Unanticipated consequences of ocean acidification: A noisier ocean at lower pH

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[1]   We show that ocean acidification from fossil fuel CO_2 invasion and reduced ventilation will result in significant decreases in ocean sound absorption for frequencies lower than about 10 kHz. This effect is due to known pH-dependent chemical relaxations in the $B(OH)_3/B(OH)_4^-$ and HCO_3^-/CO_3^{2-} systems. The scale of surface ocean pH change today from the +105 ppmv change in atmospheric CO_2 is about -0.12 pH units, resulting in frequency dependant decreases in sound absorption (α = dB/km) exceeding 12%. Under reasonable projections of future fossil fuel CO_2 emissions and other sources a pH change of 0.3 units or more can be anticipated by mid-century, resulting in a decrease in α by almost 40%. Ambient noise levels in the ocean within the auditory range critical for environmental, military, and economic interests are set to increase significantly due to the combined effects of decreased absorption and increasing sources from mankind's activities. **Citation:** Hester, K. C., E. T. Peltzer, W. J. Kirkwood, and P. G. Brewer (2008), Unanticipated consequences of ocean acidification: A noisier ocean at lower pH, *Geophys. Res. Lett.*, *35*, L19601, doi:10.1029/2008GL034913.

1. Introduction

[2]   Ocean acidification from the invasion of fossil fuel CO_2 from the atmosphere is now a well recognized phenomenon of widespread concern [*Cicerone et al.*, 2004; *Feely et al.*, 2004; *Sabine et al.*, 2004]. The negative effects are likely to be felt on biological processes such as calcification [*Orr et al.*, 2005; *Kleypas et al.*, 2006] and on the respiration of deep-sea animals [*Portner et al.*, 2004]. But so large is this signal, and so pervasive is the oceanic CO_2 system in structuring the fundamental chemical fabric of the fluid, that basic geophysical properties are also being affected. In this paper we show that the absorption of sound within the auditory range of $0.01 - 10$ kHz has been decreasing and will be substantially reduced due to ocean acidification.

[3]   While the pH dependence of sound absorption in the ocean has been known for a considerable time [*Fisher and Simmons*, 1977] and has been linked to ocean geochemical cycles [*Brewer et al.*, 1995], the emerging impacts of the fossil fuel CO_2 and climate-induced changes on sound absorption in the ocean have not yet been addressed. There are already well established concerns over rising levels of ocean ambient noise [*National Research Council of the National Academies*, 1994, 2003, 2005] from increased maritime activities of all kinds – the effects described here will add to those concerns.
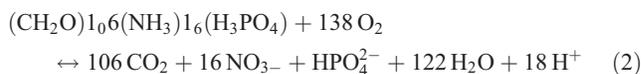
[4]   There are now at least three drivers of changing ocean pH acting in concert and these will all reduce ocean sound absorption:

[5]   1. The accumulated amount of fossil fuel CO_2 in the upper ocean is now some 530 billion tons, and the invasion rate is some 1 million tons per hour. The principal effect of adding fossil fuel CO_2 to sea water is a loss of carbonate ion to form bicarbonate and reduce pH (Figure 1) as in:

$$CO_2 + H_2O + CO_3 \rightarrow 2HCO_3^- \qquad (1)$$
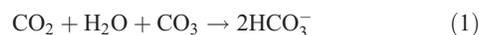
The addition of fossil fuel CO_2 alone does not change alkalinity. Simple projections based upon the Intergovernmental Panel on Climate Change (IPCC) scenarios show that by mid-century a reduction in surface ocean water pH from this invasion of around 0.3 pH units [*Brewer*, 1997] and could well exceed this number.

[6]   2. There is a well-documented on-going decline in sub-surface ocean dissolved oxygen levels as a result of decreased ventilation and ocean warming [*Gamo*, 1999; *Chen et al.*, 1999; *Jenkins*, 2008; *Stramma et al.*, 2008]. The decline in dissolved oxygen that is simply associated with lower solubility of the gas in warmer water will not reduce pH; but by far the greater fraction of the changes now being observed is from reduced ventilation/increased respiration and this is necessarily accompanied by an increase in dissolved CO_2 (and hence a further reduction in pH) in the proportions established by the well-known Redfield ratio as in:

$$(CH_2O)1_06(NH_3)1_6(H_3PO_4) + 138\,O_2$$
$$\leftrightarrow 106\,CO_2 + 16\,NO_{3-} + HPO_4^{2-} + 122\,H_2O + 18\,H^+ \quad (2)$$

[7]   The addition from the decomposition reaction of respiratory CO_2 at depth is accompanied by changes in the oxidation state of the nitrogen species, and this will change alkalinity and reduce ocean buffering capacity [*Brewer and Goldman*, 1976], thus magnifying the pH change over addition of CO_2 alone (Figure 1).

