

# Impacts of Atmospheric Anthropogenic Nitrogen on the Open Ocean

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Increasing quantities of atmospheric anthropogenic fixed nitrogen entering the open ocean could account for up to about a third of the ocean's external (nonrecycled) nitrogen supply and up to ~3% of the annual new marine biological production, ~0.3 petagram of carbon per year. This input could account for the production of up to ~1.6 teragrams of nitrous oxide (N<sub>2</sub>O) per year. Although ~10% of the ocean's drawdown of atmospheric anthropogenic carbon dioxide may result from this atmospheric nitrogen fertilization, leading to a decrease in radiative forcing, up to about two-thirds of this amount may be offset by the increase in N<sub>2</sub>O emissions. The effects of increasing atmospheric nitrogen deposition are expected to continue to grow in the future.

**N**itrogen is an essential nutrient in terrestrial and marine ecosystems. Most nitrogen in the atmosphere and ocean is present as N<sub>2</sub> and is available only to diazotrophs, a restricted group of microorganisms that can fix

N<sub>2</sub>. Most organisms can only assimilate forms of reactive nitrogen (fixed nitrogen, N<sub>r</sub>), including oxidized and reduced inorganic and organic forms. The availability of N<sub>r</sub> limits primary production, the conversion of inorganic carbon to organic carbon (*I*), in much of the ocean. Reactive nitrogen enters the ocean via rivers, N<sub>2</sub> fixation, and atmospheric deposition. It is removed via N<sub>2</sub> formation by denitrification and anaerobic ammonium oxidation (anammox), nitrous oxide (N<sub>2</sub>O) and ammonia emissions, and burial of organic matter in sediments. Human activities have severely altered many coastal ecosystems by increasing the input of anthropogenic nitrogen through rivers and groundwater, direct discharges from wastewater treatment, atmospheric deposition, and so forth, resulting in increasing eutrophication. Human activities have also added large quantities of atmospheric N<sub>r</sub> to central ocean regions.

Riverine input of N<sub>r</sub> to the oceans is estimated as 50 to 80 Tg N year<sup>-1</sup> (2–4). However, much is either lost to the atmosphere after N<sub>2</sub> conversion or buried in coastal sediments, never reaching oceanic regions (5). We assume that riverine N<sub>r</sub> has a negligible impact on the open ocean nitrogen inventory, and we do not consider it further. Estimates of global ocean N<sub>2</sub> fixation range from 60 to 200 Tg N year<sup>-1</sup> (2, 6–8). Although impacts of the amplified nitrogen inputs to terrestrial systems are being continuously evaluated (3, 9), here we show that atmospheric transport and deposition is an increasingly important pathway for N<sub>r</sub> entering the open ocean, often poorly represented in analyses of open ocean anthropogenic impacts (10–16). Atmospheric N<sub>r</sub> input is rapidly approaching global oceanic estimates for N<sub>2</sub> fixation and is predicted to increase further due to emissions from combustion of fossil fuels and production and use of fertilizers. Our objective is to highlight the growing im-

portance of anthropogenic atmospheric N<sub>r</sub> (AAN) deposition to the oceans and evaluate its impact on oceanic productivity and biogeochemistry.

## Atmospheric Emission and Deposition of Nitrogen Species

Atmospheric emissions of N<sub>r</sub> are primarily oxidized nitrogen species, NO<sub>x</sub> (NO + NO<sub>2</sub>) and NH<sub>3</sub>. Recent studies suggest that atmospheric water-soluble organic nitrogen is far more abundant than conventionally thought, constituting ~30% of total N<sub>r</sub> deposition (13, 17–20). Given the uncertain origins and complex composition of this material, the importance of direct emissions and secondary formation of organic nitrogen is unclear. However, measurements suggest that an important fraction is anthropogenic (13, 17). We therefore assume that in 1860, the relationship between organic and inorganic nitrogen deposition was the same as it is today and increase our 1860 estimate so that organic nitrogen represents 30% of total N<sub>r</sub> deposition. The uncertainties associated with this assumption emphasize the need for further research on atmospheric organic nitrogen.

