Effects of Fossil Fuel CO_2 Emissions on the pH of the Oceans

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Abstract

Surface seawater samples from the Pacific, Atlantic, Gulf of Mexico, North Sea, Baltic Sea, Black Sea and the St. Lawrence Seaway were tested in-situ and under laboratory conditions for pH, CO_2 vapor pressure, and rates of CO_2 absorption. Laboratory tests were conducted on each sample under atmospheric CO_2 partial pressures of between 0ppm and 4,000ppm. The pH of every sample = $A – B.log_e(CO_2$ vapor pressure), where A represents the pH when the sample CO_2 vapor pressure is 1ppm, and B is the slope of the logarithmic function. A is approximately 10.6 and B is approximately 0.4. The R^2 correlation for each sample was about 0.98. The in-situ tests confirmed National Oceanic and Atmospheric Administration (NOAA) data showing that CO_2 vapor pressure averaged 7% lower than the atmospheric CO_2 partial pressure. This difference is the driving force for CO_2 absorption by the oceans. The in-situ seawater pH ranged from 7.9 to 8.5 corresponding to CO_2 vapor pressures of 410ppm to 250ppm. The average pH was 8.08 with a CO_2 vapor pressure of 378ppm. This study shows that the average surface seawater pH would decrease to 7.8 if the atmospheric CO_2 increased to 800ppm and to 7.2 if CO_2 increased to 4,000ppm. The increase in seawater acidity may be explained solely by the increases in fossil fuel CO_2 emissions. The average ocean pH could be maintained at 8.08 by reducing fossil fuel CO_2 emissions to 15Gt/year from approximately 35Gt/year. The longer this reduction in fossil fuel emissions is delayed, the lower the ocean's pH will drop. The differential CO_2 concentration at the ocean surface results from the absorption and reaction of the dissolved CO_2 by plants, and the change in chemical equilibrium. This paper examines the causes of the observed variation in differential CO_2 concentration at the ocean's surface.

Introduction

In 2011 the following equation was developed to represent the annual increase in atmospheric CO_2 concentration. $\delta CO_2 = \delta Ef + 5.0 – 0.017CO_2$ where δCO_2 is the increase in atmospheric CO_2 concentration in ppm in a calendar year, δEf is the fossil fuel CO_2 emissions in ppm in that year, and CO_2 is the average atmospheric carbon dioxide concentration in January of that year. This equation is based on mass transfer theory and reaction kinetics described by Levenspiel (1) and Lewis and Whitman (2). The basis for this equation and the calculation of the rate constant is shown in a supplementary Excel file. The values of pre-1958 atmospheric CO_2 concentrations were from ice-core samples (3) and the values of post-1958 atmospheric CO_2 concentrations were measured at Mauna Loa (4). Annual fossil fuel emissions δEf were from Energy Information Administration (EIA) (5), Carbon Dioxide Information analysis Center (CDIAC) (6) and International Energy Agency (IEA) (7). The 1980 equation was accurate through 2017 and it was determined that the two equation constants had not changed between 1750 and 2017. The prediction of atmospheric CO_2 concentration between 1750 and 2017 is shown in figure 1.

In 2017 and 2018 samples of the oceans' surface seawater were analyzed to determine their CO_2 vapor pressures and pHs. This analysis confirmed that the net oceanic absorption was proportional to the atmospheric CO_2 concentration. Fossil fuel emissions were the only significant contributor to the rising atmospheric CO_2 concentrations (8). This paper establishes the relationship between pH and atmospheric CO_2 concentrations and predicts average oceanic pH through 2100 for different rates of fossil fuel emissions.

A supplementary Ecel file contains all data used for calculations and predictions, and includes statistical and sensitivity analyses.
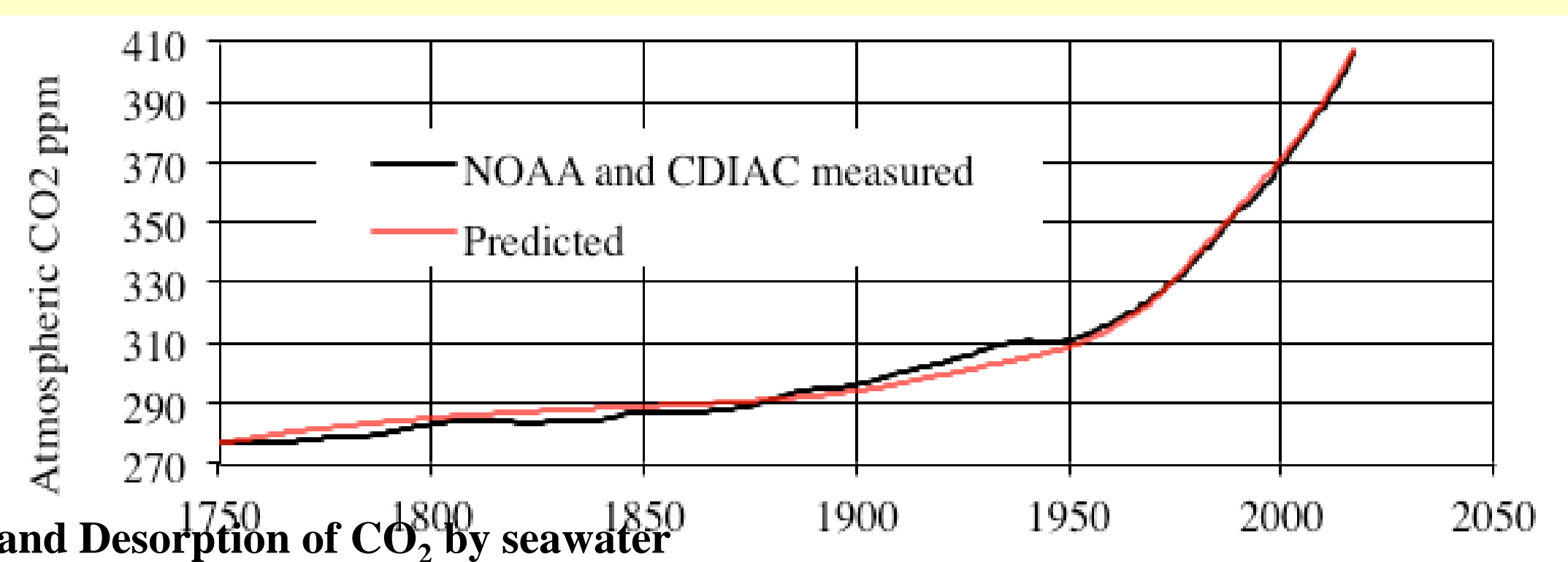

