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

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1. Introduction

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 [*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.

Insert Table 1

2. Equilibration of calcite with CO_2 in seawater

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].

Changes in seawater pH (Table 1) calculated using widely-used CO_2-system software [*Lewis and Wallace.*, 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].

Century-scale CO_2 increases cause carbonate-ion concentrations ($[CO_3^{2-}]$) to decline and carbonate-mineral saturation states to diminish. The change from pre-industrial (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

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 CO_2 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).

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 in *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 CO_2-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 CO_2 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 CO_2 will have direct physiological effects [*Seibel and Fabry,* 2003; *Barry et al.,* 2005].

4. Conclusions

Currently, about one-third of the CO_2 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 CO_2 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 CO_2 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 CO_2 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.

References

Andersson, A. J., F.T. Mackenzie, and L.M. Ver (2003), Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO_2, *Geology,* 31, 513-516.

Archer, D. (2005), Fate of fossil fuel CO_2 in geologic time, *J. Geophys. Res.*, 110, doi:10.1029/2004JC002625.

Archer, D.E, H. Kheshgi, and E. Maier-Reimer (1998), Dynamics of fossil fuel CO_2 neutralization by marine $CaCO_3$, *Global Biogeochem. Cycles,* 12, 259-276.

Barry, J. P., K. R. Buck, C. Lovera, L. Kuhnz, and P. J. Whaling (2005), Utility of deep sea CO_2 release experiments in understanding the biology of a high-CO_2 ocean: Effects of hypercapnia on deep sea meiofauna, *J. Geophys. Res.*, 110, C09S12, doi:10.1029/2004JC002629.

Caldeira, K., and M. E. Wickett (2003), Anthropogenic carbon and ocean pH, *Nature*, 425, 365-365.

Caldeira, K., M. Akai, P. Brewer, B. Chen, P. Haugan, T. Iwama, P. Johnston, H. Kheshgi, Q. Li, T. Ohsumi, H. Poertner, C. Sabine, Y. Shirayama, and J. Thomson (2005), Ocean storage. In: *IPCC Special Report on Carbon Dioxide Capture and Storage***.** Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

Caldeira, K., and M. E. Wickett (2005), Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean, *J. Geophys. Res.*, 110, C09S04, doi:10.1029/2004JC002671.

Dickson, A. G. (1981) An exact definition of total alkalinity, and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Res.* 28, 609-623.

Dickson, A. G. and F. J. Millero (1987). A comparison of the equilibrium constants equilibrium constant for the dissociation of carbonic acid in a seawater media. *Deep-Sea Res. A.*, 34, 1733-1743. (Corrigenda: *ibid*. 36, 983.).

Feely, R.A., C.L. Sabine, K. Lee, W. Berelson, J. Kleypas, V.J. Fabry, and F.J. Millero (2004), Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans, *Science*, 305, 362-366.

Gattuso, J.-P., D. Allemand, and M. Frankignoulle (1999), Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. *Am. Zoologist*, 39, 160-183.

González-Dávila, M., J. M. Santana-Casiano,. M. J. Rueda, O. Llinás and E. González-Dávila (2003), Seasonal and interanual variability of sea-surface carbon dioxide species at the European station for Time Series in the Ocean at the Canary Islands (ESTOC) between 1996 and 2000. *Global. Biogochem. Cycles*, 17, 1076, doi:10.1029/2002GB001993.

IPCC (Intergovernmental Panel on Climate Change) (2001), *Climate Change 2001: The Scientific Basis*, J. T. Houghton et al. (editors), Cambridge University Press, Cambridge UK, 881 pp.

Kleypas, J.A., R.W. Buddemeier, D. Archer, J.P. Gattuso, C. Langdon, and B.N. Opdyke (1999), Geochemical consequences of increased atmospheric carbon dioxide on coral reefs, *Science*, 284, 118-120.

Lewis, E., and D. W. R. Wallace. (1998), Program Developed for CO_2 System Calculations, ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN.

Loáiciga, H. A. (2006), Modern-age buildup of CO_2 and its effects on seawater acidity and salinity, *Geophys. Res. Letters,* 33, L10605, 10610.11029/12006GL026305.

Mehrbach C., Culberson C. H., Hawley J. E., and Pytkowicz R. M. (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18, 897–907.

Orr, J. C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G.-K. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M.-F. Weirig, Y. Yamanaka, and A. Yool (2005), Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, 437, 681-686.

Pörtner, H.O., M. Langenbuch, and A. Reipschlager. 2004. Biological impact of elevated ocean CO_2 concentrations: lessons from animal physiology and Earth history? *J. Oceanogr.,* 60, 705-718.

Sabine, C.L. R.A. Feely, N. Gruber, R.M. Key, K. Lee, J.L. Bullister, R. Wanninkhof, C.S. Wong, D.W.R. Wallace, B. Tilbrook, F.J. Millero, T.-H. Peng, A. Kozyr, T. Ono, and A.F. Rios, 2004: The Oceanic Sink for Anthropogenic CO_2, *Science,* 305, 367-371.

Seibel, B. A., and V. J. Fabry (2003), Marine biotic response to elevated carbon dioxide, *Adv. Appl. Biodiversity Sci.,* 4, 59-67.

Stumm, W., and J. J. Morgan (1996), *Aquatic Chemistry, 3rd ed.*, 1022 pp., Wiley & Sons, New York.

Sundquist, E. T. (1985), Geological perspectives on carbon dioxide and the carbon cycle, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations, Archean to Present*, edited by E. T. Sundquist and W. S. Broecker, pp. 5-59.

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

Zachos, J.C., U. Rohl, S.A. Schellenberg, A. Sluijs, D.A. Hodell, D.C. Kelly, E. Thomas, M. Nicolo, I. Raffi, L.J. Lourens, H. McCarren, and D. Kroon (2005), Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum, *Science*, 308, 1611-1615.

Zeebe, R. E., and D. Wolf-Gladrow (2001), *CO_2 in Seawater: Equlibrium, Kinetics, Isotopes*, 346 pp., Elsevier Science, B.V., Amsterdam.

Table 1. pH changes from natural "mid 18th century" conditions and carbonate mineral saturation states (= $[Ca^{2+}][CO_3^{2-}]/K_{sp}$) at three temperatures for a number of different atmospheric CO_2 concentrations. K_{sp} is the solubility product for calcite or aragonite.

Atm. CO_2 (ppm)	pH change			Calcite saturation			Aragonite saturation		
	0ºC	15ºC	30ºC	0ºC	15ºC	30ºC	0ºC	15ºC	30ºC
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

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}, a phosphate concentration of 0.5 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* [1987].