Estimated total N<sub>r</sub> and AAN emissions in 1860, 2000, and 2030 (Table 1) show that anthropogenic emissions have significantly increased since the mid-1800s and future increases are expected (21). Over the next 20 to 25 years, the proportion of NH<sub>3</sub> emissions will likely increase due to enhanced atmospheric emission controls predicted to be more effective for NO<sub>x</sub> than NH<sub>3</sub> (Table 1) (21). An important fraction of atmospheric N<sub>r</sub> emissions is deposited on the ocean (Table 1). In 1860, this amounted to ~20 Tg N year<sup>-1</sup>, of which ~29% was anthropogenic. By 2000, the total N<sub>r</sub> deposition to the ocean had more than tripled to ~67 Tg N year<sup>-1</sup>, with ~80% being anthropogenic. This is greater than the 39 Tg N year<sup>-1</sup> reported by (14), in part because our estimate includes water-soluble organic nitrogen. Estimates of anthropogenic emissions for 2030 indicate a ~4-fold increase in total atmospheric N<sub>r</sub> deposition to the ocean and an ~11-fold increase in AAN deposition compared with 1860 (22).

The spatial distribution of atmospheric deposition has also changed greatly (Fig. 1, A and B). Deposition to most of the ocean was <50 mg N m<sup>-2</sup> year<sup>-1</sup> in 1860, with very few areas >200 mg N m<sup>-2</sup> year<sup>-1</sup>. Most oceanic deposition was from natural sources; anthropogenic sources impacted only a few coastal regions. By 2000, deposition over large ocean areas exceeded 200 mg N m<sup>-2</sup> year<sup>-1</sup>, reaching >700 mg N m<sup>-2</sup> year<sup>-1</sup> in many areas. Intense deposition plumes extend far downwind of major population centers in Asia, India, North and South America, around Europe, and west of Africa (Fig. 1B). A direct comparison of deposition in 1860 and 2000 shows almost all ocean surface areas now being affected by AAN deposition (Fig. 1, A and B). Predictions for 2030 (fig. S1) indicate similar patterns, but with

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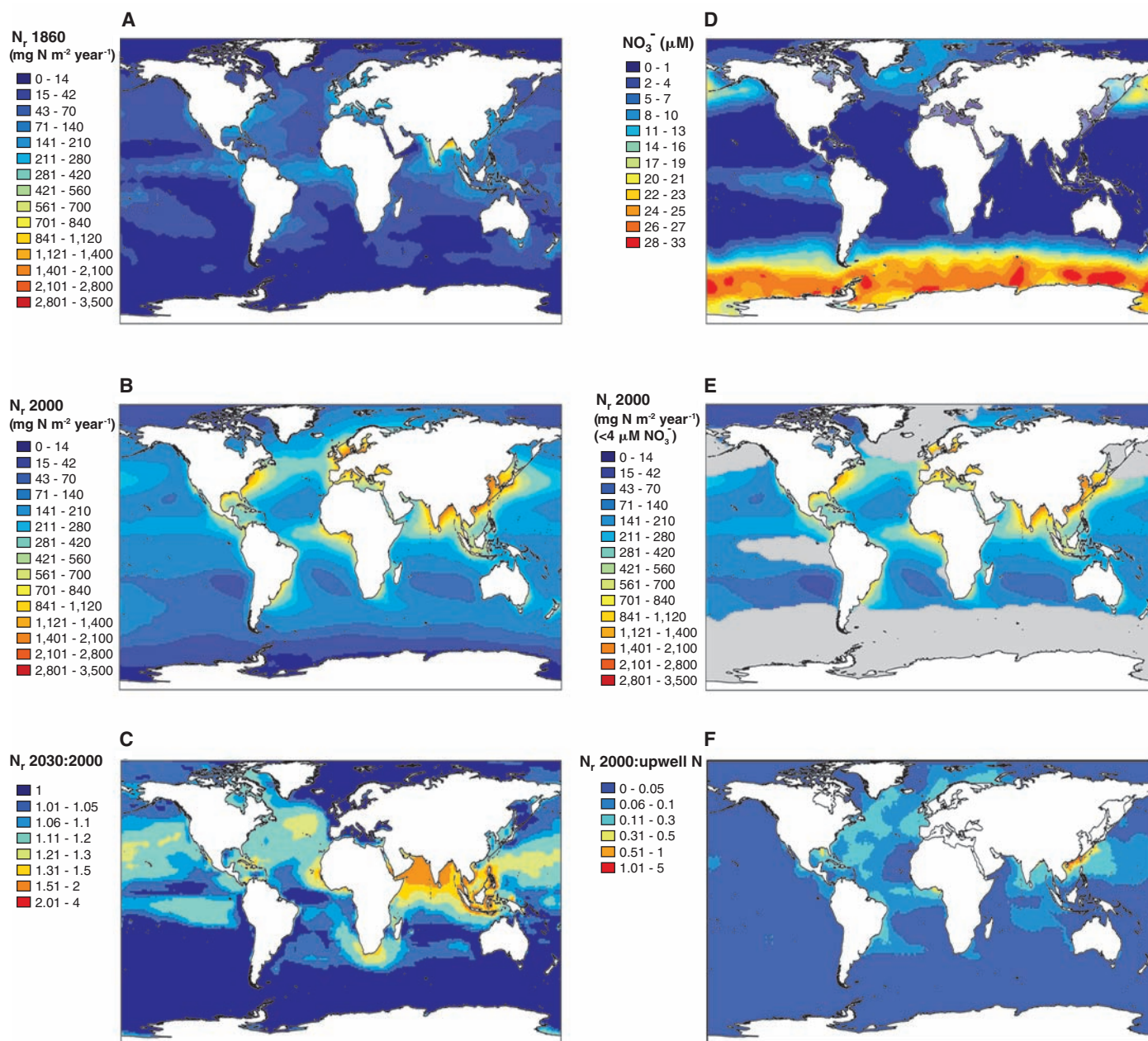
increased deposition further into open ocean regions (21, 22). The ratio of 2030-to-2000 deposition rates (Fig. 1C) shows up to a factor of 2 increase in Southeast Asia, the Bay of Bengal, and the Arabian Sea; up to a 50% increase off western Africa; and up to 30% increase essentially all the mid-latitude North Atlantic and North Pacific. As Galloway *et al.* (9) conclude, controlling  $\text{NO}_x$  emissions using maximum feasible reductions could substantially decrease future emissions, so

