



## RESEARCH ARTICLE

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## Key Points:

- A new estimate of total atmospheric fixed nitrogen inputs to the ocean ( $39 \text{ Tg N yr}^{-1}$ ) and its spatial distribution is presented
- The effects of atmospheric deposition on the oceans are estimated as an increase of productivity equivalent to  $0.15 \text{ Pg C yr}^{-1}$
- Four key uncertainties in these estimates are identified

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## A reevaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean

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**Abstract** We report a new synthesis of best estimates of the inputs of fixed nitrogen to the world ocean via atmospheric deposition and compare this to fluvial inputs and dinitrogen fixation. We evaluate the scale of human perturbation of these fluxes. Fluvial inputs dominate inputs to the continental shelf, and we estimate that about 75% of this fluvial nitrogen escapes from the shelf to the open ocean. Biological dinitrogen fixation is the main external source of nitrogen to the open ocean, i.e., beyond the continental shelf. Atmospheric deposition is the primary mechanism by which land-based nitrogen inputs, and hence human perturbations of the nitrogen cycle, reach the open ocean. We estimate that anthropogenic inputs are currently leading to an increase in overall ocean carbon sequestration of  $\sim 0.4\%$  (equivalent to an uptake of  $0.15 \text{ Pg C yr}^{-1}$  and less than the Duce et al. (2008) estimate). The resulting reduction in climate change forcing from this ocean  $\text{CO}_2$  uptake is offset to a small extent by an increase in ocean  $\text{N}_2\text{O}$  emissions. We identify four important feedbacks in the ocean atmosphere nitrogen system that need to be better quantified to improve our understanding of the perturbation of ocean biogeochemistry by atmospheric nitrogen inputs. These feedbacks are recycling of (1) ammonia and (2) organic nitrogen from the ocean to the atmosphere and back, (3) the suppression of nitrogen fixation by increased nitrogen concentrations in surface waters from atmospheric deposition, and (4) increased loss of nitrogen from the ocean by denitrification due to increased productivity stimulated by atmospheric inputs.

### 1. Introduction

Oceanic biogeochemical cycles play many important roles in the Earth system, including sustaining marine productivity by the cycling of carbon and the key nutrients N, P, Si, and Fe [Falkowski et al., 1998, 2000]. Marine productivity in turn affects air-sea gas exchange of greenhouse gases and thereby planetary radiative balance and climate. The oceans represent a very large planetary reservoir of fixed or reactive nitrogen, i.e., nitrogen that is in forms other than the unreactive gaseous  $\text{N}_2$ . Henceforth, fixed nitrogen will be simplified to “nitrogen,” and when we specifically include dinitrogen gas,  $\text{N}_2$ , this will be stated. The internal cycling of this nitrogen within the oceans, predominantly as nitrate in deep water, supports much of the primary production in the surface ocean on annual to decadal time scales. External inputs of nitrogen to the oceans from rivers, groundwater and direct waste discharges, atmospheric deposition, and oceanic dinitrogen ( $\text{N}_2$ ) fixation (henceforth nitrogen fixation) may further augment ocean productivity. These

inputs, together with those of other key potentially limiting nutrients such as P and Fe [Krishnamurthy *et al.*, 2010; Moore *et al.*, 2013; Okin *et al.*, 2011], regulate the long-term biological productivity of the ocean and hence ocean carbon storage.

Prior to human intervention, we assume a steady state for the ocean nitrogen budget in which external inputs should balance losses. These losses occur primarily by denitrification and anaerobic ammonia oxidation or anammox (subsequently simplified to denitrification in the text). The nitrate ocean residence time is <3000 years [Voss *et al.*, 2013; Bianchi *et al.*, 2012; Gruber and Galloway, 2008; Landolfi *et al.*, 2015]

The global nitrogen cycle is now being massively perturbed by human activity, particularly on land, and this affects the coastal oceans [Fowler *et al.*, 2013; Gruber and Galloway, 2008; Rockstrom *et al.*, 2009]. Although exact budgets are uncertain, estimated anthropogenic release of nitrogen into the global environment ( $160 \text{ Tg N yr}^{-1}$ ,  $T_g = 10^{12} \text{ g}$ ) is now of similar magnitude to all natural nitrogen fixation ( $250 \text{ Tg N yr}^{-1}$ ) and may increase in the future with a growing global population, depending on societal progress in limiting nitrogen fluxes [Gruber and Galloway, 2008]. The increasing inputs of nitrogen from human activity, predominantly from land-based activities, have the potential to modify oceanic, and even global, biogeochemical systems. However, our understanding of the scale and impact of such perturbations on the oceans is even less complete than on land [Fowler *et al.*, 2013; Gruber and Galloway, 2008].

Duce *et al.* [2008], Suntharalingam *et al.* [2012], Yang and Gruber [2016], and Krishnamurthy *et al.* [2007] have recently provided estimates of atmospheric inputs of fixed nitrogen to the world oceans and the impact of this deposition on ocean biogeochemistry. Duce *et al.* [2008] also argued that atmospheric deposition is the dominant mechanism by which anthropogenic perturbations of the nitrogen cycle affect the open ocean, because of effective removal of fluvial nitrogen inputs on shelves by denitrification. Recognizing that there has been considerable new information on atmospheric emissions and their deposition to the oceans, as well as improved modeling capability of their impacts since the publication of Duce *et al.* [2008], many of the authors of that paper have come together to reevaluate their earlier conclusions. In this contribution we therefore update the Duce *et al.* [2008] study, reporting improved estimates of the preindustrial and modern atmospheric nitrogen inputs to the ocean. We also report improved models to describe the distribution and impact of these inputs on the oceans and their impacts on the exchange of some important greenhouse gases. We also consider possible future changes in the nitrogen fluxes. In addition, we reconsider the assumption in the Duce *et al.* paper that fluvial nitrogen is completely removed by denitrification on shelves and hence does not affect the nitrogen budget of the open oceans.

We begin by considering the three main external nitrogen sources to the oceans, fluvial, atmospheric, and biological nitrogen fixation, before moving on to consider the impacts of changing atmospheric nitrogen inputs on ocean biogeochemistry. As shown in earlier work [Duce *et al.*, 2008] nitrogen fixation by lightning is quantitatively a very small component of the global nitrogen cycle compared to other inputs:  $\sim 5 \text{ Tg N yr}^{-1}$  [Fowler *et al.*, 2013]. It is included in the models here and is assumed to be unaffected by human activity and hence not explicitly discussed further.

## 2. Fluvial Inputs to the Oceans

Freshwater nitrogen inputs to the world oceans include riverine and submarine groundwater inputs plus some direct discharges. River inputs dominate and hence are our focus here [Jickells and Weston, 2011]. Riverine nitrogen fluxes at the freshwater/saltwater boundary have now been modeled and validated against available data, with associated uncertainty, [Seitzinger *et al.*, 2005, 2010]. These authors report a global flux estimate of  $23 \text{ Tg N yr}^{-1}$  for dissolved inorganic nitrogen (DIN) and  $11 \text{ Tg N yr}^{-1}$  for dissolved organic nitrogen (DON). The total river input of nitrogen to the coastal seas has approximately doubled over the last few hundred years [Beusen *et al.*, 2016; Moore *et al.*, 2013; Seitzinger *et al.*, 2010]. This input is also now dominated by nitrate, although in preindustrial times organic N may have made a much higher relative contribution [Jickells and Weston, 2011; Seitzinger *et al.*, 2005]. The general agreement between independent estimates [Beusen *et al.*, 2016; Seitzinger *et al.*, 2010] provides confidence in the estimated fluvial N fluxes. The validation, calibration, and bias evaluations of the models' estimates are discussed in the individual papers.

Models and field data have suggested that much of the riverine nitrogen input is consumed on continental shelves, primarily by sediment denitrification fueled by organic carbon derived from shelf sea primary

production [Duce *et al.*, 2008; Fennel *et al.*, 2006; Seitzinger *et al.*, 2006]. This leads to the suggestion that shelf seas are a global ocean nitrogen sink rather than a source to the open ocean. The significance of this shelf sea fluvial nitrogen sink is, however, uncertain and depends, at least in part, on the water residence time on the shelf and how and where the open ocean/shelf sea boundaries are placed. We next consider how much of the nitrogen delivered by rivers reaches the open ocean and how much is utilized and denitrified on the shelf based on Sharples *et al.* [2016].

