GEOPHYSICAL RESEARCH LETTERS, VOL. 38, L13602, doi:10.1029/2011GL047720, 2011

Impacts of anthropogenic SO_x, NO_x and NH_3 on acidification of coastal waters and shipping lanes

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Received 13 April 2011; revised 22 May 2011; accepted 24 May 2011; published 7 July 2011.

[1] The acidification of the ocean by anthropogenic CO_2 absorbed from the atmosphere is now well-recognized and is considered to have lowered surface ocean pH by 0.1 since the mid-18th century. Future acidification may lead to undersaturation of $CaCO_3$ making growth of calcifying organisms difficult. However, other anthropogenic gases also have the potential to alter ocean pH and CO_2 chemistry, specifically SO_x and NO_x and NH_3. We demonstrate using a simple chemical model that in coastal water regions with high atmospheric inputs of these gases, their pH reduction is almost completely canceled out by buffering reactions involving seawater HCO_3^- and CO_3^{2-} ions. However, a consequence of this buffering is a significant decrease in the uptake of anthropogenic CO_2 by the atmosphere in these areas. **Citation:** Hunter, K. A., et al. (2011), Impacts of anthropogenic SO_x, NO_x and NH_3 on acidification of coastal waters and shipping lanes, *Geophys. Res. Lett.*, *38*, L13602, doi:10.1029/2011GL047720.

1. Introduction

[2] There is considerable concern about the effects of anthropogenic CO_2 absorbed by the ocean on its carbonate chemistry, and associated pH-dependent processes, collectively termed *ocean acidification* (OA) [*Caldeira and Berner*, 1999; *Doney et al.*, 2009; *Orr et al.*, 2005; *The Royal Society*, 2005]. This process is independent of human-derived global warming, but shares a common cause. A number of potential effects of OA are recognized, including making calcification of marine organisms more difficult, and altering the availability of CO_2 for metabolism, with resultant ecosystem changes [*The Royal Society*, 2005]. However, as recently pointed out by *Doney et al.* [2007] other anthropogenic gases can also alter ocean pH by absorption from the atmosphere, specifically oxides of sulfur and nitrogen (which enter the ocean mainly after oxidation to H_2SO_4 and HNO_3 respectively), and ammonia.

[3] *Doney et al.* [2007] presented a detailed analysis of the impact of these gases on the pH of the global surface ocean. Their approach comprised a 3D circulation model of the ocean combined with estimated regional air-to-sea fluxes of the relevant species. They found that the anthropogenic alkalinity flux is negative (becoming more acidic) in temperate regions of the North Atlantic that are dominated by fossil fuel sources of SO_2 and NO_x but that the flux is positive (becoming more alkaline) in the tropics because of a dominance of NH_3 input. The latter position is reversed if a substantial portion of the ammonia undergoes nitrification. On a global scale, the authors concluded that the alterations in surface water chemistry from anthropogenic nitrogen and sulfur input are rather small, only a few percent at most of those caused by the uptake of anthropogenic CO_2. However, they did conclude that more substantial impacts might be expected in coastal waters. Here we examine this possibility in more detail.

[4] Recently, measurements of pH and chemical compositions of rainfall at Bermuda have confirmed that in this region of the subtropical North Atlantic the contribution to OA from sulfur and nitrogen gases is at most 2% of that caused by anthropogenic CO_2 [*Bates and Peters*, 2007]. While this agrees with the predictions of the global model [*Doney et al.*, 2007], Bermuda is not a heavily impacted region and there appears to be no comparable analysis made for coastal waters or shipping lanes where the impacts of sulfur and nitrogen gases are expected to be greater. It is known that the global distribution of shipping density correlates well with emissions of various pollutants derived from ship exhausts, including SO_2, NO_x and particulates [*Endresen et al.*, 2005, 2003; *Streets et al.*, 1997, 2000]. Therefore, we have conducted a feasibility analysis on the likely relative impacts of CO_2 versus the other anthropogenic gases in such waters, focusing in more detail on these areas than done by Doney et al., as well as considering these impacts in a non-model based framework.

