

Fundamentals of Ocean pH

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1 Introduction

We are often told that the CO₂ released from burning fossil fuels will cause dangerous ocean acidification. Actually the oceans will remain comfortably alkaline and hospitable to life for the foreseeable future. This brief note is a quantitative review of the physical chemistry of ocean pH. High school chemistry and algebra should provide enough background to follow the discussion. An excellent introduction to the chemistry of the oceans can be found in the book: *Seawater: Its Composition, Properties and Behavior*, by Wright and Colling[1]. More details on ocean pH can be found in a recent review by Tans [2].

2 Alkalinity of the Unbuffered Ocean

Ocean water is salty because of the weathering of the earth's rocks by rainwater, and because of salts dissolved from the ocean floor, especially near plate-spreading boundaries. The salt water contains positive ions (cations), mainly sodium Na⁺, magnesium Mg²⁺, calcium Ca²⁺ and potassium K⁺. For clarity, we can think of the ions as coming from the strong bases NaOH, and potassium hydroxide, KOH (lye) and much less soluble magnesium hydroxide, Mg(OH)₂ and calcium hydroxide Ca(OH)₂ (slaked lime). The ocean also contains negative ions (anions), mainly chloride Cl⁻ and sulfate SO₄²⁻, which we can think of the anions as coming from the strong acids, hydrochloric acid, HCl and sulfuric acid, H₂SO₄. For want of a better word, we will refer to the cations of strong bases, and anions of strong acids as *pH-independent* ions. The concentration of pH-independent ions is unaffected by normal changes in the pH of water.

The electrical charge of the pH-independent positive ions slightly exceeds that of pH-independent negative ions. The excess charge is called the *alkalinity* [A]. In ocean water with a typical salinity of 35 g kg⁻¹ (grams of salt per kg of water) the alkalinity is about

$$[A] \approx 2.3 \times 10^{-3} M \tag{1}$$

For ocean chemistry the unit of alkalinity M (or equivalent) is usually taken to be one mole of elementary charge (one Faraday) per kg of water.

If there were nothing but pH-independent ions of strong acids and strong bases in the ocean, the excess positive charge would be compensated the negative charge of hydroxyl ions,

OH^- . Recall that the H_2O molecules of liquid water can dissociate into positive hydrogen ions H^+ and negative hydroxyl ions OH^- in the reaction



The concentrations, in the traditional oceanographic unit of moles per kilogram (M), are related by

$$[\text{H}^+][\text{OH}^-] = K_w, \quad \text{where} \quad K_w = 1.00 \times 10^{-14} \text{ M}^2 . \quad (3)$$

Some of the equilibrium “constants” can vary substantially over the range of temperatures and pressures of the oceans. For example, the dissociation coefficient of water (3) increases slowly with temperature, because it is easier to spontaneously break up H_2O molecules in warmer water. Here and elsewhere we will use a water temperature of 25 C, and we will neglect any pressure dependence of the equilibrium coefficients. This will reasonably characterize the first 500 m of ocean waters in low to mid latitudes where most of the earth’s oceans and much of its aquatic life are found. We will ignore small difference between the concentration of the ion, for example $[\text{H}^+]$, and the thermodynamic activity $a(\text{H}^+)$, the quantity that rigorously goes into laws of mass action like (3).

The concentration of H^+ ions in solutions is traditionally written in terms of a dimensionless number, the pH, as

$$[\text{H}^+] = 10^{-\text{pH}} \text{ M}, \quad \text{or} \quad \text{pH} = -\log([\text{H}^+]/\text{M}) \quad (4)$$

For charge neutrality we must have

$$[\text{A}] + [\text{H}^+] = [\text{OH}^-] . \quad (5)$$

Using (3) in (5) we find the quadratic equation for $[\text{H}^+]$,

$$[\text{H}^+]^2 + [\text{A}][\text{H}^+] - K_w = 0 . \quad (6)$$

The quadratic equation (6) for $[\text{H}^+]$ has an unphysical solution where $[\text{H}^+]$ is a negative real number, and the solution of interest to us

$$[\text{H}^+] = \frac{1}{2}(\sqrt{4K_w + [\text{A}]^2} - [\text{A}]) = 4.35 \times 10^{-12} \text{ M} . \quad (7)$$

The representative alkalinity (1) was used to evaluate (7). Substituting (7) into (4) we find that the pH-independent ions would give the ocean a pH of

$$\text{pH} = 11.4 . \quad (8)$$

This is about the same pH as household ammonia, and considerably more alkaline than California’s celebrated Mono Lake (pH = 9.8). But bacteria that can thrive in waters of pH=11.4 are known to exist.

