# Quantifying the impact of anthropogenic nitrogen deposition on oceanic nitrous oxide

Parvadha Suntharalingam,<sup>1</sup> Erik Buitenhuis,<sup>1</sup> Corinne Le Quéré,<sup>1</sup> Frank Dentener,<sup>2</sup> Cynthia Nevison,<sup>3</sup> James H. Butler,<sup>4</sup> Hermann W. Bange,<sup>5</sup> and Grant Forster<sup>1</sup>

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[1] Anthropogenically induced increases in nitrogen deposition to the ocean can stimulate marine productivity and oceanic emission of nitrous oxide. We present the first global ocean model assessment of the impact on marine N<sub>2</sub>O of increases in nitrogen deposition from the preindustrial era to the present. We find significant regional increases in marine N2O production downwind of continental outflow, in coastal and inland seas (15-30%), and nitrogen limited regions of the North Atlantic and North Pacific (5-20%). The largest changes occur in the northern Indian Ocean (up to 50%) resulting from a combination of high deposition fluxes and enhanced N2O production pathways in local hypoxic zones. Oceanic regions relatively unaffected by anthropogenic nitrogen deposition indicate much smaller changes (<2%). The estimated change in oceanic N2O source on a global scale is modest (0.08–0.34 Tg N yr<sup>-1</sup>,  $\sim$ 3–4% of the total ocean source), and consistent with the estimated impact on global export production (~4%). Citation: Suntharalingam, P., E. Buitenhuis, C. Le Quéré, F. Dentener, C. Nevison, J. H. Butler, H. W. Bange, and G. Forster (2012), Quantifying the impact of anthropogenic nitrogen deposition on oceanic nitrous oxide, Geophys. Res. Lett., 39, L07605, doi:10.1029/2011GL050778.

## 1. Introduction

[2] Intensification of fossil fuel combustion and nitrogenous fertilizer application since the pre-industrial era has increased global emissions of inorganic reactive nitrogen (primarily nitrogen oxides and ammonia species (NOy + NHx)), and associated atmospheric nitrogen deposition on the ocean [*Duce et al.*, 1991; *Dentener et al.*, 2006]. This flux to the ocean provides a supplemental nutrient source to marine ecosystems in nitrogen limited regions, with potential for significant impacts on productivity, ocean pH, and ocean-atmosphere fluxes of greenhouse gases such as N<sub>2</sub>O [*Prospero et al.*, 1996; *Krishnamurthy et al.*, 2007; *Doney et al.*, 2007; *Duce et al.*, 2008]. N<sub>2</sub>O is the third most significant contributor to radiative forcing of the long-lived

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greenhouse gases [*Forster et al.*, 2007], and current emissions, weighted by ozone depleting potential, are now estimated to exceed those of other ozone depleting agents [*Ravishankara et al.*, 2009].

[3] NHx and NOy have atmospheric lifetimes of hours to days and can be transported over large spatial scales  $(10^2 - 10^3 \text{ km})$ ; *Dentener et al.* [2006] estimate that over 80% of current oceanic deposition of these species occurs over the open ocean, with the remainder on coastal and shelf regions. Present-day levels of total reactive nitrogen (Nr) deposition on the ocean are estimated to be 38–96 Tg N yr<sup>-1</sup> [*Duce et al.*, 2008, hereinafter D2008]. This flux is comparable to other external nitrogen inputs to the upper ocean; c.f., 60–200 Tg N yr<sup>-1</sup> from marine nitrogen fixation [*Gruber*, 2008], and 50–80 Tg N yr<sup>-1</sup> from river input [*Galloway et al.*, 2004; *Seitzinger et al.*, 2005].