2. Theory

[5] The theory describing the chemical equilibria of CO_2 in seawater are well established, along with the methods for

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0094-8276/11/2011GL047720

characterizing the CO_2 system by measurement [*Dickson et al.*, 2007]. The uptake of CO_2 from the atmosphere is governed by the Henry's Law equilibrium

$$K'_H = \frac{[H_2CO_3^*]}{fCO_2} \tag{1}$$

where fCO_2 is the fugacity of CO_2 in the gas phase and K'_H is the Henry's law constant, which is a function of temperature and salinity. The quantity $[H_2CO_3^*]$ conventionally represents the stoichiometric concentration of undissociated CO_2, i.e., either CO_2(aq) or H_2CO_3. $[H_2CO_3^*]$ further dissociates to form bicarbonate and carbonate ions:

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+ \tag{2a}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{2b}$$

The corresponding equilibrium constant expressions for these two reactions are expressed in a conditional way, defined in terms of the concentrations of the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} and a suitable pH scale. Reactions (2a) and (2b) can be combined to produce a single equilibrium linking all 3 species of CO_2 which is useful for visualizing the fate of atmospheric CO_2 taken up by the ocean:

$$H_2CO_3^* + CO_3^{2-} \rightleftharpoons 2\ HCO_3^- \tag{3}$$

The equilibrium constant for (3) is large ($\approx 10^3$) indicating that anthropogenic CO_2 taken up by the ocean will react almost completely with residual CO_3^{2-} in seawater (provided sufficient CO_3^{2-} remains). While (3) does not explicitly depend on pH, the consequent increase in the ratio of HCO_3^- to CO_3^{2-} means that the pH of the seawater will decrease.

[6] Seawater alkalinity A_T is defined as the excess of weak bases present in seawater relative to the condition of pure CO_2 in water [*Dickson*, 1981, 1992]. As a result, the absorption of CO_2 by the ocean does not involve any initial change in A_T. However, the total dissolved inorganic carbon (DIC) of the water will increase with CO_2 uptake

$$DIC = \left[H_2CO_3^*\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right] \tag{4}$$

[7] Alkalinity changes will occur if CO_2 uptake subsequently gives rise to dissolution of $CaCO_3$. In principle this will happen when $[CO_3^{2-}]$ has decreased, through reaction (3) to the point when $CaCO_3$ becomes undersaturated. From this derives concerns about the effects of OA on calcifying organisms.

3. Sulfur and Nitrogen Gases

[8] Large amounts of SO_2 and NO_x are emitted by human activities, particularly fuel combustion. Shipping is particularly important because ships tend to use heavy bunker oils as fuel which can be rich in sulfur [*Tsyro and Berge*, 1997] relative to other fuels. In the atmosphere, these gases are rapidly converted to acid species (H_2SO_4, HNO_3) following emission and are the main forms in which these acidic gases eventually leave the atmosphere. The effects of these acids on freshwater systems and on rain composition are well known (acid rain). Significant quantities of these pollutants also make their way into the ocean, especially in coastal waters where shipping is usually more concentrated.

[9] The effects of H_2SO_4 and HNO_3 absorption by seawater are different from that of CO_2 in two essential respects. First, when CO_2 is absorbed by seawater, reaction (3) takes place and the DIC of seawater increases by the amount of CO_2 absorbed, with alkalinity remaining constant. By contrast, uptake of H_2SO_4 by seawater causes a decrease in alkalinity, with each mole of H_2SO_4 causing a decrease in A_T by 2 equivalents because of the diprotic nature of H_2SO_4. Essentially adding H_2SO_4 increases acidity in the ocean, which means a decrease in alkalinity. Similarly HNO_3 formed by oxidation of NO_x as a monoprotic strong acid causes a decrease in alkalinity of 1 equivalent per mole of HNO_3 absorbed.