A typical ocean pH is 8.1, much less than the value (8) that would be produced by the pH-independent ions. The reason is the presence of weak acids, notably carbonic acid H_2CO_3 , boric acid $\text{B}(\text{OH})_3$ and silicic acid $\text{Si}(\text{OH})_4$. Of these, carbonic acid is by far the most important. If we ignore the other weak acids, we find that the pH of ocean water in contact with the atmosphere depends on the concentration of atmospheric CO_2 as shown in Fig. 1. The pH values were calculated with Eq. (20), which we discuss below, and (4). Also shown in Fig. 1 is the pH of pure rain water, uncontaminated by the oxides of sulfur or nitrogen. Current CO_2 concentrations would give pure rainwater a pH of about 5.4, mildly acidic (ordinary vinegar has pH \approx 3).

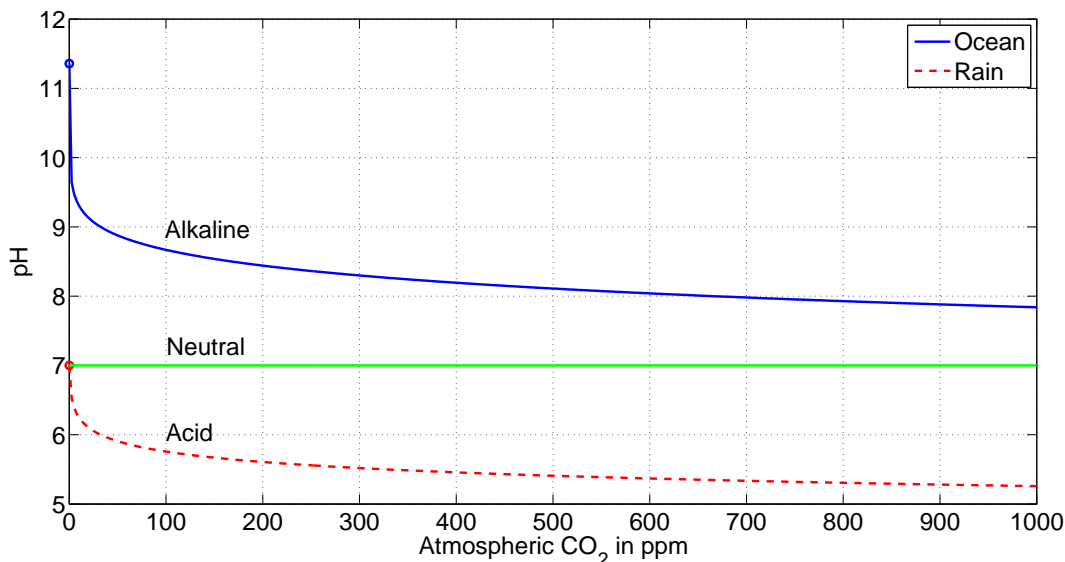


Figure 1: pH of ocean water and rain water versus concentration of CO₂ in the atmosphere. Calculated with (20); Ocean alkalinity [A] = 2.3 × 10⁻³ M. Rain alkalinity [A] = 0. Temperature $T = 25$ C.

3 Buffering by Weak Acids

For conceptual clarity, we begin by imagining an atmosphere free of CO₂ and an ocean with only pH-independent ions, and therefore with the high pH = 11.4 of (8). Now imagine adding CO_{2g} molecules to the atmosphere, and maintaining a fixed atmospheric level by adding still more CO_{2g} molecules to replace the large number that dissolve into the ocean according to the reaction



A small fraction of the dissolved CO_{2aq} molecules will attach water molecules to become molecules of undissociated carbonic acid, H₂CO₃. The ratio of the concentrations of the two uncharged species of dissolved inorganic carbon will be independent of pH, but will depend on temperature. For simplicity, we will let the symbol [CO₂] describe the total concentration of uncharged, inorganic carbon molecules in solution

$$[\text{CO}_2] = [\text{CO}_{2aq}] + [\text{H}_2\text{CO}_3] \quad (10)$$

The concentration of uncharged inorganic carbon molecules in the surface water will be proportional to the partial pressure P_{CO_2} (in atmospheres) of the CO₂ molecules in the gas phase

$$[\text{CO}_2] = \alpha P_{\text{CO}_2}, \quad \text{where } \alpha = 2.84 \times 10^{-2} \text{ M atm}^{-1}. \quad (11)$$

The numerical value of the coefficient α for Henry's law (11) is from the work of Weiss [3] for a temperature of 20 C.

