Correspondence to Nature Geoscience

A Comment on: Kuffner, I.B., A. J. Andersson, P. L. Jokiel, K. S. Rodgers & F. T. MacKenzie (2008). "Decreased abundance of crustose coralline algae due to ocean acidification." Nature Geoscience 1: 114-117.

To the Editor -- In a recent article appearing in this journal, Kuffner et al.[1] purported to show the impact of ocean acidification caused by rising levels of carbon dioxide in the atmosphere on the recruitment and growth of crustose corralline algae (CCA). While the experiment was carefully done, close inspection of their methods reveals that they choose to increase the pCO_2 of the seawater in their mesocosms by lowering pH by addition of hydrochloric acid. This means of "ocean acidification" differs in kind from the passive absorption of carbon dioxide from the atmosphere into the oceanic mixed layer which leads to an increase in pCO_2 and TCO_2 and a decrease in pH while alkalinity remains constant.[2] The difference in these two approaches can be seen in Table 1. The experiment of Kuffner et al. more appropriately mimics the impact of acid rain.[3]

[Insert Table 1 here.]

Table 1 reveals small but significant differences in bicarbonate (HCO_3^-) and carbonate ($CO_3^=$) ion concentrations between the two treatments. By adding a dilute strong acid instead of CO_2, Kuffner et al. achieved their elevated pCO_2 at a lower $CO_3^=$ ion concentration. If the ability to form a calcareous precipitate is the limiting factor in CCA settlement (as opposed to the ambient pH or pCO_2) then the acid treatment used in this study will over-estimate the impact of ocean acidification from increasing atmospheric pCO_2. While their study has focused on the impact of acidification in surface waters, we are also concerned about the impact of CO_2 enrichment in the mid-depth, low oxygen waters where extensive cold-water coral reefs occur.[6]

The point of this commentary is to raise a cautionary note for the many investigations of ocean acidification from fossil fuel CO_2 enrichment now underway. Given the small differences in the carbonate ion concentrations involved, had they done the experiment by CO_2 enrichment, the results would most probably be similar. Indeed, another recent publication[3] notes the impact of acid rain in coastal areas has a small but significant impact on the carbonate system as well. Because this form of "ocean acidification" is due to the addition of a strong acid, the work of Kuffner et al. is more closely germane to the potential impact of acid rain on CCA settlement. Other studies on the impact of ocean acidification on corals do not describe the means of acidification (acid titration or CO_2 enrichment).[7]

If we are truly concerned about investigating the impact of higher levels of CO_2 on the ocean biosphere, we would be well advised to simulate those future changes as closely as possible. For ocean acidification that means CO_2 enrichment not acid titration.

References:

1. Kuffner, I. B., A. J. Andersson, P. L. Jokiel, K. S. Rodgers and F. T. MacKenzie (2008). Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geoscience 1: 114-117. doi:10.1038/ngeo100.

2. Orr, J. C., et al. (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437: 681-686. doi:10.1038/nature04095.

3. Doney, S. C., et al. (2007). Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. Proc. Nat. Acad. Sci. 104: 14580-14585. doi:10.1073/pnas.0702218104.

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Table 1.

Case	T	S	TAlk	pH	TCO2	pCO2	xCO2	HCO3	CO3
	deg C	pss-78	µmol/kg		µmol/kg	µatm	µmol/mol	µmol/kg	µmol/kg
0	24.1	34.3	2156	8.17	1888.3	399.5	411.4	1692.4	184.2
1	24.1	34.3	2027.4	7.905	1888.3	765.0	787.9	1761.7	104.2
2	24.1	34.3	2156.0	7.930	2001.7	765.0	787.9	1862.9	116.6
Δ			128.6	0.025	113.4	0		101.2	12.4
%Δ			6.3		6.0			5.7	11.9

Table 1. Concentrations of the various components of the carbonate system for seawater from Kaneohe Bay[1] with and without treatment. *Case 0* shows the concentrations of the various ions for the mean conditions of Kaneohe Bay during the time period of their experiment. In *case 1*, HCl was added to increase the pCO_2 to ambient plus 365 µtam; TCO_2 is held constant and TAlk was varied until pCO_2 = 765 µtam. In *case 2*, sufficient CO_2 is added to achieve the same pCO_2 as for the acid treatment (765 µtam) while TAlk was held constant. Calculations were performed using CO2sys[4], as per Kuffner et al., and using the same constants that they selected.[5] xCO_2 is the mole fraction of CO_2 in dry air corresponding to the pCO_2 of air in equilibrium with seawater at the appropriate temperature.