Comment on “Modern-age buildup of CO$_2$ and its effects on seawater acidity and salinity” by Hugo A. Loáiciga

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1. Introduction

[1] A doubling of present atmospheric CO$_2$ concentrations (to 760 ppm) may occur by the end of this century in the absence of efforts to diminish CO$_2$ emissions from fossil-fuel combustion [Intergovernmental Panel on Climate Change (IPCC), 2001]. Based on inappropriate assumptions and erroneous thermodynamic calculations, Loáiciga [2006] mistakenly reports that atmospheric CO$_2$ concentrations of 760 ppm will lower the pH of the surface ocean by 0.28 relative to the natural “mid 18th century” conditions. He implies that a drop of this magnitude will have minimal biological impact, neglecting numerous recent experiments and observations showing that this decrease in pH would substantially affect the physiology and health of marine organisms. Here, we focus on two fundamental flaws in the published analysis that invalidate his conclusions: (1) he assumes instantaneous chemical equilibration of the ocean with carbonate minerals although this process is known to take five to ten thousand years and (2) contrary to what is implied by Loáiciga, many marine organisms are sensitive to a pH decrease of 0.2 units.

2. Equilibration of Calcite With CO$_2$ in Seawater

[2] The calculations of Loáiciga [2006] assume that chemical equilibration with calcite will occur instantaneously in response to an increase in atmospheric CO$_2$, resulting in an increase in alkalinity and a significant buffering of seawater pH. The carbonate system in seawater does react with calcium carbonate minerals, but the rate of reaction is limited both kinetically and physically. The behavior of open ocean surface waters differs from that of ground waters in contact with carbonate rocks [Stumm and Morgan, 1996]. Ocean surface waters are not in contact with enough carbonate mineral to allow local equilibration; thus equilibration of the ocean with carbonate minerals involves various transport processes and takes five to ten thousand years [Sundquist, 1985; Archer et al., 1998; Archer, 2005; Caldeira and Wickett, 2003]. Reaction of anthropogenic CO$_2$ with carbonate minerals will ultimately cause the average ocean alkalinity to increase; however, observations to date show little or no change in ocean alkalinity [Andersson et al., 2003; González-Dávila et al., 2003; Feely et al., 2004].

[1] Changes in seawater pH (Table 1) calculated using widely-used CO$_2$-system software [Lewis and Wallace, 1998].
Table 1. pH Changes From Natural “Mid 18th Century” Conditions and Carbonate Mineral Saturation States at Three Temperatures for a Number of Different Atmospheric CO₂ Concentrations

<table>
<thead>
<tr>
<th>Atm. CO₂, ppm</th>
<th>pH Change</th>
<th>Calcite Saturation</th>
<th>Aragonite Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0°C</td>
<td>15°C</td>
<td>30°C</td>
</tr>
<tr>
<td>280</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>380</td>
<td>-0.12</td>
<td>-0.11</td>
<td>-0.10</td>
</tr>
<tr>
<td>500</td>
<td>-0.23</td>
<td>-0.21</td>
<td>-0.20</td>
</tr>
<tr>
<td>760</td>
<td>-0.40</td>
<td>-0.38</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

*Carbonate mineral saturation states = [Ca²⁺][CO₃²⁻]/Ksp, Ksp is the solubility product for calcite or aragonite. Calculated according to Lewis and Wallace [1998] (see http://cdiac.ornl.gov/oceans/co2rprt.html) using a salinity of 35, an alkalinity concentration of 2310 μmol kg⁻¹, and a silicate concentration of 7.0 μmol kg⁻¹, and carbonate dissociation constants from Mehrbach et al. [1973] as refit by Dickson and Millero [1987a, 1987b].

1998], with the assumption of constant alkalinity [Dickson, 1981] appropriate for estimating century-scale changes in ocean chemistry, are substantially larger than those reported by Loáiciga [2006] (for example, see González-Dávila et al. [2003]). There is a further significant problem with Loáiciga’s calculations; his equation 7 is not appropriate to seawater. As written, it implies that the concentration of alkalinity is twice that of calcium, whereas in the real ocean the concentration of alkalinity is far less than that of calcium [Stumm and Morgan, 1996].

4. Conclusions

[7] Currently, about one-third of the CO₂ released to the atmosphere from the burning of coal, oil, and gas (and land cover change) is absorbed by the surface ocean [IPCC, 2001; Sabine et al., 2004]. This CO₂ drives well known changes in the aqueous carbonate system that result in decreases of both ocean pH and carbonate-ion concentrations [Stumm and Morgan, 1996; Zeebe and Wolf-Gladrow, 2001]. A body of literature describes observed and modeled penetration of CO₂ into the ocean and its impact on ocean chemistry [e.g., Caldeira and Wickett, 2003; Feely et al., 2004; Sabine et al., 2004; Caldeira and Wickett, 2005; Orr et al., 2005]. There is a substantial and growing body of evidence that the projected changes in oceanic pH and dissolved CO₂ will have direct physiological effects [Seibel and Fabry, 2003; Barry et al., 2005].

3. Sensitivity of Marine Organisms to pH Change

[5] The U.S. Environmental Protection Agency [1976] Quality Criteria for Water state: “For open ocean waters where the depth is substantially greater than the euphotic zone, the pH should not be changed more than 0.2 units outside the range of naturally occurring variation . . .” Atmospheric CO₂ concentrations would need to be stabilized at <500 ppm for the ocean pH decrease to remain within the 0.2 limit set forth by the U.S. Environmental Protection Agency [1976] (Table 1).

[6] The assumption made by the U.S. Environmental Protection Agency [1976] that a pH decrease of 0.2 units in the ocean will not harm marine biota is fundamentally to the conclusions made by Loáiciga [2006]. However, this criterion was established prior to the development of an extensive body of research showing that a decrease of this magnitude would pose a risk to the physiology and health of a variety of marine organisms (much of this research is reviewed by Gattuso et al. [1999], Kleypas et al. [1999], Seibel and Fabry [2003], Pörtner et al. [2004], and Caldeira et al. [2005]). The best-studied effect of CO₂-driven pH changes in seawater is the reduction in calcification rates of several major groups of organisms that secrete calcium carbonate shells and skeletons (e.g., corals and coccolithophores). For example, studies in general show that calcium carbonate minerals are produced by corals at rates approximately proportional to the degree of aragonite supersaturation. Average decreases in coral reef calcification of about 30% to 60% have been reported for a doubling of CO₂ over pre-industrial concentrations, raising concern that calcification rates in coral reefs may fall behind rates of erosion and dissolution. Predicted decreases in calcite and aragonite saturation in both cold and warm waters risk important adverse impacts on food webs and key biogeochemical processes throughout the water column [Orr et al., 2005].

References


Environmental Protection Agency (1976), Quality Criteria for Water, Washington, D. C.


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