GEOPHYSICAL RESEARCH LETTERS, VOL. 40, 2731–2736, doi:10.1002/grl.50521, 2013

Shipping contributes to ocean acidification

Ida-Maja Hassellöv,[1] David R. Turner,[2] Axel Lauer,[3,4] and James J. Corbett[5]

Received 26 March 2013; revised 26 April 2013; accepted 29 April 2013; published 6 June 2013.

[1] The potential effect on surface water pH of emissions of SO_X and NO_X from global ship routes is assessed. The results indicate that regional pH reductions of the same order of magnitude as the CO_2-driven acidification can occur in heavily trafficked waters. These findings have important consequences for ocean chemistry, since the sulfuric and nitric acids formed are strong acids in contrast to the weak carbonic acid formed by dissolution of CO_2. Our results also provide background for discussion of expanded controls to mitigate acidification due to these shipping emissions. **Citation:** Hassellöv, I.-M., D. R. Turner, A. Lauer, and J. J. Corbett (2013), Shipping contributes to ocean acidification, *Geophys. Res. Lett.*, *40*, 2731–2736, doi:10.1002/grl.50521.

1. Introduction

1.1. Ocean Acidification

[2] Rising concentration of CO_2 in the atmosphere results in a slow acidification of the surface ocean, also known as "the other CO_2 problem" [*Doney et al.*, 2009]. Anthropogenic acidification from emissions of sulfur and nitrogen oxides (SO_X, NO_X) has been understood in terms of acidification and eutrophication of land and freshwater ecosystems [*Greaver et al.*, 2012] and in terms of atmospheric aerosol effects on regional and global climate, but deposition also occurs over ocean surface water in the form of sulfuric and nitric acids [*Brydges and Wilson*, 1990; *Dhondt et al.*, 1994; *Kaufman and Chou*, 1993; *von Feilitzen and Lugner*, 1910].

1.2. Shipping as a Source of Acidification

[3] Since the late 1990s [*Corbett and Fischbeck*, 1997], international shipping has been recognized as a significant contributor of SO_X and NO_X to the atmosphere on local, regional, and global scales. Although identified as a limited contributor to coastal acidification [*Capaldo et al.*, 1999; *Endresen et al.*, 2003], the acidifying effects on the marine environment have generally been considered negligible due to the inherent buffering capacity of seawater [*Doney et al.*, 2007; *Hunter et al.*, 2011]. One reason for this perception is that proximal acidification impacts attributable to international shipping have not heretofore been considered explicitly with adequate spatial and temporal resolution.

[4] Sulfur oxides (SO_X) are produced during combustion of sulfur-containing fuels, and nitrogen oxides (NO_X) form primarily from nitrogen in the air during high-temperature/high-pressure combustion. While NO_X formation depends mainly on the combustion temperature, the amount of SO_X produced is directly related to the sulfur content of the fuel, recently subject to international regulation through the establishment of Emission Control Areas (ECA) (Table 1). Table 2 shows the timetable for increasingly strict control of the maximum sulfur content allowed in fuel [*International Maritime Organization (IMO)*, 1992]. For comparison, the corresponding limit for road transport in the European Union (EU) is 10 ppm (0.001%) as from January 2011 [*European Union (EU)*, 2009]. Presently, two alternatives can meet the ECA regulations: (a) switch to much more expensive low sulfur fuel or (b) use abatement technology that removes the SO_X from the exhausts. One promising technique is seawater scrubbing where the natural high solubility of SO_X in seawater and the natural high buffering capacity of seawater are utilized to eliminate the emission of acidifying SO_X to the atmosphere [*An and Nishida*, 2003; *Andreasen and Mayer*, 2007; *Wang et al.*, 2007].

