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Variability of Carbonate Chemistry of seawater of the central Atlantic coastline of Ghana

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Abstract

Variability of carbonate chemistry of seawater has attracted high interest due to their impact on coastline and living things. The purpose of the study was to monitor the carbonate chemistry parameters of seawater along selected parts of the Central Atlantic Coastline of Ghana and assess the variability trend of the carbonate chemistry over the one-year. The study was carry out in five fish landing beaches in Ghana with the samples collected and analysed four times in every month for the study period. Sample were analysed using United States Geological Survey (USGS) computer software programme, USGS CO2calc V4.0.9 to determine the carbonate chemistry parameters The results showed that there was a high concentration value for Partial Pressure of Carbon dioxide (pCO2) and total carbon dioxide in the coastline. There was evidence of decreasing trends of carbonate ion concentration, calcite and aragonite saturation states and pH, whiles the Revelle factor was at an increasing trend. These findings suggest that seawater of the coastline in Ghana is gradually losing its buffer potency and may pose danger to the lives of marine organism especially shell forming organism that provide food nutrients for people in the study area.

Keywords: Calcite and Aragonite saturation, Partial Pressure of Carbon dioxide (pCO2), pH, Revelle factor, Total alkalinity.

Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

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1.0 **Introduction**

Oceans play important roles in global biogeochemical cycles which contribute immensely to biodiversity of the planet. They also serve as a carbon dioxide sinks thereby regulating atmospheric carbon dioxide (Turley and Gattuso, 2012). About 20% of carbon dioxide (CO_2) has been added the sink (Ocean) (Takahashi et al., 2009). The ocean presently takes up about a quarter of our annual CO_2 emissions (Le Qu´er´e et al., 2013) at least one quarter of Earth's anthropogenic surface warming is being absorbed by the ocean (Ramanathan and Feng, 2009). In fact, the continual increase in the absorption of Carbon dioxide and other human activities by the Ocean alters the other components of the carbonate chemistry in surface waters (Borges and Gypens, 2010). These have the tendency of lowering the oceanic pH and carbonate ion concentrations, that can result in the decreasing of the saturation state of seawater with respect to calcium carbonate (Feely et al., 2004). Global evidence already stipulates that oceanic pH is 0.1 units lower than pre-industrial era (Vezina and Hoegh-Guldberg, 2008) and it is projected to decrease by another 0.3 to 0.4 units by 2100 (Munday et al., 2009). This may lead to ocean acidification which has potentially dangerous consequences for humans and marine biodiversity. Under-saturated of seawater with respect to calcium carbonate, marine organisms can no longer form calcium carbonate shells (Raven et al., 2005). The reduction of the calcifying rate of shell forming organisms such as mollucs and crustaceans (Barnard and Grekin, 2010), consequently leads to imbalances in the ecosystem and these has effects on food chain and food web (Turley and Gattuso, 2012; Hall- Spencer et al., 2008). This situation has a toll on fish catch recently, as study by FASD (2011) revealed that globally, income generated by each coastal fishery canoe dropped by 40%.

Most of the people along the coast are fishers and depends solely on fishing. Fish is an important source of animal protein, with consumption approximately 22 kg yr-1 per person (FAO, 2014). The fisheries' sector is estimated to employ about 2.2 million people that can be translated to ten percent (10%) [Bank of Ghana, 2008] of the active workforce either directly or indirectly and generate well over one billion United State Dollars in revenue yearly. This accounts for at least 4.5% of Ghana's Gross Domestic Product (Republic of Ghana Fisheries and Aquaculture Development, 2008; Aseidu and Nunoo, 2013).

Not only does the incidence of ocean acidification affects the global fish stock but in Ghana where fisheries provides fish catch has fallen short of Ghana's fish requirement (Bard and Koranteng, 1995) coupled with emergence of Harmful Algal Bloom (HABs) in the Ghanaian marine environment, various Bio-Economic models have been used to predict revenue losses to the Fisheries sector of the Ghanaian economy (Atta-Mills et al., 2004; Sumaila et al., 2006). However, there is scarce data on the seawater quality on the Ghanaian marine environment due to Climate Change. This has made it difficult for marine scientists to make predictions on the Ghanaian situation. Therefore, there must be the need for constant monitoring of seawater quality in order to generate data.

However there has not been enough research on the carbonate chemistry parameters of seawater in the Central Atlantic Coastline of Ghana. This study therefore sort to monitor the carbonate chemistry parameters of seawater along selected parts of the Central Atlantic Coastline of Ghana and assess the variability trend of the carbonate chemistry over the one-year period.

2.0 **Materials and Methods**

Five landing beaches was selected for this research as identified in the following figure1. They include, Tsokomey/Bortianor (TB), kokrobitey (KB), Gomoah Nyanaynor (GN), Senya Breku (SB) and Gomoah Fettey (GF).

