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# ECS 202 Assignment

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## OCEAN ACIDIFICATION

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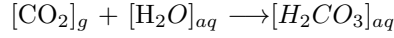
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# 1 PART A

## 1.1 The Oceanic Carbonate Buffer and its pH regulation:

The Ocean is a rich source of Minerals, especially Carbonates, Sulphates, and Chlorides. The term ‘**Oceanic Carbonate buffer**’ is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean  $H^+$  concentration, and thus pH. [4].

Carbon dioxide from the atmosphere dissolves in seawater by reacting with the water molecules ( $H_2O$ ) to form carbonic acid ( $H_2CO_3$ ).

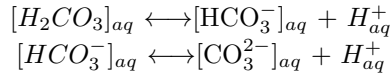


It is important to note that not all the  $CO_2$  dissolved in seawater reacts to make carbonic acid, and therefore, seawater contains some amount of dissolved gaseous  $CO_2$ . The carbonic acid in solution and carbon dioxide in the atmosphere are related via **Henry’s law**: The concentration of  $CO_2$  in air is proportional to that of the solution of carbonic acid.

$$[H_2CO_3] = K_H^* pCO_2$$

$K_H$  is Henry Constant for  $CO_2$

Carbonic acid is a **weak diprotic** acid and partly dissociates first into a bicarbonate ion ( $HCO_3^-$ ) and a proton, and subsequently, the bicarbonate dissociates partly into carbonate ion ( $CO_3^{2-}$ ) and a proton. The relevant reactions are:



For which we can write equilibrium relations:

$$\begin{aligned} K_1 &= \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \approx 10^{-6.35} \\ K_2 &= \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \approx 10^{-10.3} \end{aligned}$$

The relative concentrations of  $[H_2CO_3]$ ,  $[HCO_3^-]$  and  $[CO_3^{2-}]$  are governed by the pH (ie  $-\log_{10}[H^+]$ ) of the solution. Carbonic acid is the dominant species at pH values below the pK1 ( $-\log_{10}K_1$ ), bicarbonate dominates between the pK1 and pK2 values and the carbonate ion dominates at pH values above the pK2.[3]

In a process, such as  $CO_2$  dissolution, **addition of  $H^+$**  to seawater, results in consumption of  $H^+$  by carbonate ( $[CO_3^{2-}]$ ) ion that is later converted into bicarbonate ( $[HCO_3^-]$ ). Since initially most of the added  $H^+$  would be consumed in this way, the **change in pH is much less** than it would otherwise be. However, this process also consumes some carbonate ion and thus pH buffering capacity would diminish as  $CO_2$  concentrations increase.

Interaction with  $CaCO_3$ -rich sediments further tends to buffer the chemistry of the seawater so that changes in pH are diminished. Dissolution of carbonate minerals provides  $[CO_3^{2-}]$  ions that can react to consume  $H^+$ . Thus, the dissolution of carbonate minerals tends to decrease  $[H^+]$  (increase pH). However the  $H_2CO_3$  formed yields  $CO_{2g}$  and  $H_2O_{aq}$  (in excess).  $CO_{2g}$  diffuses from the ocean to the atmosphere, thereby maintaining the pH.[2]

Thus Carbonate Buffer acts to **stabilise the average pH of seawater** at approximately pH = 8 because of the following two processes: (i) uptake of  $CO_2$  from the atmosphere and (ii) interaction of seawater with oceanic sediments composed of  $CaCO_3$ . Since  $CaCO_3$  is abundant in sediments, the pH of the deep oceans cannot change by large amounts over timescales of 10,000 years. However, over historical timescales, significant changes in surface and near surface ocean pH can occur.

