

Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system

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Fossil fuel combustion and agriculture result in atmospheric deposition of 0.8 Tmol/yr reactive sulfur and 2.7 Tmol/yr nitrogen to the coastal and open ocean near major source regions in North America, Europe, and South and East Asia. Atmospheric inputs of dissociation products of strong acids (HNO₃ and H₂SO₄) and bases (NH₃) alter surface seawater alkalinity, pH, and inorganic carbon storage. We quantify the biogeochemical impacts by using atmospheric and ocean models. The direct acid/base flux to the ocean is predominately acidic (reducing total alkalinity) in the temperate Northern Hemisphere and alkaline in the tropics because of ammonia inputs. However, because most of the excess ammonia is nitrified to nitrate (NO₃⁻) in the upper ocean, the effective net atmospheric input is acidic almost everywhere. The decrease in surface alkalinity drives a net air-sea efflux of CO₂, reducing surface dissolved inorganic carbon (DIC); the alkalinity and DIC changes mostly offset each other, and the decline in surface pH is small. Additional impacts arise from nitrogen fertilization, leading to elevated primary production and biological DIC drawdown that reverses in some places the sign of the surface pH and air-sea CO₂ flux perturbations. On a global scale, the alterations in surface water chemistry from anthropogenic nitrogen and sulfur deposition are a few percent of the acidification and DIC increases due to the oceanic uptake of anthropogenic CO₂. However, the impacts are more substantial in coastal waters, where the ecosystem responses to ocean acidification could have the most severe implications for mankind.

alkalinity | biogeochemistry | global change | ocean chemistry | nutrient eutrophication

Humans are dramatically altering the global nitrogen and sulfur budgets, with one result being the release of large fluxes of nitrogen oxides (NO_x, ≈2 Tmol/yr), ammonia (NH₃, ≈4 Tmol/yr), and sulfur dioxide (SO₂, ≈2 Tmol/yr) to the atmosphere (1). Globally, fossil fuel combustion and biomass burning fluxes of NO_x exceed the natural fluxes from land to the atmosphere (2); NH₃ fluxes to the atmosphere are overwhelmed by those from human activities, mainly livestock husbandry (3); and oxidized sulfur fluxes from land are ≈10 times the natural fluxes, again because of combustion of fossil fuels and biomass burning (2). After chemical transformations in the atmosphere, much of the anthropogenic nitrogen and sulfur is deposited to the surface as the dissociation products of nitric acid (HNO₃) and sulfuric acid (H₂SO₄). HNO₃ and H₂SO₄ are strong acids that completely dissociate in water:



Because of the relatively short lifetime of reactive nitrogen and sulfur species in the atmosphere (days to about a week), the majority of the acid deposition occurs on land, in the coastal ocean, and in the open ocean downwind of the primary source regions in

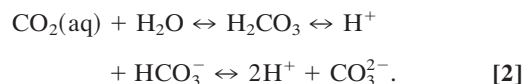
eastern North America, Europe, and South and East Asia (4–7). The subsequent acidification of terrestrial and freshwater ecosystems by dry deposition and more acidic rainfall is a well known environmental problem (8–11).

Anthropogenic nitrogen and sulfur deposition to the ocean surface alters surface seawater chemistry, leading to acidification and reduced total alkalinity. Lower pH and resulting lower CO₃²⁻ concentrations are of particular concern for a range of benthic and pelagic organisms that form calcareous (CaCO₃) shells (e.g., corals, coralline algae, foraminifera, pteropods, and coccolithophores) (12, 13). The acidification effects, although not as large globally as those of anthropogenic CO₂ uptake (14, 15), could be significant in coastal ocean regions because these regions are already vulnerable to other human impacts, including nutrient fertilization (15, 16), pollution, overfishing, and climate change. Here we compute bounds on the potential impact of anthropogenic nitrogen and sulfur deposition on seawater chemistry, using simulated atmospheric deposition fields applied to a coupled 3D ocean ecosystem–biogeochemical model (see *Methods*). We also compare these model results with field observations for U.S. coastal regions.

Basic Principles of the Effects of Atmospheric C, N, and S Deposition on Seawater Chemistry.

It is useful to frame the impact of anthropogenic nitrogen and sulfur inputs in terms of the changes in surface water dissolved inorganic carbon (DIC) and total alkalinity (Alk). DIC and Alk are conservative quantities with respect to mixing and temperature and pressure changes and, together with temperature and salinity, determine seawater pH and the partial pressure of carbon dioxide, pCO₂ (17), an important factor driving air-sea CO₂ exchange. Processes that increase DIC or decrease Alk lower seawater pH (ocean acidification) and raise pCO₂.

