Impacts of Atmospheric Anthropogenic Nitrogen on the Open Ocean
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Impacts of Atmospheric Anthropogenic Nitrogen on the Open Ocean


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 (N2O) 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 N2O emissions. The effects of increasing atmospheric nitrogen deposition are expected to continue to grow in the future.

Nitrogen is an essential nutrient in terrestrial and marine ecosystems. Most nitrogen in the atmosphere and ocean is present as N2 and is available only to diazotrophs, a restricted group of microorganisms that can fix atmospheric nitrogen to form ammonia (NH3). Recent studies suggest that atmospheric water-soluble organic nitrogen is far more abundant than conventionally thought, constituting ~30% of total N 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).

Atmospheric Emission and Deposition of Nitrogen Species

Atmospheric emissions of N are primarily oxidized nitrogen species, NOx (NO + NO2) and NH3. Recent studies suggest that atmospheric water-soluble organic nitrogen is far more abundant than conventionally thought, constituting ~30% of total N deposition (13, 17). 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 deposition. The uncertainties associated with this assumption emphasize the need for further research on atmospheric organic nitrogen.

Estimated total N 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 NH3 emissions will likely increase due to enhanced atmospheric emission controls predicted to be more effective for NOx than NH3 (Table 1) (21). An important fraction of atmospheric N emissions is deposited on the ocean surface areas now being affected by AAN deposition (21).

Riverine input of N to the oceans is estimated as 50 to 80 Tg N year−1 (2–4). However, much is either lost to the atmosphere after N2 conversion or buried in coastal sediments, never reaching oceanic regions (5). We assume that riverine N has a negligible impact on the open ocean nitrogen inventory, and we do not consider it further. Estimates of global ocean N2 fixation range from 60 to 200 Tg N year−1 (2, 6–8). Although impacts of the amplified nitrogen inputs to terrestrial systems are being continuously evaluated (3, 9), we here show that atmospheric transport and deposition is an increasingly important pathway for N2 entering the open ocean, often poorly represented in analyses of open ocean anthropogenic impacts (10–16). Atmospheric N2 input is rapidly approaching global oceanic estimates for N2 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 importance of anthropogenic atmospheric N deposition to the oceans and evaluate its impact on oceanic productivity and biogeochemistry.
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% across essentially all the mid-latitude North Atlantic and North Pacific. As Galloway et al. (9) conclude, controlling NO\textsubscript{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 ~50 Pg C year\textsuperscript{−1} (23), equivalent to ~8800 Tg N year\textsuperscript{−1}, assuming Redfield stoichiometry (Table 2). Because ~78% of this production is driven by regeneration of Nr 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 ~11 Pg C year\textsuperscript{−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...
(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 \( \text{N}_2 \) and \( \text{CO}_2 \) 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 \( \text{CO}_2 \) exchange.

Only external (to the ocean) sources of \( \text{N}_2 \), that reach the surface mixed layer can affect the steady-state balance of the biologically mediated flux of \( \text{CO}_2 \) across the air-sea interface. The two known open ocean sources of external \( \text{N}_2 \) are biological \( \text{N}_2 \) fixation \((c \text{ in Fig. 2}) \) and atmospheric deposition \((d \text{).} \) Together these contribute a net oceanic input of \( \text{N}_2 \) that can support "completely new production" and hence influence global oceanic \( \text{N}_2 \) and the net atmosphere-to-ocean exchange of \( \text{CO}_2 \), assuming an adequate supply of other nutrients (P, Fe). Although \( \text{N}_2 \) fixation must have dominated the flux of external new nitrogen in the preindustrial world, atmospheric \( \text{N}_2 \) deposition is now approaching \( \text{N}_2 \) fixation as a result of the dramatic increase in the anthropogenic component (Table 2).