[4] The anthropogenic component of this deposition flux to the ocean has increased almost ten-fold since 1860, to  $\sim$ 54 (31–77) Tg N yr<sup>-1</sup> in 2000. It is s estimated to account for  $\sim 3\%$  of current global oceanic export production ( $\sim 0.31$ (0.18–0.44) Pg Cyr<sup>-1</sup> (D2008)). D2008 also highlight the potential impact on oceanic N<sub>2</sub>O evolution and suggest that increases in atmospheric nitrogen deposition since 1860 could account for a third ( $\sim 1.6$  Tg Nyr<sup>-1</sup>) of present-day ocean N2O emissions, with likely increases over the coming decades. Oceanic N<sub>2</sub>O is formed during the sub-surface remineralization of organic matter. The dominant formation pathway in well-oxygenated environments is believed to be nitrification during the oxidation of ammonium to nitrate [Cohen and Gordon, 1979; Frame and Casciotti, 2010; Santoro et al., 2011, and references therein]. However, N2O cycling mechanisms display sensitivity to local oxygen level; higher yields are noted at low O<sub>2</sub> levels, ascribed to alternate source pathways such as enhanced nitrification, denitrification, and interactions between the two [Codispoti et al., 2001; Naqvi et al., 2000]. Denitrification in anoxic regions can also provide a sink for N<sub>2</sub>O. Marine sub-oxic zones, such as those in the Eastern Tropical Pacific and the Arabian Sea, are important net sources of N<sub>2</sub>O to the atmosphere [Bange et al., 2001; Naqvi et al., 2010], and potentially contribute a significant portion (25–50%) of global ocean emissions [Codispoti, 2010]. Increases in anthropogenic nitrogen input to these regions is predicted to intensify local N<sub>2</sub>O formation and the ocean-to-atmosphere flux [Naqvi et al., 2000; Bange et al., 2010].

[5] Ocean biogeochemistry model analyses have assessed the impact of increased Nr deposition on marine productivity [*Krishnamurthy et al.*, 2007] and ocean acidification [*Doney et al.*, 2007], and report a spatially varied response with noted coastal amplification. The response of the marine  $N_2O$ cycle, however, has not been investigated in similar detail.

<sup>&</sup>lt;sup>1</sup>School of Environmental Sciences, University of East Anglia, Norwich, UK.

<sup>&</sup>lt;sup>2</sup>Institute for Environment and Sustainability, Joint Research Centre, European Commission, Ispra, Italy.

<sup>&</sup>lt;sup>3</sup>Institute of Arctic and Alpine Research, University of Colorado at Boulder, Boulder, Colorado, USA.

<sup>&</sup>lt;sup>4</sup>Global Monitoring Division, Earth System Research Laboratory, NOAA, Boulder, Colorado, USA.

<sup>&</sup>lt;sup>5</sup>Helmholtz Centre for Ocean Research Kiel (GEOMAR), Kiel, Germany.

Simulation	lpha (mol/mol)	eta (mol/mol)	Global Ocean N <sub>2</sub> O Source 'Background' Deposition (Tg N yr <sup>-1</sup> )	Global Ocean $N_2O$ Source 'Year 2000' Deposition (Tg N yr <sup>-1</sup> )	Change in $N_2O$ Source = Difference of 'Year 2000' and 'Background' Simulations (Tg N yr <sup>-1</sup> )
Standard	$0.75\times10^{-4}$	0.01	4.42	4.57	0.15
			Sensitivity Simulations <sup>b</sup>		
NitrificationOnly 0.75	$0.75 \times 10^{-4}$	0	2.97	3.05	0.08
NitrificationOnly 0.5	$0.5  imes 10^{-4}$	0	1.98	2.04	0.06
NitrificationOnly 1.0	$1.0  imes 10^{-4}$	0	3.96	4.07	0.11
LowO2x2	$0.75 \times 10^{-4}$	0.02	5.86	6.08	0.22
LowO2x3	$0.75 \times 10^{-4}$	0.03	7.31	7.59	0.28
LowO2x4	$0.75 \times 10^{-4}$	0.04	8.76	9.10	0.34
Nevison_2003 <sup>c</sup>			5.95	6.25	0.30

Table 1.	Impact of	Change in Nr	Deposition on	1 Oceanic N <sub>2</sub> O	Source: Summar	y of Results for t	he N <sub>2</sub> O Simulations <sup>3</sup>
		0				_	2

<sup>a</sup>Global oceanic  $N_2O$  source for 'Background' and 'Year 2000' deposition scenarios (columns 4 and 5); model estimated impact of anthropogenic Nr deposition on oceanic  $N_2O$  production (column 6).

<sup>b</sup>The 'NitrificationOnly' and 'LowO2' sensitivity simulations use variations of the N<sub>2</sub>O source parameterization of equation (1), with different values of  $\alpha$  and  $\beta$ , to change the weighting on the 'Nitrification' and 'Low-oxygen' N<sub>2</sub>O source pathways.