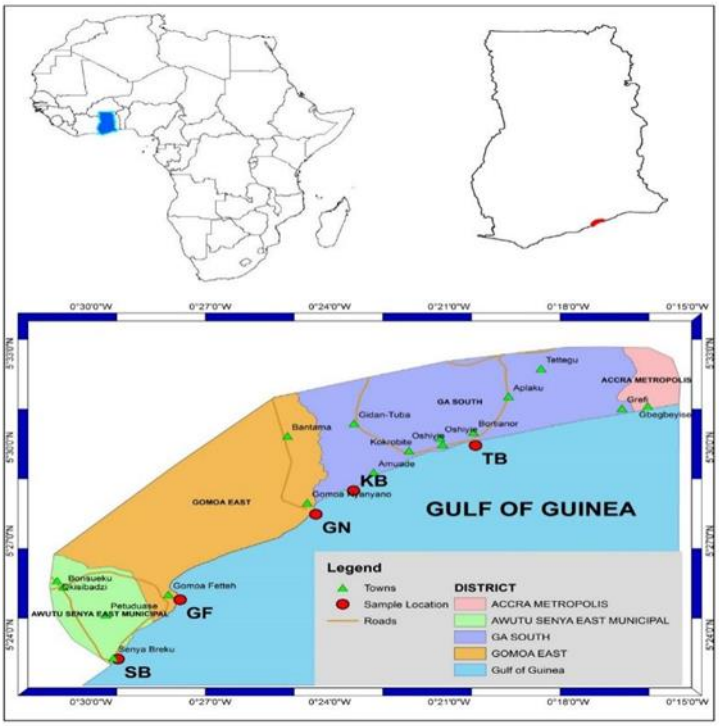

Fig. 1: Map showing the landing beaches used for the study

2.1 Sampling

The sampling of seawater was done four times every month over a twelve-month (12) period (June 2016 to May 2017) and an average for each month computed and recorded after the analysis.
Sampling containers [500 mL of well pre-conditioned High Density Polyethylene sampling bottles (HDPB)] were cleaned thoroughly by immersing all them in a 10% (v/v) HNO_3 solution for at least forty-eight hours (48 hrs). Subsequently, the containers were rinsed with double-distilled water Mahapatra et al., (2001) and labelled with special codes.
Seawater samples were collected at a distance of about 100 m offshore aboard a motorized marine vessel with a multi-meter probe. Prior to the collection of seawater samples, the sampling bottles where first rinsed three (3) times with the sampled water in large container. Physico-chemical parameters such as pH, temperature, salinity and conductivity were measured in-situ, with HANNA HI 9829 multi-parameter probe. Three replicates' readings were taken. Three replicates of water samples were collected from each sampling sites.
Samples for major cations determination were acidified with two (2) drops of concentrated 65% HNO_3 immediately after the collection of the seawater samples; The samples were kept on ice in thermally insulated containers for transportation to the Marine Chemistry laboratory of the Ghana Atomic Energy Commission (GAEC), Kwabenya, Accra. At the laboratory, the samples were kept in a refrigerator at 4 oC and analyzed within 48 hours.

2.2 Determination of Total Alkalinity (TA)

Fifty-milliliter (50 mL) aliquot of the seawater sample was transferred into a 250 mL conical flask. Followed by addition of two drops of bromcresol green indicator. The content of the conical flask was mixed thoroughly by swirling to develop a blue colour. The water sample was then titrated against 0.02 M H_2SO_4 solution from the burette until the colour changed from colour blue to colour yellow signifying the end point of the titration. The titration was stopped and the volume of the titrant (H_2SO_4) in the burette was recorded. Two replicate titrations were done and the mean titre value calculated.
Total alkalinity was calculated using the following equation:

Alkalinity (mg/L $CaCO_3$) = (B × N × 50000)/(mL Sample)

Where: B = total mL of titrant used to bromcresol green end point (mean volume of standard H_2SO_4 used), N = normality of titrant (H_2SO_4 solution)

2.3 Determination of Carbonate Chemistry Parameters

The United States Geological Survey (USGS) computer software programme, USGS CO2calc V4.0.9 (Robbins et al., 2010) was used for the computation (based on measured pH, total alkalinity, temperature, and salinity) of carbonate chemistry parameters. The parameters are partial pressure of carbon dioxide (pCO_2); total carbon dioxide (TCO_2) or dissolved inorganic carbon (DIC); carbonate ion concentration (CO_3^{2-}); mineral saturation states for calcite (Ωca) and aragonite (Ωar); revelle factor (RF) and bicarbonate (HCO_3^-). The calculations were done based on Wallace (1998) with carbonate acid dissociation constants proposed by Mehrbach et al., (1973) as refitted by Dickson and Millero (1987) with the dissociation constant for boric acid was determined by Dickson (1990).

3.0 Results and Discussion

To ascertain the significance of the differences in the observed parameters across the sites, Analysis of Variance (ANOVA) was employed. Here, the Null Hypothesis of Equality of Mean of Measurement was tested. The results are presented in Table 1.

Table 1: ANOVA test of equality of mean of carbonate chemistry parameters

Chemistry Parameter	F statistic	p – value
pCO_2	10.84	0.0000
Carbonate ion (CO_3^{2-})	7.31	0.0000
pH	11.11	0.0000
Total Alkalinity (TA)	4.16	0.0050
Total Carbon Dioxide (TCO_2)	5.11	0.0010
Dissolved CO_2	11.53	0.0000
Revelle Factor (RF)	11.39	0.0000
Aragonite (ΩAr)	11.42	0.0000
Calcite (Ωcal)	6.72	0.0000
Atmospheric CO_2	10.72	0.0000

From Table 1, it can be observed that there is a significant difference in the observed measures for the carbonate chemistry parameters with respect to the sites (all p – values are less than 0.05 at 5% level of significance).

3. 2 Variability of Observed Salinity and Temperature

Salinity of seawater is averaged to be 35ppt. But for our monitoring, it was observed across the study sites of the study that, salinity of seawater averaged a little over 34ppt instead of high density of seawater due to evaporation. This was probably due to addition of fresh water leading to the decrease in density of seawater.