[10] Second, on time scales of a few months to a year, these initial changes in pH and CO_2 chemistry brought about by the absorption of strong acid gases induce an increase in seawater pCO_2 with the result that CO_2 is vented to the atmosphere as the ocean-atmosphere system re-equilibrates [*Doney et al.*, 2007]. Figure 1a shows the calculated change in pH of seawater of typical composition after the absorption of CO_2, H_2SO_4 or HNO_3. Despite the fact that CO_2 and HNO_3 influence the speciation of CO_2 in seawater in fundamentally different ways (increasing DIC versus decreasing A_T) the consequent initial changes in pH are very similar. This is because HNO_3 is a strong acid, and will therefore participate in a reaction similar in nature to (3)

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^- \tag{5}$$

This gives rise to a smaller change in the CO_3^{2-} to HCO_3^- ratio than H_2CO_3, but this is enhanced by the fact that DIC does not increase. By contrast, the decrease in pH caused by H_2SO_4 is greater than the other two acids because of the diprotic nature of H_2SO_4.

[11] Figure 1a demonstrates that to decrease ocean pH by 0.1 requires approximately 30 μM of H_2SO_4 and almost twice as much of CO_2 or HNO_3. It would be very difficult to detect an increase in surface ocean sulfate of this magnitude because the background sulfate concentration in seawater is 1000 times greater (0.028 M). However, addition of 60 μM of nitrate would be highly significant in terms of this important micronutrient, and easily detectable. Anthropogenic CO_2 levels of up to 60 μM are observed in the present-day surface ocean [*Feely et al.*, 2004; *Sabine et al.*, 2004].

[12] A decrease in surface ocean pH by whatever form of acidification also leads to an increase in surface water CO_2 partial pressure pCO_2, which then acts to oppose further absorption of atmospheric CO_2 by decreasing the partial pressure gradient between ocean and atmosphere. Figure 1b shows the pCO_2 changes resulting from the initial acidification observed in Figure 1a. These results cannot be directly compared with the actual changes in atmospheric CO_2 except in a rough manner because the calculations have only been performed at one temperature. However, Figure 1b shows that a 100 ppmv increase in pCO_2 results from an increase in DIC of about 60 μM, and is consistent with the observed increase from 280 ppmv in 1750 to 390 ppmv at the present-day.

[13] As surface waters with this enhanced pCO_2 re-equilibrate with the atmosphere over time scales of a few months, the equilibrium pH increases again. The dotted