[5] Recent studies have begun to focus on the potential contribution of total anthropogenic SO_X, NO_X, and ammonia to ocean acidification, assuming that deposited ammonia is also oxidized to nitric acid. A global modeling study concluded that the contribution of these gases is no more than a few percent [*Doney et al.*, 2007] but noted that the effects may be larger in coastal waters. A regional modeling study [*Hunter et al.*, 2011] concluded that input of sulfur and nitrogen gases would lead to reduced uptake of CO_2 and that the combined effect on pH would be small. However, both these studies considered relatively large sea areas on an annual basis and focused on the total anthropogenic gas production. In order to examine the effects of shipping-based emissions in more detail, we have modeled the resulting acidification on a 1° × 1° grid on a monthly basis.

[6] The aim of this work is to identify those oceanic areas where shipping-derived acidification can make a significant contribution to the total anthropogenic acidification. At the current state of knowledge, it is not possible to separate the contributions of CO_2 and strong acids to the observed acidification of the ocean. We therefore explicitly add ship-derived acids to the observed state of the surface ocean in order to provide a time-resolved and geospatial comparative estimate of expected contributions from shipping to ocean acidification.

2. Methods

[7] The input data are for the years 2000 and 2002, before the establishment of ECAs (Table 1). We have used monthly

---

[1] Department of Shipping and Marine Technology, Chalmers University of Technology, Gothenburg, Sweden.

[2] Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden.

[3] International Pacific Research Center, University of Hawaii, Honolulu, Hawaii, USA.

[4] Now at IASS Institute for Advanced Sustainability Studies, Potsdam, Germany.

[5] College of Earth, Ocean, and Environment, University of Delaware, Newark, Delaware, USA.

Corresponding author: D. R. Turner, Department of Chemistry and Molecular Biology, University of Gothenburg, SE-412 96, Gothenburg, Sweden. (davidt@chem.gu.se)

0094-8276/13/10.1002/grl.50521

Table 1. Establishment of Emission Control Areas (ECAs)

Area	Emission Control	Adopted	Date of Entry into Force	In Effect From
Baltic Sea	SO_X	26 Sep 1997	19 May 2005	19 May 2006
North Sea	SO_X	22 Jul 2005	22 Nov 2006	22 Nov 2007
North American	SO_X, NO_X, PM[a]	26 Mar 2010	1 Aug 2011	1 Aug 2012
United States Caribbean Sea	SO_X, NO_X, PM[a]	26 Jul 2011	1 Jan 2013	1 Jan 2014

[a] Particulate matter.

global surface water distributions, mapped on a 1° × 1° grid, of salinity [*Conkright et al*., 2002], temperature [*Conkright et al*., 2002], mixed layer depth [*Monterey and Levitus*, 1997], alkalinity [*Lee et al*., 2006], and carbon dioxide partial pressure for the year 2000 [*Takahashi et al*., 2009]. Monthly SO_X deposition rates resulting from shipping were obtained from model simulations with the global aerosol-climate model EMAC/MADE [*Jöckel et al*., 2006; *Lauer et al*., 2007; *Lauer et al*., 2009]. EMAC/MADE is a general circulation model that includes a detailed representation of aerosol microphysical processes, tropospheric NO_X-HO_X-CH_4-CO-O_3 chemistry and the sulfur cycle, as well as transport and removal (dry and wet deposition) of aerosol particles and trace gases. The aerosols are interactively coupled to the model's chemistry, cloud microphysics, and the radiation scheme. The impact of shipping on aerosols and the deposition rates of SO_X and NO_X is estimated by calculating differences between model simulations with and without ship emissions. The ship emission inventory used provides monthly mean emissions representative for the year 2002 [*Wang et al*., 2008]. The annual emission totals from shipping are 9.2 Tg for SO_2, 0.35 Tg for primary SO_4, and 16.4 Tg(NO_2) for NO_X.