Figure 1 Predicted Atmospheric CO2 1750 to 2017

Absorption and Desorption of CO_2 by seawater

Without photosynthesis the oceans' surface waters would be in equilibrium with the atmosphere and the CO_2 vapor pressure would equal the atmospheric CO_2 partial pressure. Photosynthesis removes CO_2 from the surface water, whereas absorption from the atmosphere, biomass respiration, decay and decomposition add CO_2. These mechanisms are functions of CO_2 concentration, temperature, sunlight availability and intensity, and the density of surface plants, plankton and nutrients. Some of the carbohydrates produced by photosynthesis are ultimately converted to calcium carbonate in shells, fish bones, and coral reefs. The global average CO_2 vapor pressure (VPCO2) was approximately 7% below the atmospheric CO_2 partial pressure (PCO2) between 1990 and 2012 NOAA(9). The atmospheric CO_2 partial pressure "PCO2" used in this section of the paper is similar to the atmospheric CO_2 concentration "CO2" used in the introduction because both use ppm as their unit of measurement. The average difference between PCO2 and VPCO2 for all samples was 7% and increased as PCO2 increased. The absorption rate equation was similar for all seawater locations. 10 locations are listed in figure 3 and 4. The absorption/desorption rate r = $k_n a(PCO_2 – VPCO_2)$. The absorption rate constant k_a was calculated from measured values of r, PCO2, VPCO2, PCO2 and a (absorption area). The calculations are shown in a supplementary Excel file. The results show that the net CO_2 absorbed or desorbed from air in a sealed vessel containing seawater was proportional to PCO2 in the sealed container. The results confirm that the net CO_2 removal from the atmosphere was proportional to the atmospheric CO_2 concentration. The rate constant was similar at all locations. An absorption and desorption plot is shown in figure 2 for a seawater sample from the Gulf of Mexico at the Galveston San Luis Hotel breakwater. The k_a.a was –0.14ppm/hour/ppm. The CO_2 in the sealed container at any time t could be calculated from $PCO_{2\ at\ time\ t} = e^{-0.14t}(PCO_{2c\ initial} – PCO_{2equilibrium}) + PCO_{2equilibrium}$ where "t" is time in hours from initial absorption. The equivalent global oceanic rate constant k_a was -4.57E-08mt/year/m^2/ppm and k_a.a was –0.0047ppm/year/ppm. The global rate constants are calculated from the measured rate constants. Different ocean areas were used to calculate k_a.a. The area selected as most representative assumes that the effective area is 2.24 times the flat or calm water area with no waves. The calculations are shown in a supplementary Excel file.
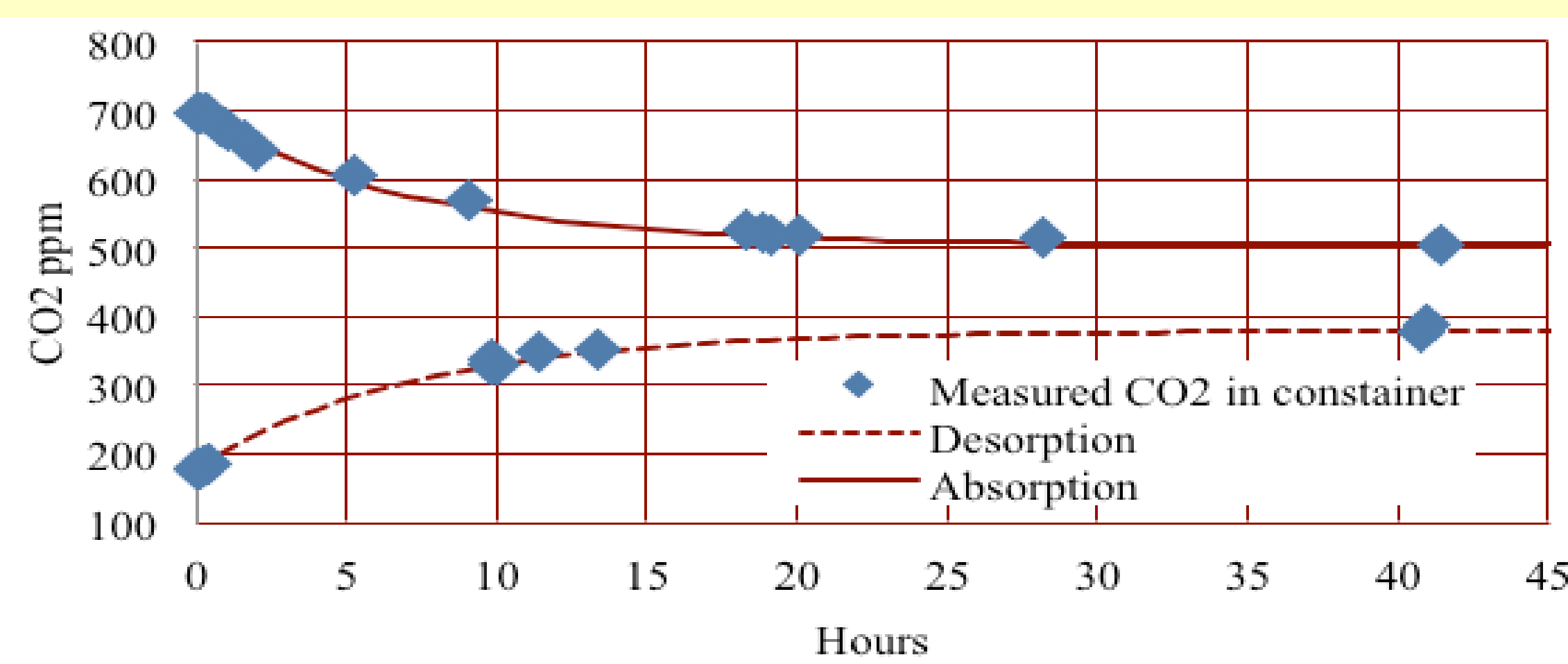