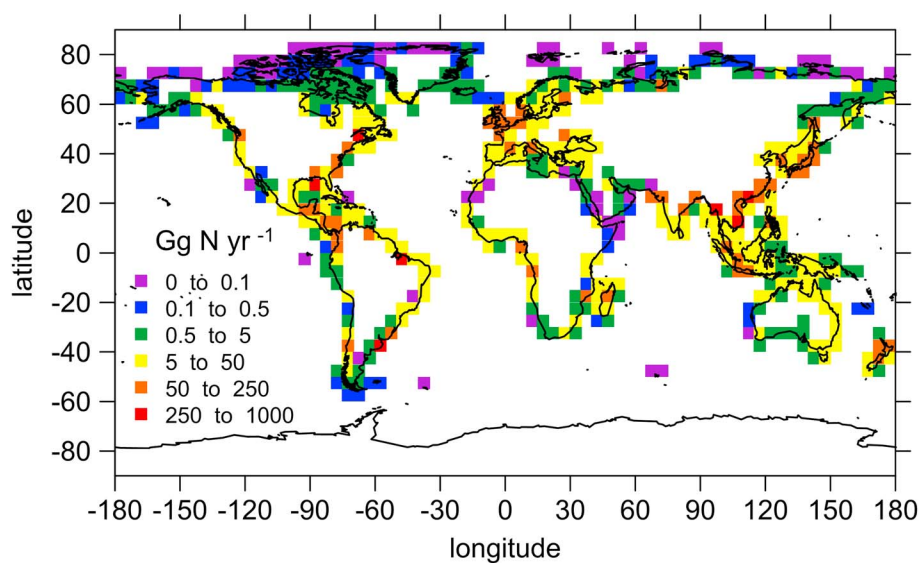
Fluvial particulate organic nitrogen (along with other fluvial particulate matter) is effectively trapped in estuaries at low salinity by particle flocculation [e.g., Slattery and Phillips, 2011] or on the shelf [Muller-Karger *et al.*, 2005]. However, it may be subsequently degraded to dissolved forms of nitrogen and thereby escape this particulate matter trap.

The main mechanism for long-term trapping of fluvial dissolved inorganic nitrogen on the shelf is the microbial consumption of nitrate by denitrification in shelf sediments [Voss *et al.*, 2013]. The effectiveness of shelf sea fluvial nitrate retention is then a function of both the rates of shelf sedimentary denitrification and the residence time of water on the shelf [Seitzinger *et al.*, 2006]. The residence time of fluvial water on the shelf is not well known but can be anticipated to be very variable, being influenced by the width of the shelf, flow rates within the coastal buoyant plumes, and the net rates of water exchange across the shelf break. At a global scale, a key influence on circulation is the Coriolis force which acts to turn freshwater plumes to the right in the Northern Hemisphere and to the left in the Southern Hemisphere, as the buoyant water exits the estuary. This tends to retain the estuary discharge within the shelf sea, inhibiting the freshwater and associated nitrogen from directly crossing the shelf. This increases the water residence time on the shelf. The Coriolis force is highly dependent on latitude, and the analysis of Sharples *et al.* [2016] suggests that only near the equator (within about 20° latitude) is the Coriolis force weak enough to allow direct across-shelf movement of river plumes. Elsewhere, the Coriolis force moves freshwater flows along shelf. This creates freshwater residence times on the shelf that are sufficiently long (months to years) to allow effective removal of most riverine nitrogen, although slowly degrading riverine DON will be exported [Fennel *et al.*, 2006; Letscher *et al.*, 2013; Sharples *et al.*, 2016].

The limited influence of the Coriolis force near the equator means that the residence time of the freshwater on the shelf there may be sufficiently short (days to weeks) that freshwater inputs will rapidly cross the shelf to reach the open ocean, and hence, there may not be time for fluvial dissolved nitrogen inputs to be denitrified. By contrast, at higher latitudes the residence times of river water on shelf are increased by the Coriolis force to the point (many months or longer) where sediment denitrification can utilize effectively all of the riverine nitrogen input [Sharples *et al.*, 2016].

The rivers discharging in tropical equatorial region include many with high flows per unit catchment area, due to high rainfall [Syvitski *et al.*, 2005], and many with globally important total water flows such as the Amazon, Zaire, and Fly. These rivers may also have relatively low inorganic nitrogen concentrations, because of both less intensive catchment agriculture and dilution of nitrogen inputs by the high river flow. However, these rivers still deliver important total nitrogen loads due to the high water flows [Seitzinger *et al.*, 2005, 2010]. Dissolved organic nitrogen (DON) is often a significant component of the total dissolved nitrogen flux in these tropical river systems [Jickells and Weston, 2011; Seitzinger *et al.*, 2005]. This material contains a complex mixture of compounds and the rate of degradation of these DON components is very poorly known [Hansell, 2013]. Assuming that the relatively biogeochemically labile DON is degraded on a time scale of about 50 days [Lønborg and Álvarez-Salgado, 2012], then such biologically labile DON may escape across the shelf to the open ocean from low latitude equatorial rivers due again to the shorter shelf residence times of freshwater in these systems. At high latitudes the labile DON may be degraded on the shelf and will then be retained along with nitrate on the shelf. More slowly degraded DON may be transported to the open ocean [Letscher *et al.*, 2013, 2015].

Sharples *et al.* [2016] estimate that net global fluvial dissolved inorganic nitrogen (DIN) inputs across the shelf break to the open ocean are about  $17 \pm 4 \text{ Tg N yr}^{-1}$ . This implies that globally about 75% of fluvial DIN is transported across the shelf to the oceans with the main inputs occurring near the equator (Figure 1). This DIN flux will be augmented by a riverine DON flux ( $11 \text{ Tg N yr}^{-1}$ ), although the uncertainties in our understanding of the composition and reactivity of this material mean that we cannot estimate the shelf-wide retention of this flux with any confidence. These fluxes contrast to the Duce *et al.* [2008] assumption of complete nitrogen



**Figure 1.** N supply across shelf and to the open ocean in  $5^\circ \times 5^\circ$  boxes based on NEWS (global nitrogen export from watersheds) river inputs [S. P. Seitzinger *et al.*, 2010] and shelf retention estimates [Sharples *et al.*, 2016] illustrating the dominance of tropical rivers as nitrogen sources capable of transporting nitrogen across the shelf to the open ocean [Sharples *et al.*, 2016].