[8] The additional acidification due to nitrogen gases was assumed to be proportional to the SO_X-derived acidification: for the gross emissions (Figure 1), the acidification due to NO_X and NH_4 was taken to be twice that of SO_X [*Hunter et al*., 2011], while for the shipping-based emissions, the acidification due to NO_X was taken to be equal to that of SO_X [*McLaren et al*., 2012]. The added protons are distributed evenly over the grid square down to the mixed layer depth, and the change in pH calculated. The pH change was calculated assuming that the total inorganic carbon remained constant, while the alkalinity was reduced by the added protons. Calculations were carried out over a period of 12 consecutive months beginning in January. The alkalinity reduction from January was carried over to February but reduced by dilution if the mixed layer depth deepened. This procedure was continued throughout the 12 month period in order to estimate the cumulative effects of acid deposition.

3. Results

[9] The largest effects of SO_X and NO_X input from shipping are seen in parts of the northern hemisphere, where ~85% of all shipping emissions [*Corbett et al*., 1999] coincide with seasonal stratification thus concentrating the acid emissions within a relatively shallow surface mixed layer. Figure 1 shows the calculated pH change for January and August: the significant coastal acidification shown for August then decreases during the autumn as mixing of surface and deeper waters occurs. Figure 2 shows corresponding calculations for the shipping-derived input of SO_X and NO_X. Several well-trafficked shipping routes are clearly visible in the August distribution, and seasonal coastal acidification in the range 0.0015–0.002 pH is observed. This is of the same order of magnitude as the annual surface water acidification in the open ocean due to increased atmospheric CO_2 [*Bates and Peters*, 2007; *Byrne et al*., 2010; *Dore et al*., 2009]. Figure 3 shows the August distributions in the North Atlantic and the North Pacific, where the largest pH effects are observed. The lack of data close to the coasts is due to the limitations of the global oceanographic atlases used (represented in white boundaries near continents). We can expect that pH changes close to the coasts may well be larger than those calculated in more open waters, particularly due to heavy shipping traffic in the vicinity of major ports, even if the contribution from continental runoff may increase relative to shipping.

4. Discussion

[10] The acidification contribution from international shipping is spatially nonuniform, but important for the global understanding of the pH changes in the surface ocean. This study suggests opportunities for improved understanding of the net contribution of human activity on ocean acidification: (i) to reduce uncertainties, (ii) to enhance comparability with regional models, and (iii) to properly include both natural changes (e.g., seasonality) and changes in shipping contributions (e.g., resulting from policy measures to take place over this decade).

4.1. Modeling Assumptions

[11] The modeling approach used here makes a number of implicit assumptions:

[12] 1. that the acid thus deposited is uniformly distributed over a mixed layer depth: this is reasonable for a monthly time step, particularly in the shallower mixed layers where significant acidification is calculated;

[13] 2. that this acid is retained within the grid square during a 12 month period: inclusion of horizontal advection processes could result in somewhat less focused hot spot areas;

[14] 3. that there is no re-equilibration of CO_2 with the atmosphere following the acidification: in the areas undersaturated in CO_2 (Figure 4, the majority of the most acidified grid squares), the effect would be to minimize the uptake of

Table 2. Present and Upcoming Fuel Oil Sulfur Limits[a] Inside and Outside ECAs

Outside an ECA	Inside an ECA
4.50% m/m prior to 1 Jan 2012	1.50% m/m prior to 1 Jul 2010
3.50% m/m on and after 1 Jan 2012	1.00% m/m on and after 1 Jul 2010
0.50% m/m on and after 1 Jan 2020[b]	0.10% m/m on and after 1 Jan 2015

[a] expressed as % sulfur by weight in the fuel.

[b] depending on the outcome of a review, to be concluded in 2018, as to the availability of the required fuel oil, this date could be deferred to 1 January 2025.