CO₂ combines with water to form carbonic acid (H₂CO₃), which then undergoes a series of acid/base dissociation reactions:



DIC concentration ([DIC]; μmol/kg) is

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Abbreviations: Alk, total alkalinity; DIC, dissolved inorganic carbon.

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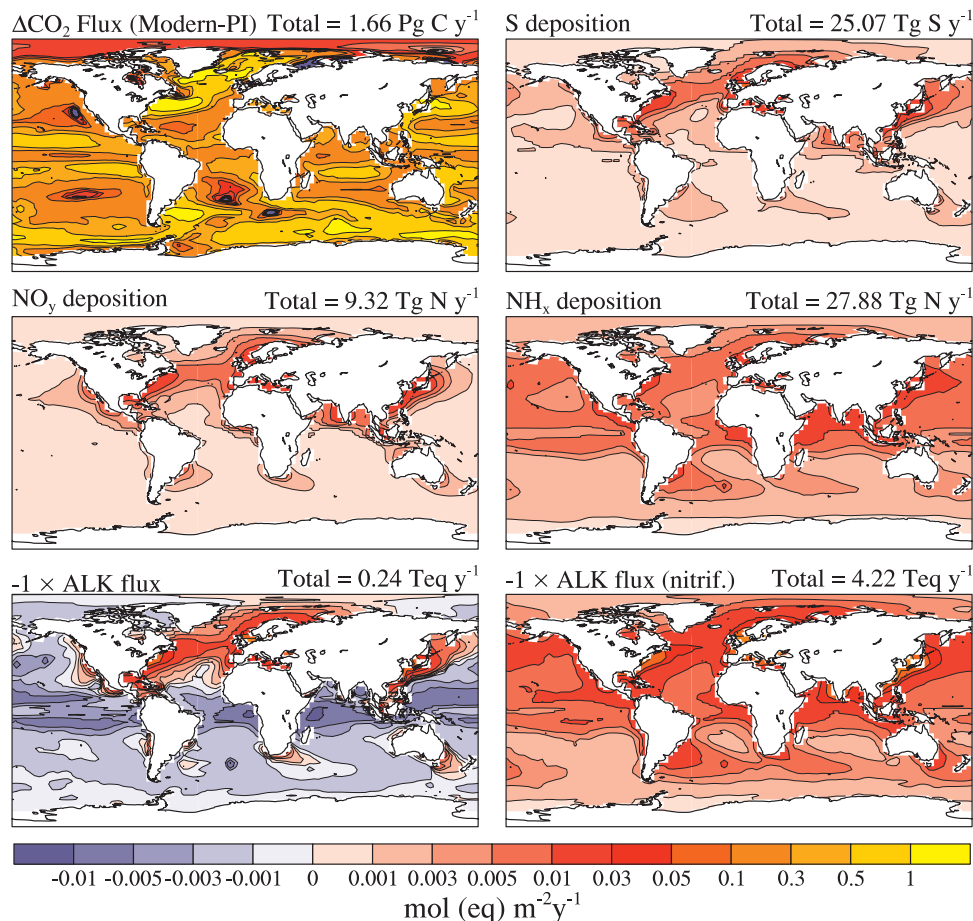


Fig. 1. Model-estimated anthropogenic (1990–2000 minus preindustrial) atmospheric deposition fluxes for carbon, nitrogen, and sulfur ($\text{mol}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$); alkalinity; and potential alkalinity, assuming complete nitrification of $\text{NH}_4^+ + \text{NH}_3$ ($\text{eq}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$).

Model ocean anthropogenic CO_2 uptake is $138 \text{ Tmol}\cdot\text{y}^{-1}$, with spatial $f\text{DIC}$ fluxes ranging from 0.1 to $2.0 \text{ mol C m}^{-2}\cdot\text{y}^{-1}$. Highest anthropogenic $f\text{DIC}$ values occur in regions of upwelling and water mass transformation (2, 24, 25). Globally, the ocean alkalinity reduction due to anthropogenic sulfur and nitrogen deposition, $f\text{Alk}_{\text{nitrif}}$, is at most, assuming full nitrification of ammonium deposition, approximately -3% of the $f\text{DIC}$ inputs because of anthropogenic CO_2 uptake. However, the alkalinity fluxes can be significant relative to anthropogenic $f\text{DIC}$ fluxes in some coastal ocean and margin areas. Previous modeling studies (Terrestrial Ocean Atmosphere Ecosystem Model, TOTEM; refs. 26 and 27) estimate anthropogenic atmospheric nitrogen deposition to the global coastal ocean of $0.03 \text{ mol}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ for the

turn of the 21st century, very similar to the estimates in Table 1. It was also shown that this flux will increase significantly during the next several decades, as will the reactive nitrogen flux to the coastal ocean from anthropogenic sources via rivers and groundwaters.

