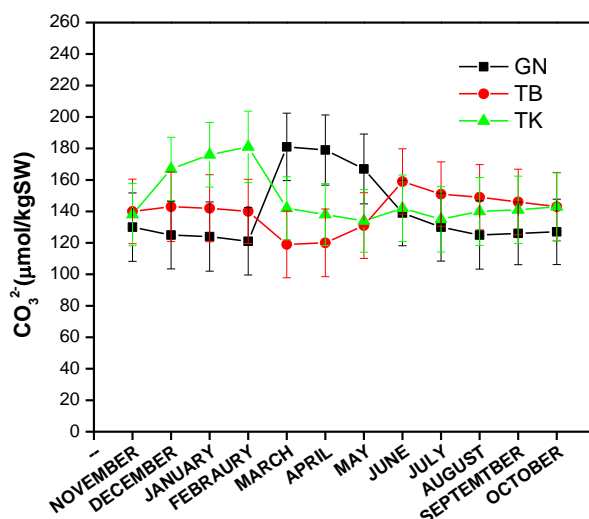


Figure 4. The concentrations of  $\text{CO}_3^{2-}$  in the studied sample sites

### 3.4 Variability of pH Observed at the Different Sites of 1-Year

The pH value from all the three study sites was determined over twelve months in other to evaluate the relationship between it and the anthropogenic  $\text{CO}_2$ . This was important because of the earlier report that



the increase in atmospheric CO<sub>2</sub> concentration facilitates the ocean continuously absorbs anthropogenic CO<sub>2</sub> from the atmosphere, leading to global ocean acidification (Zhang and Wang, 2019; Cao Wang, Zheng, and Zhang 2014). The result from Figure 5 shows relatively constant and high pH values (between 8.07 - 8.15) in the months of June to December for all the sampling sites. Even though these pH values are considered to be high, they are within the worrying rate of reduction in the industry and developed countries like China [Zhang and Wang, 2019]. The variation of pH is vividly seen from January to May in each sampling sites. The observed similar and high pH values that seen to be constant at all the study sites from June to December was attributed to the raining season that most human activity that reduce the release of CO<sub>2</sub> into the atmosphere for ocean uptake are reduced and also presence of more plant in the area absorbing a lot of the atmospheric CO<sub>2</sub>. Obviously different pH for all the sampling sites from January to May was attributed to observe different human activities and plantations, as well as inputs of contaminants and nutrients from run-offs, waste products of animals and discharge systems around the areas of study (NOAA, 2009). The lowest and highest pH values among the three sites were observed in the January and March respectively at GN site. These months witnessed several and different human and industrial activities of the sites. The other two sites (TK and KB sampling sites) recorded opposing decrease of their pH from January to march, with TB showing the lowest value in March. This variation and the decreasing trend of pH in most of the landing beaches are a confirmation previous reports (Kpaliab and Bawa, 2022; Bates 2007): Bates *et al.*, 2012), suggesting that variation in seawater pH occurs over time in a year and thus ocean acidity around the landing beaches is not constant within a year. One major indicator accounting for ocean acidification is pH (Bates et al., 2012), due to the Global decreasing pH with a corresponding increase in acidity of the oceans is dissolving of carbon dioxide from the atmosphere into the sea (Armstrong et al., 2010). It was therefore concluded that the release of anthropogenic CO<sub>2</sub> (in the landing beach of the sampling site) induces decrease of pH, indicating the ocean acidification of those areas.

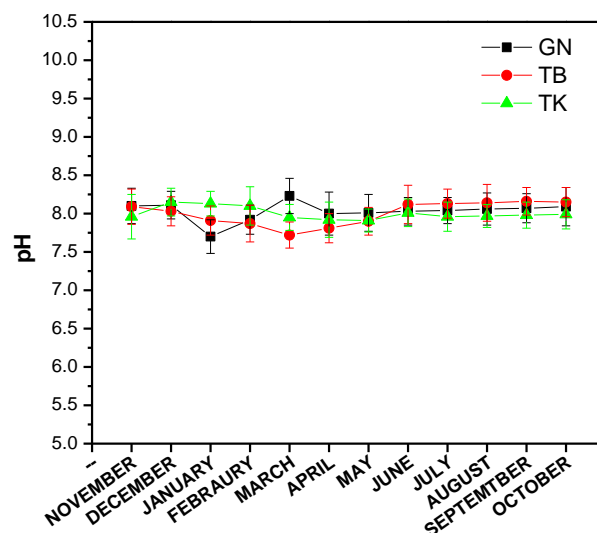


Figure 5. The pH in the different studied sample sites and months

### 3.5 Results of Carbonate Chemistry Parameters of Seawater

Carbonate chemistry parameters measured in this study for the twelve (12) months were summary into one-year results by finding the total mean for each site. Additionally, the mean result for the study areas was determined to find out the carbonate parameters and pH in the year 2022.

The determined result is presented in Table 1.