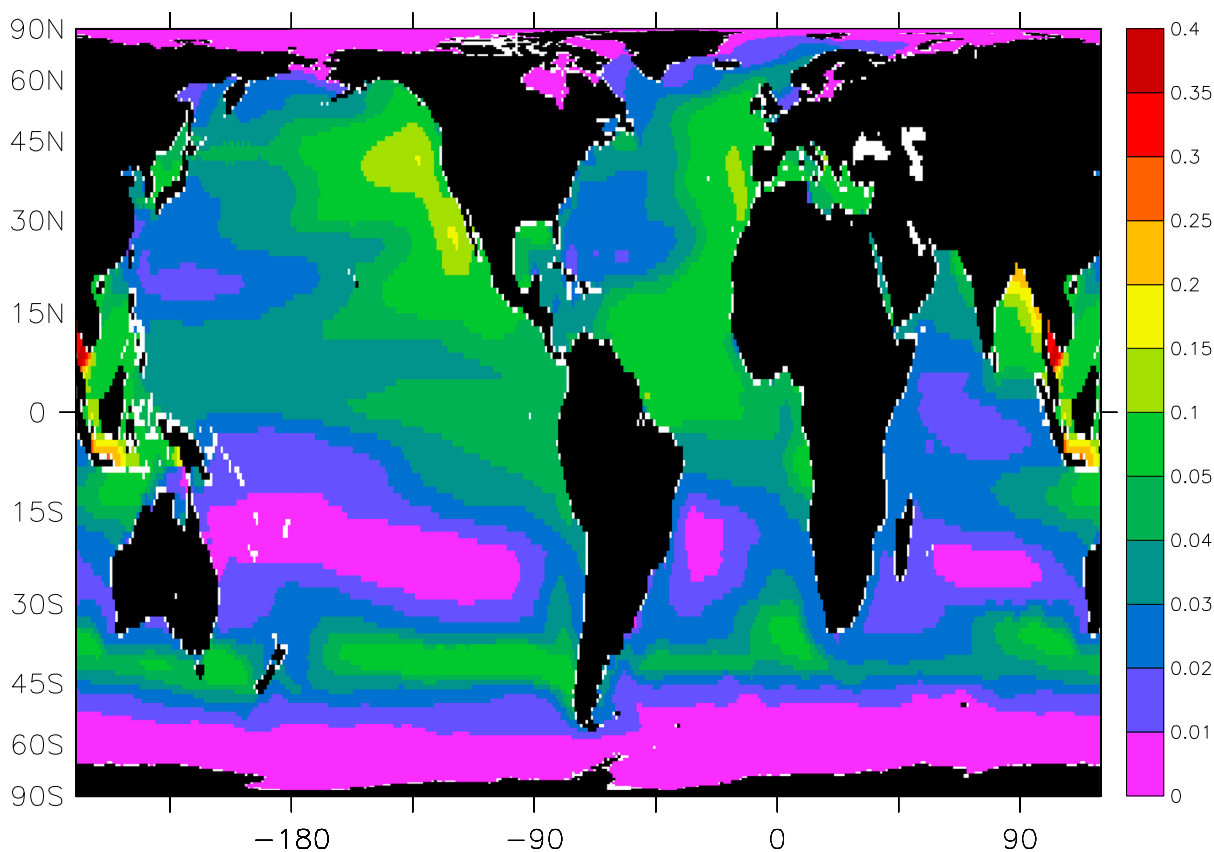
retention on the shelf. The Sharples *et al.* [2016] flux estimation excludes estuarine nitrogen retention and thus is an upper limit on nitrogen inputs to the open ocean.

As noted earlier global fluvial nitrogen fluxes to the oceans have probably doubled since 1860 [Beusen *et al.*, 2016; Moore *et al.*, 2013]. Seitzinger *et al.* [2010] suggest that riverine fluxes of nitrogen may increase by  $-3$  to  $+10\%$  by 2030, depending on the assumed development scenario. Hence, the overall eutrophication pressures on coastal systems from nitrogen loading are likely to continue. An important control on shelf nutrient retention is associated with physical oceanographic factors particularly the Coriolis force, and we suggest that the spatial distribution of fluvial inputs, and hence the physical controls on the effectiveness of shelf retention of these inputs, is likely to remain similar between 2005 and 2030. Thus, the overall changes in the fluvial nitrogen fluxes to the open ocean are likely to be small, although locally large changes in Arctic regions may follow from global warming.

### 3. Biological Nitrogen Fixation

Biological nitrogen ( $N_2$ ) fixation offers the marine phytoplankton community a mechanism to relieve nitrogen limitation. However, biochemical mechanisms for nitrogen fixation require considerable energy expenditure. Biological nitrogen fixation also requires relatively large amounts of iron [Grosskopf and LaRoche, 2012; Kustka *et al.*, 2003]. Nitrogen fixation is restricted to a small group of prokaryotic planktonic organisms, although evidence from genetic studies suggests that the range of organisms able to fix nitrogen may be greater than previously thought [Bombar *et al.*, 2016]. Estimates of global nitrogen fixation rates and controls are very uncertain [Landolfi *et al.*, 2015; Mahaffey *et al.*, 2005; Somes and Oschlies, 2015; Somes *et al.*, 2013]. At regional and basin scales nitrogen fixation rates can be estimated using direct measurements, abundance estimates of nitrogen fixers, and from estimates of nitrogen abundance relative to phosphorus,  $N^*$  [e.g., Singh *et al.*, 2013]. However, at a global scale, estimates of nitrogen fixation rates have been derived from three different approaches: (1) plankton biogeochemical models constrained by marine chemistry data [e.g., Benavides *et al.*, 2013; Mills and Arrigo, 2010], (2) self-assembling ecosystem models, which do not prescribe biological rates directly but derive them to achieve the best fit to geochemical data [Dutkiewicz *et al.*, 2012], and (3) extrapolations of direct measurements of biological nitrogen fixation [e.g., Grosskopf *et al.*, 2012]. Some recent studies have reported methodological issues that may cause earlier direct measurements of nitrogen fixation rates to be inaccurate [Dabundo *et al.*, 2014; Grosskopf *et al.*, 2012].

The most recent direct measurement based estimates of global ocean nitrogen fixations rate is about  $177 \text{ Tg N yr}^{-1}$  [Grosskopf *et al.*, 2012]. The self-assembly ecosystem models estimate nitrogen fixation rates



**Figure 2.** Nitrogen fixation rate estimates from PlankTOM model (see text) as  $\text{mol N m}^{-2} \text{yr}^{-1}$ , averaged over the period 1990–1999.

to be  $85 \text{ Tg N yr}^{-1}$  (range 66–135) [Dutkiewicz *et al.*, 2012], while other recent model estimates range from 91 to  $137 \text{ Tg N yr}^{-1}$  [Bianchi *et al.*, 2012; Landolfi *et al.*, 2015]. The PlankTOM model used here to assess the impacts of atmospheric deposition on the oceans [Buitenhuis *et al.*, 2013; Le Quere *et al.*, 2005] estimates global ocean nitrogen fixation rates of  $164 \text{ Tg N yr}^{-1}$  (Figure 2), broadly consistent with these other estimates and somewhat higher than, but within the uncertainties of, the estimate of 100 (60–200)  $\text{Tg N yr}^{-1}$  used in Duce *et al.* [2008]. Nitrogen fixation rates are high in warm tropical oligotrophic waters and where there is sufficient availability of water column P and Fe [Luo *et al.*, 2012; Somes and Oschlies, 2015]. The model results (Figure 2) also predict high nitrogen fixation in some coastal areas in SE Asia, which probably reflects stimulation by riverine phosphorus inputs. The global models are rarely able to fully capture the complex and episodic nature of nitrogen fixation blooms, and we note, for example, that high rates of nitrogen fixation have been observed in the Arabian Sea [Gandhi *et al.*, 2011].

Based on current estimates [Bianchi *et al.*, 2012] of nitrogen loss from the ocean by burial and denitrification ( $260 \text{ Tg N yr}^{-1}$ ), only at the high end of this range of estimated nitrogen fixation rates is the ocean nitrogen cycle balanced. This has led to a discussion of whether the preindustrial ocean nitrogen system is in steady state or not after recovery from glaciation and the restoration of the current continental shelves [Bianchi *et al.*, 2012; Codispoti, 2007; Grosskopf *et al.*, 2012; Somes *et al.*, 2013]. The usual biogeochemical assumption of ocean steady state may be inappropriate if the oceanic nitrogen system is still responding to postglacial maximum sea level rise when there was little or no continental shelf, and hence, the ocean nitrogen cycle may have been very different. The nitrogen isotopic composition record of organic matter preserved in foraminifera within ocean sediments does suggest a major reorganization of the oceanic nitrogen cycle between glacial and interglacial conditions [Straub *et al.*, 2013]. In regions like the Arabian Sea oxygen depleted zones, denitrification has been shown to fluctuate on even shorter (century) time scales [Altabet *et al.*, 2002; Suthhof *et al.*, 2001], due to regional changes in environmental conditions. However, with nitrogen fixation and other input and removal rates of the order proposed above, and assuming steady state, the

ocean residence time of nitrogen becomes short enough (of the order of 3000 years) that postglacial maximum reequilibration should have been achieved [Somes *et al.*, 2013]. Hence, a pre-Anthropocene steady state should apply. The oceanic residence times of N and phosphorus (P) are therefore quite distinctly different, despite their close ocean scale coupling as is evident from the Redfield ratio. This coupling is due to large-scale thermohaline water mixing that smooths out the effects of the different internal ocean biogeochemical N and P cycling [Martiny *et al.*, 2013; Singh *et al.*, 2015; Weber and Deutsch, 2010]