Figure 2 Absorption and desorption of CO2 in sealed container
Galveston San Luis

Ocean pH as a function of CO_2 vapor pressure for 2017 and 2018 water samples

During seawater testing to measure CO_2 vapor pressure (VPCO2) it was observed that VPCO2 could be derived directly from seawater pH, saving many hours of testing per sample, and minimizing post sampling contamination. The pH vs. VPCO2 is shown in figures 3, 4 and 5 for normal salinity (35g/kg) and low salinity (15g/kg). As pH is the log function of H^+ ion concentration, pH of seawater was a logarithmic function of VPCO2. The average pH of normal salinity samples was $–0.42Ln(VPCO_2) – 10.55$ whereas the pH of the low salinity samples was $–0.39Ln(VPCO2) – 10.57$. $PCO_2 – VPCO_2$ or ΔCO_2 may be calculated from ΔpH using figure 6 for Galveston seawater. $\Delta pH = pH_e – pH_i$, where pH_i is the surface water pH measured in-situ and pH_e is the sample pH after it has equilibrated in the atmosphere at the sample site. If a CO_2 meter is not available, PCO2 and the equilibrium VPCO2 can be estimated from pH using figure 6. This is an exponential curve $\Delta CO_2 = 397 – e^{((\Delta pH – 2.5)/-0.42)}$ .It may be approximated as linear over the range of pH measured. The linear equation is $\Delta CO_2 = 766\ \Delta pH +3.8$
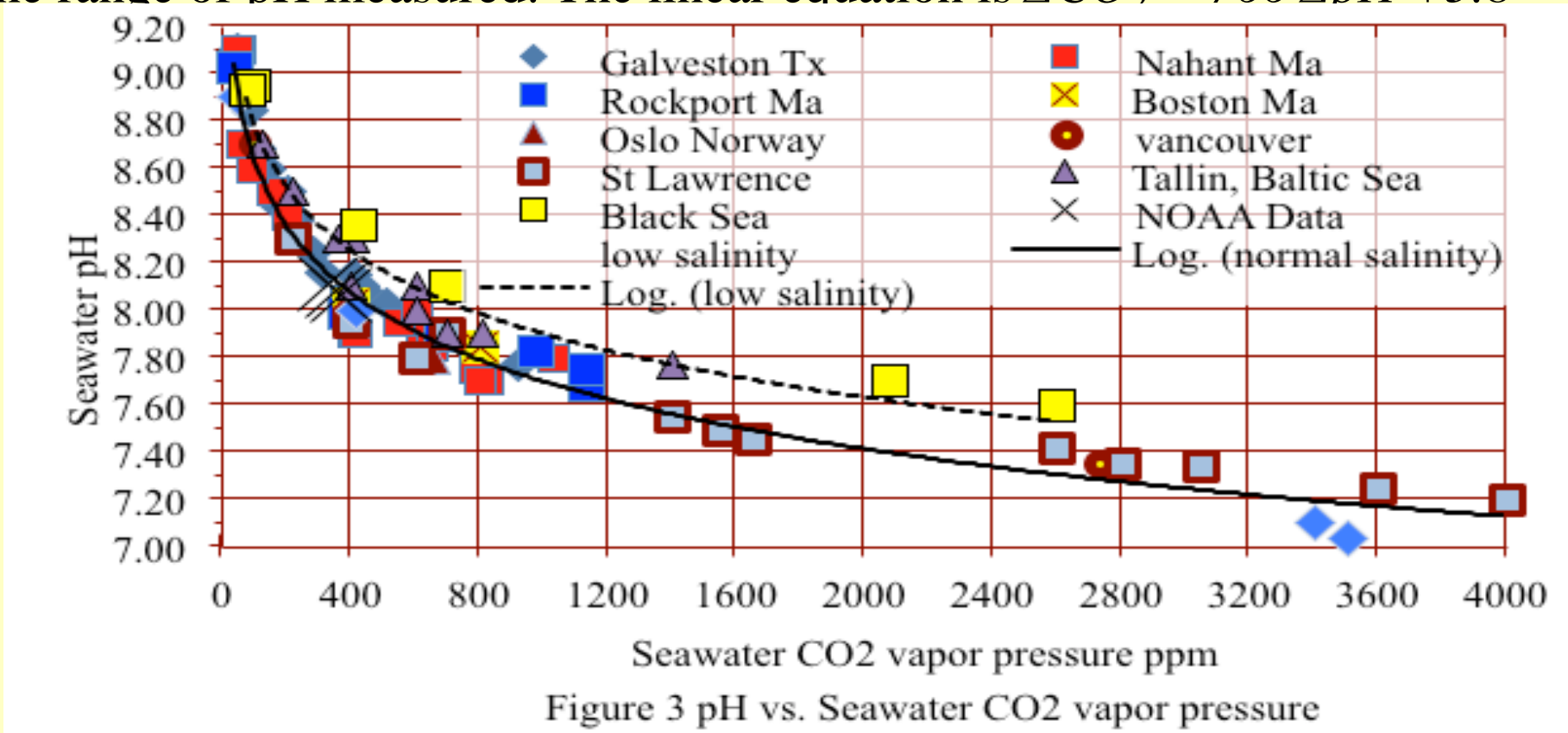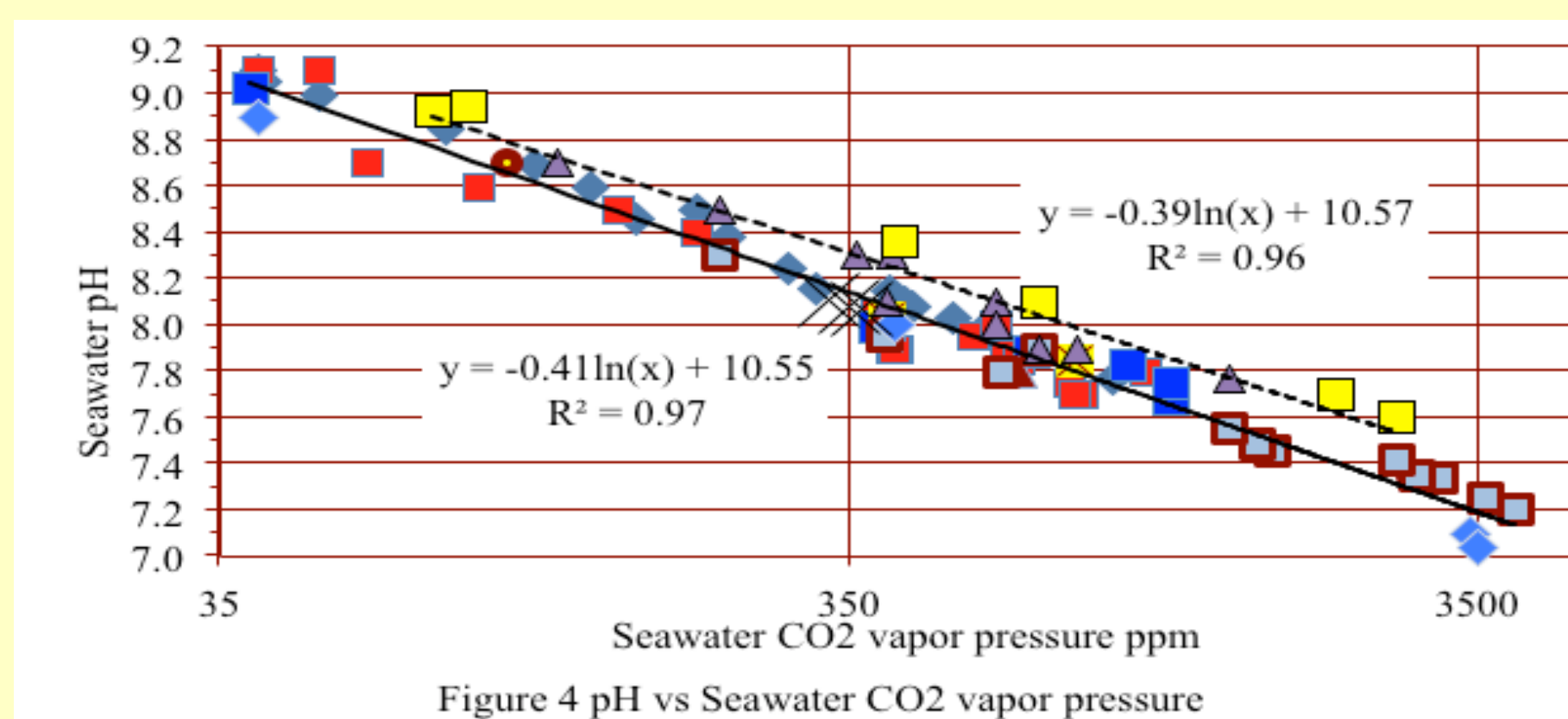