[8]   3. The combustion of fossil fuels results not only in CO_2 emissions, but in the deposition of 0.8 Tmol/yr reactive sulfur and 2.7 Tmol/yr nitrogen primarily to coastal oceans. These atmospheric additions of strong acids change ocean alkalinity and pH, and while there are offsetting reactions the net effect is acidification [*Doney et al.*, 2007]. Ship emissions are a significant component of this and are directly linked to oceanic deposition of acidic species [*Corbett and Fischbeck*, 1997].

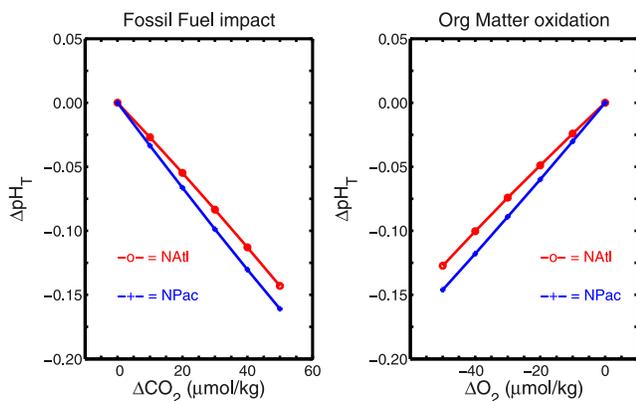[1]Monterey Bay Aquarium Research Institute, Moss Landing, California USA.

Figure 1. Predicted pH shifts (on the total pH scale) resulting from the invasion of fossil fuel derived carbon dioxide from the atmosphere (left panel) or from increased in situ respiration due to the slowing of oceanic ventilation allowing more time for the bacterial oxidation of organic matter (right panel) for two representative sites. The North Atlantic water sample is from a depth of 595 m while the North Pacific water sample is from 841 m. The greater impact per mole (CO_2 addition or O_2 consumption) in the Pacific Ocean reflects the greater preformed CO_2 concentration in this older water mass reducing the natural buffer capacity, making it more sensitive to further additions.

[9] The summation of the above processes leads to the conclusion that predictions of long term pH changes of sea water based upon the fossil fuel CO_2 signal alone [*Brewer*, 1997; *Caldeira and Wickett*, 2003], large though they may be, are likely significant underestimates. Thus waters in the upper ocean are now undergoing an extraordinary transition in their fundamental chemical state and at a rate not seen on Earth for millions of years, and the effects are being felt not only in biological impacts but also on basic geophysical properties including ocean acoustics.

2. Ocean Acoustics and Dependence on Ocean Chemistry

[10] Acoustic relaxations occur due to pressure-dependent volume changes, such as with the $MgSO_4$ ion-pair relaxation where an OH^- group poised between Mg and SO_4 ions is displaced by a high-frequency (10–1000 kHz) sound wave [*Eigen and Tamm*, 1962]. Early field observations of an apparent pH dependence of low-frequency sound absorption in seawater around 1 kHz [*Thorp*, 1965] were followed by laboratory studies which identified boric acid species as the primary cause [*Yeager et al.*, 1973]. The use of positively-correlated pH dependent terms based upon these results is now fully accepted and embedded in all modern calculations of sound absorptivity [*Francois and Garrison*, 1982].

[11] While ocean sound absorption can be successfully calculated based on empirical correlations, there does appear to be some uncertainty over the exact mechanism of the chemical relaxation involved, and the chemical description of the relaxation process has been described in various

ways. The "boric acid" relaxation in seawater is used to describe the chemical relaxation which involves complex coupled $B(OH)_3/B(OH)_4^-$ and HCO_3^-/CO_3^{2-} equilibria with ion-pairing. *Mellen et al.* [1981] proposed the following coupled exchange reaction:

$$CO_3^{2-} + B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + HCO_3^- \qquad (3)$$
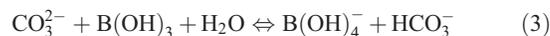
with the caveat that this could represent an approximation of a more complicated process. *Zeebe et al.* [2001] concluded that equation 3 best represented acid-base coupling in the boric acid and carbonic acid systems with minimal, if any, effect from Ca^{2+}. However, sound absorption was too small using the above mechanism to explain sea water measurements; the addition of Ca^{2+} ion-pairing was required [*Mellen et al.*, 1981]. A complex four-state exchange mechanism was introduced to account for the coupled systems with ion-pairing [*Mellen et al.*, 1983]. Further work is needed to full understand the role of Ca^{2+} ions in sea water sound absorption.