Temperature is a critical water quality parameter since it directly influences the amount of dissolved carbon dioxide, oxygen and other physico-chemical parameters that is available to marine organisms. Water bodies undergo temperature variations along with normal climatic fluctuations. These variations

occur seasonally and, in some water bodies, over periods of 24 hours.
The recommended temperature of ocean surface water is averaged at 17oC. But for all the study sites, decrease in temperature was observed for the first quarter (June to August) except Senya Breku (SB) this may be due to addition of fresh water into the sea. There was up and down fluctuation in temperature over the entire study period. The temperature of water is influenced by many factors but it may exceed recommended criteria due to exposures to radiation (Washington State, 1998). The fluctuations and accumulation of temperature has shown that it is a crucial factor in the distribution of aquatic species and also influences the rate of reactions occurring within the water body (Chapman, 1996).

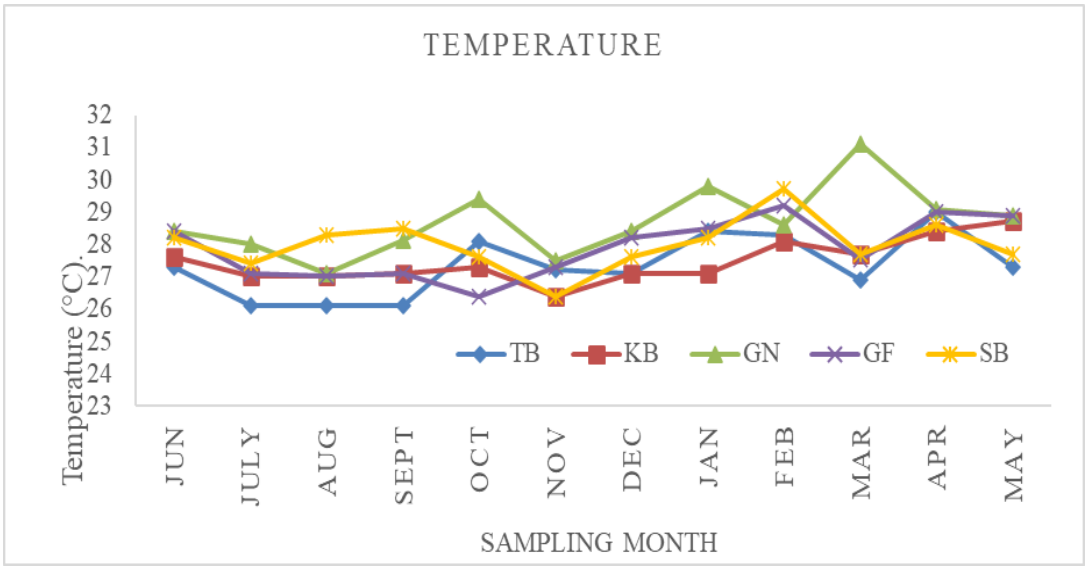

Fig. 2: Temporal variation of temperature

On average, temperature was observed to be high as 28oC (Fig.2). this suggest that there is a gradual warming of the ocean due to the absorption of most of the excess heat from the greenhouse gas emissions and can cause coral bleaching and loss of breeding grounds for marine species and the ecosystem as a whole.

3.3 Variability of pH Observed at the Five Sites

From Fig. 2, the observed pH for the first half (June to November) which happens to be the peak season which incidentally coincided with the raining season. The study appeared to be constant on the average at all the study sites. For the second half (December to May) of the study, appreciable variability was observed; with study site Gomoa Nyanyanor (GN) experiencing the high variability in March, followed by subsequent decline. Senya Breku (SB) recorded the least amount and variability of pH across the study period. On the average pH from the study sites started declining from March except Gomoa Nyanyanor that showed a slight appreciation (Fig.3). The decreasing trend of pH in most of the landing beaches are in agreement with work done by Bates (2007) and Bates et al. (2012). Both study recorded a decrease in seawater pH over extended periods of time, thus, an occurrence of acidity of the oceans may be identified with the landing beaches that recorded decreasing trend of pH

The greatest indicator of ocean acidification is pH (Bates et al., 2012), and decreasing pH correlates with an increase in acidity of the oceans as a result of increased absorbance of carbon dioxide from the atmosphere (Royal society, 2005). Values of pH recorded from all the sampling sites vary very marginally within the months in a decreasing trend (Fig. 2), but the variations were significant (Table 1). The decreasing trend of the pH observed across the sampling sites seem to be confirming the projected decrease in the ocean's pH by 0.3 to 0.4 units by 2100 (Munday et al., 2009). The reason for the declining trend of pH from December may be attributed to nearshore inputs of contaminants and nutrients from run-offs, waste products of animals and discharge systems.