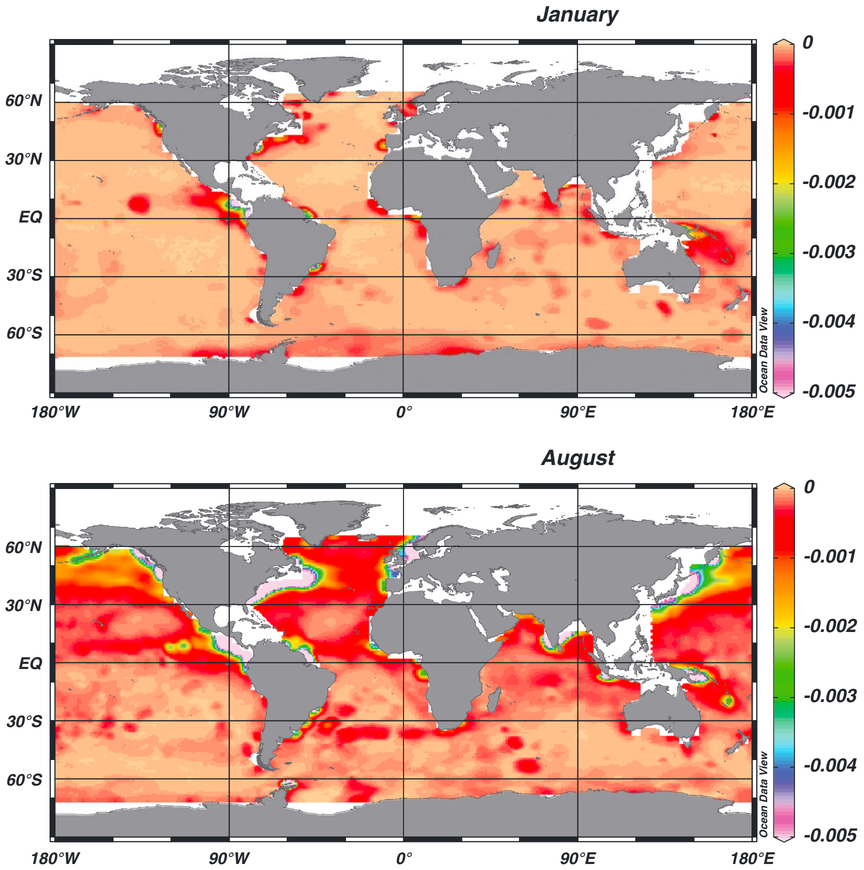

Figure 1. Calculated surface water pH changes arising from total inputs of SO_X, NO_X, and NH_4. Calculations begin with the month of January. It is assumed that these inputs are fully oxidized to sulfuric and nitric acids, respectively, within the monthly time step.

CO_2 in these grid squares, thus decreasing the effect of CO_2-driven acidification; in other areas, the acidification would result in outgassing of CO_2 as suggested in previous modeling exercises [*Doney et al.*, 2007; *Hunter et al.*, 2011].

[15] Since our alkalinity and pCO_2 input data are based on observations, they include the cumulative effects of previous acidification, which will be particularly significant in the hot spot areas. Taking these assumptions into account, we conclude that the location of the most acidified hot spot areas and the order of magnitude of the calculated acidification are sufficiently accurate to support our conclusions and recommendations.

4.2. Comparison With Previous Studies

[16] Two previous studies have calculated the acidification due to SO_X, NO_X, and NH_4: both studies have used the total anthropogenic emissions as source functions, so that they should be compared with Figure 1 rather than Figures 2 and 3, which use only the shipping-derived emissions.

[17] *Doney et al.* [2007], in a global model, calculated a maximum annual acidification of ca. 0.0004 pH. While our estimates of annual acidification show a strong spatial dependence (Figure 5), the global mean (0.00037) and median (0.00018) values are consistent with Doney's estimate.

[18] *Hunter et al.* [2011], in three regional models, calculated annual acidifications of 0.0014, 0.00046, and 0.0008 for the North Sea, Baltic Sea and South China Sea, respectively. Hunter et al. made the assumption that the surface water pCO_2 was in equilibrium with the atmosphere before acidification and then calculated the effect of CO_2 loss due to the acidification. Since we have used pCO_2 values based on observations, most of which are far from equilibrium with the atmosphere, we cannot make a meaningful comparison with the unrealistic "equilibrated values" of Hunter et al. Furthermore, our model lacks data for the Baltic and South China Seas but includes partial coverage of the North Sea (Figure 3). Our estimates give mean and median annual North Sea acidification of 0.0024 and 0.0018 pH, which, given the difference in coverage, compares well with Hunter et al.'s unequilibrated estimate of 0.0014 pH.