Nitrogen fixation in the oceans is controlled in part by the availability of P and Fe [Ito *et al.*, 2016; Moore *et al.*, 2009; Somes and Oschlies, 2015; Srinivas and Sarin, 2013]. Hence, it is coupled to the larger ocean biogeochemical cycle, particularly N loss processes [Landolfi *et al.*, 2015; Mahaffey *et al.*, 2005; Meyer *et al.*, 2016; Moore and Doney, 2007; Moore *et al.*, 2006; Somes *et al.*, 2013]. Nitrogen fixation is also known to be suppressed by the presence of dissolved nitrogen species in the water column. This physiological suppression effect is species dependent, but the available evidence [Grosskopf and LaRoche, 2012; Krupke *et al.*, 2015; Meyer *et al.*, 2016; Sohm *et al.*, 2011] suggests that this only occurs at relatively high dissolved N concentrations (several micromolar). This threshold is much higher than the likely increase in surface water nitrogen concentrations from individual atmospheric N deposition events over the open ocean [Duce *et al.*, 2008; Grosskopf and LaRoche, 2012; Michaels *et al.*, 1993; Somes *et al.*, 2016], which are likely to be in the range of nanomolar rather than micromolar [Michaels *et al.*, 1993]. This argument suggests that suppression of nitrogen fixation by atmospheric deposition events is unlikely. However, this assertion merits further study in field populations, mesocosms, and laboratory cultures, although this is challenging because only a few nitrogen-fixing marine microbes are currently in culture. In our modeling of the N cycle here we evaluate the impacts of atmospheric deposition on the oceans with and without this potential inhibition of nitrogen fixation (see later).

We suggest that nitrogen fixation rates are unlikely to change in the near future as a result of anthropogenic N inputs to the ocean. However, changes in dust input might change the iron supply and hence change the rates [Ito *et al.*, 2016; Jickells *et al.*, 2005; Moore *et al.*, 2006] as may ocean acidification [Hutchins *et al.*, 2015].

#### 4. Atmospheric Deposition

The third important external source of fixed nitrogen to the oceans is from the atmosphere. As a result of anthropogenic nitrogen emissions, the total atmospheric nitrogen input to the ocean is now comparable in magnitude to the other external nitrogen sources, although the balance between them will vary regionally. The atmospheric input is made up of inorganic oxidized (nitrate and nitric acid) and reduced (ammonia and ammonium) nitrogen and organic nitrogen. In this context, organic nitrogen is defined as nitrogen available to inorganic nitrogen analysis after oxidation [Cape *et al.*, 2011]. On a global basis these three forms contribute in approximately equal amounts to the total nitrogen deposition [Duce *et al.*, 2008; Kanakidou *et al.*, 2012], although there are substantial temporal and regional variations in fluxes and composition as discussed later. Atmospheric nitrogen fluxes are now greatly enhanced (approximately tenfold) by human activity. Combustion is the main source of oxidized nitrogen, emitted as  $\text{NO}_x$  and converted on time scales of a day or so to nitric acid and nitrate. Agricultural emissions are the main source of ammonia [Duce *et al.*, 2008]. Most emissions originate on land, although shipping emissions are becoming increasingly important [Eyring *et al.*, 2005] (Table 1). Rapid and efficient atmospheric transport allows these emissions to reach the open oceans within days, hence much faster and more effectively than fluvial inputs [Fowler *et al.*, 2013].

The magnitude of nitrogen emissions and their deposition to the oceans are uncertain and generally poorly constrained by both data and models. However, a recent detailed comparison of models and data for the Atlantic Ocean suggested reasonable agreement between model estimates and observations, providing increased confidence in the estimates presented here [Baker *et al.*, 2010, 2017].

The estimates of atmospheric deposition here are based on the TM4-ECPL model [Daskalakis *et al.*, 2015; Tsigaridis *et al.*, 2014] which includes for the first time an explicit scheme for estimating atmospheric dissolved organic nitrogen deposition [Kanakidou *et al.*, 2012]. In contrast, Duce *et al.* [2008] ran their present-day simulation of atmospheric nitrogen deposition for the year 2000 based on a synthesis of global models [Dentener *et al.*, 2006]. The simulation reported here is for 2005, although the impacts of this change in year are trivial, when considering the large spatial scales here. The estimates from the TM4-ECPL model agree well with other model outputs and with data [Kanakidou *et al.*, 2016]. The spatial distribution derived from the

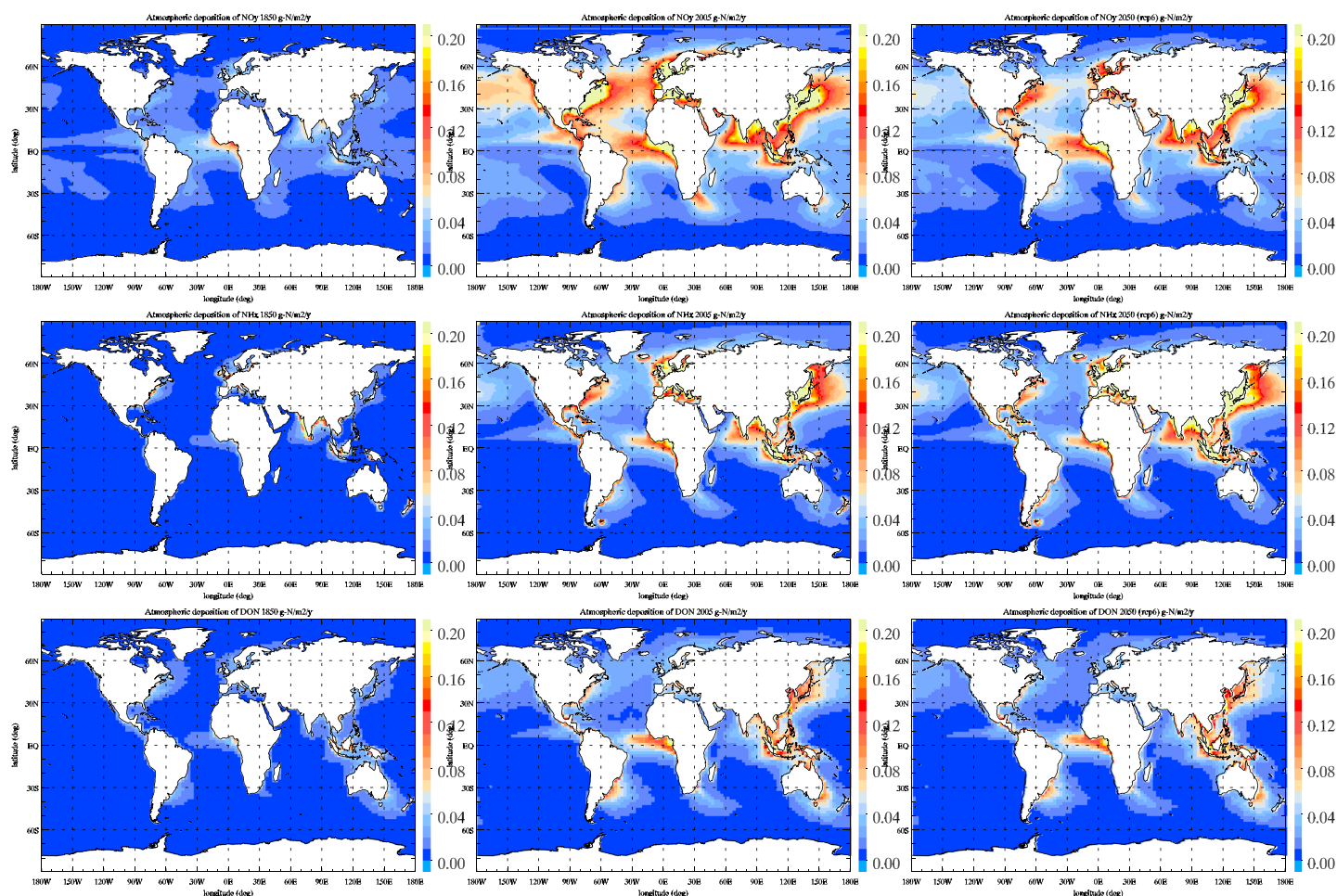
**Table 1.** TM4-ECPL Model Estimated Global Atmospheric N Emissions by Source for 1850, 2005, and 2050, the Latter Based on the RCP6.0 Scenario