the increases we predict on deposition rates (Fig. 1C) may represent upper limits.

### Impact on New Primary Production and the Biological Pump

Present global open ocean primary production is estimated at  $\sim 50 \text{ Pg C year}^{-1}$  (23), equivalent to  $\sim 8800 \text{ Tg N year}^{-1}$ , assuming Redfield stoichiometry (Table 2). Because  $\sim 78\%$  of this production is driven by regeneration of  $\text{N}_r$  within surface

waters (24) (*a* in Fig. 2), it is more relevant to evaluate the impact of AAN deposition on oceanic productivity and biogeochemistry by comparing AAN with global new production, estimated at  $\sim 11 \text{ Pg C year}^{-1}$  (24–26). New production (*b* in Fig. 2 and Table 2) is dominated by nitrate regenerated at depth from sinking organic matter and subsequently returned to the euphotic zone via physical transport (*b'* in Fig. 2) (27). Over sufficiently large space and time scales



**Fig. 1.** (A) Total atmospheric reactive nitrogen ( $\text{N}_r$ ) deposition in 1860 in  $\text{mg m}^{-2} \text{ year}^{-1}$  [ $\text{NH}_x$  and  $\text{NO}_y$  are derived from (3), with the addition of 30% of the total nitrogen as organic nitrogen]. Total atmospheric  $\text{N}_r$  deposition in 1860 was  $\sim 20 \text{ Tg N year}^{-1}$ , AAN was  $\sim 5.7 \text{ Tg N year}^{-1}$ . (B) Total atmospheric reactive nitrogen ( $\text{N}_r$ ) deposition in 2000 in  $\text{mg m}^{-2} \text{ year}^{-1}$  [derived from (21) with the addition of 30% of the total nitrogen as organic nitrogen]. Total atmospheric  $\text{N}_r$  deposition in 2000 was  $\sim 67 \text{ Tg N year}^{-1}$ , AAN was  $\sim 54 \text{ Tg N year}^{-1}$ . (C) Ratio of the projected flux of  $\text{N}_r$  to the ocean in 2030 to

that in 2000. (D) Nitrate concentrations ( $\mu\text{M}$ ) in the surface (0 to 1 m) waters of the ocean (43). (E) Similar to (B), but with regions where surface nitrate  $> 4 \mu\text{M}$  has been masked out. Total atmospheric  $\text{N}_r$  deposition in 2000 to the nonmasked areas was  $\sim 51 \text{ Tg N year}^{-1}$ , AAN was  $\sim 41 \text{ Tg N year}^{-1}$ . (F) Ratio of total  $\text{N}_r$  deposition to dissolved inorganic nitrogen (DIN) supply into the upper 130 m as diagnosed from a model fitted to oceanic tracer observations (44). To reduce noise, computation of the ratio has been limited to areas with DIN supply exceeding  $0.05 \text{ mol m}^{-2} \text{ year}^{-1}$ .