The anthropogenic alkalinity perturbation is redistributed by ocean circulation and initiates feedbacks by means of alterations in surface pH, air–sea CO_2 flux, and [DIC]. Biogeochemical transformations must also be considered because of nitrogen buildup or eutrophication of surface waters, stimulating increased ocean primary production and organic matter export (27–30). We evaluate the responses by using a 3D marine physical/ecological/biogeochemical model (see *Methods*), focusing on three sensitivity

Table 1. Model-estimated anthropogenic (1990–2000 minus preindustrial) and preindustrial atmospheric deposition fluxes

Flux	Integrated anthropogenic deposition, Tmol/y or Teq/y (preindustrial)		Anthropogenic coastal ocean flux, mol or $\text{eq}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$	
	Global	Ocean-only	Model	Observed
$f\text{CO}_2$	—	138	0.10 to 2.00	
$f\text{NH}_4^+ + f\text{NH}_3$	4.11 (0.00)	1.99 (0.00)	0.00 to 0.03	0.02
$f\text{NO}_3^-$	1.84 (1.18)	0.67 (0.73)	0.00 to 0.03	0.02
$f\text{SO}_4^{2-} + f\text{SO}_2$	2.21 (0.58)	0.78 (0.49)	0.00 to 0.03	0.01
$f\text{Alk}$	$-2.15 (-2.34)$	$-0.24 (-1.71)$	-0.01 to $+0.01$	
$f\text{Alk}_{\text{nitrif}}$	$-10.37 (-2.34)$	$-4.22 (-1.71)$	-0.01 to -0.10	

Field observations are shown for comparison (4, 5).