A dissolved carbonic acid molecule can dissociate into a bicarbonate ion and a free proton



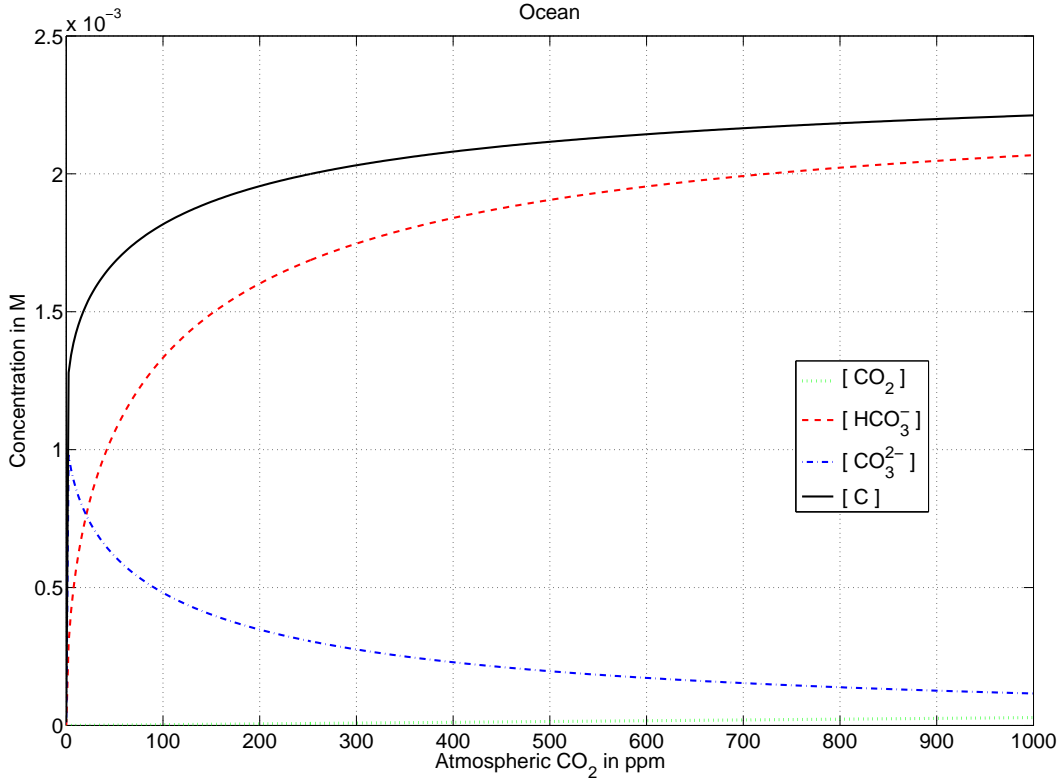


Figure 2: Inorganic carbon in ocean water: uncharged $[\text{CO}_2]$, bicarbonate $[\text{HCO}_3^-]$, carbonate $[\text{CO}_3^{2-}]$ and total $[\text{C}]$ of (18) versus concentration of CO_2 in the atmosphere. Calculated with (20), (17), (14) and (11), under the assumption of complete chemical equilibrium. The ocean alkalinity is $[\text{A}] = 2.3 \times 10^{-3} \text{ M}$ and the temperature is $T = 25 \text{ C}$.

We can write the equilibrium concentrations of dissolved inorganic carbon species associated with the reaction (12) as

$$[\text{H}^+][\text{HCO}_3^-] = K_1[\text{CO}_2], \quad \text{where } K_1 = 10.00 \times 10^{-7} \text{ M}. \quad (13)$$

The numerical value for the equilibrium coefficient K_1 is from the work of Merbach [4] for 20 C. Using (13) and (11) we find that the concentration of bicarbonate ions is

$$[\text{HCO}_3^-] = \frac{K_1}{[\text{H}^+]} \alpha P_{\text{CO}_2}. \quad (14)$$

A bicarbonate ion can dissociate to a positive hydrogen ion and a carbonate ion



The equilibrium concentrations are related by

$$[\text{H}^+][\text{CO}_3^{2-}] = K_2[\text{HCO}_3^-], \quad \text{where } K_2 = 7.69 \times 10^{-10} \text{ M}. \quad (16)$$

The bicarbonate dissociation coefficient K_2 is several orders of magnitude smaller than the carbonic acid dissociation coefficient K_1 because energy needed to remove a proton from H_2CO_3 in water is much less than the energy to remove a proton from HCO_3^- . Using (16) with (15) and (14) we find

$$[\text{CO}_3^{2-}] = \frac{K_1 K_2}{[\text{H}^+]^2} \alpha P_{\text{CO}_2}. \quad (17)$$

The total concentration of dissolved inorganic carbon is

$$[\text{C}] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (18)$$

The dissolved CO_2 molecules will release bicarbonate and carbonate ions, in accordance with the reactions (12) and (15), so the equation of charge neutrality (5) must be modified to give

$$[\text{A}] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \quad (19)$$

Substituting (17) and (14) into (19) and using (3) we find

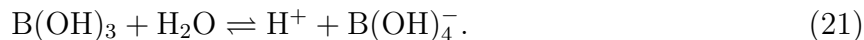
$$[\text{H}^+]^3 + [\text{A}][\text{H}^+]^2 - (K_w + K_1 \alpha P_{\text{CO}_2})[\text{H}^+] - 2K_2 K_1 \alpha P_{\text{CO}_2} = 0. \quad (20)$$