<sup>c</sup>The 'Nevison 2003' simulation implements the N<sub>2</sub>O source parameterization of *Nevison et al.* [2003].

Previous estimates of the impact of anthropogenic Nr deposition on marine  $N_2O$  have been derived from simple scaling analyses (e.g., D2008). Here, we use a global ocean biogeochemistry model, which includes representation of the  $N_2O$  cycle, to quantify the impact of the increases in reactive nitrogen deposition on ocean biogeochemistry and specifically on the marine  $N_2O$  source. This is the first spatially resolved analysis of this impact on marine  $N_2O$ , and enables us to identify sensitive regions where anthropogenic deposition has the most significant influence on marine  $N_2O$  formation.

## 2. Methods and Model Configuration

#### 2.1. Ocean Biogeochemistry Model

[6] We use the PlankTOM5 ocean biogeochemistry model [*Le Quéré et al.*, 2005; *Vogt et al.*, 2010], embedded in the prognostic global ocean general circulation model NEMO v2.3 [*Madec et al.*, 1999], and forced by daily meteorological data from the NCEP reanalysis. PlankTOM5 combines a representation of ecosystem dynamics, based on five plankton groups, with ocean biogeochemistry parameterizations from the PISCES model [*Aumont and Bopp*, 2006]. The model is run at a horizontal resolution of ~2° with higher resolution (up to 0.5°) in tropical and polar latitudes, and 31 vertical levels with 10 m resolution in the upper 100 m. Model global export production is 9.5 Pg C yr<sup>-1</sup>, consistent with recent estimates (9–12 Pg C yr<sup>-1</sup> [*Schlitzer*, 2002], 3–20 Pg C yr<sup>-1</sup> [*Najjar et al.*, 2007]). Additional details on model configuration and evaluation are given by *Cotrim da Cunha et al.* [2007] and *Vogt et al.* [2010].

## 2.2. N<sub>2</sub>O Model

[7] NEMO-PlankTOM5 has been extended to simulate the  $N_2O$  cycle, based on the parameterization of *Suntharalingam et al.* [2000], which relates  $N_2O$  production to marine organic matter remineralization via the oxygen consumption rate:

N<sub>2</sub>O Source =  $\alpha$  . [Oxygen Consumption Rate] + $\beta$  .  $f(O_2)$  . [Oxygen Consumption Rate] (1)

The two terms account for separate formation pathways representing (i) nitrification in the oxygenated ocean, and (ii) the enhanced yield of N<sub>2</sub>O at low oxygen levels.  $\alpha$  is a scalar multiplier derived from observed correlations between  $\Delta$ N<sub>2</sub>O('excess N<sub>2</sub>O') and Apparent Oxygen Utilization (AOU) [*Suntharalingam and Sarmiento*, 2000]. The parameterization of the high-yield N<sub>2</sub>O source in low oxygen zones follows the methods of *Suntharalingam et al.* [2000], where  $\beta$  is a linear scaling parameter, and  $f(O_2)$  accounts for the functional dependence of N<sub>2</sub>O yield on oxygen level. N<sub>2</sub>O loss by denitrification is represented at oxygen levels below 5  $\mu$ mol/L [*Friederich et al.*, 1985].

[8] Our 'Standard' simulation uses values  $\alpha = 0.75 \times 10^{-4}$  mol/mol and  $\beta = 0.01$  mol/mol. We also evaluate a set of sensitivity simulations (Table 1) varying the values of  $\alpha$  and  $\beta$  to account for reported regional variation in N<sub>2</sub>O yield in oxic and sub-oxic waters [*Law and Owens*, 1990; *Freing et al.*, 2009]). We evaluate, as an additional sensitivity, the parameterization of *Nevison et al.* [2003], which additionally accounts for the influence of water-mass mixing on measurements of AOU and  $\Delta$ N<sub>2</sub>O. The primary aim of the sensitivity analyses is to characterize the uncertainty in the N<sub>2</sub>O source function, when estimating the impact of anthropogenic Nr deposition on marine N<sub>2</sub>O.