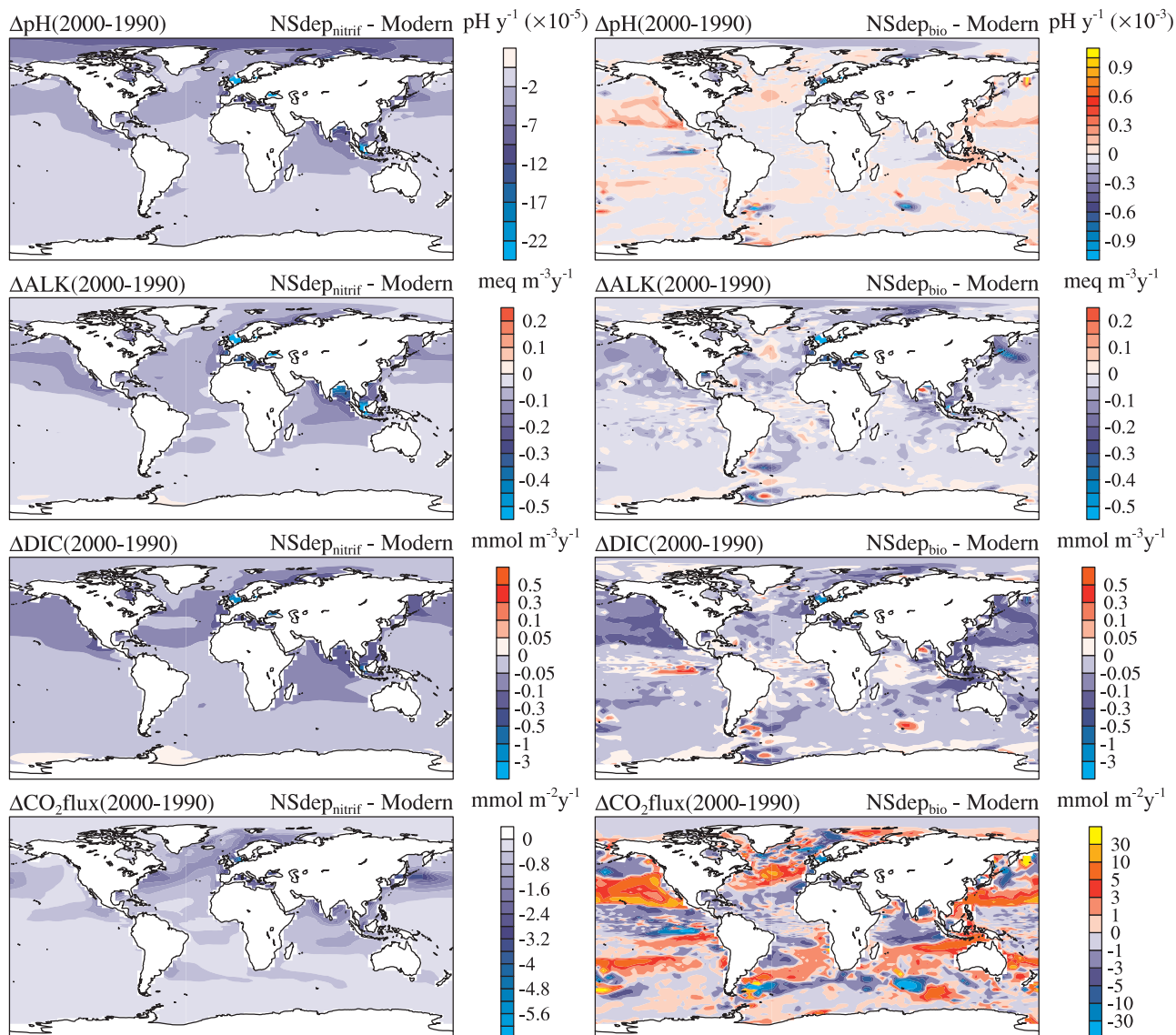


Fig. 3. Perturbation maps of simulated surface water pH, DIC, and total alkalinity trends and air-sea CO_2 flux due to anthropogenic atmospheric nitrogen and sulfur deposition.

significant threat to ecosystems, including coral reefs and coastal benthic and planktonic foodwebs dominated by calcifying organisms (10–13). Our study highlights the need to also consider the effects of non- CO_2 acidification sources from atmospheric nitrogen and sulfur deposition, both through their direct effects on reducing ocean alkalinity and their indirect effects through nitrogen fertilization of marine phytoplankton.

Uncertainties regarding the magnitude of non- CO_2 ocean acidification arise from errors in the anthropogenic sulfur and nitrogen deposition fluxes to the ocean, ocean circulation, and marine biogeochemical responses. Global deposition depends strongly on total emissions, with emission ranges of approximately $\pm 16\%$ for NO_x (total plus lightning) (7, 33), $\pm 27\%$ for NH_x (7, 34), and $\pm 20\%$ for SO_2 (35). Spatial differences in emissions and atmospheric transport pathways will change the downwind deposition fluxes to the oceans. The overall spatial patterns are generally similar across most models but can vary locally because of small shifts in steep deposition gradients. For example, sulfate residence times for models range between 3 and 5 days (35), with our model at 3.4 days. This means that deposition to remote regions in other models could be larger, but that uncertainties should be within $\approx 50\%$, even in

remote regions. The response of seawater carbonate thermodynamics to acidification is well constrained. Better estimates of the uncertainties due to ocean circulation and biology require exploration of the effect in other numerical models and against field observations.

Here we highlight the first-order impacts associated with anthropogenic atmospheric nitrogen and sulfur. More comprehensive studies on global change and coastal acid/base chemistry would need to include a range of additional processes. The extent of atmospheric neutralization of acidic compounds may be varying because of changes in mineral dust emissions and alkaline fly ash from coal-fired power plants. There is evidence, for example, of reduced atmospheric deposition of basic cations (e.g., Ca^{2+}) (36). Although much of the acidity flux that falls on land will likely be neutralized by soils, some fraction may be transported to the ocean (10, 11, 29), and there are substantial riverine inputs of anthropogenic nitrogen and organic matter to the coastal domain (27, 30, 37). In the water column, second-order biological effects arise from altered rates of nitrogen fixation, water-column and sediment denitrification, calcification, and CaCO_3 remineralization (14, 15, 38–40).

Methods

Preindustrial and current nitrogen deposition (including nitrate and ammonia) are simulated (33) in the MOZART model (41), based on climate simulations from the Parallel Climate Model (42) for 1890 and 1990, respectively. Emissions for both preindustrial and present-day come from the EDGAR-HYDE inventory (43). Present-day emissions of ammonia follow ref. 7, whereas preindustrial emissions are assumed to be zero. For the sulfate species, simulations are conducted within the Community Atmospheric Model (CAM3) (44), using sulfate chemistry based on ref. 45. Emissions for preindustrial and current climate for sulfur are based on ref. 46, and the preindustrial and current climates were simulated by using slab ocean model versions (47).

The ocean model combines a state-of-the-art marine ecosystem module (48) with phytoplankton functional groups (pico/nanoplankton, diatoms, diazotrophs, and calcifiers), multiple limiting nutrients (N, P, Si, and Fe), zooplankton, and several detrital pools. The model explicitly tracks both NO_3^- and NH_4^+ pools and

includes nitrification, nitrogen fixation, and water-column denitrification (39, 49). The biogeochemistry module (50) has full carbonate system thermodynamics (21), and air-sea CO_2 fluxes follow a quadratic wind-speed gas exchange relationship. The ecobiogeochemistry is embedded in the low-resolution (zonal 3.6° ; meridional 0.8° – 1.8° ; 25 vertical layers with a 12-m-thick surface layer) National Center for Atmospheric Research ocean physical model (CCSM3.1), based on the Parallel Ocean Program (51). This model is integrated with a repeat annual cycle of surface forcing based on National Centers for Environmental Prediction reanalysis and satellite data products (52–54).

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