For positive alkalinity $[\text{A}] > 0$ and partial pressure $P_{\text{CO}_2} > 0$, the cubic equation (20) for $[\text{H}^+]$ has three solutions, two un-physical solutions where $[\text{H}^+]$ is either a negative real number or has an imaginary part, and the solution of interest to us, where $[\text{H}^+]$ is a positive real number. The partitioning of dissolved inorganic carbon in the ocean between uncharged species, bicarbonate and carbonate ions is shown in Fig. 2, which was calculated with (20), (17), (14) and (11). At current atmospheric levels of CO_2 , about 400 ppm, most of the dissolved inorganic carbon consists of bicarbonate ions. As atmospheric CO_2 levels increase, the concentration of bicarbonate ions will slowly increase, and the concentration of carbonate ions will slowly decrease.

In Fig. 3 we show the partitioning of dissolved inorganic carbon between uncharged species, bicarbonate and carbonate ions in uncontaminated rain water. Unlike the ocean, where most of the inorganic carbon consists of bicarbonate ions, most of the dissolved inorganic carbon in pure rainwater is the uncharged species CO_2 of (10).

3.1 Boron

Although most of the buffering of ocean alkalinity is due to dissolved CO_2 , other weak acids make a minor contribution. Consider boric acid, $\text{B}(\text{OH})_3$, the next most important buffering species in the ocean after dissolved CO_2 . A boric acid molecule can attach an OH^- from a water molecule and release a free proton



We can write the equilibrium concentrations of dissolved boron species associated with the reaction (21) as

$$[\text{H}^+][\text{B}(\text{OH})_4^-] = K_B [\text{B}(\text{OH})_3], \quad \text{where } K_B = 2.512 \times 10^{-9} \text{ M}. \quad (22)$$

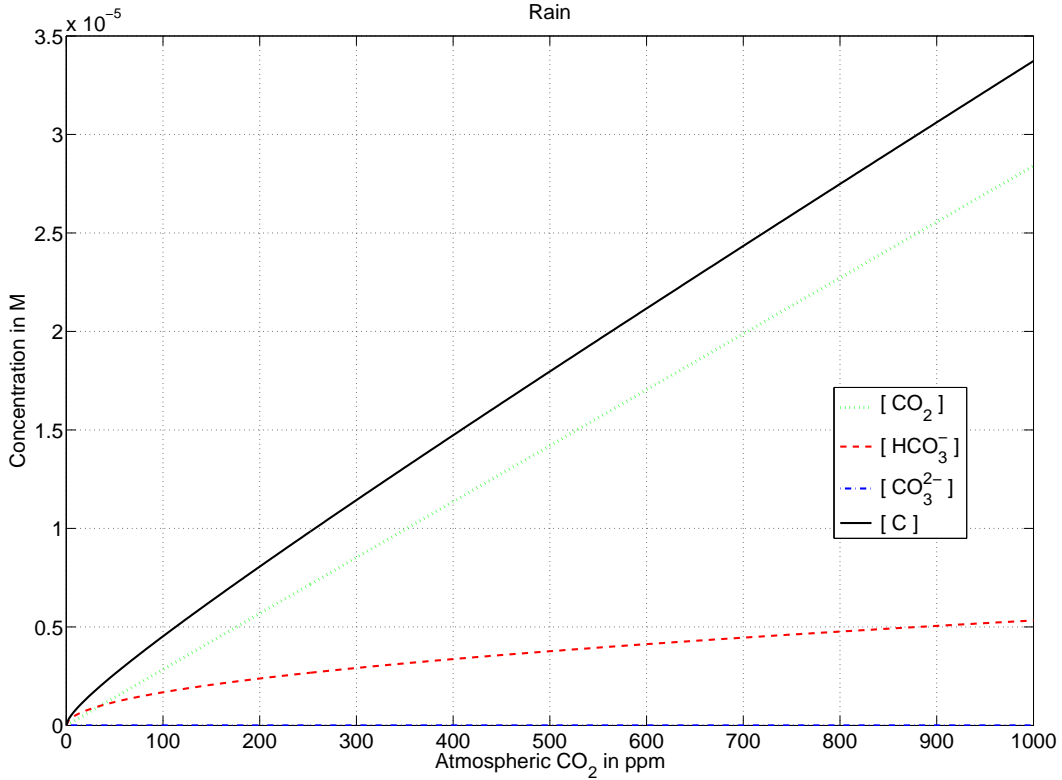


Figure 3: Inorganic carbon in pure rain water, with no contamination by oxides of sulfur or nitrogen; uncharged $[\text{CO}_2]$, bicarbonate $[\text{HCO}_3^-]$, carbonate $[\text{CO}_3^{2-}]$ and total $[\text{C}]$ of (18) versus concentration of CO_2 in the atmosphere. Calculated with (20), (17), (14) and (11), under the assumption of complete chemical equilibrium. The rain alkalinity is $[A] = 0$, and the temperature is $T = 25 \text{ C}$.