[9] Our N<sub>2</sub>O simulations have been evaluated with a compilation of oceanic measurements from the cruises listed in Text S1 in the auxiliary material.<sup>1</sup> Figure S1 presents a comparison of model sensitivity simulations (Table 1) against N<sub>2</sub>O measurements for different oceanic regions characterizing both oxygenated (North and South Atlantic, Western Pacific), and low-oxygen zones (Eastern Equatorial Pacific, Arabian Sea). The 'Standard' and the 'Nevison2003' model simulations, sampled at the measurement locations, provide the best match to the observations capturing the magnitude and depth of the observed sub-surface N2O maximum in the majority of the regions. We note that both 'Standard' and the 'Nevison2003' simulations overestimate observed N<sub>2</sub>O in the Arabian Sea; this results from a poor representation of the local monsoonal upwelling and associated biogeochemical fluxes in coarse grid ocean models [Aumont and Bopp, 2006; Suntharalingam and Sarmiento, 2000]. The global oceanic N<sub>2</sub>O source in the 'Standard'

<sup>&</sup>lt;sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011GL050778.



**Figure 1.** (a) Change in reactive nitrogen deposition;  $\Delta Nr$  Deposition = 'Year 2000' minus 'Background' deposition distributions. (Units : mg N m<sup>-2</sup> yr<sup>-1</sup>). Data sources: *Duce et al.* [2008]; *Dentener et al.* [2006]; gridded distributions provided by K. Altieri (personal communication, 2009). (b) Change in organic carbon export estimated from NEMO-PlankTOM5 model (Units : g C m<sup>-2</sup> yr<sup>-1</sup>);  $\Delta C$  Export = Difference between ocean model simulations forced with 'Year 2000' and 'Background' Nr deposition distributions. (c) Change in oceanic N<sub>2</sub>O production (column integral, Units : mg N m<sup>-2</sup> yr<sup>-1</sup>);  $\Delta N_2O$  Source = Difference between ocean model simulations forced with 'Year 2000' and 'Background' Nr deposition distributions. (d) Percentage change in oceanic N<sub>2</sub>O production (Units: % change in column integral);  $\Delta N_2O$  Source expressed as a percentage of the ocean N<sub>2</sub>O source for the 'Background' scenario ('Standard' N<sub>2</sub>O model simulation).

simulation is 4.6 Tg N yr<sup>-1</sup> (comprised of 3.0 Tg N yr<sup>-1</sup> from the 'nitrification' pathway, and 1.6 Tg N yr<sup>-1</sup> from the lowoxygen pathway). The sensitivity simulations yield an oceanic N<sub>2</sub>O source range of 2.0–9.1 Tg N yr<sup>-1</sup> (Table 1), consistent with recent estimates (1.8–5.8 Tg Nyr<sup>-1</sup> [*Denman et al.*, 2007], and 3–11 Tg Nyr<sup>-1</sup> [*Bange*, 2006]).

#### 2.3. Nitrogen Deposition Simulations

[10] For all the simulations discussed in this analysis, we force the NEMO-PlankTOM5 model with a climatological meteorology (NCEP decadal average for 1996–2005) to minimize the influence of inter-annual meteorological variation, as our primary aim is evaluation of the impact of the change in anthropogenic Nr deposition on marine N<sub>2</sub>O through the assessment of different deposition scenarios. The inorganic carbon system tracers were initialized using the Global Ocean Data Analysis Project (GLODAP) [*Key et al.*, 2004], macro-nutrient initialization is from the World Ocean Atlas [*Garcia et al.*, 2006], and the other biological variables were initialized with values from a previously equilibrated model run [*Vogt et al.*, 2010]. For the sensitivity analyses presented here, the ocean model

was run for a further 60 years, and we report averaged values from the last decade of these simulations.

[11] Atmospheric Nr deposition fluxes are taken from D2008 ( $1^{\circ} \times 1^{\circ}$  gridded fields provided by K. Altieri (personal communication, 2009)), and account for inorganic and organic reactive nitrogen. We implement separate deposition distributions for (i) pre-industrial ('Background'), and (ii) present-day ('Year 2000'), conditions, with global Nr deposition totals on the ocean of 13.3 Tg N  $yr^{-1}$  and 67 Tg N yr<sup>-1</sup> respectively (D2008). The change in Nr deposition between these scenarios is illustrated in Figure 1a, and indicates significant increases in coastal and inland seas downwind of populated regions of East Asia, North America, the Indian sub-continent, and Western Europe. The largest open-ocean change occurs in the northern Indian Ocean (up to a ten-fold increase). Open-ocean gyre regions of the North Atlantic and North Pacific indicate two to fivefold increases (D2008).