4.3. Significance

[19] The calculated near-coastal seasonal acidification of 0.0015–0.002 pH is without a doubt significant: deposition of shipping emissions not only matches the CO_2-driven acidification but also reduces the alkalinity of the water. Future studies of the impact of CO_2 on acidification in these areas can no longer ignore the spatial and seasonal components of strong acid acidification attributable to heavy shipping traffic. As the potential impact peak coincides with the seasonal activity peak of biological processes, such as plankton spring bloom or hatching of fish, potential effects on the ecosystem may spread on both temporal and spatial scales [*Halpern et al.*, 2008; *Heath*, 2008].

[20] The ECAs established by the IMO regulate sulfur emissions in some areas of the North Atlantic and North

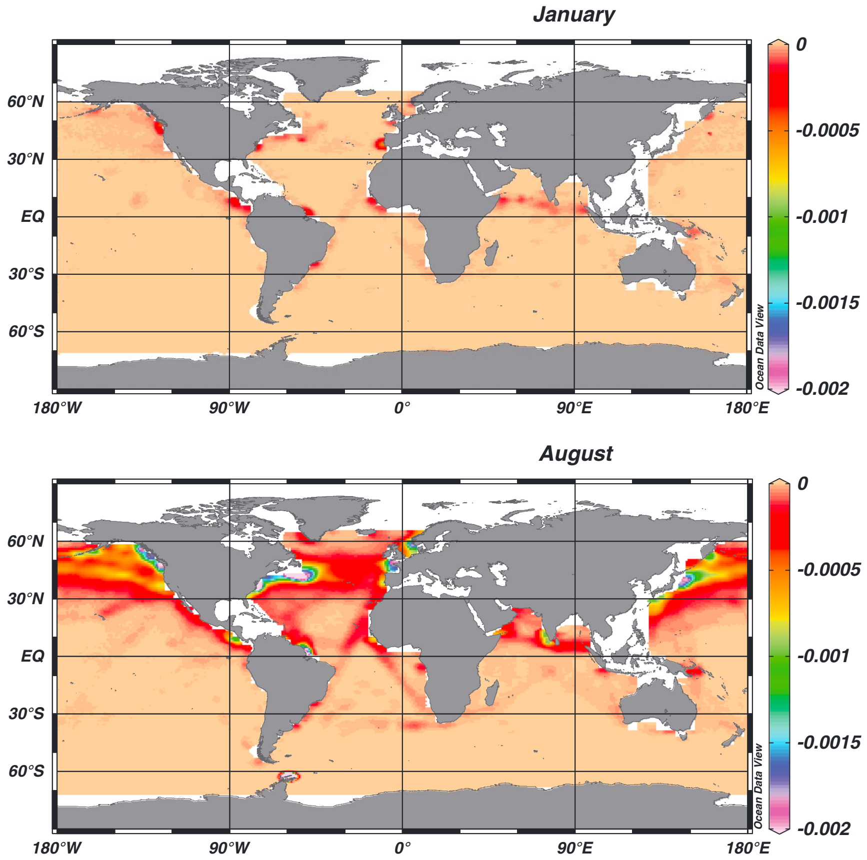

Figure 2. Calculated surface water pH changes arising from shipping-derived inputs of SO_X and NO_X. Calculations begin with the month of January.

