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Modern-age buildup of CO_2 and its effects on seawater acidity and salinity

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[1] The impacts of increases in atmospheric CO_2 since the midst of the 18th century on average seawater salinity and acidity are evaluated. Assuming that the rise in the planetary mean surface temperature continues unabated, and that it eventually causes the melting of terrestrial ice and permanent snow, it is calculated that the average seawater salinity would be lowered not more than 0.61‰ from its current 35‰. It is also calculated –using an equilibrium model of aqueous carbonate species in seawater open to the atmosphere- that the increase in atmospheric CO_2 from 280 ppmv (representative of 18th-century conditions) to 380 ppmv (representative of current conditions) raises the average seawater acidity approximately 0.09 pH units across the range of seawater temperature considered (0 to 30°C). A doubling of CO_2 from 380 ppmv to 760 ppmv (the $2 \times CO_2$ scenario) increases the seawater acidity approximately 0.19 pH units across the same range of seawater temperature. In the latter case, the predicted increase in acidity results in a pH within the water-quality limits for seawater of 6.5 and 8.5 and a change in pH less than 0.20 pH units. This paper's results concerning average seawater salinity and acidity show that, on a global scale and over the time scales considered (hundreds of years), there would not be accentuated changes in either seawater salinity or acidity from the observed or hypothesized rises in atmospheric CO_2 concentrations. **Citation:** Loáiciga, H. A. (2006), Modern-age buildup of CO_2 and its effects on seawater acidity and salinity, *Geophys. Res. Lett.*, *33*, L10605, doi:10.1029/2006GL026305.

1. Introduction

[2] Heightened fossil-fuel CO_2 emissions in the post-Industrial Revolution era (that is, after 1750) have lead to a planetary energy imbalance estimated to be about 1 W/m². The Earth is absorbing more solar energy than it reflects, or emits to outer space as long-wave radiation [*Hansen et al.*, 2005]. It has been estimated that – if fossil-fuel CO_2 emissions continue to increase at the approximate annual rate of 2 % observed during the last decade- the mean global surface temperature could increase 2 to 3°C by 2100 [*Hansen*, 2005]. Many authors have pondered the likely regional and global-scale consequences of modern-age (i.e., post-Industrial Revolution) global warming and associated climate change [see, e.g., *Budyko*, 1977; *Zektser and Loáiciga*, 1993; *Loáiciga et al.*, 1996; *Sala et al.*, 2000; *Vörösmarty et al.*, 2000; *Loáiciga*, 2003; *Houghton*, 2004; *Hansen*, 2005; *Schröter et al.*, 2005].

[3] There are linkages between the ongoing increase of atmospheric CO_2 (and other greenhouse gases) and average seawater characteristics. One, indirect, linkage is established through the reduced mass of terrestrial ice (through melting of polar ice, mountain glaciers, permanent snow, and permafrost) caused by higher mean surface temperature. This input of melted terrestrial ice to the oceans modifies the average seawater salinity. The latter currently fluctuates within a narrow range of 33×10^3 to 37×10^3 ppm (or ‰) by mass over 97% of the world's seawater [*Stumn and Morgan*, 1996]. A second, direct, linkage arises from the dissolution of atmospheric CO_2 in seawater [*Zeebe and Wolf-Gladrow*, 2001]. This process is an important component of the series of chemical reactions that govern the aqueous carbonate system in seawater open to the atmosphere. The dissolution of atmospheric CO_2 in seawater depends on its partial pressure and on the temperature and salinity of seawater.