[12] There is one additional piece of emerging geochemical complexity. *Fisher* [1979] presented evidence from field data of a third chemical relaxation term at 3 kHz. From the work of *Mellen et al.* [1979], the most probable explanation is the existence of relaxation associated directly with the dissolved CO_2 system, but *Fisher* [1979] expressed uncertainty as to whether the relaxation involved $MgCO_3$ or $Mg(HCO_3)^+$. Both occur in similar amounts in spite of the 10-fold excess of HCO_3^- due to the very strong pairing of the CO_3^{2-} ion. But the evolution of the geochemical signals will evolve along different paths as ocean acidification proceeds: the HCO_3^- terms will slightly increase and the CO_3^{2-} terms will strongly decrease. Thus the trend in the acoustic presence of the small third relaxation term is still not well known, but the overall picture of declining sound absorption due to changes in ocean chemical composition is very clear.

3. Results

[13] Figure 1 shows the impact in terms of decreased pH of the addition of fossil fuel CO_2 and the in situ generation of CO_2 from the bacterial oxidation of organic matter on two representative seawater samples. These samples, selected near the oxygen minimum at each station to emphasize the impact of enhanced bacterial respiration of changing ocean pH, were from a North Atlantic station (39.887 N 52.359 W at 595 m depth) and a North Pacific station (40.674 N 152.022 W at 841 m depth). Because the bacterial oxidation of organic matter both reduces alkalinity and increases total CO_2, the impact of one mole of O_2 consumption is nearly the same (88.9% and 90.7%) in terms of pH reduction as the addition of a mole of CO_2 even though it produces (equation 2) only 76.8% of the amount of CO_2. The greater impact per mole, whether from CO_2 addition or O_2 consumption at the Pacific Ocean site reflects the greater initial CO_2 concentration in this older water mass. This higher total CO_2 concentration reduces the natural buffer capacity of the water making the pH change more sensitive to further additions of CO_2 or changes in alkalinity.
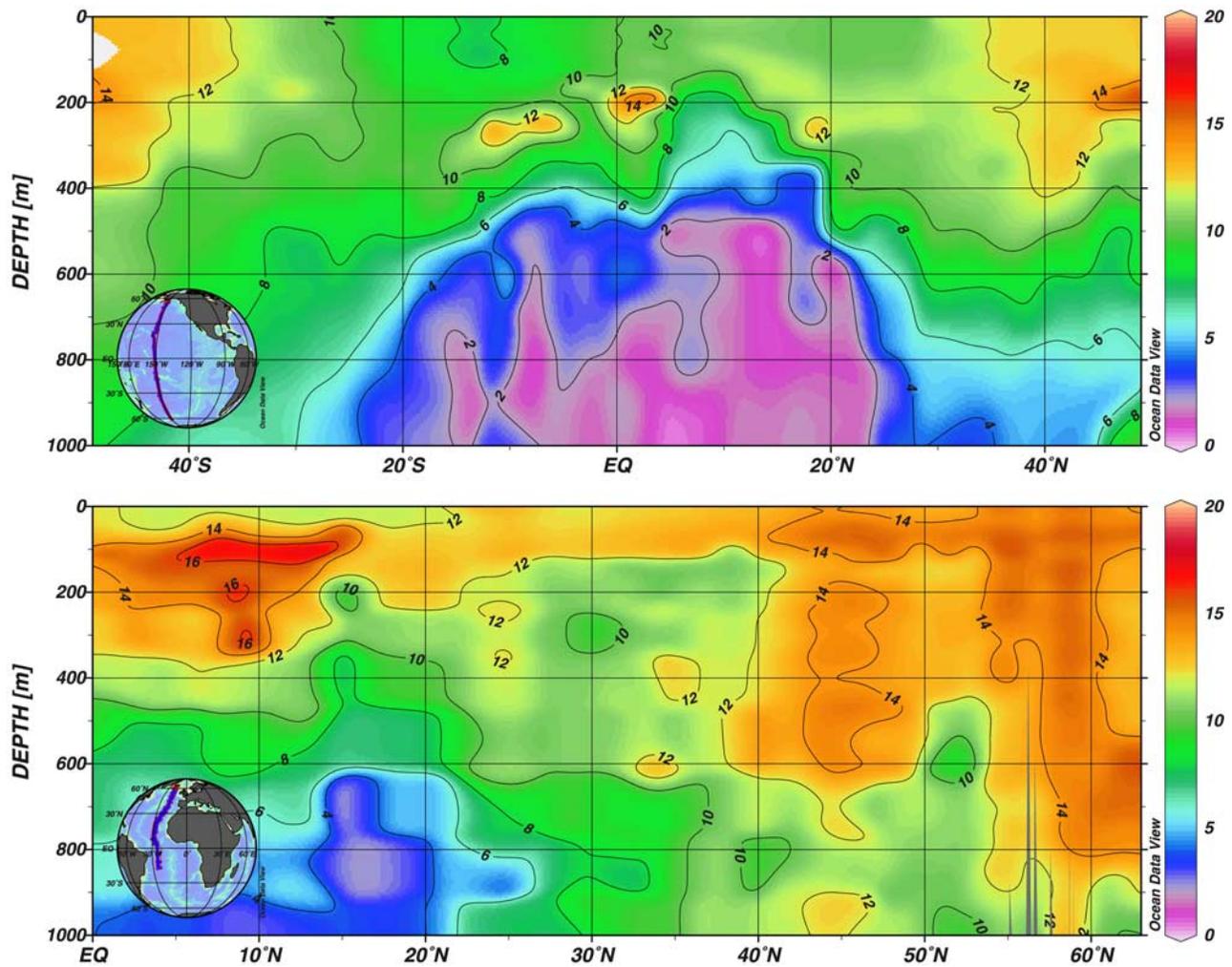
Figure 2. Calculated percent change in sound absorption at 0.44 kHz from the change in pH resulting from the fossil fuel CO_2 invasion for meridional sections in the Pacific (upper panel) and Atlantic (lower panel) oceans. Oceanic data from the GLODAP bottle dataset [*Key et al.*, 2004; *Sabine et al.*, 2005].