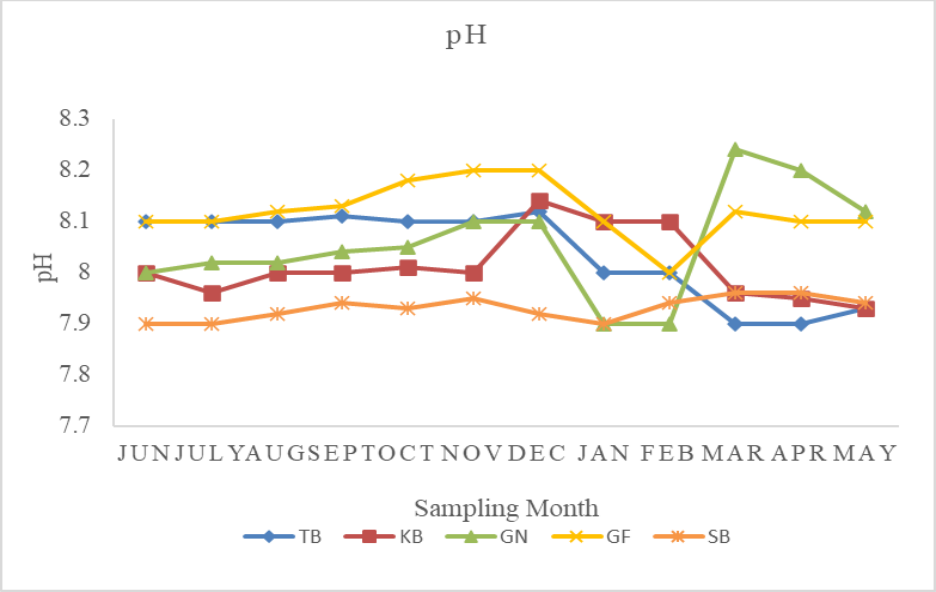

Fig. 3: Temporal variation of pH

3.4 Observed Variability in Partial Pressure of Carbon Dioxide (pCO_2)

From Figure 4, the variation of the observed partial pressure of carbon dioxide (pCO_2) concentration had a minimum decreasing trend during the peak season (June to December) across all study sites. During the lean season all study sites experienced an increase in partial pressure of carbon dioxide (pCO_2) between December and January (Lean season) and started declining again from February through to May. Here, Senya Breku (SB) and Gomoa fetteh (GF) respectively recorded the highest and least partial Pressure of carbon dioxide (pCO_2) over the study period. Partial Pressure of carbon dioxide (pCO_2) recorded in 2007 was 384 µatm and by 2100 it must get to 793 µatm (Gattuso et al., 2009) but as at the period of the research, the least Partial Pressure of carbon dioxide (pCO_2) concentration was 414.08 ± 96.6 at Gomoa Fetteh whiles Senya Breku (SB) had the highest concentration of 715.5 ± 105.4. The fluctuation of partial pressure of carbon dioxide, may be attributed to the fluctuations in temperature for the study period and anthropogenic waste. Increase in pCO_2 concentration of seawater has the tendency of reducing the survival rate some marine organisms.

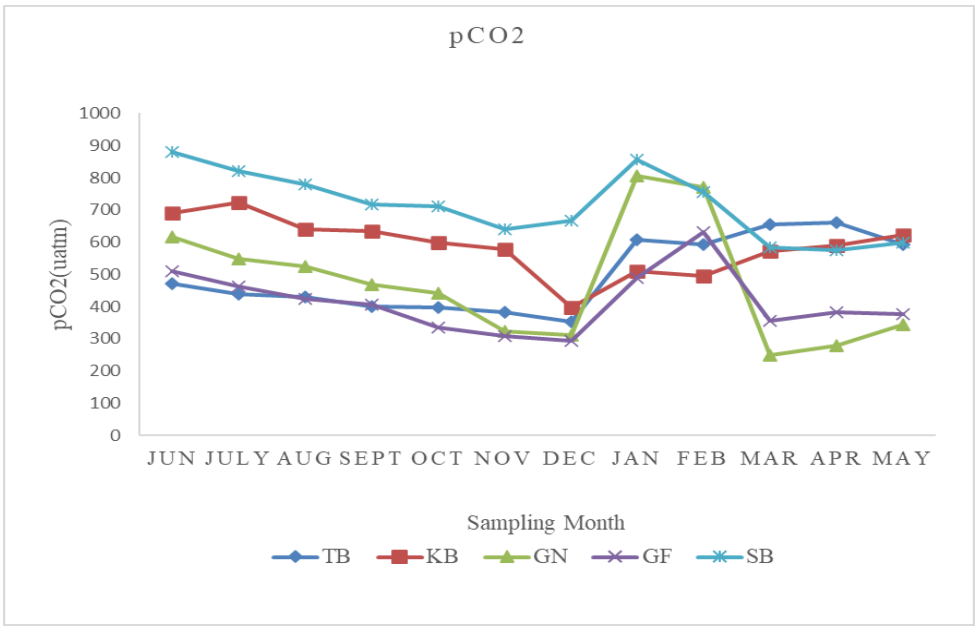

Fig. 4: Temporal variation of pCO_2

3.5 Temporal Variation of Total Alkalinity

From Figure 5, there was also steady decrease in the amount of total alkalinity (TA) concentration across all study sites between June and December and an increase in January. The pattern of variability observed in total alkalinity (TA) was similar to that of partial pressure of carbon dioxide (pCO_2) (Table 3.3). But the difference in the observed total alkalinity (TA) across the study was lower as compared to that of partial pressure of carbon dioxide (pCO_2) with Kokrobitey (KB) recording the highest concentration of total alkalinity (TA) concentration. Decreasing trend of total alkalinity recorded across all the sampling sites for the year indicates that the capacity of the ocean to neutralize acid is decreasing in all the five sampling sites.