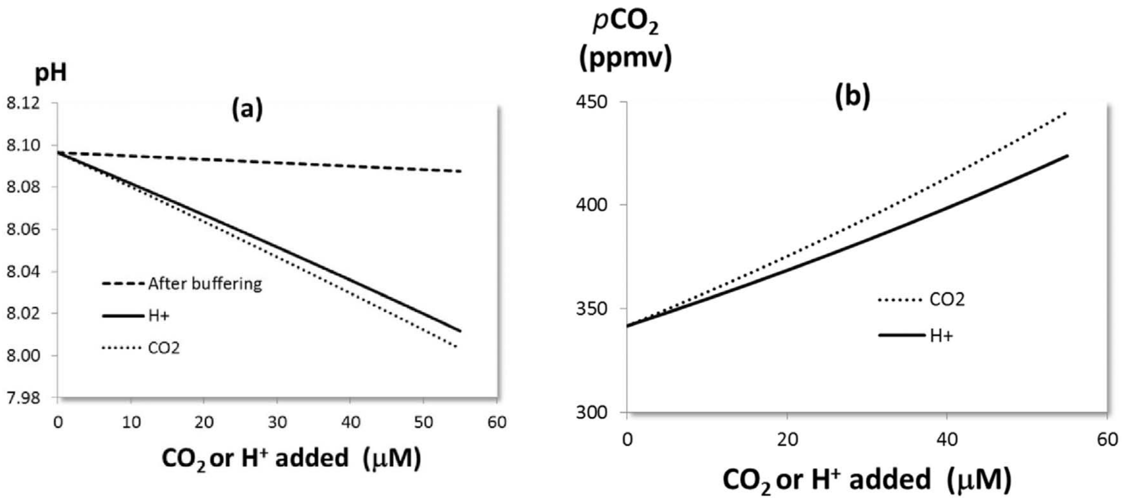

Figure 1. Calculated change in (a) pH and (b) $p\mathrm{CO_2}$ (ppmv) of seawater as a function of the concentrations of CO_2, H_2SO_4 or HNO_3 absorbed. Initial conditions DIC = 1960 μmol kg^{-1}, A_T = 2290 μmol kg^{-1}, S = 35, T = 25°C, pH on the total scale, CO_2 equilibrium constants of *Mehrbach et al.* [1973] as refit by *Dickson and Millero* [1987]. In Figures 1a and 1b, solid lines show the initial changes in pH and $p\mathrm{CO_2}$ after addition of strong acid H^+ while the dotted lines show the corresponding changes caused by CO_2 uptake. In Figure 1a the dashed line shows the final pH changes from H^+ addition after re-equilibration of CO_2 with the atmosphere. Software used SWCO2 (available at http://neon.otago.ac.nz/swco2).

curves in Figure 1a show that after allowance is made for re-equilibration, the final pH decrease induced by the strong acid gases is essentially negligible compared to that arising from anthropogenic CO_2, as indicated originally [*Doney et al.*, 2007].

4. Effects of Ammonia Input

[14] The input of nitrogen species to the ocean is not limited to HNO_3 formed by atmospheric oxidation of NO_x. Ammonia is also found in the atmosphere. Dry deposition of NH_3 will increase A_T, while wet deposition of NH_4^+ has the same effect because the formation of NH_4^+ in rainwater involves formation of OH^- as a counter-ion [*Doney et al.*, 2007]. Thus in both cases, the oceanic uptake of ammonia results in an *increase* in A_T. However, subsequent nitrification can change the impact of these $NH_3 + NH_4^+$ fluxes

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O \qquad (6)$$

This reverses the effect of ammonia input to a decrease in A_T. After complete nitrification of deposited ammonia, the net effect is the same as that of an equivalent amount of HNO_3 formed from NO_x [*Doney et al.*, 2007].

[15] An additional factor whereby atmospheric processes can alter surface ocean pH is through the prior dissolution of atmospheric limestone dusts by acidic rainwater. This process increases ocean A_T by an amount equivalent to twice the flux of Ca^{2+} entering the ocean, assuming most Ca^{2+} in rainwater derives from $CaCO_3$ dissolution [*Doney et al.*, 2007].

5. Model for Comparing pH Effects

[16] We now describe a simple model for comparing the effects of sulfur and nitrogen gases on surface ocean pH with that of anthropogenic CO_2. The model is based on the principles used in the global assessment [*Doney et al.*, 2007]. We apply this model to three case studies of coastal waters for which we can make reasonable estimates of the fluxes to the ocean of sulfur and nitrogen gases.

[17] The effect of anthropogenic CO_2 on pH was calculated by using estimates of A_T for each case (together with salinity S and temperature T) to calculate pH and CO_2 speciation for an initial condition of equilibrium with an atmosphere having a $p\mathrm{CO_2}$ of 390 ppmv. Next, the $p\mathrm{CO_2}$ was augmented by +1.7 ppmv which is similar to the annual increase in $p\mathrm{CO_2}$ as recorded at Mauna Loa, Hawaii over the last few decades (http://co2now.org). The pH and CO_2 speciation were then re-computed to obtain the annual pH change resulting from additional CO_2 uptake. The CO_2 speciation calculations were carried out using the SWCO2 software package (available at http://neon.otago.ac.nz/swco2).