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## 1.2 Le Chatlier's principle to explain pH change with Atmospheric $CO_2$

Following are the equations depicting the Dynamic equilibrium between Oceanic  $CO_3^{2-}$  and Atmospheric  $CO_2$ :

1.  $[CO_2]_g + [H_2O]_{aq} \longleftrightarrow [CO_2]_{aq} + [H_2O]_{aq}$
2.  $[CO_2]_{aq} + [H_2O]_{aq} \longleftrightarrow [H_2CO_3]_{aq}$
3.  $[H_2CO_3]_{aq} \longleftrightarrow [HCO_3^-]_{aq} + H_{aq}^+$
4.  $[HCO_3^-]_{aq} \longleftrightarrow [CO_3^{2-}]_{aq} + H_{aq}^+$
5.  $[CaCO_3]_s \longleftrightarrow [Ca^{2+}]_{aq} + [CO_3^{2-}]_{aq}$

**Le Chatelier's principle** states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.

Here if the amount of Atmospheric  $CO_2$  increases then reaction(1) proceeds rightwards. The rate of the forward reaction of the buffering system increases until the system reaches a new equilibrium. This results in higher production of Carbonic Acid ( $H_2CO_3$ ) that further dissociates, giving two  $H^+$  along with bicarbonate and carbonate anions. Since the concentration of  $H^+$  increases, **pH of seawater decreases**.

The chemical changes in the oceans caused by increases in the concentration of  $CO_2$  in the atmosphere will include a (i)lowering of the pH; (ii)an increase in dissolved  $CO_2$ ; (iii)a reduction in the concentration of carbonate ions and an (iv)increase in bicarbonate ions.

## 1.3 Effects of decreased Ocean pH:

(A decreased pH implies increased acidity)

### 1.3.1 Effects on Marine lifeforms:

1. The major primary producers in the oceans are the benthic photosynthetic organisms, such as seaweed, sea grasses and corals. Changes in pH will affect the availability of nutrients and this may alter rates of growth and photosynthesis.
2. Increased acidity may lead to a change in cellular composition of the primary producers which could alter the nutritional value made available to the organisms that feed on them.
3. Larger marine animals that live in the oceans and do not breathe air (fish and some zooplankton), take up oxygen and lose respired  $CO_2$  through their gills. Increased  $CO_2$  and decreased pH could have a major effect on this respiratory gas exchange system.
4. A low pH and increased  $CO_2$  concentration in seawater causes acidification of bodyfluids in marine organisms. This symptom is known as "Hypercapnia" and is detrimental to survival.
5. Metals exist in two forms in seawater; complex and free dissolved. Metal ions in low pH are generally the free dissolved form that is most toxic. A decrease in pH generally increases the proportion of free dissolved forms of toxic metals that is hazardous to many marine organisms.[4]
6. The formation of shells or plates of  $CaCO_3$ , by calcification, is a widespread biological phenomenon among marine organisms (molluscs, corals, echinoderms and calcareous algae).To make these structures, seawater has to be supersaturated with calcium ( $Ca^{2+}$ ) and carbonate ( $CO_3^{2-}$ ) ions. Lower pH reduces the carbonate saturation of the seawater, making calcification harder and also weakening any structures that have been formed.This causes tremendous loss of marine biodiversity and destruction of marine communities.

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### 1.3.2 Effects on Long and Short term Carbon cycles

The carbon cycle refers to the flow of carbon between the atmosphere, rocks, oceans and biosphere (all of Earth's life forms). The long-term reservoir contains about 99.9 percent of the total carbon which is found mainly in rocks and fossil fuels and takes up to millions of years to recycle carbon dioxide. In the short-term reservoir, carbon is stored in the atmosphere, oceans and biosphere with the ocean containing the largest amount of carbon.[1]

1. Decreased pH of the oceans will reduce their ability to absorb additional  $CO_2$  from the atmosphere, which will in turn affects the rate and scale of global warming.
2. Increased  $[H^+]$  in seawater affects the natural process of calcareous shell formation in marine organisms and this directly retards the deposition of carbonate rocks on the seabed.
3. The process whereby carbon is transferred from the atmosphere to the deep ocean waters is referred to as the 'biological pump'. A decreased pH changes the strength of this pump. This significantly alters the amount of carbon being sequestered to the deep ocean environments and therefore removed from the atmosphere.
4. The carbonate rocks formed in deep oceans are fundamentally different due to different pH conditions. This affects the rate of future fossil fuel formation and alters the natural processes of carbonate extraction.