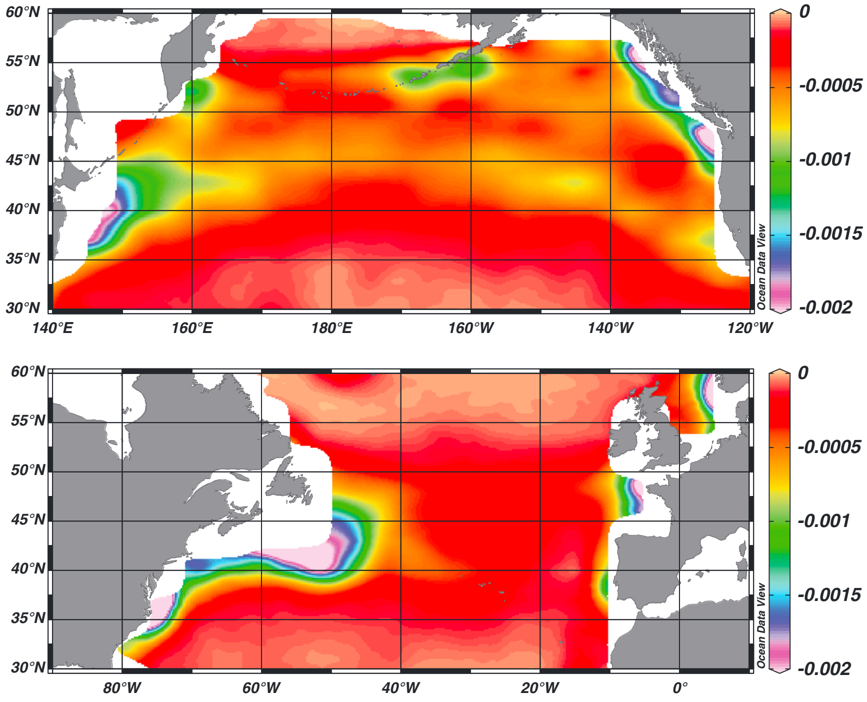

Figure 3. Calculated North Pacific and North Atlantic surface water pH changes for August arising from shipping-derived inputs of SO_X and NO_X. Calculations begin with the month of January.

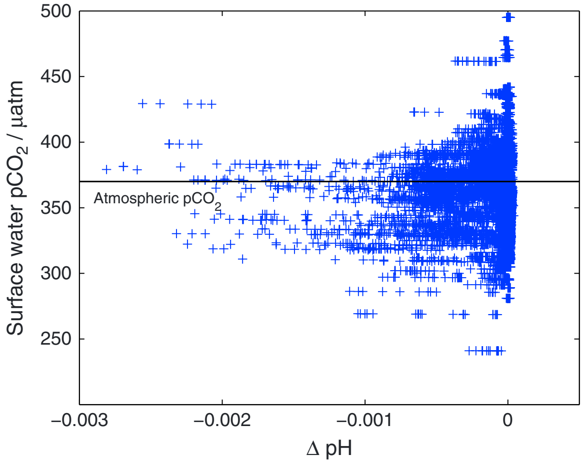

Figure 4. Calculated shipping-derived acidification (ΔpH) for the month of August together with surface water pCO$_2$: and (horizontal line) atmospheric pCO$_2$ for the year 2000 (30,688 data points).

Pacific with greatest potential impact (Table 1 and observable in the figures). Future work in these areas should focus on regional studies in these hot spot areas. These regional studies should include oceanographic models in order to investigate the accumulation of acidity on a multiyear basis. Such models will provide a basis for the assessment of the effects of future emission control regimes in these areas. Other areas identified in this work include the Pacific coastal regions around Asian nations, Mexican and Central American coastlines (e.g., shipping routes to the Panama Canal), and parts of the Indian Ocean (e.g., shipping routes connecting Indonesia and the Suez Canal).

[21] Some northern hemisphere hot spots are already subject to ECA regulation (Tables 1 and 2). In these areas, large-scale implementation of seawater scrubbing for sulfur abatement on board, if not accompanied by neutralization with a base other than seawater before discharge, simply acts as an efficient mechanism for transferring the acid to the surface water. This would result in a focused shipping-derived acidification in regions where biodiversity or commercial aquaculture (e.g., shellfisheries) may be most negatively impacted. Future work using more highly resolved regional models could examine shipping sulfur impacts where our study could not discern among land-based impacts to coastal ocean areas, such as the Mediterranean Sea, the Indo-Asian-Australian coastlines, the US-Mexico Gulf, and the Caribbean seas. Policy-focused analyses should also consider the current, pending, and potential implications of policy measures and business choices that lower marine fuel sulfur content (Table 2).