Although oceanic alkalinity is said to be relatively stable, research has shown it to vary over time, especially through ocean acidification (Doney et al., 2009). This is because total alkalinity is calculated from the ions in the ocean and thus a change in chemical composition is evident due to increasing anthropogenic carbon dioxide, would alter alkalinity. The decreasing trend thus observed is not out of place and only seeks to affirm the ongoing ocean acidification phenomenon. According to Doney et al., (2009), total alkalinity varies over time, especially through ocean acidification. Moreover, since the carbonate chemistry of the ocean was changing as inferred from reducing carbonate ion concentrations (Fig. 3), variation of total alkalinity was very significant with p-value of 0.0050 which is less than alpha value of 0.05 (Table 4). This may be a much watch out situation.

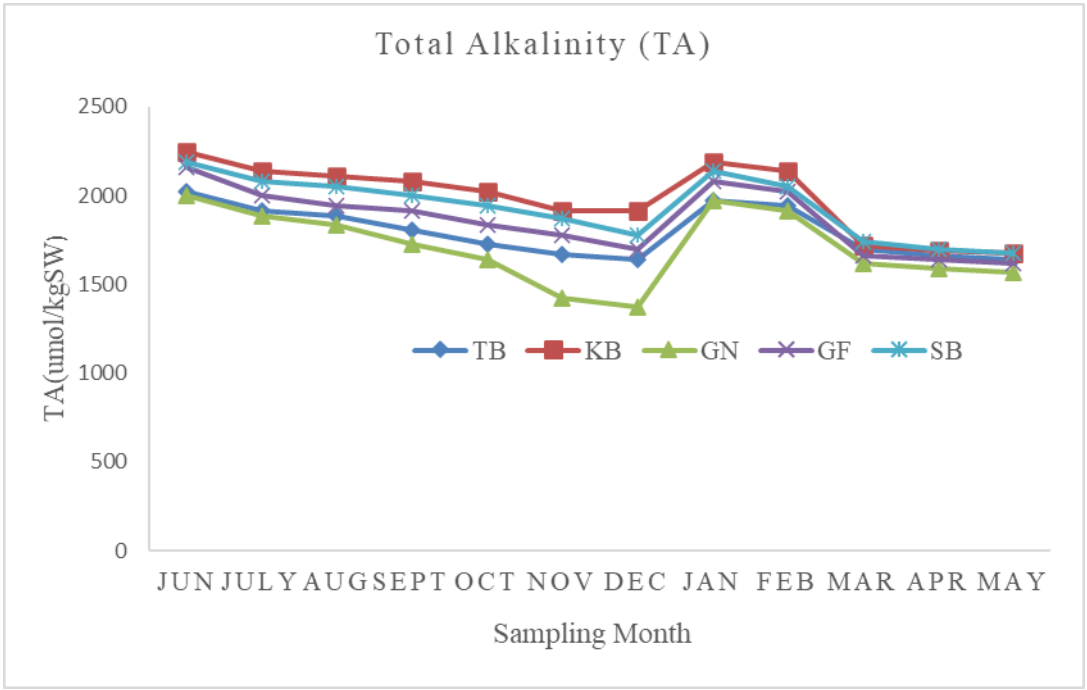

Fig. 5: Temporal variation of total alkalinity (TA)

3.6 Variation of Total carbon dioxide

It is interesting to note that, in Fig. 6, the trend of variability in the total carbon dioxide (TCO_2) concentration across the study site was like that of the concentration of total alkalinity (TA) (Fig 4) and partial pressure of carbon dioxide (pCO_2) (Fig 4.3) over the study period. Again, Kokrobitey (KB) recorded the highest total carbon Dioxide (TCO_2) concentration (Fig. 5). The concentration of total carbon dioxide was observed to be declining from June to December, and raised for a month and started declining. One will have taught that, since the Total Alkalinity was observed to be declining as in Fig 4 owing to the fact that, the Ocean may be gradually losing its ability to neutralize, Total Carbon dioxide and Partial Pressure of carbon dioxide should have been on the rise. Total Carbon dioxide and Partial Pressure of carbon dioxide are also on the decline trend and these decline may be as a result of increase in the Revellel factor

of the ocean. Because the ocean's capacity to hold more carbon dioxide from the atmosphere is inversely proportional to the Revelle buffer factor (Egleston et al., 2010). Other factors can be offshore and human activities.