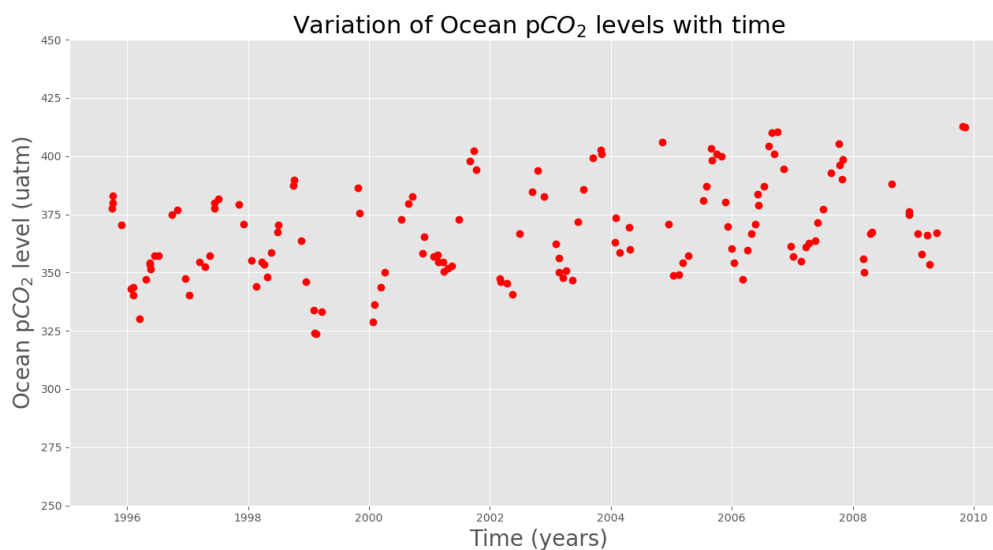
Therefore an increased  $H^+$  ion concentration in oceans causes severe ramifications to the global carbon cycle by modifying the every stable states of the interacting dynamic feedback systems.

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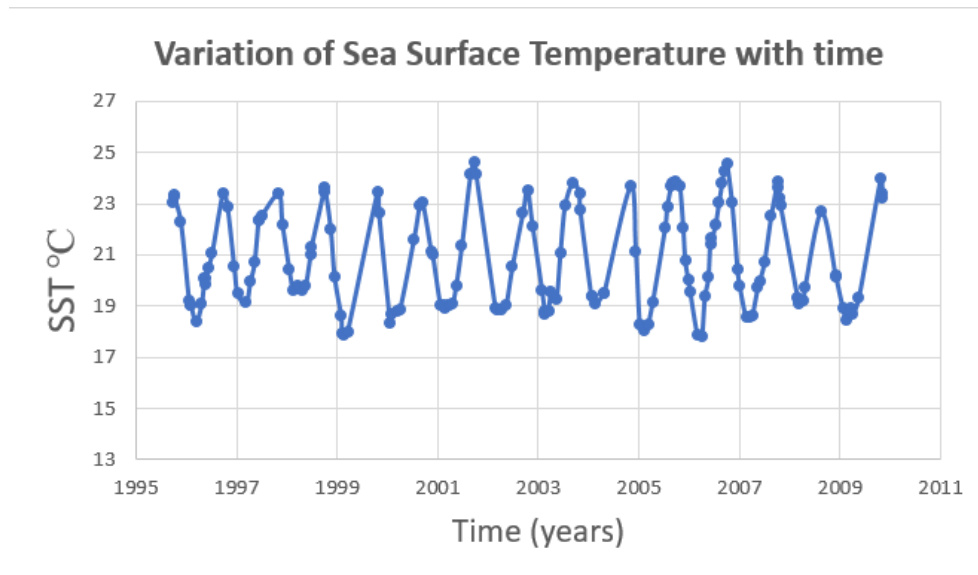
## 2 PART B

**Q1** Reverse geocoded Address: Cádiz - La Palma (Northwestern Africa - Mauritania)

**Q2** Variation of  $pCO_2$  levels (aperiodic oscillations/fluctuations)



### Q3 Variation of Sea surface temperature



We observe an **oscillating trend** in sea surface temperature values. These oscillations have an approximate period of one to one-and-a-half years. The **annual temperature range** is between 19°C to 22°C whereas the minima is 17°C and maxima is 24°C.