The dissociation coefficient[5] of (22) is intermediate between that of carbonic acid (13) and the bicarbonate ion (16). In analogy to (18), we write the total concentration[5] of boron-containing molecules in sea water as

$$[\text{B}] = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-] \approx 0.42 \times 10^{-3} M. \quad (23)$$

Combining (23) with (22) we find, in analogy to (14) and (17) that the concentration of borate ions is

$$[\text{B}(\text{OH})_4^-] = \frac{K_B [\text{B}]}{K_B + [\text{H}^+]}. \quad (24)$$

If the boric acid were the only buffer for ocean alkalinity, the equation (19) of charge neutrality would become

$$[A] + [\text{H}^+] = [\text{OH}^-] + [\text{B}(\text{OH})_4^-]. \quad (25)$$

Substituting (3) and (24) into (25), we see that the hydrogen-ion concentration is given by the solution of the cubic equation

$$[\text{H}^+]^3 + ([A] + K_B)[\text{H}^+]^2 - (K_w + \{[\text{B}] - [A]\}K_B)[\text{H}^+] - K_w K_B = 0. \quad (26)$$

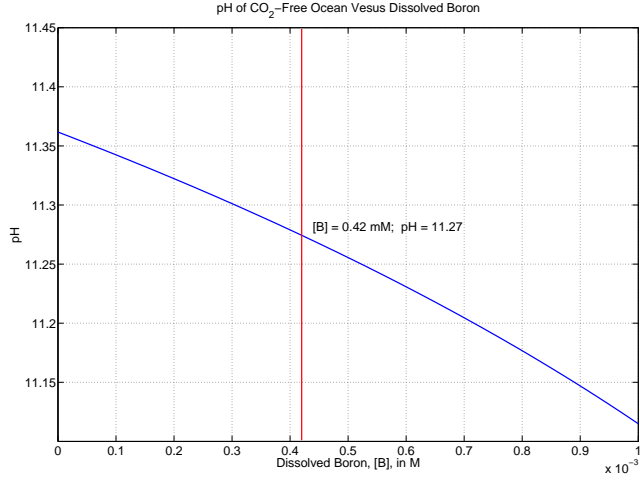


Figure 4: pH of CO_2 -free ocean water versus boron concentration $[\text{B}]$. Calculated with (26). Ocean alkalinity $[\text{A}] = 2.3 \times 10^{-3}$ M. The current concentration of boron in the oceans[5], $[\text{B}] = 0.42 \times 10^{-3}$ M, is indicated by the vertical line. Temperature $T = 25$ C.

Like (20), the cubic equation (26) for $[\text{H}^+]$ has three solutions, two un-physical solutions where $[\text{H}^+]$ is either a negative real number or has an imaginary part, and the solution of interest to us, where $[\text{H}^+]$ is a positive real number. Solutions of (26) for boron concentrations comparable to those in the oceans are shown in Fig. 4. There is not enough boron in the oceans to make much change to the pH. For otherwise pure water with $[\text{B}] = 0.42$ mM of dissolved boric acid we can use (26) with $[\text{A}] = 0$ to find $[\text{H}^+] = 1.031 \times 10^{-6}$ or $\text{pH} = 5.99$. Adding the concentration (23) of boric acid to the CO_2 -free ocean only decreases the pH for about 11.36 to 11.27, still harshly alkaline. A solution of pure boric acid at the concentration of (23) has about the same acidity as rainwater at around 30 ppm of atmospheric CO_2 . There is not much boric acid in the oceans and it is a weak acid to begin with.

For an ocean buffered by both boric acid and dissolved CO_2 , the equation (19) of charge neutrality would become

$$[\text{A}] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-]. \quad (27)$$

Substituting (24), (17) and (14) into (19) and using (3) we find

$$[\text{H}^+]^4 + ([\text{A}] + K_B)[\text{H}^+]^3 - (K_w + \{[\text{B}] - [\text{A}]\}K_B + K_1\alpha P_{\text{CO}_2})[\text{H}^+]^2 - (K_wK_B + \{K_B + 2K_2\}K_1\alpha P_{\text{CO}_2})[\text{H}^+] - 2K_BK_2K_1\alpha P_{\text{CO}_2} = 0. \quad (28)$$

The quartic equation (28) for $[\text{H}^+]$ has four solutions, three un-physical solutions where $[\text{H}^+]$ is either a negative real number or has an imaginary part, and the solution of interest to us, where $[\text{H}^+]$ is a positive real number. Solutions of (28) are shown in Fig. for $[\text{B}] = 0.42$ mM, approximately the current ocean value, and for a range of atmospheric CO_2 concentrations. Boron has much less effect on ocean pH than dissolved CO_2 .