(1 to ~1000 years), nitrate-driven new production is balanced by the biologically mediated export of particulate and dissolved organic matter from the surface layer ( $b''$  in Fig. 2). On a similar time scale, this component of new production is almost neutral in terms of carbon assimilation (28) because degradation processes release  $N_r$  and  $CO_2$  in stoichiometric amounts equivalent to the initial elemental composition of the organic matter. In the absence of denitrification and other fixed nitrogen losses in the ocean interior, nitrate-based new production can be considered a closed loop within which the biologically mediated carbon export ( $b''$ ) is balanced by a return flux of dissolved inorganic carbon ( $b'$ ), resulting in near-zero net air-sea  $CO_2$  exchange.

Only external (to the ocean) sources of  $N_r$  that reach the surface mixed layer can affect the steady-state balance of the biologically mediated flux of  $CO_2$  across the air-sea interface. The two known open ocean sources of external  $N_r$  are biological  $N_2$  fixation ( $c$  in Fig. 2) and atmospheric deposition ( $d$ ). Together these contribute a net oceanic input of  $N_r$  that can support “completely new production” and hence influence global oceanic  $N_r$  and the net atmosphere-to-ocean exchange of  $CO_2$ , assuming an adequate supply of other nutrients (P, Fe). Although  $N_2$  fixation must have dominated the flux of external new nitrogen in the preindustrial world, atmospheric  $N_r$  deposition is now approaching  $N_2$  fixation as a result of the

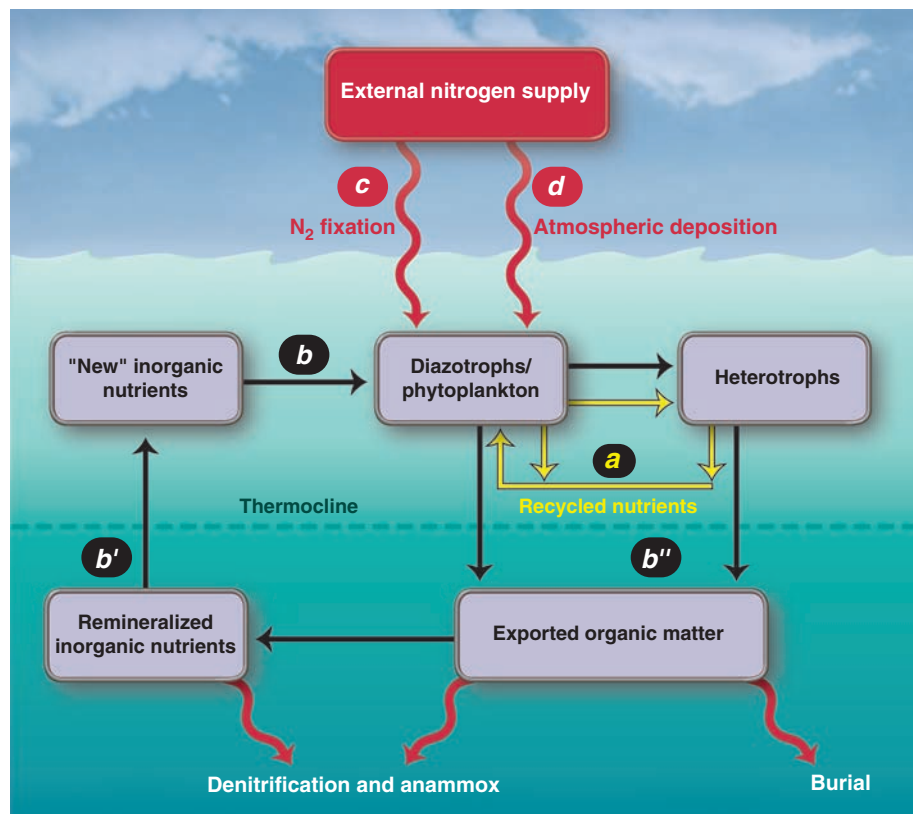
dramatic increase in the anthropogenic component (Table 2).