Figure 3 pH vs. Seawater CO2 vapor pressure
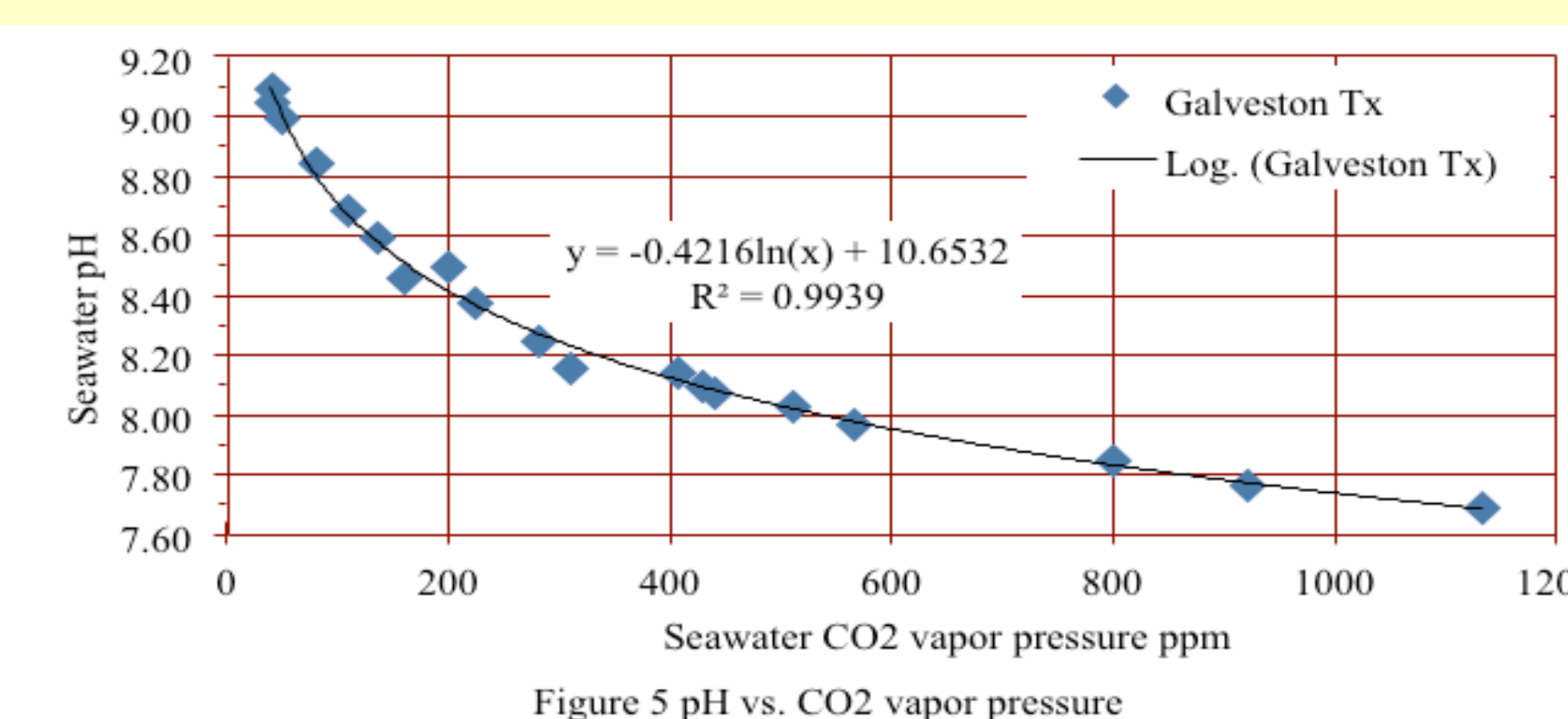