[18] Next, to assess the impacts of H_2SO_4, HNO_3 and NH_3 on pH, the alkalinity of the seawater was adjusted to take account of the effects of these 3 species (both with and without nitrification):

$$A_T^{adj} = A_T - 2 \cdot f[H_2SO_4] - f[HNO_3] + f[NH_3](\text{initial}) \qquad (7a)$$

$$A_T^{adj} = A_T - 2 \cdot f[H_2SO_4] - f[HNO_3] - f[NH_3](\text{after nitrification}) \qquad (7b)$$

where f[X] is the annual increase in the concentration of X in the affected water mass as a result of uptake from the atmosphere. The adjusted A_T was then combined with the final DIC value obtained from the CO_2 calculation to re-calculate the new pH. By making these calculations in steps, i.e., setting some sulfur and nitrogen terms to zero, it was possible to assess the effects of the individual species. We calculated the f[X] terms by combining estimates of the atmospheric deposition rate to the sea surface (mol m^{-2}yr^{-1}) of the anthropogenic sulfur and nitrogen gases with a knowledge of the depth

Table 1. Input Parameters Used for Each Case Study

	Region		
	North Sea	Baltic Sea	South China Sea
Mean depth (m)	36	55	100 (mixed layer)
Salinity (psu)	34	7	35
Temperature (°C)	12	10	25
A_T (μmol kg^{-1})	2260	910	1995
H_2SO_4 flux (mmol m^{-2} yr^{-1})	24	2.4	50
HNO_3 flux (mmol m^{-2} yr^{-1})	48	4.8	40
NH_3 + NH_4^+ flux (mmol m^{-2} yr^{-1})	48	4.6	80
$f[H_2SO_4]$ (μM yr^{-1})	0.67	0.043	0.50
$f[HNO_3]$ (μM yr^{-1})	1.33	0.086	0.40
$f[NH_3]$ (μM yr^{-1})	1.33	0.086	0.80
f = ratio A_T to CO_2 fluxes (Figure 2)	0.91	0.25	0.10

of the water mass affected. This represents a worse case scenario in which the rate of flushing of the water mass is much smaller than the increase in [X].

[19] The results of this calculation represent the initial pH decrease caused by the sulfur and nitrogen gases before re-equilibration with the atmosphere. In the next calculation step, the CO_2 composition of the seawater with altered alkalinity was then re-adjusted to be in equilibrium with the current atmospheric pCO_2 for each time step in order to restore equilibrium.

[20] We chose 3 case studies (Table 1). The first is the southern North Sea region between the U.K. and France, Belgium and the Netherlands, which is an area of very dense shipping. Estimates of the oxidized sulfur and nitrogen fluxes into this region in were taken from the EMEP report for 1997 [*Tsyro and Berge*, 1997]. For oxidized sulfur, a flux of 24 mol S m^{-2} yr^{-1} was assumed, which is equivalent to an acidity flux of 48 mol m^{-2} yr^{-1}, similar to the value of 30 mol m^{-2} yr^{-1} assumed by *Doney et al.* [2007] for average coastal waters. We also assumed the average water depth in this region to be 36 m.

[21] The second case is the Baltic Sea which is a region of low surface water salinity and A_T, making it potentially more susceptible to acidic gases. The data reported by EMEP [*Tsyro and Berge*, 1997] indicates that the likely H_2SO_4 deposition rate for this region is about a factor of 10 lower than the North Sea case. Based on published bathymetric data, we chose an average depth of affected water as 55 m.

[22] HNO_3 fluxes for these two regions were estimated from the same data source [*Tsyro and Berge*, 1997]. However, we could find no data for NH_3 inputs. Therefore, we estimated these by assuming that each is twice the corresponding H_2SO_4 flux (on a molar basis). *Doney et al.* [2007, Table 1] report this ratio for the anthropogenic coastal water fluxes, while a value of 2.5 can be calculated from data presented by *Endresen et al.* [2005].