| Source   | Emissions (Tg N yr <sup>-1</sup> ) |       |       |
|--|------------------------------------|-------|-------|
|  | 1850                               | 2005  | 2050  |
| NO <sub>x</sub>                                |                                    |       |       |
| Terrestrial anthropogenic NO <sub>x</sub>      | 0.6                                | 27    | 20.2  |
| Shipping NO <sub>x</sub>                       |                                    | 5.3   | 3.1   |
| Aircraft NO <sub>x</sub>                       |                                    | 0     | 0     |
| Biomass burning NO <sub>x</sub>                | 0.5                                | 5.5   | 5.7   |
| Natural NO <sub>x</sub> soils + lightening     | 11.8                               | 11.6  | 11.6  |
| NH <sub>x</sub>                                |                                    |       |       |
| Terrestrial anthropogenic NH <sub>x</sub>      | 5.4                                | 32.9  | 43.7  |
| Biomass burning NH <sub>x</sub>                | 0.9                                | 9.2   | 9.4   |
| Natural NH <sub>x</sub> soils                  | 2.4                                | 2.4   | 2.4   |
| Natural NH <sub>x</sub> ocean emissions        | 8.2                                | 8.2   | 8.2   |
| Total inorganic N                              | 29.8                               | 102.1 | 104.3 |
| Organic N (ON)                                 |                                    |       |       |
| Anthropogenic and biomass burning              | 1.3                                | 7.0   | 6.8   |
| Natural biogenic particles and soil dust       | 9.3                                | 9.3   | 9.3   |
| ON insoluble on marine aerosol                 | 1.1                                | 1.1   | 1.1   |
| ON soluble on marine aerosol and marine amines | 5.8                                | 5.8   | 5.8   |
| Total ON                                       | 17.5                               | 23.2  | 23    |
| Total N emissions                              | 47.2                               | 125.2 | 127.3 |

TM4-ECPL model of nitrogen deposition (Figure 3) and present-day global nitrogen emission estimates (Table 1, 125 Tg N yr<sup>-1</sup>) are very similar to those in *Duce et al.* [2008], 116 (uncertainty range 68–164) Tg N yr<sup>-1</sup>. However, the net nitrogen deposition estimates to the oceans (Table 2) are rather different as discussed below, with a net deposition here of 39 Tg N yr<sup>-1</sup> compared to 67 (uncertainty range 38–96) Tg N yr<sup>-1</sup> in *Duce et al.* [2008].

The difference reflects a slightly lower (18 versus 23 Tg N yr<sup>-1</sup>) oxidized nitrogen deposition to the ocean. This arises in part because some of the oxidized nitrogen emission is assumed to react to form atmospheric organic nitrogen (about 10 Tg N yr<sup>-1</sup> produced mainly over land), of which 2 Tg N yr<sup>-1</sup> is deposited to the ocean [*Kanakidou et al.*, 2012]. Other formation pathways for inorganic nitrogen involving ammonia have been suggested [*Altieri et al.*, 2012]. The major differences between the budget here and that of *Duce et al.* [2008] reflects changes in the model estimates of *net* organic nitrogen and reduced inorganic nitrogen (NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub>) deposition. This highlights the potential importance of the role of recycled marine emissions in these fluxes in particular, since redeposition of marine emissions will not create a net increase in marine productivity. The specific major changes to these flux estimates compared to *Duce et al.* [2008] are detailed below:

1. The TM4-ECPL explicit modeling of organic nitrogen yields a total deposition flux of dissolved organic nitrogen to the ocean of 15 Tg N yr<sup>-1</sup>, somewhat lower than the flux of 20 (uncertainty range 10–30) Tg N yr<sup>-1</sup> estimated by *Duce et al.* [2008] who used a simple assumption (based on literature estimates) that DON represents 30% of total N deposition. The deposited DON has uncertain, complex, and poorly quantified sources that may include some marine emissions that are redeposited [*Jickells et al.*, 2013]. TM4 model estimates about 6 Tg N yr<sup>-1</sup> of this DON to be of marine origin and redeposited to the ocean, resulting in a net flux of 9 Tg N yr<sup>-1</sup>. This estimation of an important recycled marine component of DON is consistent with estimates from observational studies on Bermuda [*Altieri et al.*, 2016], although at other locations anthropogenic terrestrial sources have been argued to dominate the DON [*Jickells et al.*, 2013]. The DON model results reported here estimate gross DON deposition at 15–20% of total N deposition (Figure 3) which is broadly in line with recent measurements of the proportion of DON in aerosols and rainwater over the Atlantic, 7–10% [*Zamora et al.*, 2011], ~24% [*Lesworth et al.*, 2010], and 19% [*Altieri et al.*, 2016], and Pacific, 16% [*Martino et al.*, 2014]. However, the proportion varies greatly regionally from 4 to 62% [*Zamora et al.*, 2011]. Thus, the major change in the flux estimate here compared to that of *Duce et al.* [2008] is the suggestion that the gross DON deposition may include an important marine recycled component, leading to a reduction in the net DON deposition. The sources of organic nitrogen in marine



**Figure 3.** Deposition fields to the oceans for (left column) 1850, (middle column) 2005, and (right column) 2050 for (top row) oxidized ( $\text{NO}_y$ ), (middle row) reduced ( $\text{NH}_x$ ), and (bottom row) organic N (in  $\text{g N m}^{-2} \text{yr}^{-1}$ ); scale maximum has been fixed to 0.20 for readability and easier comparison.

deposition are uncertain, and there is also evidence for an important terrestrial and anthropogenic component to the deposition [Cape *et al.*, 2011]. Hence, further studies of atmospheric organic nitrogen are required.

- In the case of reduced nitrogen ( $\text{NH}_x$ =ammonia+ammonium), the new model estimate of ammonia/ammonium deposition to the oceans presented here ( $12 \text{ Tg N yr}^{-1}$ ) is only half of that reported by Duce *et al.* [2008], 24 (uncertainty range 14–32)  $\text{Tg N yr}^{-1}$ . This difference arises because in the new model estimate, while gross  $\text{NH}_x$  deposition is  $20 \text{ Tg N yr}^{-1}$  (broadly similar to the earlier estimate),  $8 \text{ Tg N yr}^{-1}$  of this is estimated to be associated with redeposition of  $\text{NH}_x$  emitted as ammonia from the oceans. This compares to an estimate of recycled ammonia of only  $3 \text{ Tg N yr}^{-1}$  in Duce *et al.* [2008].

**Table 2.** Deposition to the Oceans ( $\text{Tg N yr}^{-1}$ ) All With 2005 Meteorology and Using the RCP 6.0 Scenario for 2050<sup>a</sup>

| Flux                                   | 1850 | 2005 | 2050 |
|--|------|------|------|
| Inorganic $\text{NO}_y$                | 4    | 18   | 13   |
| $\text{NH}_y$ from land                | 2    | 12   | 14   |
| $\text{NH}_y$ from ocean (redeposited) | 8    | 8    | 8    |
| ON from land                           | 4    | 9    | 9    |
| ON from ocean (recycled)               | 6    | 6    | 6    |
| Total N input                          | 24   | 53   | 50   |
| Net N input                            | 10   | 39   | 36   |

<sup>a</sup>Note that total N includes insoluble organic nitrogen.



Thus, as with the dissolved organic nitrogen, the marine recycling flux estimation results in an important change in the net flux estimates. There is relatively limited direct experimental evidence to substantiate the large-scale marine emission of ammonia suggested by these models [Johnson *et al.*, 2008], but it is consistent with one recent detailed study on Bermuda in the tropical Atlantic [Altieri *et al.*, 2014]. We suggest that the magnitude and direction of the air-sea ammonia flux (and the organic nitrogen flux) deserves further investigation.