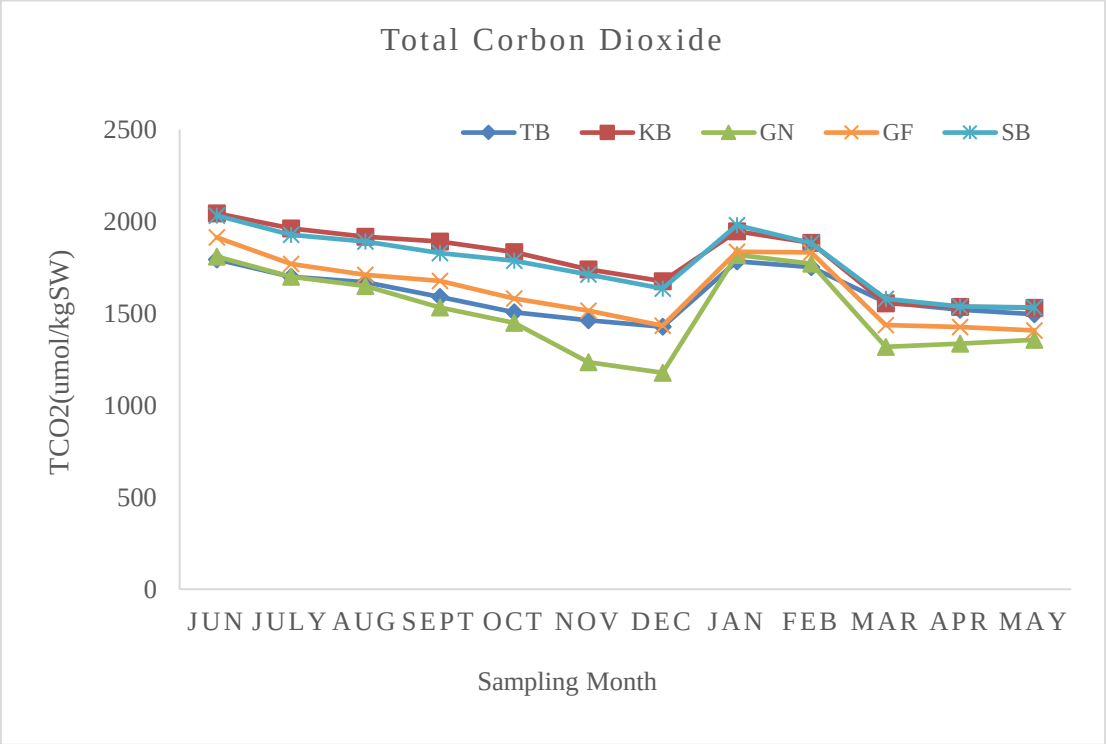

Fig. 6: Temporal Variation of Total Carbon Dioxide (TCO2)

3.7 Variability of Carbonate Ion Observed in the Five Study Sites

From Fig. 7, there was a significant variability during the second half of the study period (December to May). Study sites KB and GN experienced a high increase in Carbonate ion (CO3-) between November to February and February to March respectively. However, the change in Carbonate ion (CO3-) from June to November there was marginal variation but the variations ware statistically significant across the study sites, as the p-value for carbonate ion concentration was 0.0000 a P – value < 0. 05 from table 1. Reduced carbonate ion concentrations raise the saturation horizon closer to the surface, giving room for increased under saturation. Bates et al. (2014). From fig 6, the decrease or low levels of carbonate ion concentration has a dire consequence on marine organisms, this goes to reiterate and emphasize research conducted by Barnard and Grekin, 2010 that Coralline algae, crustose, some phytoplankton, warm and cold-water corals are all organisms that use carbonate minerals to form shells and skeletons.

3.8 Variation of Revellel Factor Observed in the Five Study sites across the Year

Figure 8 depicts the pattern of variability in Revelle factor across the study sites over the study period. The ocean's capacity to hold more carbon dioxide from the atmosphere is inversely proportional to the Revelle buffer factor (Egleston et al., 2010), thus the higher the factor, the lower the capacity of the ocean uptake atmospheric CO2. The Revelle factor was averagely constant over the study period for the entire study site. However, between December and January, there was an observed increase for all study sites with Gomoa Fetteh (GF) recording the least Revelle factor on the average. The gradual increasing trend of Revelle factor observed over the one-year period seem to suggest research conducted earlier that, waters of the North Atlantic were gradually losing capacity to absorb carbon dioxide from the atmosphere due to identified increasing Revelle factor (Bates et al., 2012) (Fig. 8). The most important direct feedback associated with ocean acidification is the changing of the Revelle buffer factor (Gehlen et al., 2011) of the ocean by increasing its value. The range of Revelle factor according to Sabina et al., 2004 is 8 to 13. The least Revellel Factor recorded at Gomoa Fettey is 9.62 ± 0.72, this implies that our