Can this atmospheric  $N_r$  deposition be rapidly assimilated into primary production? It will impact the biogeochemistry of oceanic areas that are either perennially or seasonally depleted in surface nitrate, but will have little effect in high-nutrient, low-chlorophyll (HNLC) regions where the concentration of surface nitrate is always high. Comparing surface nitrate concentrations (Fig. 1D) and total  $N_r$  deposition (Fig. 1B) shows the relatively small overlap between high  $N_r$  deposition and significant surface nitrate concentrations. In regions where surface nitrate is seasonally depleted (i.e., where productivity is nitrogen limited), atmospheric deposition would likely be assimilated during the year. Although  $N_r$  generally is seasonally exhausted in regions where mean annual nitrate is  $<7 \mu M$ , a more conservative value of  $<4 \mu M$  is used to calculate the distribution of the atmospheric  $N_r$  deposition in present-day nitrogen-depleted waters (Fig. 1E). The calculated global  $N_r$  deposition to regions with mean nitrate  $<4 \mu M$  is  $\sim 51 \text{ Tg N year}^{-1}$ , or  $\sim 76\%$  of the total atmospheric  $N_r$  deposited in the ocean, compared to  $\sim 56 \text{ Tg N year}^{-1}$  ( $\sim 84\%$  of total deposition) if  $<7 \mu M$  is used as a threshold. Corresponding values for AAN are  $\sim 41$  and  $\sim 45 \text{ Tg N year}^{-1}$ . Using the areas delineated by the  $<4 \mu M$  and  $<7 \mu M$  nitrate concentrations above, we calculate that  $\sim 67$  to  $75\%$  of oceanic

surface waters are potentially seasonally nitrogen limited, although some of these areas may not be exclusively nitrogen limited but rather colimited (1). It has recently been assumed that only 40% of the ocean is nitrogen limited (14), although this estimate did not allow for N/P colimitation such as seen in the North Atlantic and other areas designated P-limited in (14). These are likely underestimates because much of the  $N_r$  is deposited upstream of  $N_r$ -depleted regions (e.g., HNLC Southern Ocean) and will eventually be advected into thermocline waters of nitrogen-limited regions of the Southern Hemisphere and North Atlantic and thus are important to future (decades to centuries) productivity and biogeochemistry (29).

The total atmospheric deposition plus  $N_2$ -fixation flux to the ocean is  $\sim 167 \text{ Tg N year}^{-1}$  (Table 2). Assuming complete assimilation, these external  $N_r$  sources can support a maximum biologically mediated flux of  $\sim 1.0 \text{ Pg C year}^{-1}$ , of which  $\sim 0.4 \text{ Pg C year}^{-1}$  is from atmospheric deposition. Deposition of AAN alone could support up to  $\sim 0.3 \text{ Pg C year}^{-1}$ , or  $\sim 3\%$  of all new production, including that from nutrients upwelled from deep waters, and  $\sim 32\%$  of the productivity derived from external  $N_r$  supply (Table 2). In 1860, AAN supported a biologically mediated carbon flux of only  $\sim 0.03 \text{ Pg C year}^{-1}$ , so from 1860 to the present the potential impact of AAN on net primary productivity has increased  $\sim 10$ -fold. An earlier lower estimate ( $0.16 \text{ Pg C year}^{-1}$ ) of new (export) production generated by AAN deposition (14) assumed a different nitrogen-limited area, lower atmospheric fluxes, and the assumption that N enhancement will result in the replacement of diazotrophs by other phytoplankton.

Increased new production due to AAN fertilization coincides with the anthropogenic perturbation of the global carbon cycle and penetration of anthropogenic carbon in the ocean. The current anthropogenic  $CO_2$  uptake by the ocean is  $\sim 2.2 \pm 0.5 \text{ Pg C year}^{-1}$  (30), primarily attributed to physical-chemical processes (the “solubility pump”). Assuming that new production draws down atmospheric  $CO_2$  according to Redfieldian stoichiometry, up to  $\sim 10\%$  of the present anthropogenic carbon uptake could be attributed to anthropogenic nitrogen fertilization. This potentially significant enhancement of the oceanic uptake of anthropogenic carbon indicates the need to incorporate this factor in future Earth system assessments and models, as has already been done for terrestrial ecosystems (31). This estimate may be lower if the dissolved organic carbon or particulate organic carbon produced is regenerated at shallow depths (32). The efficiency and longevity of this anthropogenic nitrogen fertilization effect depend on temporal uncoupling of the new  $N_r$  inputs ( $N_2$  fixation and atmospheric deposition) from  $N_r$  removal (e.g., denitrification/anammox and burial). Assuming that all other essential nutrients are in adequate supply, it will be operational as long as the