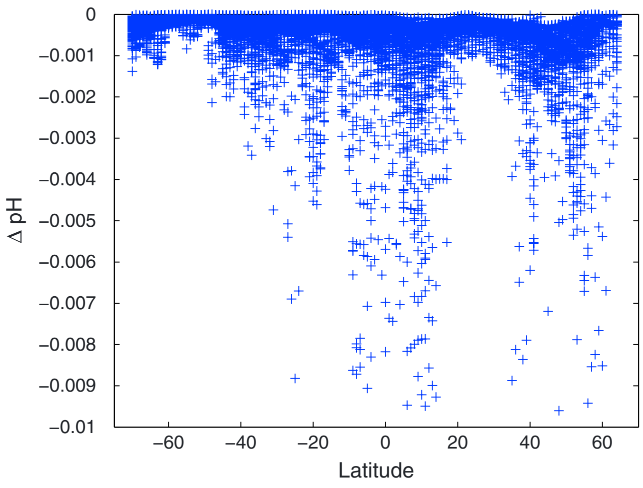

Figure 5. Calculated gross annual acidification from SO$_X$, NO$_X$ as a function of latitude (30,675 data points).

[22] **Acknowledgments.** Ida-Maja Hassellöv received partial support from Chalmers Area of Advance Transport; Axel Lauer was supported by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), by NASA through grant NNX07AG53G, and by NOAA through grant NA09OAR4320075, which sponsor research at the International Pacific Research Center; James Corbett received partial support from the University of Delaware School of Marine Science and Policy, and from Energy and Environmental Research Associates, LLC. We acknowledge the provision of the EMAC/MADE data by the SeaKLIM group (Veronika Eyring), German Aerospace Center (DLR), Germany.

[23] The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

References

An, S., and O. Nishida (2003), New application of seawater and electrolysed seawater in air pollution control of marine diesel engine, *JSME Int J., Ser. B*, *46*, 206–213.

Andreasen, A., and S. Mayer (2007), Use of seawater scrubbing for SO$_2$ removal from marine engine exhaust gas, *Energy Fuels*, *21*(6), 3274–3279, doi:10.1021/ef700359w.

Bates, N. R., and A. J. Peters (2007), The contribution of atmospheric acid deposition to ocean acidification in the subtropical North Atlantic Ocean, *Mar. Chem.*, *107*(4), 547–558, doi:10.1016/j.marchem.2007.08.002.

Brydges, T. G., and R. B. Wilson (1990), Acid rain since 1985—Times are changing, *Proc. R. Soc. Edinburgh Sect. B—Biol. Sci.*, *97*, 1–16, doi:10.1007/BF00229447.

Byrne, R. H., et al. (2010), Direct observations of basin-wide acidification of the North Pacific Ocean, *Geophys. Res. Lett.*, *37*, L02601, doi:10.1029/2009gl040999.

Capaldo, K., et al. (1999), Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean, *Nature*, *400*(6746), 743–746.

Conkright, M. E., et al. (2002), *World Ocean Atlas 2001: Objective Analyses, Data Statistics, and Figures, CD-ROM Documentation*, Silver Spring, MD, pp. 17.

Corbett, J. J., and P. Fischbeck (1997), Emissions from ships, *Science*, *278*(5339), 823–824, doi:10.1126/science.278.5339.823.

Corbett, J. J., et al. (1999), Global nitrogen and sulfur inventories for oceangoing ships, *J. Geophys. Res.*, *104*(D3), 3457–3470, doi:10.1029/1998JD100040.

Dhondt, S., et al. (1994), Surface water acidification and extinction at the Cretaceous-Tertiary boundary, *Geology*, *22*(11), 983–986, doi:10.1130/0091-7613(1994)022 < 0983:swaaea > 2.3.co;2.