Figure 4 pH vs Seawater CO2 vapor pressure

Figure 5 pH vs. CO2 vapor pressure
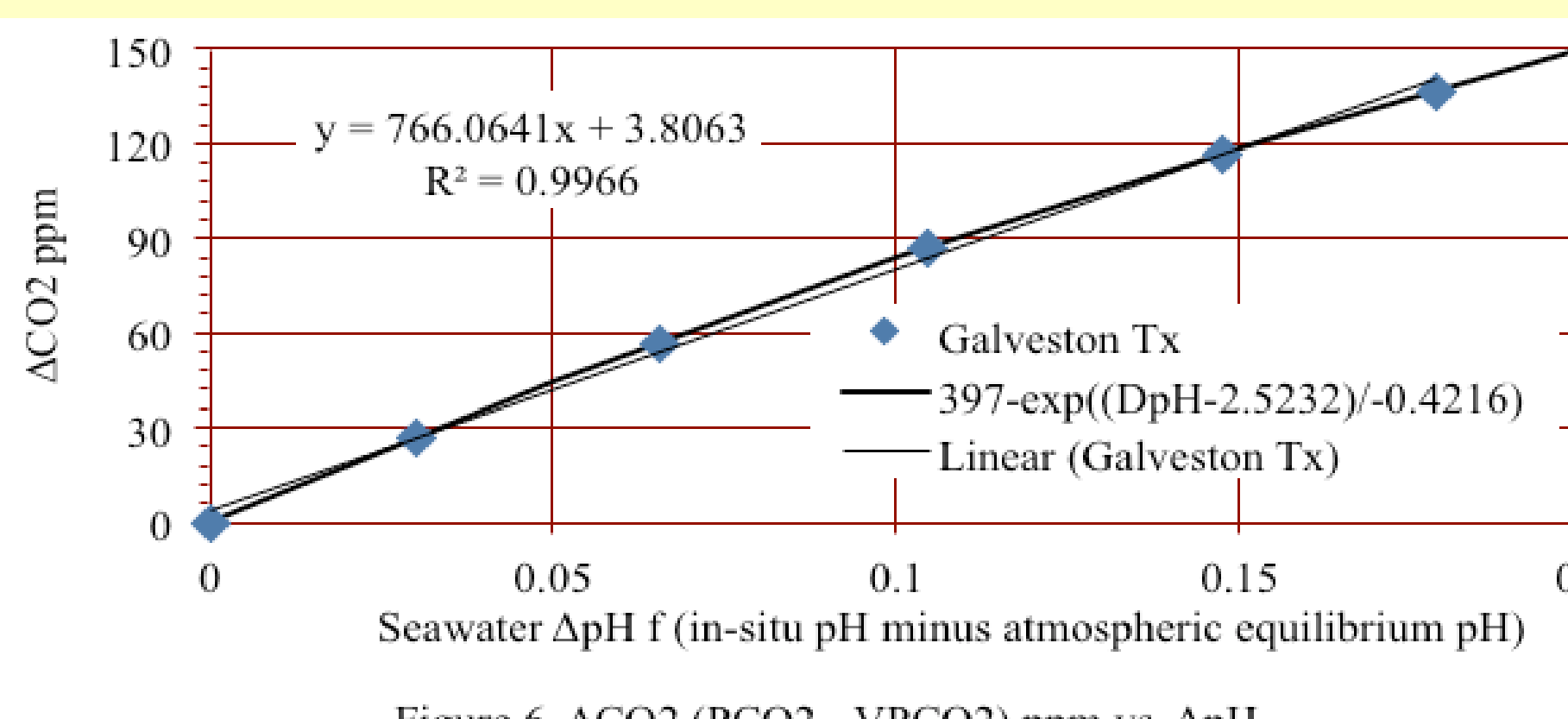

Figure 6 ΔCO_2 (PCO2 - VPCO2) ppm vs. ΔpH

Atmospheric CO_2 concentrations and ocean pHs predicted through 2100

Figures 3, 4 and 5 show that seawater pH is a function of seawater CO_2 vapor pressure. The measurements of atmospheric CO_2 and CO_2 vapor pressure at locations listed in figure 3 show that the average difference between the measured CO_2 vapor pressure and the atmospheric partial pressure was 7%. This agreed with the NOAA published results (9). As atmospheric CO_2 partial pressure increases, the difference between atmospheric CO_2 and PVCO2 increases because photosynthesis increases (10). The seawater pH for a given atmospheric CO_2 partial pressure or concentration is approximately the same as the pH of the seawater with a vapor pressure of 93% of the atmospheric partial pressure. Before predicting the oceans' pHs it was necessary to predict