**Fig. 2.** Schematic of the processes supplying nutrients for surface primary production. See text for detailed description.

increase in new  $N_r$  (and associated additional  $CO_2$  uptake) is not balanced by increased regeneration of  $N_2$  and  $CO_2$  and release at the ocean-air interface. Eventually, if AAN deposition levels off, the ocean may reach a new steady state with respect to nitrogen gains and losses that is neutral with respect to  $CO_2$  uptake over time scales similar to the oceanic N residence time (~1000 years).

The future impact of AAN on productivity must be evaluated in the context of predicted changes in productivity caused by other variables. For instance, elevated concentrations of atmospheric  $CO_2$  may have resulted in excess carbon consumption and export because of shifting C:N stoichiometry (33), and it is unclear whether projected AAN and high  $CO_2$  concentrations have synergy or compensate. El Niño–Southern Oscillation (ENSO)–induced higher

water temperatures and the associated increased stratification in low-latitude oceans may have reduced productivity by 60% in some regions (34). Thus, in a warmer climate, decreases in productivity due to restricted injection of nutrient-rich deep water would only accentuate the importance of AAN contributions to new production in low-latitude oligotrophic oceanic areas where AAN already has a strong effect. Assuming that all  $N_r$  deposition is assimilated into primary production, this  $N_r$ -driven new production could contribute as much as 20% of the total new (or export) production in such regions where upwelling is limited, e.g., the North Atlantic gyre (Fig. 1F). The contribution of  $N_r$  deposition to new production is higher in the Atlantic than the Pacific and can reach magnitudes comparable to export production along some continental areas.

**Table 1.** Atmospheric nitrogen emissions and deposition to the ocean. Assumed uncertainties—emissions: 1860:  $\pm 50\%$ ; 2000:  $NO_x \pm 30\%$ ,  $NH_3 \pm 50\%$ ; 2030: see text and (20). Deposition: 1860:  $\pm 50\%$ ; 2000:  $NO_y/NH_x \pm 40\%$ , organic N  $\pm 50\%$ ; 2030: see text and (20).

	1860* (Tg N year <sup>-1</sup> )	2000† (Tg N year <sup>-1</sup> )	2030‡ (Tg N year <sup>-1</sup> )
<i>Emission to the atmosphere</i>			
Total $NO_x$	13 (7–20)	52 (36–68)	54‡
Anthropogenic $NO_x$	2.6 (1.3–4)	38 (27–49)	43
Total $NH_3$	21 (11–32)	64 (32–96)	78‡
Anthropogenic $NH_3$	7.4 (3.7–11)	53 (27–80)	70
Total atmospheric N emissions	34 (18–52)	116 (68–164)	132
Total anthropogenic $N_r$ (AAN)	10 (5–15)	91 (54–129)	113
<i>Deposition to the ocean</i>			
Total $NO_y$	6.2 (3.1–9.3)	23 (14–32)	25
Anthropogenic $NO_y$	1.2 (0.6–1.8)	17 (10–24)	18
Total $NH_x$	8 (4–12)	24 (14–34)	29
Anthropogenic $NH_x$	2.4 (1.2–3.6)	21 (13–29)	25
Total organic $N_r$	6.1 (3.0–9.1)	20 (10–30)	23
Anthropogenic organic $N_r$	2.1 (1.0–3.1)	16 (8–24)	19
Total $N_r$ deposition	20 (10–30)	67 (38–96)	77
Total anthropogenic $N_r$ (AAN)	5.7 (2.8–8.5)	54 (31–77)	62

\*From (3). †Derived from (21); see text and (26). ‡ $NO_x$  and  $NH_3$  based on ~80% and ~90% anthropogenic, respectively [from (3)].

**Table 2.** Atmospheric nitrogen deposition to the ocean in 2000 and its impact on productivity. Global-scale estimates of total primary production (23); new production (24–26);  $N_2$  fixation (2, 6–8). Most letters in italics refer to flux pathways in Fig. 2.