3.1. Changes in Low-Frequency Sound Absorption Since the Industrial Revolution

[14] Low-frequency ambient noise in the ocean comes from both natural and anthropogenic sources [*National Research Council of the National Academies*, 1994, 2003, 2005]. The dominant natural source is wind-driven surface waves from 0.001 to 10 kHz. Man-made activities increased contribution is largely due to shipping from 0.01 to 1.0 kHz. However, other sources such as military and industrial activities create sound waves across the entire low-frequency spectra.

[15] To determine the effect to date CO_2 invasion has had on low-frequency ocean noise, we first need to determine the amount of anthropogenic CO_2 already absorbed. This estimated anthropogenic CO_2 signal is available in the GLODAP bottle dataset using an approach pioneered by *Brewer* [1978] and *Chen and Millero* [1979] and later refined by *Gruber et al.* [1996]. Knowledge of the anthropogenic CO_2 input allows for the pre-Industrial total CO_2 to be calculated and, combined with total alkalinity, pH and sound absorptivity at each location was determined.

[16] Shallow waters are of the most interest when considering the effect of anthropogenic noise on marine life and are also the first affected by atmospheric changes. At water depths up to 1000 m, Figure 2 shows the percent decrease in α at 0.44 kHz from pre-Industrial Revolution until the 1990s for meridional sections of the Atlantic and Pacific Oceans. In parts of the north Atlantic, low-frequency absorptivity has decreased over 15%, with a greater than 10% decrease common above 400 m in both the Pacific and Atlantic. It should be noted that for these calculations total alkalinity was assumed constant, ignoring inputs such as acidic ship emissions, and represent a conservative estimate on changes to date.