Can this atmospheric \( \text{N}_2 \) 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 \( \text{N}_2 \) deposition (Fig. 1B) shows the relatively small overlap between high \( \text{N}_2 \) 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 \( \text{N}_2 \) generally is seasonally exhausted in regions where mean annual nitrate is <7 \( \mu \text{M} \), a more conservative value of <4 \( \mu \text{M} \) is used to calculate the distribution of the atmospheric \( \text{N}_2 \) deposition in present-day nitrogen-depleted waters (Fig. 1E). The calculated global \( \text{N}_2 \) deposition to regions with mean nitrate <4 \( \mu \text{M} \) is ~51 Tg N year\(^{-1} \), or ~76% of the total atmospheric \( \text{N}_2 \) deposited in the ocean, compared to ~56 Tg N year\(^{-1} \) (~84% of total deposition) if <7 \( \mu \text{M} \) is used as a threshold. Corresponding values for AAN are ~41 and ~45 Tg N year\(^{-1} \). Using the areas delineated by the <4 \( \mu \text{M} \) and <7 \( \mu \text{M} \) nitrate concentrations above, we calculate that ~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 \( \text{N}_2 \) is deposited upstream of \( \text{N}_2 \)-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 \( \text{N}_2 \) fixation flux to the ocean is ~167 Tg N year\(^{-1} \) (Table 2). Assuming complete assimilation, these external \( \text{N}_2 \) sources can support a maximum biologically mediated flux of ~1.0 Pg C year\(^{-1} \), of which ~0.4 Pg C year\(^{-1} \) is from atmospheric deposition. Deposition of AAN alone could support up to ~0.3 Pg C year\(^{-1} \), or ~3% of all new production, including that from nutrients upwelled from deep waters, and ~32% of the productivity derived from external \( \text{N}_2 \) supply (Table 2). In 1860, AAN supported a biologically mediated carbon flux of only ~0.03 Pg C year\(^{-1} \), so from 1860 to the present the potential impact of AAN on net primary productivity has increased ~10-fold. An earlier lower estimate (0.16 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 \( \text{CO}_2 \) uptake by the ocean is ~2.2 ± 0.5 Pg C year\(^{-1} \) (30), primarily attributed to physical-chemical processes (the "solubility pump"). Assuming that new production draws down atmospheric \( \text{CO}_2 \) according to Redfieldian stoichiometry, up to ~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 \( \text{N}_2 \) inputs (\( \text{N}_2 \) fixation and atmospheric deposition) from \( \text{N}_2 \) 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

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**Fig. 2.** Schematic of the processes supplying nutrients for surface primary production. See text for detailed description.
increase in new N \(_2\) (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\(_2\) deposition is assimilated into primary production, this N\(_2\)-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\(_2\) 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: ±50%; 2000: NO\(_x\) ±30%, NH\(_3\) ±50%; 2030: see text and (20). Deposition: 1860: ±50%; 2000: NO\(_x)/NH\(_3\) ±40%, organic N ±50%; 2030: see text and (20).

<table>
<thead>
<tr>
<th>Emission to the atmosphere</th>
<th>2000†</th>
<th>2030‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total NO(_x)</td>
<td>13 (7–20)</td>
<td>52 (36–68)</td>
</tr>
<tr>
<td>Anthropogenic NO(_x)</td>
<td>2.6 (1.3–4)</td>
<td>38 (27–49)</td>
</tr>
<tr>
<td>Total NH(_3)</td>
<td>21 (11–32)</td>
<td>64 (32–96)</td>
</tr>
<tr>
<td>Anthropogenic NH(_3)</td>
<td>7.4 (3.7–11)</td>
<td>53 (27–80)</td>
</tr>
<tr>
<td>Total atmospheric N emissions</td>
<td>34 (18–52)</td>
<td>116 (68–164)</td>
</tr>
<tr>
<td>Total anthropogenic N, (AAN)</td>
<td>10 (5–15)</td>
<td>91 (54–129)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Deposition to the ocean</th>
<th>2000†</th>
<th>2030‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total NO(_x)</td>
<td>6.2 (3.1–9.3)</td>
<td>23 (14–32)</td>
</tr>
<tr>
<td>Anthropogenic NO(_x)</td>
<td>1.2 (0.6–1.8)</td>
<td>17 (10–24)</td>
</tr>
<tr>
<td>Total NH(_3)</td>
<td>8 (4–12)</td>
<td>24 (14–34)</td>
</tr>
<tr>
<td>Anthropogenic NH(_3)</td>
<td>2.4 (1.2–3.6)</td>
<td>21 (13–29)</td>
</tr>
<tr>
<td>Total organic N,</td>
<td>6.1 (3.0–9.1)</td>
<td>20 (10–30)</td>
</tr>
<tr>
<td>Anthropogenic organic N,</td>
<td>2.1 (1.0–3.1)</td>
<td>16 (8–24)</td>
</tr>
<tr>
<td>Total N deposition</td>
<td>20 (10–30)</td>
<td>67 (38–96)</td>
</tr>
<tr>
<td>Total anthropogenic N, (AAN)</td>
<td>5.7 (2.8–8.5)</td>
<td>54 (31–77)</td>
</tr>
</tbody>
</table>

*From (3). †Derived from (22); 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.