the atmospheric CO_2. From 2013 to 2015, global fossil fuel CO_2 emissions were nearly constant at 33Gt/year although they increased to 35Gt/year in 2016. Figure 7 shows predicted atmospheric CO_2 for several scenarios. If fossil fuel emissions remain at 33Gt/year from 2018 through 2100, and there are no changes in other factors, atmospheric CO_2 will be 501ppm in 2100. Atmospheric CO_2 will ultimately reach equilibrium at 529ppm. However, if annual fossil fuel emissions were to increase at 1.8%/year, which was the average annual increase in fossil fuel emissions between 1980 and 2010, atmospheric CO_2 would be 838ppm by 2100 and continue to increase. A 54% reduction in fossil fuel emissions from 33Gt/year to 15.16Gt/year in 2018, and maintaining 15.16Gt/year indefinitely, atmospheric CO_2 will equilibrate at 400ppm. If fossil fuel CO_2 emissions were eliminated in 2018, CO_2 would be 315ppm in 2100 and would equilibrate at 290ppm.
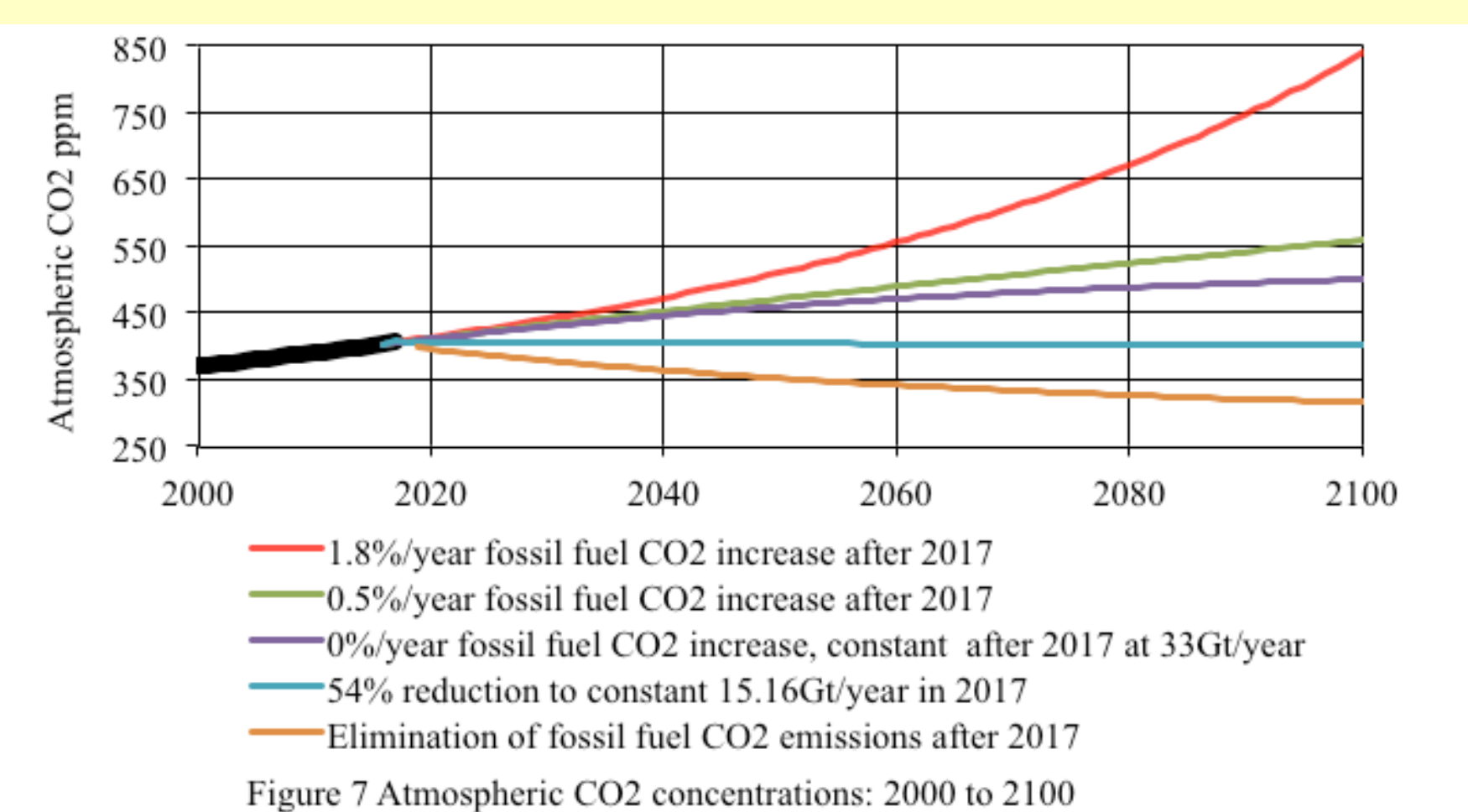