[4] This paper's objectives are twofold. First, a mass-balance approach is used to estimate the change in average seawater salinity caused by the melting of terrestrial ice and permanent snow in a warming Earth. Second, it applies a chemical equilibrium model for the concentration of carbonate species in seawater open to the atmosphere. The model is used to estimate the effect of changes in atmospheric CO_2 on the acidity of seawater. One estimation uses the current atmospheric CO_2 concentration of approximately 380 ppmv (equivalent to a partial pressure $P_{CO2} = 10^{-3.420}$ atm). Seawater temperature is allowed to vary from 0 to 30°C, depending on its geographical location. A second estimation uses twice the current concentration, or 760 ppmv ($P_{2 \times CO2} = 10^{-3.119}$ atm), and the same temperature range. The $2 \times CO_2$ scenario is widely used in the assessment of likely impacts of global warming [see, e.g., *Loáiciga*, 2003]. For the sake of historical perspective, a third estimation of seawater acidity uses the CO_2 atmospheric concentration prevalent in the midst of the 18th century (280 ppmv or $P_{CO2} = 10^{-3.553}$ atm [*Ramanathan et al.*, 1989]). Seawater acidity and salinity are of biological, physical, and chemical significance [*U.S. Environmental Protection Agency*, 1976], and have been identified as variables of concern regarding the rise of atmospheric CO_2 [*Stumn and Morgan*, 1996; *Kerr*, 1998]. The *U.S. Environmental Protection Agency* [1976] recommended a range of pH in seawater between 6.5 and 8.5 for marine aquatic life, but not more than 0.2 pH units outside the normally occurring range. This paper ascertains the likely impacts of atmospheric CO_2 rise on average seawater salinity and acidity.

2. Melting of Terrestrial Ice and Its Effect on Average Seawater Salinity

[5] There are about 24.4×10^6 km³ of water held in polar ice sheets, mountain glaciers, permanent snow and perma-

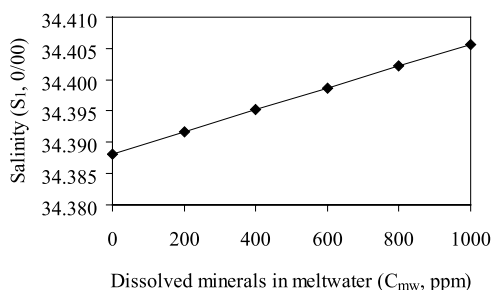[1]Department of Geography, University of California, Santa Barbara, California, USA.

Figure 1. Average seawater salinity as a function of the dissolved mineral content of meltwater. It is assumed that the totality of terrestrial ice and permanent snow melt as the planetary mean surface temperature increases. See text for details.

frost [*Shiklomanov and Sokolov*, 1983]. This compares with a volume $V_{sw} = 1.338 \times 10^9$ km³ of seawater [*Shiklomanov and Sokolov*, 1983]. The latter has an average salinity $S_0 = 35 \times 10^3$ ppm by mass (=35‰). The increase in mean global surface temperature observed during the 20th and 21st centuries has been hypothesized as a plausible cause for the melting of terrestrial ice, which could bring about numerous impacts on humans and ecosystems, and accelerated sea-level rise (see *Houghton* [2004] for a review of possible global-warming impacts). This section calculates the effect that terrestrial ice melting would have on average seawater salinity. The calculation considers the case in which the totality of the $V_{mw} = 24.4 \times 10^6$ km³ of terrestrial ice and permanent snow melt and mix with seawater. The calculation relies on a mass-balance equation for the modified average seawater S_1 following the melting of terrestrial ice and permanent snow. The average density of seawater prior to terrestrial meltwater mixing is $\rho_{sw} = 1025$ kg/m³. That of terrestrial meltwater equals $\rho_{mw} = 1000$ kg/m³. The average concentration of dissolved mineral material in terrestrial meltwater is denoted by C_{mw}. C_{mw} is allowed to vary between 0 and 1000 ppm by mass. Thus:

$$S_1 = \frac{S_0 \rho_{sw} V_{sw} + C_{mw} \rho_{mw} V_{mw}}{\rho_{sw} V_{sw} + \rho_{mw} V_{mw}} \quad (1)$$

[6] Figure 1 shows a graph of S_1 vs. the dissolved mineral content of meltwater (C_{mw}). The graph indicates that the largest possible reduction in average seawater salinity is about 0.61 ppm, that is, from 35‰ to 34.39‰ when $C_{mw} = 0$. The calculations of average seawater salinity shown on Figure 1 establish that this variable can be safely set at its current value of 35‰ when calculating changes in the average seawater pH as a function of atmospheric CO_2 concentration.