<table>
<thead>
<tr>
<th>Global ocean nitrogen (Tg N year(^{-1}))</th>
<th>Resultant global ocean productivity (Pg C year(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total primary production (a+b+c+d)</td>
<td>~8000 (7000–10,500)</td>
</tr>
<tr>
<td>New production (NP) (b)</td>
<td>~1900 (1400–2600)</td>
</tr>
<tr>
<td>Marine N(_2) fixation (c)</td>
<td>~100 (60–200)</td>
</tr>
<tr>
<td>Total net N(_2) deposition (d) (NO(_x)+NH(_3)+Organic N)</td>
<td>~67 (38–96)</td>
</tr>
<tr>
<td>Total external nitrogen supply (c+d)</td>
<td>~167 (98–296)</td>
</tr>
<tr>
<td>Anthropogenic N deposition (AAN) (e)</td>
<td>~54 (31–77)</td>
</tr>
</tbody>
</table>

| Marine N\(_2\) fixation as % NP N | \(c/b\) | ~3.3% (2.3–14.3%) |
| Total N\(_2\) deposition as % NP N | \(d/b\) | ~3.5% (1.5–6.9%) |
| AAN as % NP N | \(e/b\) | ~2.8% (1.2–5.5%) |
| Total N\(_2\) deposition as % external N supply | \(d/(c+d)\) | ~40% (13–98%) |
| AAN as % external N supply | \(e/(c+d)\) | ~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\(_2\) deposition has a very small effect on the surface seawater ambient N\(_2\) 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\(_2\) concentration by only ~45 nM (35), which is too small to suppress N\(_2\) fixation (36)]. Atmospheric N\(_2\) 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\(_2\) 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\(_2\) (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 in 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\(_2\)O Emissions from the Ocean**

Another important issue is whether increasing atmospheric N\(_2\) inputs to the ocean can alter marine emissions of nitrous oxide (N\(_2\)O), a major greenhouse gas. Estimates of global sea-to-air N\(_2\)O fluxes vary considerably. Two recent estimates are the Intergovernmental Panel on Climate Change (IPCC) assessment (30) (3.8 Tg N year\(^{-1}\) as N\(_2\)O) and the calculation by Bange of the mean from data in (40) (6.2 Tg N year\(^{-1}\)). Using the mean (5.0 Tg N year\(^{-1}\)) and the range of these two estimates, and assuming that the nitrogen in
this “recent” N2O flux originally entered the oceans from N2 fixation (100 Tg N year⁻¹) and atmospheric deposition (67 Tg N year⁻¹), then the emission of 5.0 Tg N year⁻¹ as N2O results from nitrification and denitrification of part of this 167 Tg N year⁻¹ entering the surface ocean. This assumes that N2O production in the near-surface ocean is at steady state and there are no significant time lags between atmospheric input and N2O formation. Normalizing the N2O 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 N₂O-N year⁻¹, or about a third of total oceanic N₂O emissions. This approach suggests that in 1860, only ~0.2 Tg N year⁻¹ (~5%) of the sea-to-air flux of N₂O was driven by atmospheric anthropogenic inputs, assuming simplistically that N₂O 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 N₂O 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 N₂O emission from the oceans. Calculations and estimates of increases for 2030 are in table S1.

While oceanic AAN deposition may result in increased N₂O emissions, increasing radiative forcing, AAN also increases primary production (up to ~0.3 Pg C year⁻¹ detailed above) and export production to the deep ocean, removing CO₂ from the atmosphere and therefore decreasing radiative forcing. With a Global Warming Potential of 298 for N₂O (42), the net balance suggests that about two-thirds of the decrease in radiative forcing from CO₂ uptake could be offset by the increase due to N₂O emissions. The uncertainty in our estimates is considerable; however, the estimates suggest the potential importance of AAN to N₂O emissions and therefore the need for future research in regions such as the Oceanic Oxygen Minimum Zones (OMZs), which, although small in area, are potentially important for N₂O 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 quantify 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 N₂ 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 CO₂) may result from this fertilization. In addition, AAN inputs may stimulate N₂O emissions, with possibly about two-thirds of the decrease in radiative forcing from increased CO₂ uptake by the ocean being offset by the increase in radiative forcing from increased N₂O 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 N₂O deposition to the ocean, coupled with measuring N₂O 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 N₂O 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 N₂O emissions and the duration of the enhanced (anthropogenic) CO₂ uptake.

References and Notes