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Comment on “Modern-age buildup of CO₂ and its effects on seawater acidity and salinity” by Hugo A. Loáiciga

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1. Introduction

[1] A doubling of present atmospheric CO₂ concentrations (to 760 ppm) may occur by the end of this century in the absence of efforts to diminish CO₂ 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 CO₂ 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 CO₂ in Seawater

[2] The calculations of Loáiciga [2006] assume that chemical equilibration with calcite will occur instantaneously in response to an increase in atmospheric CO₂, 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 Wickert*, 2003]. Reaction of anthropogenic CO₂ 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].

[3] Changes in seawater pH (Table 1) calculated using widely-used CO₂-system software [*Lewis and Wallace*,

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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^a

Atm. CO ₂ , ppm	pH Change			Calcite Saturation			Aragonite Saturation		
	0°C	15°C	30°C	0°C	15°C	30°C	0°C	15°C	30°C
280	0	0	0	2.90	4.84	7.18	1.82	3.11	4.81
380	-0.12	-0.11	-0.10	2.28	3.94	6.08	1.43	2.53	4.07
500	-0.23	-0.21	-0.20	1.81	3.23	5.15	1.14	2.08	3.45
760	-0.40	-0.38	-0.35	1.26	2.33	3.89	0.79	1.50	2.61

^aCarbonate mineral saturation states = $[Ca^{2+}][CO_3^{2-}]/K_{sp}$. K_{sp} 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 $\mu\text{mol kg}^{-1}$, a phosphate concentration of 0.5 $\mu\text{mol kg}^{-1}$, and a silicate concentration of 7.0 $\mu\text{mol kg}^{-1}$, 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] Century-scale CO₂ increases cause carbonate-ion concentrations ($[CO_3^{2-}]$) to decline and carbonate-mineral saturation states to diminish. The change from preindustrial (280 ppm) to present-day (380 ppm) conditions has already nearly halved the degree of aragonite supersaturation in cold surface ocean waters (Table 1). An increase to 760 ppm would cause aragonite minerals to dissolve in cold ocean waters (aragonite saturation <1; Table 1) [Caldeira and Wickett, 2005; Orr *et al.*, 2005]. This is in stark contrast to Loáiciga’s model which requires a constant equilibrium with calcite and hence a significant undersaturation with respect to aragonite, even in the pre-industrial ocean.

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 fundamental 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]. There is also 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].

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]. An additional body of literature shows that changes in ocean chemistry within the ranges predicted for the next decades and centuries present significant risks to marine biota, especially those that make their shells or skeletons from carbonate minerals (see references in Gattuso *et al.* [1999], Kleypas *et al.* [1999], Seibel and Fabry [2003], and Pörtner *et al.* [2004]). The effects of increasing atmospheric CO₂ concentrations on the carbonate system in seawater are not reversible on human time scales, and thousands of years will be required before the system can “recover” to pre-industrial conditions [Archer *et al.*, 1998; Archer, 2005; Zachos *et al.*, 2005]. The paper by Loáiciga [2006] makes incorrect assumptions about the role of alkalinity in seawater chemistry, and ignores modern research on the effects of changes in seawater chemistry on marine biota, and thus draws erroneous conclusions that simply do not apply to the real ocean.

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