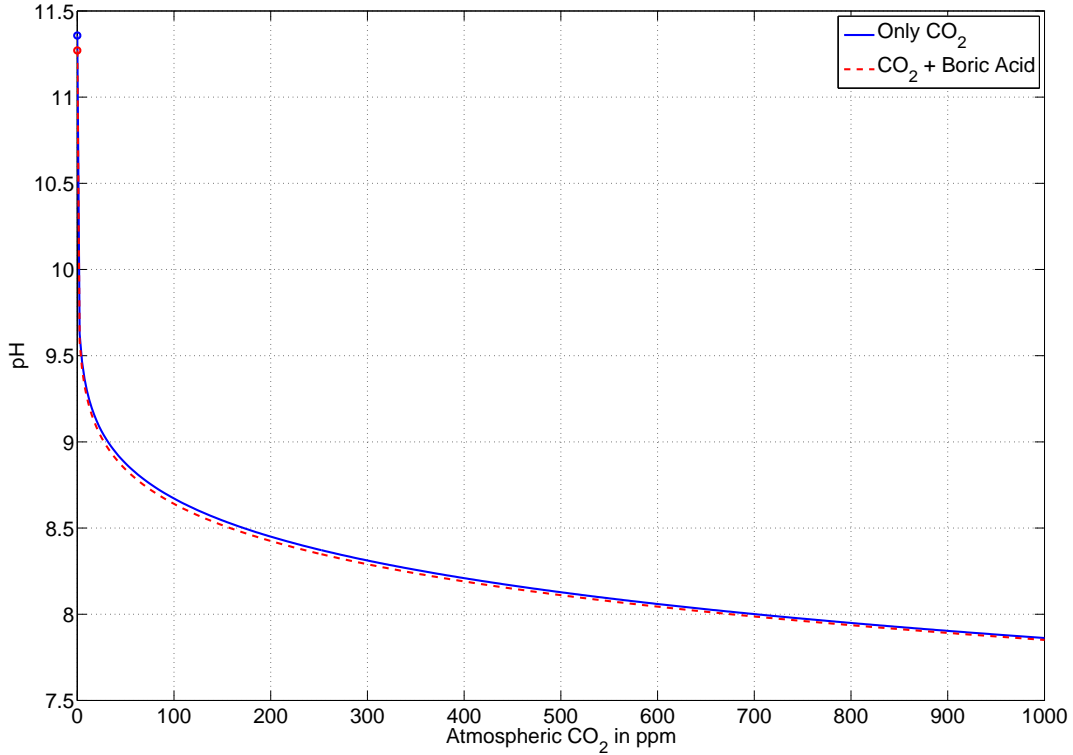


Figure 5: pH of ocean water with alkalinity $[A] = 2.3 \times 10^{-3}$ M, versus atmospheric concentration of CO_2 , without boron and with a boron concentration of $[B] = 0.42 \times 10^{-3}$ M. Temperature $T = 25$ C.

4 Equilibrium CO_2 in Atmosphere and Ocean

In hydrostatic equilibrium the atmospheric pressure p (in dynes cm^{-2}) at altitude z is given by the barometric equation

$$\frac{dp}{dz} = \frac{-gmp}{k_{\text{B}}T}. \quad (29)$$

Here m is the mean mass of an atmospheric molecule, T is the absolute atmospheric temperature in K at altitude z , and k_{B} is Boltzmann's constant. We neglect the weakening of the acceleration of gravity g with altitude and set $g = 981$ cm s^{-1} . Then we can use the ideal gas law $p = NkT$ to write (29) as

$$dp = -gmNdz. \quad (30)$$

which has the solution

$$\int_z^\infty N' dz' = \frac{p(z)}{gm}. \quad (31)$$

Here $N' = N(z')$ is the number density of molecules at altitude z above the surface. For a sea-level ($z = 0$) pressure of $P(0) = 1$ atm or $p(0) = 1.013 \times 10^6$ dyne cm^{-2} , we find the