[12] We evaluate the impact of anthropogenic Nr deposition on the marine  $N_2O$  source using the difference between two ocean model simulations, one subject to a pre-industrial 'Background' level of Nr deposition, and one with Nr deposition levels for 'Year 2000'; this follows similar methodology to previous such evaluations [*Krishnamurthy et al.*, 2007; *Doney et al.*, 2007].

# 3. Results

[13] Our model estimate of the impact of anthropogenic Nr deposition on global export production is 0.4 Pg C yr<sup>-1</sup> (~4% of global export); this is derived as the difference in export between 'Background' (9.5 Pg C yr<sup>-1</sup>) and 'Year2000' (9.9 Pg C yr<sup>-1</sup>) simulations. This estimate is comparable to those of recent investigations: 0.31 (0.18–0.44) Pg C year<sup>-1</sup> (D2008), and 0.2 Pg C yr<sup>-1</sup> [*Krishnamurthy et al.*, 2007] (for a lower present-day Nr deposition flux of 47 Tg N yr<sup>-1</sup>). The spatial distribution of the impact on export (Figure 1b) indicates largest changes in regions of high anthropogenic Nr deposition; specifically, coastal oceans (export increases >30%), the northern Indian ocean (up to 50%), and nitrate-depleted regions of northern hemispheric ocean basins (10–20%). Regions relatively unaffected by polluted continental outflow (e.g., much of the Southern Hemisphere) show export changes of less than 2%.

[14] Figures 1c and 1d illustrate the distribution of absolute and proportionate (in %) change in column-integrated N<sub>2</sub>O source for the 'Background' to 'Year 2000' change in Nr deposition ('Standard' N<sub>2</sub>O simulation shown). They indicate significant increases in N<sub>2</sub>O production in regions of high Nr deposition, e.g., coastal and inland seas (15– 30%), and North Atlantic and North Pacific basin regions downwind of continental outflow (5–20%). The largest impact is associated with the oceanic low oxygen zone of the Arabian Sea, where high levels of Nr deposition coincide with the dominant influence of the enhanced-yield N<sub>2</sub>O source pathway. N<sub>2</sub>O production in the 300–1000 m depth range of the low-oxygen zone of the Arabian Sea increases by ~50%.

[15] These local impacts correspond to measurable changes in the water column concentration of N<sub>2</sub>O; largest changes are associated with low oxygen regions, e.g., 2– 2.5 nmol L<sup>-1</sup> for the 100–300 m depth range in the Eastern Equatorial Pacific, and 5–6 nmol L<sup>-1</sup> in the 200– 500 m range of the Arabian Sea. Smaller, but still detectable changes occur in oxygenated waters, in particular, immediately downwind of continental outflow, e.g., 0.4–0.5 nmol L<sup>-1</sup> in the 200–500 m depth range of the western North Atlantic downwind of the outflow from the North American continent; and 0.3–0.4 nmol L<sup>-1</sup> at 400–700 m depth in the Western Pacific downwind of Asian outflow. We use as our criteria for detection limits the values reported by *Upstill-Goddard et al.* [1996] of ~ 40 picomol L<sup>-1</sup>.

[16] Table 1 summarizes the global results for the N<sub>2</sub>O sensitivity simulations; the increase in net marine N<sub>2</sub>O production ranges between 0.06–0.34 Tg Nyr<sup>-1</sup>, representing a 3–4% change in the global ocean source. This estimate of impact on global N<sub>2</sub>O production is smaller than that suggested by D2008 (~1.6 (1.2–2.0) Tg Nyr<sup>-1</sup>). Our model estimate of the impact on export production (0.4 Pg Cyr<sup>-1</sup>), however, is of comparable magnitude to that of D2008 of 0.18–0.44 Pg Cyr<sup>-1</sup>. The discrepancy in estimated impact on N<sub>2</sub>O between our global model result and that of D2008 arises from the differing underlying methods. In our model simulations, the main determinants of the marine N<sub>2</sub>O

source are (i) the magnitude of organic matter remineralization in the aphotic zone (primarily driven by organic carbon export), and (ii) the local oxygen level. A change imposed on sub-surface organic matter remineralization (i.e., via a change in export due to increased Nr deposition) induces an associated change in N<sub>2</sub>O formation. Our estimate of the impact of anthropogenic Nr deposition on N<sub>2</sub>O source is based on this change in organic matter remineralization (between the 'Background' and 'Year 2000' simulations), and is stoichiometrically consistent with the impact on export.