3. Average Seawater Acidity and Increased CO_2 Atmospheric Concentration

[7] This section relies on an approximate seawater model system in which calcite ($CaCO_3(s)$) dissolves in water and equilibrates with atmospheric CO_2 at a given seawater temperature and salinity [*Millero*, 1995]. Because the relative proportions of the major ions in seawater are constant [see *Stumn and Morgan*, 1996], this approximate seawater

model can be expressed in terms of a few chemical species and seawater equilibrium constants. Expressing their concentrations in mol/(kg of seawater), these species are (after *Millero* [1995]): total hydrogen ion $[H_{sws}^+] = [H^+] + [HSO_4^-] + [HF^-]$, total hydroxide ion $[OH^-]_T = [OH^-] + [MgOH^+] + [CaOH^+]$, total bicarbonate $[HCO_3^-]_T = [HCO_3^-] + [NaHCO_3] + [CaHCO_3^+] + [MgHCO_3^+] + [Ca(HCO_3)_2] + \ldots$, total concentration of calcium $[Ca^{2+}]_T$ (equal to the concentration of soluble C_a^{2+} plus the concentrations of carbonate complexes with medium ions), total soluble carbonate $[CO_3^{2-}]_T$, and total dissolved CO_2 defined by $[H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3]$, for six unknown concentrations. Atmospheric CO_2-whose partial pressure P_{CO2} is specified- dissolves in seawater according to Henry's law. The pH scale used in this aper (that is, defined in terms of $[H_{sws}^+]$) is an attempt to capture the effect of ionic interactions in seawater, which introduce theoretical and measurement difficulties in the characterization of seawater pH [*Dickson*, 1984; *Millero*, 1995; *Stumn and Morgan*, 1996]. *Millero* [1995] reported a set of seawater equilibrium constants (all valid on the mol per kg of solution scale) consistent with the approximate seawater model system as a function of salinity (0 to 45‰) and seawater temperature (0 to 45°C). Those equilibrium constants govern the concentrations of the chemical species considered in the approximate seawater model system, and are as follows:

Ion product of water:

$$K_w^{sw} = [H_{SWS}^+][OH^-]_T \quad (2)$$

Aqueous CO_2 system:

$$K_1^{sw} = [H_{sws}^+][HCO_3^-]_T \Big/ [H_2CO_3^*] \quad (3)$$

$$K_2^{sw} = [H_{sws}^+][CO_3^{2-}]_T \Big/ [HCO_3^-]_T \quad (4)$$

Solubility of calcite ($CaCO_3$):

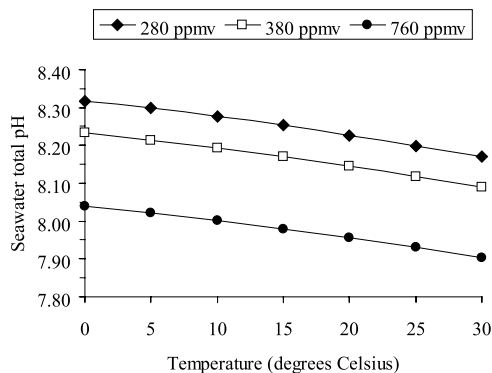$$K_{cal}^{sw} = [Ca^{2+}]_T[CO_3^{2-}]_T \quad (5)$$

Figure 2. Calculated total pH of seawater as a function of seawater temperature for three values of CO_2 atmospheric concentrations. The 280, 380, and 760 ppmv concentrations correspond to mid 18th century, year 2005, and $2 \times CO_2$ conditions. See the text for details.

Table 1. Equilibrium Constants for Salinity 35‰ and Pressure 1 atm for the Given Seawater Temperatures (After *Millero* [1995])