Doney, S. C., et al. (2007), Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, *Proc. Natl. Acad. Sci. U. S. A.*, *104*(37), 14580–14585, doi:10.1073/pnas.0702218104.

Doney, S. C., et al. (2009), Ocean acidification: The other CO$_2$ problem, *Annu. Rev. Mar. Sci.*, *1*, 169–192, doi:10.1146/annurev.marine.010908.163834.

Dore, J. E., et al. (2009), Physical and biogeochemical modulation of ocean acidification in the central North Pacific, *Proc. Natl. Acad. Sci. U.S.A.*, *106*, 12235–12240, doi:10.1073/pnas.0906044106.

Endresen, O., et al. (2003), Emission from international sea transportation and environmental impact, *J. Geophys. Res. D: Atmos.*, *108*(D17), 4560, doi:10.1029/2002JD002898.

EU (2009), Directive 2009/30/EC, European Parliament and Council, Brussels.

von Feilitzen, H., and I. Lugner (1910), On the quantity of ammonia and nitric acid in the rain-water collected at Flahult in Sweden, *J. Agric. Sci.*, *3*, 311–313.

Greaver, T. L., et al. (2012), Ecological effects of nitrogen and sulfur air pollution in the US: What do we know?, *Front. Ecol. Environ.*, *10*(7), 365–372, doi:10.1890/110049.

Halpern, B. S., et al. (2008), A global map of human impact on marine ecosystems, *Science*, *319*(5865), 948–952, doi:10.1126/science.1149345.

Heath, M. R. (2008), Comment on "a global map of human impact on marine ecosystems", *Science*, *321*(5895), 2, doi:10.1126/science.1157390.

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.

IMO (1992), *Sea Disposal of Liquid Carbon Dioxide*, International Maritime Organisation, London, pp. 12.

Jöckel, P., et al. (2006), The atmospheric chemistry general circulation model ECHAM5/MESSy1: Consistent simulation of ozone from the surface to the mesosphere, *Atmos. Chem. Phys.*, *6*, 5067–5104.

Kaufman, Y. J., and M. D. Chou (1993), Model simulations of the competing climatic effects of SO_2 and CO_2, *J. Clim.*, *6*(7), 1241–1252, doi:10.1175/1520-0442(1993)006 < 1241:msotcc > 2.0.co;2.

Lauer, A., et al. (2007), Global model simulations of the impact of ocean-going ships on aerosols, clouds, and the radiation budget, *Atmos. Chem. Phys.*, *7*(19), 5061–5079.

Lauer, A., et al. (2009), An assessment of near future policy instruments for international shipping: Impact on atmospheric aerosol burdens and the Earth's radiation budget, *Environ. Sci. Technol.*, *43*(15), 5992–5998, doi:10.1021/es900922h.

Lee, K., et al. (2006), Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophys. Res. Lett.*, *33*, L19605, doi:10.1029/2006gl027207.

McLaren, R., et al. (2012), A survey of NO_2:SO_2 emission ratios measured in marine vessel plumes in the Strait of Georgia, *Atmos. Environ.*, *46*, 655–658, doi:10.1016/j.atmosenv.2011.10.044.

Monterey, G. I., and S. Levitus (1997), *Seasonal Variability of Mixed Layer Depth for the World Ocean*, NOAA NESDIS Atlas 14, Washington, D.C., pp. 5.

Takahashi, T., et al. (2009), Climatological mean and decadal change in surface ocean pCO_2, and net sea-air CO_2 flux over the global oceans, *Deep Sea Res. Part II: Topical Studies in Oceanography*, *56*(8–10), 554–577, doi:10.1016/j.dsr2.2008.12.009.

Wang, C., et al. (2007), Cost-effectiveness of reducing sulfur emissions from ships, *Environ. Sci. Technol.*, *41*(24), 8233–8239, doi:10.1021/es070812w.

Wang, C., J. J. Corbett, and J. Firestone (2008), Improving spatial representation of global ship emission inventories, *Environ. Sci. Technol.*, *42*(1), 193–199, doi:10.1021/es0700799.