Sample site	CO <sub>2</sub>	CO <sub>3</sub> <sup>2-</sup> μmol/kg	pCO <sub>2</sub> μatm	pH
GN	15.36 ± 1.73	140.36 ± 21.42	561.36 ± 133.73	8.02 ± 0.21
TB	15.53 ± 1.85	140.27 ± 21.09	572.64 ± 107.23	8.00 ± 0.20
KB	17.31 ± 2.12	149.01 ± 20.85	667.09 ± 154.81	8.01 ± 0.18
Total mean	<b>16.07 ± 1.9</b>	<b>143.21 ± 21.12</b>	<b>600.36 ± 131.92</b>	<b>8.01 ± 0.20</b>

From Table 1, the mean results per a year for GN site shows minimum dissolved CO<sub>2</sub> concentration of 15.36 ± 1.73, CO<sub>3</sub><sup>2-</sup> concentration of 140.36 ± 21.42, partial pressure pCO<sub>2</sub> of 561.36 ± 133.73 and a highest pH of 8.02 ± 0.21. The mean results per a year for TB site shows a dissolved CO<sub>2</sub> concentration of 15.53 ± 1.85, CO<sub>3</sub><sup>2-</sup> concentration of 140.27 ± 21.09, pCO<sub>2</sub> of 572.64 ± 107.23 and a lowest pH of 8.00 ± 0.20. The mean results per a year for KB site shows a highest dissolved CO<sub>2</sub> concentration of 17.31 ± 2.12, highest CO<sub>3</sub><sup>2-</sup> concentration of 149.01 ± 20.85, highest partial pressure pCO<sub>2</sub> of 667.09 ± 154.81 and pH of 8.01 ± 0.18. The KB sites which shown a relatively low anthropogenic CO<sub>2</sub> concentration than TB sampling site and having lowest pH could be due to some other factors that could also contributed to this acidification of seawater. Some of the factors are the input of anthropogenic nitrogen to the ocean, unstable state of organic matter production, changes in oxidation, and deoxygenation (Strong et al., 2014),

The findings from the above results show that the study site of KB had the highest concentration of dissolved anthropogenic CO<sub>2</sub> among all the sampling sites with a relative low pH of 8.00. It is obvious from the result that TB seawater was more acidic (low pH of 7.99) compared the others sites. This variability of the seawater pH confirmed the earlier proposal that of surface ocean waters' pH that was 8.17 at 1750 AD and had been decreased to 8.06 over the years is expected to reach to 7.93 (pCO<sub>2</sub> = 560 μatm) or 7.71 (pCO<sub>2</sub> = 1000 μatm) in the near future (Kawahata et al., 2019). The low pH is also within the projected by the Lawrence Livermore National Laboratory ocean general-circulation model under IPCC SRES scenario, which point out that ocean surface pH could be decreased by 0.3–0.5 units at the end of 21<sup>th</sup> century (Caldeira and Wickett, 2005).

To determine the effects of anthropogenic CO<sub>2</sub> on the other studied ocean Chemistry parameters, correlation analysis was performed. This is based on the fact that input of anthropogenic CO<sub>2</sub> could cause changes in the ocean chemistry by making seawater more acidic, hence the ocean acidification (Zhang and Wang, 2019; Caldeira and Wickett, 2003). The result presented in the Table 2 shows that the correlation pH and the CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup> and pCO<sub>2</sub> were negative, suggesting that the high dissolving of CO<sub>2</sub> into seawater affected the pH of the ocean. Moreover, the correlation results (-0.26567) show that the relationship between dissolved CO<sub>2</sub> and ocean acidification is nonlinear and weak, which could have been because of other oceanic Chemistry cycle mitigating the acidification. This is important because if we want to mitigate ocean acidification at the study sites, there is the need to strongly reduce the anthropogenic CO<sub>2</sub> emission. Comparing to the report of Zhang and Wang (2019), which indicated that by the year 2017 sea surface pH in the East China dropped from the preindustrial level of 8.20 to 8.06 with corresponding of 35% rise in [H<sup>+</sup>], it is that the overall pH of 8.00 of the study area in Ghana show to be a high rate of rise in ocean acidification.

**Table 2: Correlation analysis among the studied chemistry parameters**

	CO <sub>2</sub>	CO <sub>3</sub>	pCO
CO <sub>2</sub>	1		
CO <sub>3</sub>	0.996152	1	
pCO	0.999829	0.994359	1
pH	-0.26567	-0.18016	-0.28348

## 6.0 Conclusion

The study was to determine the variability of CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, pCO<sub>2</sub> and pH in each month within a year and the relationship that exist between anthropogenic and pH of the studied areas in Ghana.

The relationships were validated over the year by comparing calculated means of the oceanic parameters. Among the three sample sites, the presence of ocean CO<sub>2</sub> source was higher in the landing beach site of KB in November and from June to October. However, CO<sub>2</sub> concentration was most high in the GN sampling site for the months of January and February, while highest CO<sub>2</sub> concentration was recorded at TB site from March to May, 2021. Dissolved CO<sub>2</sub> concentration was varied for different months and different samples sites. There were different pCO<sub>2</sub> and carbonate ion concentrations for each month and all sampled sites for the studied period.

The various study sites showed slightly increased in their seawater acidification. This was attributed to the contribution anthropogenic CO<sub>2</sub> dissolved into seawater in the all the studied landing beach site in Ghana. It was therefore concluded that the release of anthropogenic CO<sub>2</sub> (in the landing beach of the sampling site) induces decrease of pH, indicating the ocean acidification of those areas. This anthropogenic CO<sub>2</sub> driven ocean acidification could pose a lot of danger to marine calcifying organisms in the studied areas because the calcification rates of organisms largely decrease in acidified seawater.

## Statements and Declarations

There no conflict of interest for the study

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