Ocean Ammonia Outgassing: Modulation by CO₂ and Anthropogenic Nitrogen Deposition

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Abstract

The imprint of anthropogenic activities on the marine nitrogen (N) cycle remains challenging to represent in global models, in part because of uncertainties regarding the source of marine N to the atmosphere. While N inputs of terrestrial origin present a truly external perturbation, a significant fraction of N deposition over the ocean arises from oceanic ammonia (NH₃) outgassing that is subsequently deposited in other ocean regions. Here, we describe advances in the Geophysical Fluid Dynamics Laboratory’s (GFDL) Earth System Model 4 (ESM4.1) aimed at improving the representation of the exchange of N between atmosphere and ocean and its response to changes in ocean acidity and N deposition. We find that the simulated present-day NH₃ outgassing (3.1 TgN yr⁻¹) is 7% lower than under preindustrial conditions, which reflects the compensating effects of increasing CO₂ (−16%) and N enrichment of ocean waters (+9%). This change is spatially heterogeneous, with decreases in the open ocean (−13%) and increases in coastal regions (+15%) dominated by coastal N enrichment. The ocean outgassing of ammonia is shown to increase the transport of N from N-rich to N-poor ocean regions, where carbon export at 100 m increases by 0.5%. The implications of the strong response of NH₃ ocean outgassing to CO₂ for the budget of NH₃ in the remote marine atmosphere and its imprint in ice cores are discussed.

1. Introduction

The availability of reactive nitrogen (N) limits the productivity of the ocean over much of the low-latitude oceans (Moore et al., 2013). This has motivated considerable research on the factors that control the supply of nitrogen to the euphotic zone. Across the global ocean, the dominant N source to the well-lit euphotic zone arises from the upward transport of N-rich subsurface waters via mixing or upwelling currents (e.g., Sarmiento & Gruber, 2013). However, lateral transport (e.g., Letscher et al., 2016), N deposition (e.g., Duce et al., 2008; Jickells et al., 2017), riverine inputs (e.g., Seitzinger et al., 2005), and nitrogen fixation (Wang et al., 2019) also play an important role at the regional level. Over the last 150 years, agricultural activities and fossil fuel combustion have led to a 4 times increase in N deposition to the ocean (Jickells et al., 2017). Models suggest that such increase in the N supply has resulted in significant changes in marine productivity both globally (+0.5% to 3% Duce et al., 2008; Jickells et al., 2017; Krishnamurthy et al., 2009) and regionally (Kim, Lee, Duce, et al., 2014; Krishnamurthy et al., 2010; St-Laurent et al., 2017). However, the response of the N cycle to increasing N deposition remains challenging to quantify. While field observations show that N availability in the northwest Pacific, in the immediate atmospheric outflow of East Asia, has increased, consistent with increasing N deposition (Kim et al., 2011; Ren et al., 2017), the extent to which it affects the open ocean remains uncertain (Kim, Lee, Gruber, et al., 2014; St-Laurent et al., 2017; Wang et al., 2018; Yang & Gruber, 2016). These discrepancies highlight ongoing challenges in characterizing the impacts of anthropogenic N deposition onto the marine N cycle.

A persistent source of uncertainty in current models is the representation of the marine source of atmospheric ammonia (NH₃) and organic nitrogen (Altieri et al., 2016; Jickells et al., 2017; Kanakidou et al., 2012; Wang et al., 2018). The ocean outgassing of ammonia is well supported by field observations (Gibb et al., 1999; Jickells et al., 2003; Johnson et al., 2007, 2008; Quinn et al., 1992, 1996) with recent studies suggesting that marine emissions could be the dominant source driving the gross deposition of NH₄⁺NH₃ + NH₄⁺ even in the outflow of continental sources (Altieri et al., 2014). The magnitude of the ocean source of NH₃ remains very uncertain with estimates ranging from 2 to 23 TgN yr⁻¹ (Paulot et al., 2015). In most studies to date, marine NH₃ emissions are prescribed using a climatology (Bouwman et al., 1997). Such treatment does...
not account for the bidirectional nature of NH$_3$ outgassing, which leads to an overestimate of the net N deposition to the ocean. The use of constant ocean NH$_3$ emissions also neglects changes in outgassing associated with changes in the sea water concentration of NH$_3$ due to climate change, acidification, and N deposition.

To reduce this uncertainty and elucidate the factors driving the response of marine NH$_3$ emissions to climate change in the Anthropocene, the Earth System Model 4 (ESM4.1) developed at the Geophysical Fluid Dynamics Laboratory (GFDL) includes a detailed representation of the atmospheric flux of nitrogen to the ocean, including the bidirectional exchange of NH$_3$ between ocean and atmosphere. This study is organized as follows. First, we document the representation of reduced nitrogen in the ocean biogeochemical component of ESM4.1 (Carbon, Ocean Biogeochemistry and Lower Trophics [COBALT]) and its coupling with N deposition. We focus on changes to the representation of nitrification and uptake by phytoplankton and its impact on the simulation of surface [NH$_3$ (sw)]. We then characterize the magnitude of ocean outgassing and its response to changes in N deposition and CO$_2$ over the 1850–2014 period. We conclude by discussing how the sensitivity of NH$_3$ emissions to CO$_2$ affects the concentration of NH$_3$ in the remote atmosphere and its imprint in ice cores.