[23] The third case study we chose is the South China Sea, for which measured and model-based estimates of the deposition fluxes of all 3 anthropogenic species are available [*Wang et al.*, 2008]. In this case the separate wet and dry fluxes for SO_4^{2-}, NO_3^- and NH_4^+ were combined together. For the South China Sea we chose an average mixed layer depth of 100 m as the depth of water affected by the annual input of sulfur and nitrogen. It should be noted that atmospheric S and N inputs into the North and Baltic Seas have been declining because of air-quality controls, whereas this is probably not the case yet for the South China Sea.

[24] The input data used for the calculations are summarized in Table 1. Salinity S and temperature T were estimated from hydrographic data, although values are quite variable in the Baltic Sea. However, test calculations showed that the final results are rather insensitive to these parameters. For the North Sea and South China Sea, alkalinity A_T was estimated from S and T using reported algorithms for surface waters [*Lee et al.*, 2006]. For the Baltic Sea, we adopted a value of 900 μmol kg^{-1} based on measured values. Because of the way our model is initialized to a fixed pCO_2, it is not particularly sensitive to the actual A_T value chosen in that while the absolute pH may not be accurate, the changes in pH after a small increment of CO_2 are not strongly affected.

6. Results and Discussion

[25] The results of our model calculations are presented in Table 2. The results show that the annual decreases in pH resulting from anthropogenic CO_2 are quite similar in all three regions, both before and after re-equilibration. They are slightly larger in magnitude for the Baltic Sea because of the lower A_T and DIC in these waters. It is interesting that all three sites behave in very similar ways. While the North Sea and South China Sea regions are ones of very intense shipping activity [*Streets et al.*, 1997, 2000], and have correspondingly large atmospheric fluxes of sulfur and nitrogen, the effects on the Baltic Sea are comparable because of the much lower DIC and C_T of the latter system. This also underlines the fact (which can be demonstrated using the model) that the effects on pH are not particularly sensitive to S, T or A_T (when the system is at equilibrium with the atmosphere).

[26] While initial pH changes are comparable to measured or calculated pH changes at several oceanic sites, including BATS and HOTS resulting from CO_2 uptake [*Bates et al.*, 1996; *Byrne et al.*, 2010] the pH changes after re-equilibration induced by the sulfur and nitrogen gases in addition to anthropogenic CO_2 are negligibly small. What this means is that the strong acid gases have effectively shut down much of the ocean uptake of anthropogenic CO_2. This is demonstrated graphically in Figure 2 which shows the change in seawater DIC resulting from the net uptake of atmospheric CO_2 in the presence of acidic gases at different ratios f of the fluxes of strong acid and CO_2 respectively after re-equilibration. In this

Table 2. Annual pH Changes, Total H^+ Scale, Resulting From Absorption of Different Gaseous Species in the Three Case Studies[a]

	North Sea	Baltic Sea	South China Sea
CO_2 only	−0.00164	−0.00182	−0.00153
CO_2 +SO_x	−0.00306	−0.00228	−0.00230
Buffered	−0.00012	−0.00002	−0.00008
CO_2 +SO_x +NO_x	−0.00583	−0.00322	−0.00291
Buffered	−0.00034	−0.00006	−0.00014
CO_2 +SO_x +NO_x +NH_3	−0.00306	−0.00228	−0.00169
Buffered	−0.00012	−0.00002	−0.00002
After nitrification	−0.00861	−0.00415	−0.00414
Buffered	−0.00056	−0.00010	−0.00027

[a] Both the initial pH change and the change after buffering by re-equilibration with the atmosphere are shown.