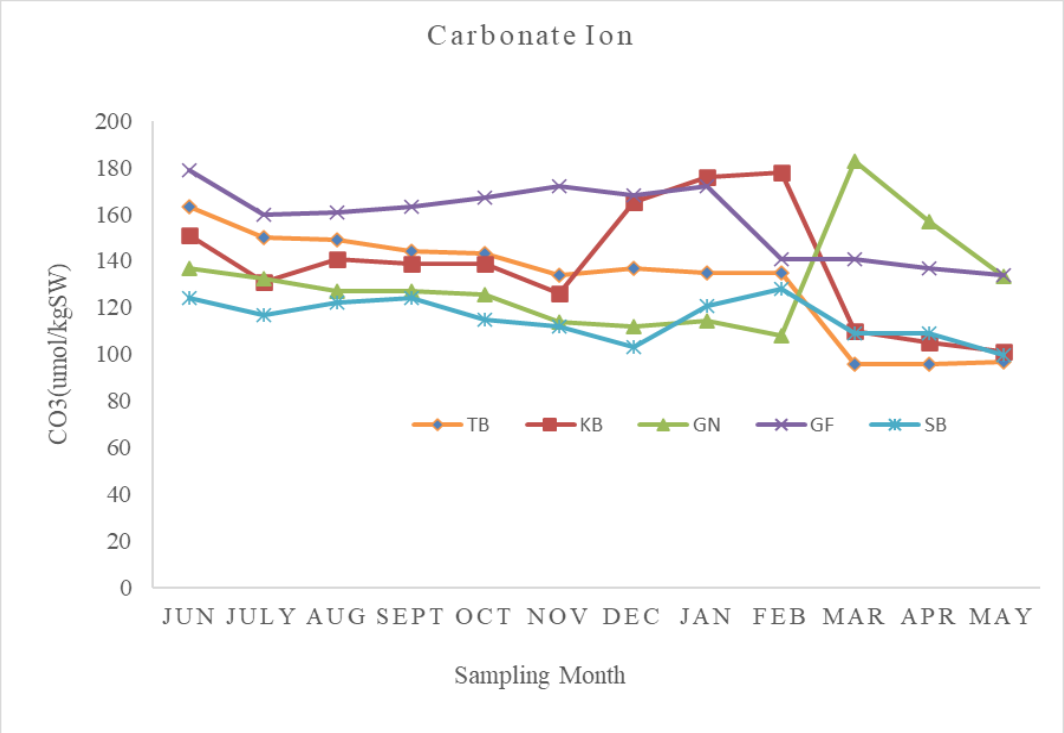

Figure 7: Temporal Variation of Carbonate ion (CO3-)

ocean is gradually losing its buffering capacity. Figs. 8, 49, and 10 present the trend of variability observed in the concentration of Aragonite and Calcite, over the study period.

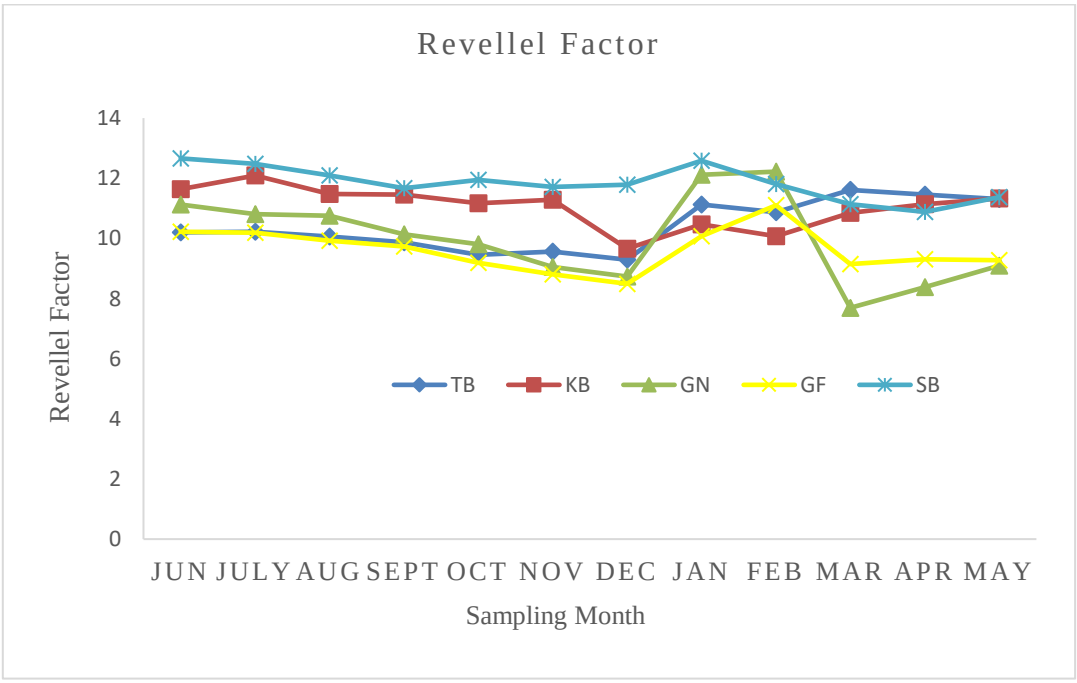

Fig. 8: Temporal Variation of Revelle Factor

3.9 Variation of Aragonite (ΩAr) Observed in the Five Study sites across the Year

The concentration of Aragonite (ΩAr) decreased gradually in study sites Tsokomey/Bortianor (TB), Gomoa Nyanyanor (GN), Gomoa Fetteh (GF), and Senya Breku (SB). However, there was an observed increase in Aragonite (ΩAr) this was observed between November and March at all study sites with Kokrobitey recording the highest in January (Fig. 9). Interestingly, the same pattern of variability was observed for Calcite concentration in all the study sites (Fig. 10). Calcite and aragonite saturation states

had declining trends in the five study sites, although mean saturation states for calcite were higher, compared to aragonite saturation. According science on space, Aragonite saturation state is used to measure the carbonate ion concentration of seawater and if it falls below 3 or less than 1, shells and other structures begin to dissolve. Generally, the aragonite saturation state of seawater of the Atlantic coastline was below the threshold of 3 to the extent that, Gomoa Nyanyanor and Sesnya Breku landing beaches in the Central region recorded aragonite saturation state to be less than one (ΩAr < 1) as in Fig 10, this seem to confirm similar decreasing trend with calcite and aragonite saturation states in the North Atlantic Ocean of an average of 0.34% per year as was observed by Bates et al., 2012, Feely et al., 2012. Generally, above the saturation horizon of seawater, saturation states have a value greater than 1 and $CaCO_3$ does not readily dissolve. However, below this depth, saturation state is less than 1 and $CaCO_3$ will readily dissolve. The low values of calcites and aragonites of the sampling sites is the dissolution of $CaCO_3$ is on the onset in such waters, and as such calcifying organisms would be heavily impacted. This situation probably may be the sea's uptake of carbon dioxide leading to the formation of bicarbonates and hence decreasing the carbonate concentration of seawater.