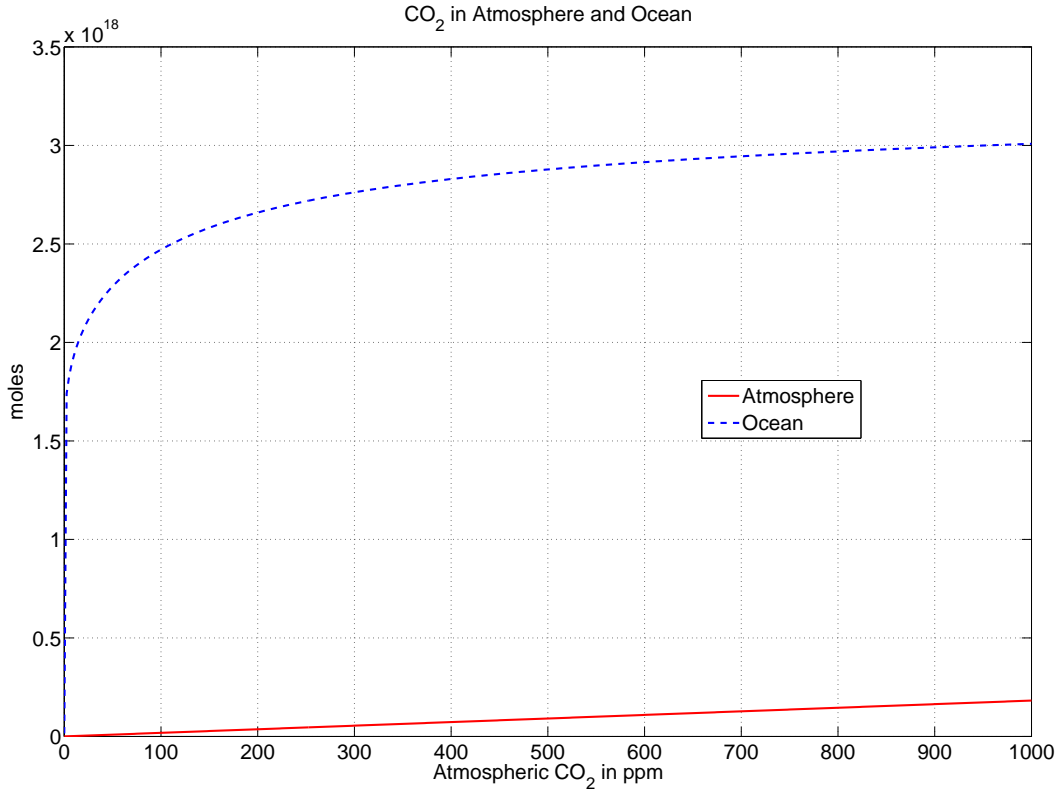


Figure 6: N_{at} , the number of moles of CO_2 in the atmosphere, and N_{oc} , number of moles of CO_2 dissolved in the oceans, versus the concentration of CO_2 in the atmosphere. The ocean alkalinity is $[\text{A}] = 2.3 \times 10^{-3} \text{ M}$ and the temperature is $T = 25 \text{ C}$.

total column density above the surface is

$$n(0) = \frac{p(0)}{gm} = 2.15 \times 10^{25} \text{ cm}^{-2}. \quad (32)$$

The molar fraction of CO_2 has the same numerical value as the partial pressure in atmospheres, P_{CO_2} , of CO_2 at sea level, so the column density of CO_2 molecules is

$$n_{\text{CO}_2} = n(0)P_{\text{CO}_2} \quad (33)$$

The earth's radius is $r_e = 6371 \text{ km}$, so its area is

$$S_e = 4\pi r_e^2 = 5.10 \times 10^{18} \text{ cm}^2. \quad (34)$$

The total number of moles of CO_2 in the atmosphere is approximately

$$N_{\text{at}} = \beta_{\text{at}}P_{\text{CO}_2}, \quad (35)$$

where the coefficient is

$$\beta_{\text{at}} = \frac{S_e n(0)}{N_A} = 1.82 \times 10^{20} \text{ moles atm}^{-1}. \quad (36)$$