Year	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009		
SST data	23.023	19.196	19.467	20.44	18.589	18.342	18.997	18.901	19.605	19.37	18.249	19.53	19.778	19.289	18.912		
	23.319	19.026	19.11	19.615	17.922	18.659	18.997	18.87	18.787	19.37	18.044	17.87	18.54	19.103	18.434		
	23.281	19.029	19.963	19.789	17.881	18.79	18.919	18.87	18.651	19.076	18.269	17.818	18.57	19.212	18.894		
	22.278	18.37	20.676	19.729	17.997	18.822	18.995	19.032	18.792	19.459	19.14	19.34	18.63	19.709	18.67		
		19.072	22.319	19.605	23.415	21.602	18.995	20.522	19.518	19.484	22.055	20.121	19.691	22.664	19.297		
		20.058	22.318	19.784	22.635	22.93	19.102	22.599	19.252	23.65	22.85	21.643	19.966	20.19	23.977		
		20.067	22.515	21.003		23.044	19.744	23.513	21.077	21.115	23.687	21.41	20.7	20.133	23.404		
		19.843	23.368	21.315		21.094	21.335	22.111	22.9		23.771	22.14	22.492		23.216		
		20.46	22.171	23.437		20.983	24.146		23.796		23.86	23.05	23.83				
		21.034		23.616			24.604		23.401		23.687	23.775	23.633				
		23.394		22.005			24.126		22.753		22.036	24.24	23.207				
		22.842		20.145							20.79	24.55	22.932				
		20.541									19.99	23.051					
												20.389					
AVRG	22.975	20.226	21.323	20.874	19.74	20.474	20.724	20.552	20.776	20.218	21.264	21.352	20.997	20.043	20.6	20.81	Yearly avg
																0.763	Std dev

The average annual temperature between 1995 and 2009 is 20.81°C with a standard deviation of 0.763°C. The highest temperature was recorded on the 270<sup>th</sup> day i.e. sometime in September whereas the lowest temperature was recorded on the 96<sup>th</sup> i.e. sometime in April.

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#### Q4 and Q5 Variation of ocean pH and pCO<sub>2</sub> through time

**The pH of seawater has decreased over time.** This is evident from the plot of pH v/s time. We obtain a linear fit with a slope of -0.0015 and  $R^2 = 0.2084$ . This implies that every year, the pH of the seawater decreases by an average amount of 0.0015. A straightforward calculation yields an annual increase in  $[H^+]$  by 0.996M.