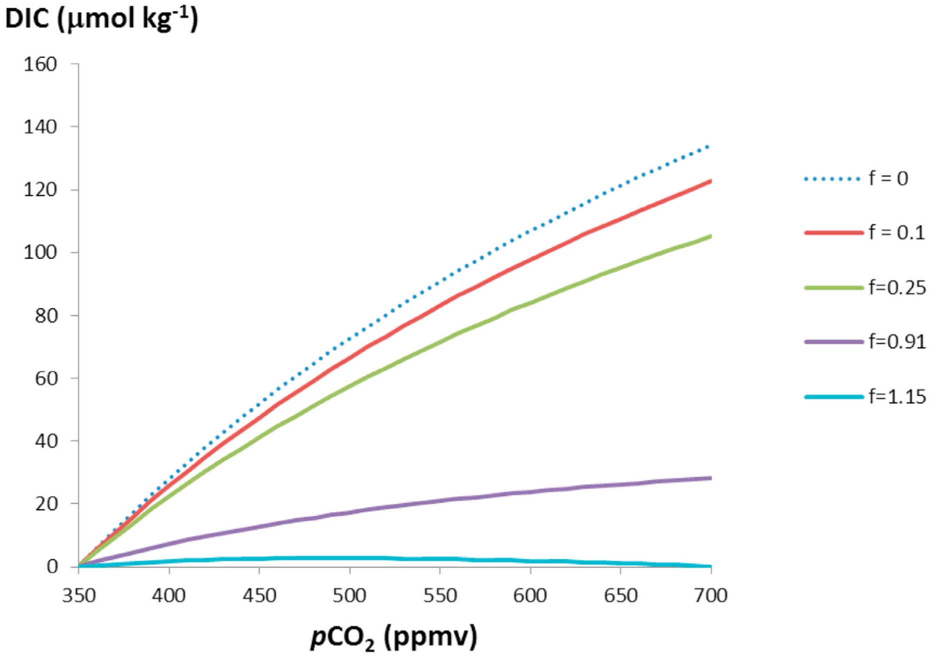

Figure 2. Calculated change in surface water DIC after re-equilibration for a combined flux of CO_2 and strong acid gases having different ratios f of strong acid to CO_2 flux. Same calculation conditions as Figure 1.

analysis, sulfur and nitrogen acids were combined as a single stoichiometric source of strong acid. The graph shows specific cases $f = 0.1$ (South China Sea), 0.25 (Baltic Sea) and 0.91 (North Sea) compared to $f = 0$ (CO_2 only). As the ratio of strong acid flux increases above $f = 0.1$, the resultant equilibrium DIC is significantly decreased. At a ratio $f = 1.15$, the system no longer takes up excess CO_2, i.e., the effects of the strong acid gases is such that the surface water maintains equilibrium with the increasing atmospheric pCO_2 without any net atmosphere-ocean exchange.

[27] This analysis, while obviously simplistic, shows that the effects of atmospheric inputs of strong acid gases, at fluxes likely to be encountered in coastal waters, is to eliminate the pH reduction which would normally accompany ocean acidification by CO_2, but at the expense of the important contribution of surface waters as a sink for anthropogenic CO_2. It should be noted that our analysis has focused purely on the effects of atmospheric inputs of N and S on the CO_2 system in coastal waters and has not taken into account other processes that may affect this. In particular, *Thomas et al.* [2009] have shown that anaerobic nitrate and sulphate reduction in shelf sediments stimulated by inputs of land-derived organic matter may be important sources of alkalinity which will offset the acidifying effects described here.

[28] **Acknowledgments.** This paper resulted from the deliberations of GESAMP Working Group 38, The Atmospheric Input of Chemicals to the Ocean. We thank the Global Atmosphere Watch (GAW) and the World Weather Research Programme (WWRP) of the World Meteorological Organization (WMO), the International Maritime Organization (IMO), the ICSU Scientific Committee on Oceanic Research (SCOR), the Swedish International Development Agency (SIDA), the University of Arizona, and the European Commission Joint Research Centre for support of this work. We thank both reviewers for very helpful comments.

[29] The Editor thanks Scott C. Doney and an anonymous reviewer for their assistance in evaluating this paper.

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