[17] The impact on N<sub>2</sub>O of D2008 is derived from a global scaling of nitrogen fluxes [Duce et al., 2008, Table S1]. This scaling estimates the contribution of anthropogenic Nr to oceanic N<sub>2</sub>O emission by multiplying the global ocean N<sub>2</sub>O flux (5.0 Tg Nyr<sup>-1</sup> by D2008) by a scaling factor which accounts for the proportionate contribution of anthropogenic Nr deposition (54 Tg Nyr<sup>-1</sup>) to the external inputs of 'new nitrogen' fuelling surface ocean productivity. D2008 define this 'new nitrogen' as the sum of nitrogen deposition and nitrogen fixation (totalling 167 Tg  $Nyr^{-1}$ ). The ratio of anthropogenic Nr deposition to this 'new nitrogen' total yields a scaling factor of  $\sim 0.32$ , and their estimate of the impact on oceanic N<sub>2</sub>O of 1.6 Tg Nyr<sup>-1</sup>. This scaling analysis, however, neglects the supply of 'new' nitrate upwelled from below (~1200 Tg N yr<sup>-1</sup> [*Gruber*, 2008]), which is relevant on the decadal to century timescales of anthropogenic Nr increase. If we modify the methodology of D2008 to account for this upwelling nitrate flux (by including this term in column 4 of Table S1 of D2008), the modified scaling factor becomes  $\sim 0.04$ , yielding an impact on oceanic  $N_2O$  of 0.19 Tg Nyr<sup>-1</sup>; this is consistent with our model estimated range of 0.06–0.34 Tg N yr<sup>-1</sup>.

[18] We are not aware of any other quantification of the impact of Nr deposition on the global oceanic N<sub>2</sub>O source. *Galloway et al.* [2004, Table 3 and Figure 1] estimate a change of 0.4 Tg N yr<sup>-1</sup> in estuarine and shelf N<sub>2</sub>O emissions due to anthropogenic reactive nitrogen impacts between 1860 and the 1990s; they assume, however, that the open ocean N<sub>2</sub>O source remains constant (at 3.5 Tg N yr<sup>-1</sup>) in this timeframe.

# 4. Uncertainties

[19] Potential uncertainties in our global model estimate could arise from uncertainties in the underlying parameterizations (for  $N_2O$ , ocean biogeochemistry and circulation), and in our assumptions on Nr assimilation by marine organisms. We note, firstly, that our methodology is designed to minimize the impact of systematic model biases (e.g., in circulation or biogeochemistry), as it relies on the difference between two simulations, that differ only in their surface deposition flux of Nr.

[20] Our model estimate of the impact of anthropogenic Nr deposition on export (0.4 Pg C yr<sup>-1</sup>) is similar to that of D2008 and *Krishnamurthy et al.* [2007] (0.18– 0.44 Pg Cyr<sup>-1</sup>), and therefore unlikely to be a cause of error in the N<sub>2</sub>O source estimate. Our N<sub>2</sub>O sensitivity simulations (Table 1) are designed to characterize uncertainty in the parameterization of the marine N<sub>2</sub>O source. The 'Standard' and 'Nevison2003' simulations produce the closest match to the observations on a global scale (Figure S1). The extreme low and high N<sub>2</sub>O scenarios characterize a range of simulated oceanic N<sub>2</sub>O distributions; e.g., the 'NitrificationOnly' simulations underestimate, and the 'LowO2x2' to'LowO2x4' simulations overestimate observed N<sub>2</sub>O throughout the water column. In this context, the impact on marine N<sub>2</sub>O associated with the 'LowO2x2' to'LowO2x4' simulations (0.22–0.34 Tg N yr<sup>-1</sup>) can be considered an upper bound. Our model analysis also assumes complete assimilation of the deposited Nr by ecosystems in nitrogen limited regions. However, components of the deposition Nr flux (e.g., water-soluble organic nitrogen [*Cornell et al.*, 2003]) may not be immediately bio-available; in this context, our model estimates must also be regarded as an upper bound.