Despite the changes in the overall fluxes, the geographic patterns of atmospheric deposition to the oceans and their temporal evolution (Figure 3) remain similar to those of Duce *et al.* [2008]. Highest inputs occur in the Northern Hemisphere downwind of large industrial and population centers in Europe, North America, and Asia. The model does not have sufficient resolution to separate deposition to coastal waters from that to the open ocean accurately, but Vet *et al.* [2014] suggest that 24% of nitrogen deposition falls in the coastal region as they define it. Because Vet *et al.* [2014] use a definition which includes some coastal land area, 24% probably represents an upper limit on the total of atmospheric nitrogen deposition that falls onto the coastal seas.

Atmospheric N inputs to the oceans are estimated to have increased sharply from 1860 to 2005 particularly in areas such as the North Atlantic and North Pacific downwind of industrialized regions. The increases in deposition to the South China Sea, for example, are already evident and now appear to be directly impacting local water column nitrate concentrations and primary production [I. N. Kim *et al.*, 2014; T. W. Kim *et al.*, 2014]. It has recently been argued that atmospheric deposition of nutrients (particularly iron, but also nitrogen) to the western Pacific can have impacts further afield in the eastern tropical Pacific, following transportation of atmospherically deposited nutrients by the ocean circulation [Ito *et al.*, 2016].

Most emission scenarios to 2050 suggest that further atmospheric deposition increases will be seen predominantly downwind of southern and Southeast Asia, reflecting industrial development plus population and affluence increases. Current projections for 2030 and 2100 under different representational concentration pathways (RCP) scenarios [Kanakidou *et al.*, 2016] suggest total N deposition to the oceans will change little between now and 2100 (−2 to +7% change by 2030, −17 to +8% by 2100 which is somewhat smaller than the projection with a different scenario of Duce *et al.* [2008]). However, the global distribution pattern will probably change (Figure 3) [Duce *et al.*, 2008]. The balance of the relative importance of oxidized (derived from NO<sub>x</sub> emissions) and reduced nitrogen (derived from ammonia emissions) is also projected to change, with an increasing proportion of ammonium compared to nitrate, due to more efficient controls on terrestrial NO<sub>x</sub> emissions compared to ammonia [Lamarque *et al.*, 2013]. These trends are already evident in deposition data with reduced nitrogen becoming relatively more important in North America in recent years [Vet *et al.*, 2014]. The trend in Southeast Asia is the reverse [Liu *et al.*, 2013] in each case reflecting regional emission changes. There are also currently large regional differences in the relative importance of oxidized and reduced nitrogen in atmospheric deposition, with the proportion of reduced to total nitrogen in deposition much higher in SE Asia than elsewhere [Vet *et al.*, 2014]. The suggested trend to a greater relative proportion of reduced to oxidized nitrogen can potentially alter atmospheric aerosol pH and the acidity of atmospheric deposition [Lamarque *et al.*, 2013]. However, this may not necessarily be the case, at least over land, where aerosol gas phase interactions maintain very acidic aerosol pH values until the ratio of acids to ammonia gas falls quite low [Weber *et al.*, 2016].

## 5. Summary of Estimated Inputs

In Table 3 we present a summary of our best estimates of contemporary nitrogen inputs to the oceans, based on the earlier discussion in the text. We therefore suggest that at least 76% of the atmospheric input is deposited beyond the shelf break, and 75% of the river DIN input escapes beyond the shelf break. We assume that all of the nitrogen fixation takes place in the open ocean. Based on the scenarios discussed earlier, it seems likely that total fluxes of nitrogen to the ocean are unlikely to change markedly over the next few decades, assuming the scenarios considered are realistic.

## 6. Impacts of Atmospheric Deposition on Water Column Productivity

The effects of atmospheric deposition have been evaluated previously using global ocean biogeochemical models [Krishnamurthy *et al.*, 2007, 2010, 2009; Suntharalingam *et al.*, 2012; Yang and Gruber, 2016] or based on various scaling procedures by Duce *et al.* [2008]. Duce *et al.* [2008] and Suntharalingam *et al.* [2012] use the same atmospheric

**Table 3.** Nitrogen Inputs to the Total Oceans Including the Continental Shelf and to the Open Ocean Beyond the Shelf Break<sup>a</sup>

| Source      | Total Ocean Flux (Tg N yr <sup>-1</sup> ) | Flux to the Open Ocean (Tg N yr <sup>-1</sup> ) |
|-------------|---|---|
| Atmospheric | 39  | >30   |
| Fluvial     | DIN 23, DON 11                            | DIN 17, Don >0 to <11                           |
| N fixation  | 164                                       | 164   |

<sup>a</sup>See text for derivation of numbers.

deposition field, while *Krishnamurthy et al.* [2007] use a separately derived field with a somewhat smaller flux, due in part to not considering organic nitrogen and also using net rather than gross ammonia/ammonium inputs, i.e., correcting for the marine ammonia emissions. All three of these models estimate the impact of increased atmospheric N deposition on export production (that which sinks to depth and should relate to ocean biological CO<sub>2</sub> uptake) to be ~0.4 Pg C/yr, reflecting predominantly the similar atmospheric nitrogen inputs used in each of the different model simulation. Studies have also considered the impact of atmospheric deposition at regional scales [*Ito et al.*, 2016; *Sundarambal et al.*, 2010; *Zamora et al.*, 2010], finding, for example, that atmospheric deposition can sustain 3% of new primary production in the northern Indian Ocean and on occasions an even higher percentage in the Atlantic [*Singh et al.*, 2012; *Spokes et al.*, 2000].

The response of the oceans to the atmospheric inputs of nitrogen has been modeled here using the PlankTOM10 model [*Le Quere et al.*, 2005; *Le Quere et al.*, 2016] to which we have added the N<sub>2</sub>O model of *Suntharalingam et al.* [2012]. This global biogeochemical model has a 2 by 1.1 degree resolution, 10 plankton functional types, and 44 state variables run within an ocean general circulation model. The model allows variable Fe:Chl:Si:C ratios in phytoplankton and particulate organic matter [*Buitenhuis et al.*, 2013] and fixed O<sub>2</sub>:C:N:P in all organic matter [*Anderson and Sarmiento*, 1994] and allows nitrogen-fixing organisms to preferentially utilize dissolved nitrogen in the water column when it is available. The atmospheric deposition field is essentially the same as that described earlier from the TM4 model, although the total flux used in the runs here was 35 rather than 39 Tg N yr<sup>-1</sup> with deposition fields as in Figure 3. The PlankTOM10 nitrogen fixation field is shown in Figure 2 and discussed earlier. The PlankTOM10 model does not fully resolve the shelf sea because of the grid square resolution, so we have used a value of riverine N input to the ocean of 16.3 Tg N/yr, similar to the estimated total DIN net river input to the open ocean. *da Cunha et al.* [2007] have previously shown, using an earlier version of this model, that the ocean productivity is relatively insensitive (on decadal time scales) to changes in the river input; for example, primary and export productivity only decrease by 7% and 3%, respectively, for a complete cessation of river inputs in the model runs, while only a 5% increase in primary productivity results from a 50% increase in riverine N inputs. However, the percentage impact on the coastal ocean productivity in each case is greater.