	Global ocean nitrogen (Tg N year <sup>-1</sup> )	Resultant global ocean productivity (Pg C year <sup>-1</sup> )
Total primary production ( <i>a+b+c+d</i> )	~8800 (7000–10,500)	~50 (40–60)
New production (NP) ( <i>b</i> )	~1900 (1400–2600)	~11 (8–15)
Marine $N_2$ fixation ( <i>c</i> )	~100 (60–200)	~0.57 (0.3–1.1)
Total net $N_r$ deposition ( <i>d</i> ) ( $NO_y+NH_x+Org. N_r$ )	~67 (38–96)	~0.38 (0.22–0.55)
Total external nitrogen supply ( <i>c+d</i> )	~167 (98–296)	~0.95 (0.56–1.7)
Anthropogenic $N_r$ deposition (AAN) ( <i>e</i> )	~54 (31–77)	~0.31 (0.18–0.44)
Marine $N_2$ fixation as % NP $N_r$	= <i>c/b</i>	~5.3% (2.3–14.3%)
Total $N_r$ deposition as % NP $N_r$	= <i>d/b</i>	~3.5% (1.5–6.9%)
AAN as % NP $N_r$	= <i>e/b</i>	~2.8% (1.2–5.5%)
Total $N_r$ deposition as % external N supply	= <i>d/(c+d)</i>	~40% (13–98%)
AAN as % external N supply	= <i>e/(c+d)</i>	~32% (10–79%)

On the basis of future scenarios for anthropogenic emissions, AAN contribution to primary production could approach current estimates of global  $N_2$  fixation by 2030. Fertilization of the surface layer by atmospheric deposition, primarily AAN, could even lead to a decrease in  $N_2$  fixation due to biological competition (14). However, atmospheric  $N_r$  deposition has a very small effect on the surface seawater ambient  $N_r$  concentrations, too little to inhibit nitrogenase activity directly [e.g., we estimate that an extremely rare and large atmospheric deposition event distributed over a 25-m mixed-layer depth could increase the  $N_r$  concentration by only ~45 nM (35), which is too small to suppress  $N_2$  fixation (36)]. Atmospheric  $N_r$  deposition more likely represents a long-term low-level fertilization of the ocean that has consequences for the natural biogeochemical cycles of nitrogen and carbon and their ongoing anthropogenic perturbations. Biological evidence suggests that phytoplankton communities in oceanic gyres are presently nitrogen limited (1). Atmospheric  $N_r$  deposition, in the absence of significant atmospheric deposition of phosphorus, may exacerbate phosphorus limitation of  $N_2$  fixation. The long-term effect of AAN deposition on  $N_2$  fixation depends on whether P or Fe limits  $N_2$  fixation and on the supply ratio of bioavailable N:P:Fe derived from atmospheric deposition (37). Atmospheric deposition of phosphorus is much less perturbed by human activity than  $N_r$  (13, 37). Hence, the overall impact of atmospheric deposition is likely to be a shift in the N/P balance of surface waters. Some marine diazotrophs can exploit dissolved organic phosphorus pools and may obtain an adequate P supply by degrading compounds such as phosphonates (38).

Changes in species composition and productivity can lead to changes in the export of nitrogen and carbon to deep ocean water, resulting in a shift of deep ocean N/P ratios away from Redfield stoichiometry, which could then influence the chemistry of upwelled waters remote from the loci of atmospheric depositions. Remineralization of this extra organic carbon flux in deep waters may reduce the deepwater  $O_2$  concentration, and the resultant microbial  $N_2$  production will act to restore the N/P ratio toward the Redfield value, as suggested to have happened in the past (39). (See Supporting Online Material, including fig. S2).

### Impact on $N_2O$ Emissions from the Ocean

Another important issue is whether increasing atmospheric  $N_r$  inputs to the ocean can alter marine emissions of nitrous oxide ( $N_2O$ ), a major greenhouse gas. Estimates of global sea-to-air  $N_2O$  fluxes vary considerably. Two recent estimates are the Intergovernmental Panel on Climate Change (IPCC) assessment (30) (3.8 Tg N year<sup>-1</sup> as  $N_2O$ ) and the calculation by Bange of the mean from data in (40) (6.2 Tg N year<sup>-1</sup>). Using the mean (5.0 Tg N year<sup>-1</sup>) and the range of these two estimates, and assuming that the nitrogen in