Temperature, °C	K_H^{sw}, mol/(kg atm)	K_1^{sw}, mol/(kg soln)	K_2^{sw}, mol/(kg soln)	K_{cal}^{sw}, mol/(kg soln)	K_w^{sw}, mol/(kg soln)
0	0.062864	7.9360×10^{-7}	4.2053×10^{-10}	4.3132×10^{-7}	5.023×10^{-15}
5	0.052131	9.0074×10^{-7}	5.2808×10^{-10}	4.3321×10^{-7}	8.690×10^{-15}
10	0.043883	1.0172×10^{-6}	6.5766×10^{-10}	4.3401×10^{-7}	1.469×10^{-14}
15	0.037463	1.1431×10^{-6}	8.1283×10^{-10}	4.3371×10^{-7}	2.421×10^{-14}
20	0.032404	1.2794×10^{-6}	9.9724×10^{-10}	4.3231×10^{-7}	3.908×10^{-14}
25	0.028392	1.4256×10^{-6}	1.2151×10^{-9}	4.2954×10^{-7}	6.166×10^{-14}
30	0.025171	1.5820×10^{-6}	1.4710×10^{-9}	4.2530×10^{-7}	9.550×10^{-14}

Dissolution of atmospheric CO$_2$ in seawater according to Henry's law (the equilibrium constant is given in mol/(kg atm) in this case):

$$K_H^{sw} = [H_2CO_3^*]/P_{CO2} \qquad (6)$$

To these equations one must add the charge-balance expression:

$$2[Ca^{2+}]_T + [H_{sws}^+] = [OH^-]_T + [HCO_3^-]_T + 2[CO_3^{2-}]_T \quad (7)$$

[8] Equations (2)–(7) involve six unknown concentrations. A series of substitutions involving equations (2)–(7) yields the following fourth-order polynomial equation on [H$_{sws}^+$]:

$$a[H_{sws}^+]^4 + [H_{sws}^+]^3 + b[H_{sws}^+] + c = 0 \qquad (8)$$

in which the coefficients a, b, c are as follows:

$$a = 2\frac{K_{cal}^{sw}}{K_H^{sw}K_1^{sw}K_2^{sw}P_{CO2}} \qquad (9)$$

$$b = -(K_w^{sw} + K_H^{sw}K_1^{sw}P_{CO2}) \qquad (10)$$

$$c = -2(K_H^{sw}K_1^{sw}K_2^{sw}P_{CO2}) \qquad (11)$$

The solution of equation (8) can be achieved numerically. Alternatively, commercially available solvers of polynomial equations can be used to obtain a closed-form solution of equation (8). Results are discussed next.

4. Results and Conclusion

[9] Table 1 shows the values of the equilibrium constants used in the solution of equation (8). They were obtained from *Millero*'s [1995] expressions with a salinity equal to 35‰, atmospheric pressure equal to 1 atm, and for seawater temperature ranging from 0 to 30°C. Figure 2 displays graphs of p[H$_{sws}^+$] as a function of the seawater temperature, for three CO$_2$ partial pressures: $P_{CO2} = 10^{-3.553}$ atm (280 ppmv, mid 18th century), $P_{CO2} = 10^{-3.420}$ atm (380 ppmv, year 2005), and $P_{2\times CO2} = 10^{-3.119}$ atm (760 ppmv, the 2 × CO$_2$ scenario).

[10] It is seen in Figure 2 that (i) for a given atmospheric concentration of CO$_2$, the p[H$_{sws}^+$] decreases with increasing temperature, that is, seawater becomes more acidic with increasing temperature, and (ii) for a given temperature, the p[H$_{sws}^+$] decreases with increasing CO$_2$ atmospheric concentration; in other words, seawater becomes more acidic with increasing CO$_2$concentrations. Figure 2 also shows that the increase in atmospheric CO$_2$ from 280 to 380 ppmv raises the seawater acidity approxi-

mately 0.09 pH units across the range of seawater temperature considered (0 to 30°C). A doubling of CO$_2$ from 380 ppmv (year 2005) to 760 ppmv (the 2 × CO$_2$ scenario) increases the seawater acidity approximately 0.19 pH units across the same range of seawater temperature. In the latter case, the increase in acidity leaves the pH within 6.5 and 8.5, with less than a 0.20 pH-unit change for any given temperature, and thus within the limits specified by water-quality criteria set by the *U.S. Environmental Protection Agency* [1976].

[11] This paper's results concerning average seawater salinity and acidity show that, on a global scale and over the time scales considered (hundreds of years), there would not be accentuated changes in either seawater salinity or acidity from the rising concentration of atmospheric CO$_2$. Yet, at smaller geographical scales, the dilution of seawater, and perhaps even changes in seawater acidity, may take greater significance.

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