In the standard PlankTOM10 configuration, nitrogen fixation suppression increases with increasing surface water nitrogen concentrations and is suppressed by 50% at 1.7 μM NH<sub>4</sub> or 7.3 μM NO<sub>3</sub>. This is based on the assumption that nitrogen-fixing organisms would preferentially utilize available fixed nitrogen in the water column. This creates a potential negative feedback on ocean nitrogen cycle from atmospheric deposition as less nitrogen is fixed if there is an increase in nitrogen deposition. As noted above, some of the available evidence suggests that such suppression only occurs at high surface water fixed N concentrations and that therefore individual atmospheric deposition events are unlikely to lead to such large increases in ambient surface water nitrogen concentrations. We have performed two model simulations, one assuming no suppression of nitrogen fixation by fixed nitrogen (Table 4, model run without N fixation suppression), and the other retaining the standard PlankTOM10 suppression (Table 4, model run including N fixation suppression). The model runs covered just over 400 years. Overall, ocean nitrogen fixation without the suppression is increased by 18 (from 146 to 164) Tg N yr<sup>-1</sup> (12% increase) over the standard run with suppression, emphasizing the potential sensitivity of the ocean biogeochemical system to such suppression as a negative feedback. Note also that nitrogen fixation is still reduced by about 4% in the model runs without suppression compared to the preindustrial run. This may reflect non-nitrogen-fixing phytoplankton outcompeting nitrogen fixers for other key nutrients (Fe and P), and thereby suppressing the growth of nitrogen fixers. Others have reported similar reductions in nitrogen fixation due to atmospheric nitrogen deposition in their model runs [*Krishnamurthy et al.*, 2007, 2010, 2009; *Okin et al.*, 2011; *Somes et al.*, 2016].

*Somes et al.* [2016] have recently reported a related study of the impacts of atmospheric deposition on ocean productivity using the UVic Earth System Climate Model. This model has more complex feedbacks than the

**Table 4.** Mean Global-Scale Fluxes Averaged Over the 1990s Are Given for PlankTOM10 (2\*1.1 Degree Resolution)<sup>a</sup>

|  | PlankTOM10                     | $\Delta$ Tg N/yr |
|--|--------------------------------|------------------|
| <i>Model Run Without Nitrogen Fixation Suppression</i> |                                |                  |
| Atmospheric N deposition <sup>b</sup>                  | 35 (177)                       | 22.3             |
| Riverine N inputs <sup>b</sup>                         | 16.3 (0)                       |                  |
| Nitrogen fixation                                      | 164 (−3.9)                     | −6.74            |
| Denitrification <sup>c</sup>                           | 212 (1.7)                      | 3.53             |
| Sedimentary organic N burial                           | 57.7 (0)                       |                  |
| Primary production                                     | 33.6 (0.44) 5135 Tg N          | 22.49            |
| Sinking POC export at 100 m <sup>d</sup>               | 2.96 (0.35)                    | 2.14             |
| Air-sea CO <sub>2</sub> flux                           | 2.83 (0.00)                    |                  |
| Air-sea N <sub>2</sub> O flux                          | 2.07 (0.5)                     | 0.01             |
| OMZ volume 20 $\mu$ M <sup>e</sup>                     | 16.9e15 m <sup>3</sup> (0.86)  |                  |
| OMZ volume 10 $\mu$ M                                  | 3.58e15 m <sup>3</sup> (0.38)  |                  |
| OMZ volume 5 $\mu$ M                                   | 1.19e15 m <sup>3</sup> (3.7)   |                  |
| <i>Model Run Including N Fixation Suppression</i>      |                                |                  |
| Atmospheric N deposition <sup>b</sup>                  | 35 (179)                       | 22.5             |
| Riverine N inputs <sup>b</sup>                         | 16.3 (0)                       |                  |
| Nitrogen fixation                                      | 146 (−7.0)                     | −11.33           |
| Denitrification <sup>c</sup>                           | 207 (1.8)                      | 3.65             |
| Sedimentary organic N burial                           | 57.7 (0)                       |                  |
| Primary production                                     | 33.7 (0.42) 5158 Tg N          | 20.94            |
| Sinking POC export at 100 m <sup>d</sup>               | 2.99 (0.54)                    | 2.37             |
| Air-sea CO <sub>2</sub> flux                           | 2.88 (0.17)                    |                  |
| Air-sea N <sub>2</sub> O flux                          | 2.55 (0.8)                     | 0.02             |
| OMZ volume 20 $\mu$ M <sup>e</sup>                     | 16.35e15 m <sup>3</sup> (0.43) |                  |
| OMZ volume 10 $\mu$ M                                  | 3.38e15 m <sup>3</sup> (1.8)   |                  |
| OMZ volume 5 $\mu$ M                                   | 1.13e15 m <sup>3</sup> (1.5)   |                  |

<sup>a</sup>Buitenhuis *et al.* [2013] and Le Quere *et al.* [2005]. Values in parentheses show the percent difference in each flux when rising atmospheric N deposition is included. Nitrogen fluxes are given in units of Tg N/yr, and carbon fluxes are in units of Pg C/yr. Total changes ( $\Delta$ ) in the atmospheric nitrogen inputs and their impacts on nitrogen fixation, denitrification, primary production, and N<sub>2</sub>O emissions are also listed.

<sup>b</sup>Dissolved inorganic N + dissolved organic N.

<sup>c</sup>All as water column denitrification in model.

<sup>d</sup>Sinking particulate organic carbon at 100 m.

<sup>e</sup>Volume of oxygen minimum zone (OMZ) waters at specified cutoff value.

PlankTOM10 model, particularly in terms of benthic and pelagic denitrification. However, this model does not resolve shelf systems well and so underestimates benthic denitrification and thereby also nitrogen fixation, which is set in the model to balance the overall denitrification losses. The Somes *et al.* [2016] simulations estimated the impact of atmospheric nitrogen inputs to the ocean at the upper end of the flux ranges considered by Duce *et al.* [2008]. The UVic model is parameterized such that at 5  $\mu$ M nitrate, nitrogen fixation is fully suppressed. The UVic model, like the PlankTOM10 model, therefore also produces quite a strong negative feedback from the suppression of nitrogen fixation by atmospheric nitrogen deposition. This model also highlights another potentially important feedback [Landolfi *et al.*, 2013]. Denitrification consumes more nitrogen than is liberated from its decomposition of organic matter. Hence, it has been demonstrated in the UVic model that increased atmospheric nitrogen deposition can lead to a negative feedback, in which increased production leads to expansion of low oxygen zones, then to net nitrogen consumption by denitrification, and hence to lower overall ocean productivity. This feedback occurs on time scales of hundreds of years reflecting the ocean circulation time scales for passing water through denitrification zones [Somes *et al.*, 2016]. Yang and Gruber [2016] reached a very similar conclusion using a different ocean biogeochemical model.

The model estimates here consider mainly the effects of nitrogen deposition on nitrogen fixation. However, there is increasing evidence that atmospheric iron deposition also plays a key role in nitrogen fixation because of the high iron requirements of nitrogen-fixing enzymes [Ito *et al.*, 2016; Martino *et al.*, 2014; Moore *et al.*, 2009; Ward *et al.*, 2013]. The dominance of nitrogen fixation we identify here, and the uncertainty in its sensitivity to atmospheric nitrogen and iron inputs and water column phosphorus cycling [Landolfi *et al.*, 2015], suggests that the magnitudes and controls on nitrogen fixation merit further research.

In the subsequent discussion to illustrate the maximum potential effects, we consider the model output run without the suppression of nitrogen fixation (Table 4, model run without rather than including N fixation suppression). We derive the changes in various ocean biogeochemical processes compared to a preindustrial atmospheric input estimate with the present-day riverine nutrient input. As noted earlier, reducing the riverine input to preindustrial levels would have little impact on the outcome in most open ocean regions [da Cunha *et al.*, 2007].

Our estimates (Table 3) indicate that atmospheric inputs dominate the increased N inputs to the oceans since the preindustrial era. This is the case even allowing for the increased inputs from rivers to the open ocean estimated here, compared to the assumption by Duce *et al.* of complete shelf nitrogen retention (Table 3). There are strong spatial gradients in the atmospheric N deposition as discussed by Duce *et al.* (see also Figure 3) with much larger inputs to the Northern Hemisphere ocean compared to the Southern Hemisphere. Within the Northern Hemisphere, deposition is particularly high in ocean regions downwind of large population centers, such as Asia (Figure 3).