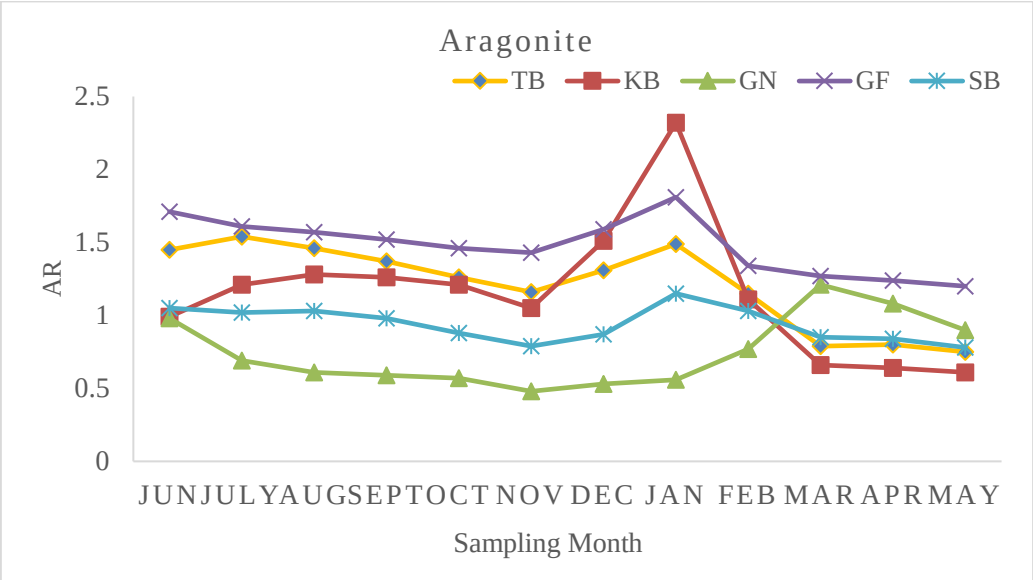

Fig. 9: Temporal Variation of Aragonite (ΩAr)

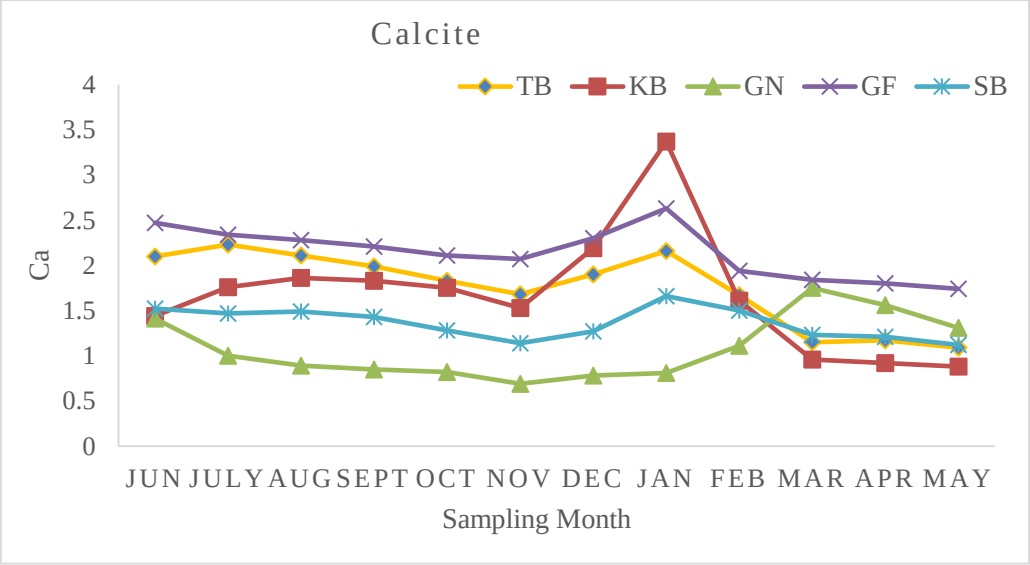

Fig. 10: Temporal Variation of Calcite

Conclusion

The study monitored the variability of carbonate chemistry of seawater of the Central Atlantic Coast of Ghana over a 1-year period. Based on the results obtained from the study, the following conclusions were drawn: The findings from the data of the monitored period indicated a High concentration value for Partial Pressure of Carbon dioxide (pCO_2) and Total carbon dioxide. Throughout the entire study period, there were also evidence of decreasing trends of carbonate ion concentration, calcite and aragonite saturation states and pH whiles the Revelle factor was at an increasing trend. These observation points to the fact that, our seawater is gradually losing its buffer potency and may pose danger to marine organism especially shell forming organism. The data generated seem to again suggest that Ocean acidification is possibly occurring in our Ghanaian waters.

Public Interest Statement

Coastal people in Ghana depend mainly on fishing and other marine organism for their protein. The increases in absorption of carbon dioxide and other components have effect on carbonate chemistry in marine, which directly affect the existence of organisms, resulting in low harvest of fishes and revenue for government. However, there was scarce data on carbonate chemistry parameters of seawater of Central Atlantic Coastline of Ghana making it difficult predict and control the parameters. For monitoring the study provided data on carbonate chemistry parameters and their variability trend of seawater of five selected Coastline of Ghana over the one-year period.

Funding

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Conflicts of Interest

There are no conflicts to be declared.

Disclaimer Statement

A portion of the thesis submitted to the University of Ghana, Under the supervision of Prof. Yaw Serfo_-Armah and Dr. Dennis Kpakpor Adotey al of the University of Ghana.

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