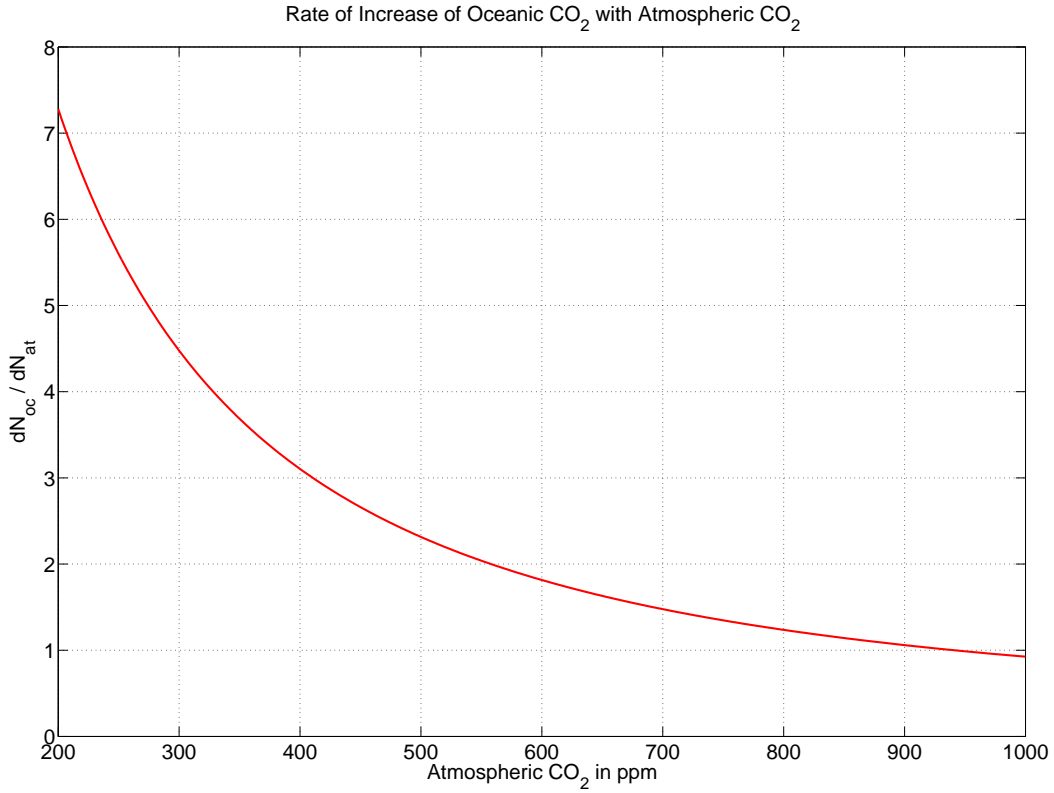


Figure 7: The equilibrium rate, dN_{oc}/dN_{at} , of increase of CO_2 in the oceans with the increase of CO_2 in the atmosphere. The ocean alkalinity is $[A] = 2.3 \times 10^{-3} \text{ M}$ and the temperature is $T = 25 \text{ C}$.

Avagadro's number is $N_A = 6.02 \times 10^{23} \text{ molecules mole}^{-1}$. The number of moles of CO_2 in the oceans is

$$N_{oc} = M_{oc}[C], \quad (37)$$

where the concentration of inorganic carbon $[C]$ was given by (18), and where the mass of ocean water is approximately

$$M_{oc} = 1.36 \times 10^{21} \text{ kg}. \quad (38)$$

The molar amounts, N_{at} and N_{oc} , of CO_2 in the atmosphere and ocean are shown in Fig. 6.

The rate of increase, dN_{oc}/dN_{at} , of CO_2 in the ocean with CO_2 in the atmosphere is shown in Fig. 7. Because of the long time (centuries) needed for additional CO_2 molecules dissolved in the ocean surface to reach the deeper ocean, the currently observed rate, $dN_{oc}/dN_{at} \approx 1$, is about three times smaller than the predicted equilibrium rate

$$\frac{dN_{oc}}{dN_{at}} = \left(\frac{M_{oc}}{\beta_{at}} \right) \frac{d[C]}{dP_{\text{CO}_2}}, \quad (39)$$

plotted in Fig. 7.

The estimates above underestimate the amount CO_2 dissolved in the ocean since they assume a uniform temperature of 25 C, while most of the deeper layers of the ocean are much colder and can hold more CO_2 . And because of the biological pump, the CO_2 levels can increase substantially with depth. Finally the dissolution calcium carbonate sinking down from the surface to more CO_2 to the deeper ocean below the lysocline.

5 Summary

This minimalist discussion already shows how hard it is to scare informed people with ocean acidification, but, alas, many people are not informed. For example:

- The oceans would be highly alkaline with a pH of about 11.4, similar to that of household ammonia, if there were no weak acids to buffer the alkalinity. Almost all of the buffering is provided by dissolved CO_2 , with very minor additional buffering from boric acid, silicic acid and other even less important species.
- As shown in Fig. 1, doubling atmospheric CO_2 from the current level of 400 ppm to 800 ppm only decreases the pH of ocean water from about 8.2 to 7.9. This is well within the day-night fluctuations that already occur because of photosynthesis by plankton and less than the pH decreases with depth that occur because of the biological pump and the dissolution of calcium carbonate precipitates below the lysocline.
- As shown in Fig. 2, doubling atmospheric CO_2 from the current level of 400 ppm to 800 ppm only decreases the carbonate-ion concentration, $[\text{CO}_3^{2-}]$, by about 30%. Ocean surface waters are already supersaturated by several hundred per cent for formation of CaCO_3 crystals from Ca^{2+} and CO_3^{2-} . So scare stories about dissolving carbonate shells are nonsense.
- As shown in Fig. 7, the ocean has only absorbed 1/3 or less of the CO_2 that it would eventually absorb when the concentrations of CO_2 in the deep oceans came to equilibrium with surface concentrations. Effects like that of the biological pump and calcium carbonate dissolution below the lysocline allow the ocean to absorb substantially more than the amount that would be in chemical-equilibrium with the atmosphere.
- Over most of the Phanerozoic, the past 550 million years, CO_2 concentrations in the atmosphere have been measured in thousands of parts per million, and life flourished in both the oceans and on land. This is hardly surprising, given the relative insensitivity of ocean pH to large changes in CO_2 concentrations that we have discussed above, and given the fact that the pH changes that do occur are small compared to the natural variations of ocean pH in space and time.

References

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