The model results (Table 4) suggest that increased anthropogenic atmospheric N deposition from preindustrial to the present could have increased ocean productivity overall by about 0.4% equivalent to 0.15 Pg C/yr. This increase in overall primary production is about half of that suggested by Duce *et al.* [2008] whose estimates were based on scaling atmospheric deposition falling on nitrogen-limited ocean regions to primary production using the Redfield ratio. The difference between the estimates here (Table 4) and this earlier estimate is essentially consistent with the reduced net atmospheric nitrogen deposition estimated here compared to the earlier paper.

Export production is the proportion of the primary production sinking to the deep ocean and the key issue in terms of removal of CO<sub>2</sub> from the atmosphere [Giering *et al.*, 2014; Laws *et al.*, 2000]. Export production only increases by 0.01 Pg C/yr over the short term in the model runs (Table 4). The proportion of the primary production exported to depth estimated here is smaller than that estimated by Duce *et al.* [2008]. This low export percentage (*f* ratio—new or export/total primary production) estimate of only 7% in PlankTOM10 compared to an assumed value of 22% in Duce *et al.* is consistent with some other lower published estimates [e.g., Laws *et al.*, 2000]. Krishnamurthy *et al.* [2007] have a similarly low sinking particulate organic carbon (POC) flux that is only 12% of productivity in their estimates of the impacts of atmospheric nitrogen deposition. Recently, Henson *et al.* [2011] have also argued more generally for such a lower value for the *f* ratio, based on direct measurements, while also emphasizing that the *f* ratio varies systematically throughout the oceans. Regardless of the short-term (years to decades) recycling of the atmospherically deposited nitrogen within the upper ocean and low export production, on the longer time scale (centuries) the atmospheric nitrogen input will eventually be lost to the deep sea and with it the associated drawdown of 0.15 Pg C/yr; the model runs are simply not long enough to capture this effect.

N<sub>2</sub>O is a powerful greenhouse gas released by nitrification and denitrification processes. Duce *et al.* [2008] noted that increases in ocean productivity can lead to expansion of low oxygen regions and an attendant increase in N<sub>2</sub>O emissions. The extent of such a feedback is sensitive to the export production and also to the area and extent of low oxygen [e.g., Bianchi *et al.*, 2012]. The impacts of atmospheric nitrogen deposition on N<sub>2</sub>O emissions by nitrification and denitrification have been modeled by Suntharalingam *et al.* [2012]. In our model runs (Table 4) we estimate the low oxygen region for N<sub>2</sub>O emissions, based on three different oxygen concentration thresholds of <20, 10, and 5 μM oxygen concentration. In the model runs the areas of low oxygen, defined by all three thresholds increase as does the overall ocean N<sub>2</sub>O flux, but the increases are generally <1% (Table 4). This increase is smaller than the 3–4% change in N<sub>2</sub>O emissions estimated by Suntharalingam *et al.* [2012]. This reduction is consistent with the reduced magnitude of net atmospheric anthropogenic nitrogen inputs used here compared to those used by Suntharalingam *et al.* [2012]. N<sub>2</sub>O can also be produced by oxidation of ammonia and DON, and changes in the surface ocean cycling of these species as a result of atmospheric deposition could also change the ocean emissions of N<sub>2</sub>O [Loscher *et al.*, 2012; Santoro *et al.*, 2011]. Although there are substantial uncertainties associated with all aspects of the oceanic N<sub>2</sub>O cycle [Zamora and Oschlies, 2014], the small size of change in N<sub>2</sub>O emissions estimated here suggests that large changes in N<sub>2</sub>O because of atmospheric nitrogen deposition are unlikely.

## 7. Conclusions

The combination of lower atmospheric deposition fluxes estimated here compared to earlier studies, a relatively high estimated rate of nitrogen fixation, and ocean biogeochemical feedbacks leads to a prediction of a

smaller impact of increasing atmospheric nitrogen deposition on ocean biogeochemical cycles and carbon uptake than that of *Duce et al.* [2008]. Our estimate of the flux of fluvial nitrogen to the open ocean is larger. The analysis and model calculations presented here highlight that this conclusion is very sensitive to four feedbacks which we identify—recycling of ammonia and organic nitrogen from seawater to the atmosphere, inhibition of nitrogen fixation by atmospheric nitrogen deposition, and the denitrification sink for nitrogen. All these feedbacks undoubtedly occur, so the key, and very difficult, challenge is the quantification of the scale of these under realistic open ocean conditions.

The calculations here suggest that the impacts of atmospheric deposition on ocean biogeochemistry can result in a net increase in primary production and CO<sub>2</sub> uptake of 0.15 Pg C yr<sup>-1</sup>. However, the resulting reduction in radiative forcing will be offset slightly by increases in N<sub>2</sub>O emissions from some regions of the oceans [Suntharalingam *et al.*, 2012].

In some areas pulses of atmospheric nutrient deposition may be sufficiently large to have short-term (days) impacts on productivity [Guieu *et al.*, 2014]. However, over most of the oceans the likely scale of short-term nitrogen inputs are relatively small compared to the existing background stock [Duce *et al.*, 2008; Michaels *et al.*, 1993]. This may not be the case for dust/iron deposition which can affect nitrogen fixation [Guieu *et al.*, 2014; Moore *et al.*, 2006].

The increases in fluvial nitrogen inputs to the ocean from human activity predominantly affect coastal systems leading to major environmental pressures [e.g., Diaz and Rosenberg, 2008]. We suggest that a quarter of fluvial inorganic nitrogen inputs are denitrified on the shelf, and the fate of fluvial dissolved organic nitrogen is particularly uncertain. Our results suggest that the effects of shelf denitrification on fluvial dissolved inorganic nitrogen fluxes is strongly latitude dependent, and further increases in nitrogen use on land in equatorial regions may therefore have a disproportionately large impact on total fluvial inputs to the open ocean. Where there are large losses of fluvial inorganic nitrogen by denitrification on the shelf, this may result in excess fluvial P inputs to the open ocean (relative to N) which could then support nitrogen fixation.

In general, the impacts of atmospheric nitrogen deposition will be greatest where the ambient surface water column nitrogen concentrations are low and hence in the ocean gyres [Duce *et al.*, 2008]. Atmospheric nitrogen deposition has strong geographic gradients, and thus it is important to consider regions where the impacts of atmospheric deposition may be particularly strong or rather different from the general pattern. We identify four such regions—the North Pacific, North Indian Ocean, Mediterranean, and tropical North Atlantic as explained below.

We predict (Figure 3) as previously [Duce *et al.*, 2008] that the western North Pacific is likely to be a focus of increasing atmospheric deposition over coming decades, even if the total net nitrogen input to the oceans may not grow. Deposition in this region is already argued to be increasing ocean productivity regionally [J. N. Kim *et al.*, 2014; T. W. Kim *et al.*, 2014]. This regional impact may be extended beyond the regions of enhanced atmospheric deposition via ocean circulation transport of deposited nutrients, where this can occur relatively rapidly on time scales of decades or less [Ito *et al.*, 2016].

In the northern Indian Ocean region, atmospheric deposition is already estimated to be contributing to new production [Singh *et al.*, 2012] and is predicted to increase. This region also contains a major deep water oxygen minimum zone where denitrification and nitrification sustain very high N<sub>2</sub>O fluxes. Here increasing nutrient inputs may lead to intensification of hypoxic conditions and increased fluxes of the greenhouse gas N<sub>2</sub>O, making this area of particular interest [Naqvi *et al.*, 2010; Suntharalingam *et al.*, 2012]. The Bay of Bengal region has low subsurface oxygen concentrations but minimal water column denitrification and N<sub>2</sub>O production at present [Bristow *et al.*, 2017]. Even modest increases in export production in the future could lead to substantial denitrification and N<sub>2</sub>O production.

The last areas we would highlight are the Mediterranean and North Atlantic subtropical gyre, which are both characterized by evidence of phosphorus limitation of primary production. This situation is enhanced by nitrogen deposition and may lead to accumulation of nitrogen in the water column and different biogeochemical impacts in such regions [Krom *et al.*, 2010; Moore *et al.*, 2009; Ward *et al.*, 2013; Yang and Gruber, 2016; Zamora *et al.*, 2010], compared to other ocean regions where nitrogen may be the proximate limiting nutrient [Moore *et al.*, 2013].

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