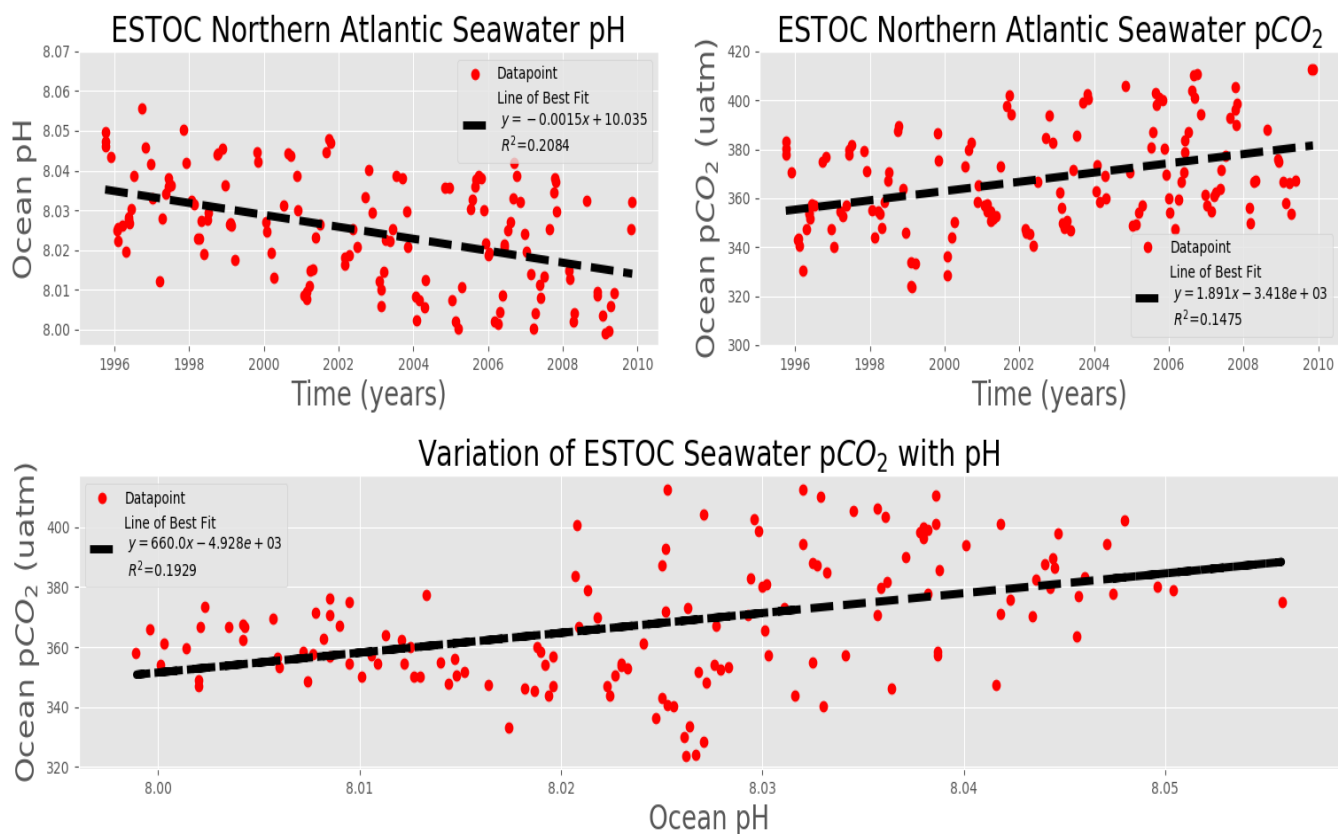
**The pCO<sub>2</sub> levels have increased over time.** This is evident from the plot of pCO<sub>2</sub> v/s time. We obtain a linear fit with a slope of 1.891 and  $R^2 = 0.1475$ . This implies that every year, the pCO<sub>2</sub> levels above the seawater increase by an average amount of 1.891 uatm.

#### pH v/s pCO<sub>2</sub> scatterplot

On performing linear regression on pH v/s pCO<sub>2</sub> data, a linear best fit is obtained with an  $R^2=0.1929$ . Such a very low  $R^2$  value indicates that the model explains very little variability of the response data around its mean. Nevertheless, we obtain a positive slope of 660.0 with a positive correlation value of  $r=0.445$ .

The model suffers from high bias but predicts that **pCO<sub>2</sub> levels increase with pH**. Physically, this is well explained by the carbonate-bicarbonate buffer in ocean water. When  $[H^+]$  increases, the bicarbonate equilibrium is shifted to the right (see PART-A, question 1). This entails higher concentration of  $H_2CO_3$ .  $H_2CO_3$  is in dynamic equilibrium with carbon dioxide and water. Thus an increased amount of  $H_2CO_3$  produces higher  $[CO_2]_{aq}$  and by Henry's Law, pCO<sub>2</sub> inceases.

### ESTOC Northern Atlantic Seawater Analysis



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## References

- [1] John. Brennan. What is carbonate buffering?
- [2] Lee R Kump, James F Kasting, Robert G Crane, et al. *The earth system*, volume 432. Pearson Prentice Hall Upper Saddle River, NJ, 2004.
- [3] Jack J Middelburg. Biogeochemical processes and inorganic carbon dynamics. In *Marine Carbon Biogeochemistry*, pages 77–105. Springer, 2019.
- [4] The Royal Society. Ocean acidification due to increasing atmospheric carbon dioxide. June, 2005.