Figure 7 Atmospheric CO2 concentrations: 2000 to 2100

The seawater CO_2 vapor pressure VPCO2 = 0.93PCO2.
Therefore pH equals $–0.42Ln((PCO_2)0.93) – 10.55$. Figure 8 shows the pH predictions through 2100.
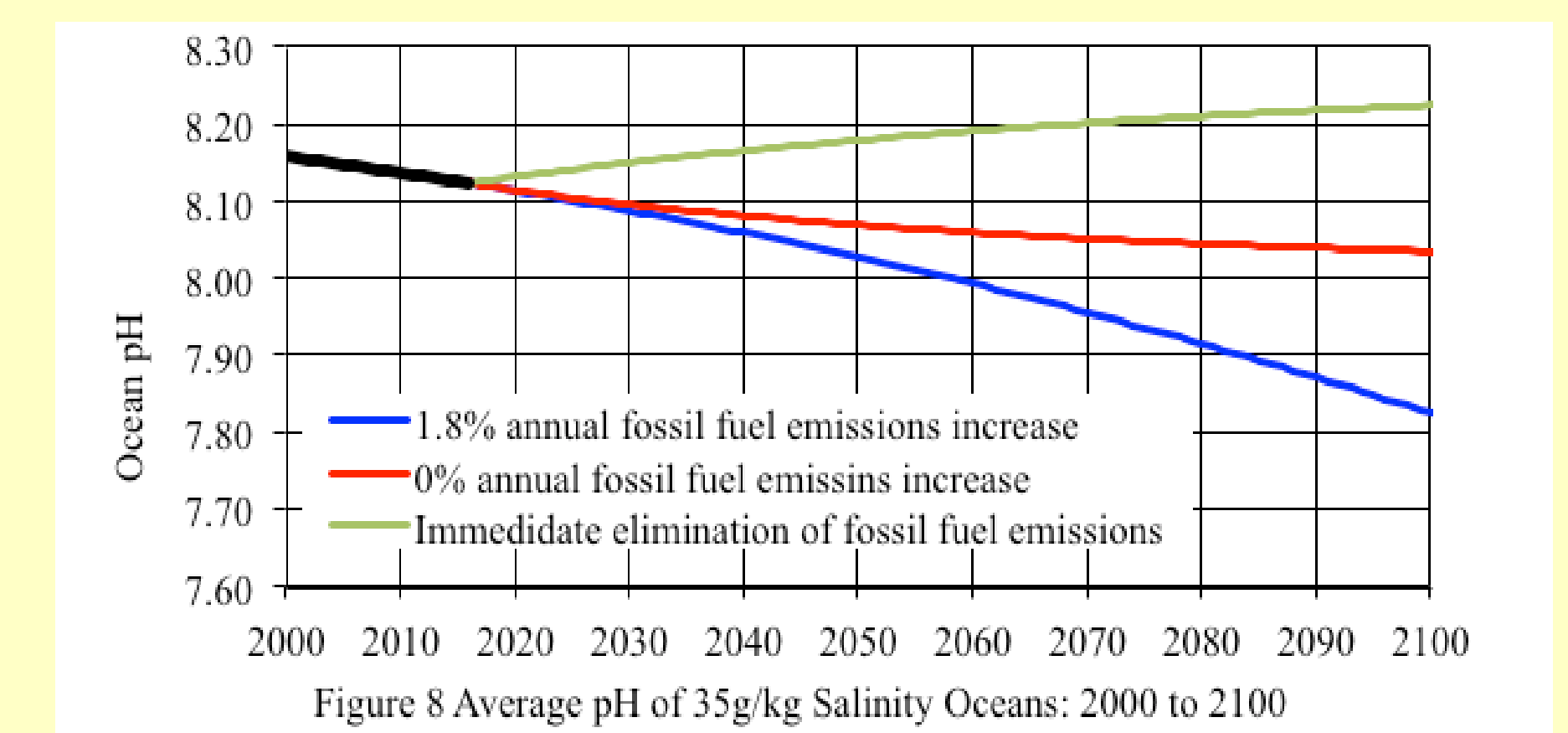

Figure 8 Average pH of 35g/kg Salinity Oceans: 2000 to 2100

Conclusions

The net rate of CO_2 removal from the atmosphere between 1750 and 2016 was proportional to the atmospheric CO_2 concentration and increased as atmospheric CO_2 increased. There were no significant changes in the average atmospheric CO_2 absorption rate constant, non-fossil fuel emissions, or total absorption surface area between 1750 and 2016. There was a 33Gt/year increase in fossil fuel CO_2 emissions, which caused 89% of the 123ppm increase in atmospheric CO_2, and a 1.95Gt/year increase in non-fossil fuel CO_2 emissions, which caused the other 11% of the increase. The average oceans' pH decreased form 8.28 to 8.12 between 1750 and 2017. Without these increases in CO_2 emissions, atmospheric CO_2 would have remained at 277ppm and the pH would have remained at 8.28. If CO_2 emissions were reduced to their 1750 level, atmospheric CO_2 would return to 277ppm and the oceans' pH would return to 8.28. This would take approximately 200 years because, as atmospheric CO_2 decreases, the rate of CO_2 removal also decreases. If CO_2 emissions were reduced by 17.84Gt/year, atmospheric CO_2 concentration would equilibrate at the 2015 level of 400ppm. This may be achieved by reducing fossil fuel CO_2 emissions from 33Gt/year to 15.16Gt/year. If fossil fuel emissions revert to their pre 2011 1.8% annual increase, the oceans 'average pH would decrease to 7.8. This would have a serious effect on the oceans' ecosystem and encourage species to evolve that can survive in the lower pH environment. If future CO_2 mass transfer dynamics and kinetics are similar to those from 1750 to 2017, and non-fossil fuel emissions continue to change slowly, fossil fuel CO_2 emissions will be the main variable affecting atmospheric CO_2 levels and oceans' pH. The reduction of fossil fuel emissions is the only effective method of increasing and stabilizing the oceans' pH.

References

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Methodology

An AZ-00002 high accuracy portable CO2 meter from CO2meter.com measured atmospheric CO2 concentrations. A PH-11 Jellas meter measured seawater pH