[21] Our analysis, and that of D2008, estimate the impact of the nutrient fertilization on N<sub>2</sub>O evolution with a link to enhanced marine productivity. In-situ iron fertilization experiments have reported contrasting results with regard to N<sub>2</sub>O; increases in sub-surface N<sub>2</sub>O saturation were observed during the Southern Ocean Iron Release Experiment (SOI-REE) [*Law and Ling*, 2001], but not during the European Iron Fertilization Experiments (EIFEX), possibly due to rapid sedimentation of resulting particulate matter in the latter [*Walter et al.*, 2005]. Additional monitoring of the fate of the export particulate phase is called for to resolve this impact on N<sub>2</sub>O [*Law*, 2008]. In view of a potentially diminished role for nutrient fertilization, our model estimates again constitute an upper bound on N<sub>2</sub>O evolution from Nr deposition.

[22] Beman et al. [2010] note a lowering of marine ammonia oxidation rates with decreasing pH (3-44% for a pH change of 0.1) and suggest associated reductions in the oceanic nitrification source of N<sub>2</sub>O with increasing ocean acidification. A detailed evaluation of the impact of the increases in ocean acidification since the pre-industrial era is beyond the scope of this study, however, in view of the potential decrease in nitrification rates [Beman et al., 2010], which is not represented in our analysis, our model estimates again provide an upper bound on the impact of Nr deposition on N<sub>2</sub>O evolution. Uncertainty in the model oxygen distribution is a potential source of error [Najjar et al., 2007], as local oxygen levels determine the magnitude and distribution of the high-yield N<sub>2</sub>O source pathway. In the simulations of Table 1, we minimize this potential error by holding model oxygen distributions to the climatological values of World Ocean Atlas [Garcia et al., 2006]. This approach, however, also limits the capability for simulating biogeochemical feedbacks between oxygen and N<sub>2</sub>O, as the model's oxygen distribution, being fixed to the observed values, does not reflect the production and consumption resulting from organic matter formation and remineralization. We have therefore conducted additional sensitivity simulations (parallel to those of Table 1), where model oxygen is allowed to change, and no longer fixed to the WOA climatology. These indicate that this feedback effect on oxygen and N<sub>2</sub>O yield is relatively small, accounting for an additional change of less than 0.01 Tg N yr<sup>-1</sup>.

## 5. Summary

[23] We have evaluated the impact on the marine  $N_2O$  source of the increase in anthropogenic reactive nitrogen deposition from the pre-industrial era to the present day using a global ocean biogeochemistry model. Our analyses

indicate relatively modest increases in the oceanic  $N_2O$  source on a global scale (0.06–0.34 Tg N yr<sup>-1</sup>). This is equivalent to a 3–4% change in the global ocean  $N_2O$  source, and consistent with the proportional impact on export production (~4%.) Our estimate for  $N_2O$  is lower than that suggested by a recent study (D2008); the discrepancy arises from the scaling methodology of D2008, which did not account for the upwelling flux of new nitrogen in their analysis. Inclusion of the flux of upwelled nitrogen in the method of D2008 yields a result of similar magnitude to our global model estimates.

[24] Our model analysis indicates significant regional impacts, however, downwind of populated zones, particularly in coastal and inland seas, in nitrogen limited regions of the North Atlantic and North Pacific, and the northern Indian Ocean. The Arabian Sea demonstrates the largest change, with regional source increases of ~50%. This results from high anthropogenic Nr deposition fluxes stimulating productivity over the hypoxic zones associated with enhanced N<sub>2</sub>O formation, and illustrates the potential sensitivity of such low-oxygen zones to changes in surface nutrient forcing. Quantifying the impact on N<sub>2</sub>O in such regions should be a priority for future investigations.

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H. W. Bange, Helmholtz Centre for Ocean Research Kiel (GEOMAR), Wischhofstr. 1-3, D-24148 Kiel, Germany.

E. Buitenhuis, G. Forster, C. Le Quéré, and P. Suntharalingam, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK. (p.suntharalingam@uea.ac.uk)

J. H. Butler, Global Monitoring Division, Earth System Research Laboratory, NOAA, 325 Broadway, Boulder, CO 80303, USA.

F. Dentener, Institute for Environment and Sustainability, Joint Research Centre, European Commission, Via E. Fermi 2749, I-21027 Ispra, Italy.

C. Nevison, Institute of Arctic and Alpine Research, University of Colorado at Boulder, Campus Box 450, Boulder, CO 80309, USA.