this “recent” N<sub>2</sub>O flux originally entered the oceans from N<sub>2</sub> fixation (100 Tg N year<sup>-1</sup>) and atmospheric deposition (67 Tg N year<sup>-1</sup>), then the emission of 5.0 Tg N year<sup>-1</sup> as N<sub>2</sub>O results from nitrification and denitrification of part of this 167 Tg N year<sup>-1</sup> entering the surface ocean. This assumes that N<sub>2</sub>O production in the near-surface ocean is at steady state and there are no significant time lags between atmospheric input and N<sub>2</sub>O formation. Normalizing the N<sub>2</sub>O flux to the atmosphere by the “completely new” nitrogen input (5.0:167) can then be used to estimate that AAN deposition has resulted in the production of up to ~1.6 Tg N<sub>2</sub>O-N year<sup>-1</sup>, or about a third of total oceanic N<sub>2</sub>O emissions. This approach suggests that in 1860, only ~0.2 Tg N year<sup>-1</sup> (~5%) of the sea-to-air flux of N<sub>2</sub>O was driven by atmospheric anthropogenic inputs, assuming simplistically that N<sub>2</sub>O production is linearly related to N supply. [We use linear scaling due to the lack of experimental and modeling studies that address the spatial and nonlinear response of N<sub>2</sub>O emissions to N deposition, although important regional variations are likely (41).] This suggests that from 1860 to the present, the increase in AAN has led to nearly an order of magnitude increase in anthropogenic N<sub>2</sub>O emission from the oceans. Calculations and estimates of increases for 2030 are in table S1.

While oceanic AAN deposition may result in increased N<sub>2</sub>O emissions, increasing radiative forcing, AAN also increases primary production (up to ~0.3 Pg C year<sup>-1</sup> detailed above) and export production to the deep ocean, removing CO<sub>2</sub> from the atmosphere and therefore decreasing radiative forcing. With a Global Warming Potential of 298 for N<sub>2</sub>O (42), the net balance suggests that about two-thirds of the decrease in radiative forcing from CO<sub>2</sub> uptake could be offset by the increase due to N<sub>2</sub>O emissions. The uncertainty in our estimates is considerable; however, the estimates suggest the potential importance of AAN to N<sub>2</sub>O emissions and therefore the need for future research in regions such as oceanic Oxygen Minimum Zones (OMZs), which, although small in area, are potentially important for N<sub>2</sub>O emissions. The future role of OMZs will be influenced not only by AAN but also by climate and other global changes.

## Conclusions

This analysis emphasizes the potential importance of the growing quantity of atmospheric reactive (fixed) nitrogen that enters the open ocean as a result of human activities and its impact on the present marine nitrogen cycle. Considering the increasing demand for energy and fertilizers, the emissions of AAN are expected to grow over the coming decades. Atmospheric deposition of anthropogenic nitrogen to the ocean may account for up to ~3% of the annual new oceanic primary productivity, but about a third of the primary productivity generated as a result of the external input of nitrogen to the ocean. The input of AAN is approaching that of

N<sub>2</sub> fixation as a source of marine reactive nitrogen. Although local AAN deposition seems unlikely to alter significantly local phytoplankton species composition, the phytoplankton community could be affected by the slow long-term fertilization of surface waters by AAN. Moreover, AAN inputs to the ocean have potentially important climatic implications. Up to about a tenth of the anthropogenic atmospheric carbon uptake by the ocean (as CO<sub>2</sub>) may result from this fertilization. In addition, AAN inputs may stimulate N<sub>2</sub>O emissions, with possibly about two-thirds of the decrease in radiative forcing from increased CO<sub>2</sub> uptake by the ocean being offset by the increase in radiative forcing from increased N<sub>2</sub>O emissions.

There is clearly much we do not know about the extent and time scale of the impacts of AAN deposition on the oceans and the feedbacks to the climate system. The issues are complex and interactive, and they must be considered in climate scenarios. Areas of particular importance include understanding more fully the sources, chemical speciation, reactivity, and availability of atmospheric organic nitrogen; developing more realistic models of N<sub>r</sub> deposition to the ocean, coupled with measuring N<sub>r</sub> deposition over extended periods of time in open ocean regions; understanding the relationships between, and impacts of, the atmospheric deposition of bioavailable N, P, and Fe; and understanding the mechanisms and time scales involved in the oceanic response to N<sub>r</sub> deposition, coupled with a new generation of Earth system models that take into account long-term low-level nitrogen fertilization of the ocean and evaluate the effect on N<sub>2</sub>O emissions and the duration of the enhanced (anthropogenic) CO<sub>2</sub> uptake.

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Table S1  
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