[17] Increases in ambient low-frequency ocean noise have already been reported, attributed largely due to human activities such as shipping, however not exclusively. *Andrew et al.* [2002] reported up to a 9 dB increase since the 1960s off Point Sur, California from 0.1–0.4 kHz, a frequency range dominated by surface winds. With no large changes in average surface winds over time, the cause of this increase is unknown. As shown, sound absorption has
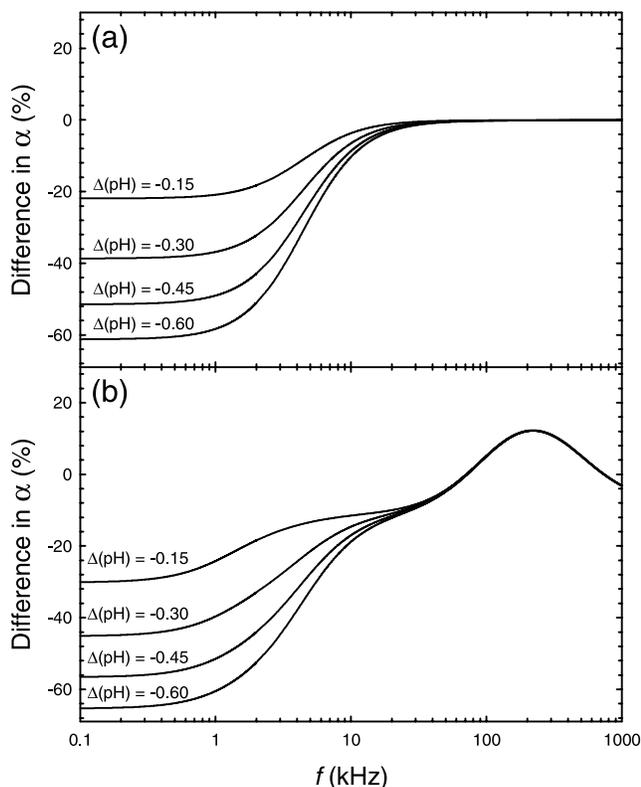
Figure 3. Percent difference in sound absorptivity in seawater between 0.01 to 1000 kHz for (a) a decrease in pH from 0.15 to 0.6 and (b) lower pH accompanied with a 3°C increase (initial conditions: S = 35, T = 12°C, pH = 8.1, D = 0.05 m).

already decreased due to pH changes and is likely already contributing to increased ambient noise levels.

3.2. Future Scenarios for Changing Ocean Acoustics

[18] With changes already exceeding 10% in the low frequency range, it is inevitable that much larger changes are to be expected. Beginning at a representative modern ocean pH of 8.1 (12°C, S = 35, D = 0.05 m), four pH perturbations were applied in a range expected to be observed over the next century. Below 1 kHz, even the highly conservative decrease of 0.15 pH units reduced α by over 20% (Figure 3).

[19] Growing atmospheric CO_2 concentration has also contributed to increased heat flux at the sea surface causing the World's oceans to warm. Temperature changes have a smaller effect than pH but also contribute to decreased sound absorption in the lower frequency range. As shown in Figure 3b, a moderate temperature increase of 3°C decreases α by a further 5–10%. This has the opposite effect at higher frequencies with greater than 10% attenuation around 200 kHz. A very realistic pH change of −0.3 [*Caldeira and Wickett*, 2003] accompanied with warming will lead to sound absorption below 1 kHz being reduced by almost half of current values.

4. Concluding Remarks

[20] The changes in ocean CO_2/pH status described here are well established, and so too is the pH dependence of the

absorption of sound within the appropriate frequency range. Thus the conclusion that sound absorption in the ocean will be reduced and that ambient noise levels will rise should not be surprising, although the scale of the change has been unanticipated. The challenge of observing these trends is real and basin scale integration from hydrographic casts sparsely sampled in space and time is notoriously difficult. But acoustic signals do offer the capability of sampling large oceanic regions [*Guoliang and Worcester*, 1989] and trends in well defined basins where the combined effects of reduced ventilation and fossil fuel CO_2 invasion are ongoing such as in the Japan Sea [*Gamo*, 1999; *Chen et al.*, 1999; *Jenkins*, 2008] may be possible and would be greatly aided by the use of modern cabled installations. It remains to be seen how marine mammals will adapt to an ocean increasingly transparent to sound at low frequencies.

5. Methods and Data

[21] Data for the pH calculations and ocean sections were taken from the GLODAP Atlas available at http://cdiac.ornl. gov/oceans/glodap/Glodap_home.htm [*Key et al.*, 2004; *Sabine et al.*, 2005]. The ocean sections were plotted using Ocean Data View (Schlitzer, 2008, available at http://odv. awi.de). Calculated pH changes due to the addition of fossil fuel CO_2 or the in situ formation of CO_2 and reduced alkalinity from the bacterial oxidation of organic matter were performed using CO2SYS [*Lewis and Wallace*, 1998] on the Total pH scale using CO_2 system constants from *Mehrbach et al.* [1973] as re-fit by *Dickson and Millero* [1987]. Ocean pH sections were computed for both pre-industrial and current (mid 1990s) conditions using the built-in pH function from the prevailing total CO_2 and alkalinity fields. For simplicity, total alkalinity was assumed to be invariant between the two cases since the impact of changing ocean circulation is just now being detected. The total CO_2 fields for the pre-industrial sections were computed by subtracting the anthropogenic CO_2 field from the prevailing total CO_2 field. Sound adsorption was calculated based on the equation provided by *Francois and Garrison* [1982].

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