2. Model Formulation

The main characteristics of GFDL-ESM4.1 are described in detail in Dunne et al. (2020) and in Adcroft et al. (2019), Zhao et al. (2018), Stock et al. (2020), and Horowitz et al. (2020) for the overall coupled, ocean dynamics, atmospheric dynamics, ocean biogeochemistry, and atmospheric chemistry components, respectively. The nominal horizontal resolution of the atmosphere and ocean models are ≃100 km and 0.5°, respectively.

We focus here on the simulation of surface seawater ammonia NH$_3$ (sw)=NH$_3$ (sw)+NH$_4^+$ (sw) and the representation of atmospheric N deposition to the ocean including the bidirectional exchange of atmospheric NH$_3$. Analysis of the model performance is based on the historical simulation averaged over three ensemble members from 1990 to 2014. Changes in the N deposition and NH$_3$ outgassing are analyzed relative to the first 400 years of the preindustrial control (piControl) simulation and years 24 to 34 of a simulation with CO$_2$ increasing at 1% yr$^{-1}$ (1pctCO2), chosen to match the CO$_2$ concentration over the 1990–2014 period.

2.1. NH$_3$ (sw) Budget in COBALTv2

Ocean biogeochemistry in ESM4.1 is simulated with version 2 of the COBALT model (COBALTv2, Stock et al., 2020). In COBALTv2, sources of NH$_3$ (sw) are dominated by biological remineralization (≃10 PgN yr$^{-1}$) with minor contributions from NH$_4^+$ deposition. Excretion of ammonium is associated with respiration of organic carbon following OCMIP- II biotic protocols (Anderson, 1995). Respiration and ammonium excretion is thus associated with feeding by all zooplankton, free living bacteria remineralizing dissolved organic material, implicit particle-attached bacteria remineralizing sinking detritus, and implicit “fish” predators consuming zooplankton. Excretion also occurs in COBALTv2 when net phytoplankton growth becomes negative (i.e., under low light conditions). More details can be found in Stock et al. (2020).

Sinks of NH$_3$ (sw) include nitrification (≃25%) and uptake by phytoplankton (≃75%). Anammox is not represented in COBALTv2 (Gruber, 2008). We focus here on the changes in the representation of the NH$_3$ sink between COBALTv1 and COBALTv2. Nitrification (jnitrif) is parameterized as

$$jnitrif = \gamma_{nitrif} \cdot f_T \cdot f_{light} \cdot f_{O_2} \cdot f_{NH_3} \cdot [NH_3(\text{sw})]^b \text{ if } [O_2] > [O_{\text{min}}]$$

$$= 0 \text{ otherwise}$$

with

$$f_T = \exp(k_T T)$$

$$f_{light} = \left(1 - \frac{I_{24}}{I_{24} + IRR}\right)$$

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Table 1

| Parameter Values Used in COBALTv2          | Value                     |
|--------------------------------------------|---------------------------|
| $f_{\text{air}}$                           | 1.35 kg mol$^{-1}$ s$^{-1}$|
| $k_{\text{NH}_x}$                          | 3.1 mmol kg$^{-1}$        |
| $k_{O_2}$                                  | 3.9 mmol kg$^{-1}$        |
| $k_T$                                      | 0.063 °C$^{-1}$           |
| IRRI                                       | 10 W m$^{-2}$             |
| $b$                                        | 2                         |
| $\kappa_{\text{NH}_x}$ (small phytoplankton) | $10^{-5}$ mmol kg$^{-1}$ |
| $\kappa_{\text{NH}_x}$ (large phytoplankton) | $5 \times 10^{-5}$ mmol kg$^{-1}$ |
| $\kappa_{\text{NH}_x}$ (diazotrophic)     | $1 \times 10^{-4}$ mmol kg$^{-1}$ |
| $\kappa_{\text{NO}_3}$ (small phytoplankton) | $5 \times 10^{-4}$ mmol kg$^{-1}$ |
| $\kappa_{\text{NO}_3}$ (large phytoplankton) | $25 \times 10^{-4}$ mmol kg$^{-1}$ |
| $\kappa_{\text{NO}_3}$ (diazotrophic)     | $5 \times 10^{-3}$ mmol kg$^{-1}$ |

$f_T$ and $f_{O_2}$ reflect the sensitivity of nitrification to temperature ($T$) and oxygen ($O_2$) with $k_T$ and $k_{O_2}$ given in Table 1. $f_{\text{light}}$ represents the inhibition of nitrification by light (Ward et al., 1982) with $IRRI$ and $I_{24}$, the light inhibition threshold (Table 1) and the 24-hr mean light irradiance, respectively. $f_{\text{nurif}}$ is a normalization factor. The sensitivity to light and $O_2$ is reduced relative to COBALTv1 following Peng et al. (2016) and Smith et al. (2014). Unlike COBALTv1, we account for the sensitivity of nitrification to the speciation of NH$_x$ via $f_{\text{NH}_x}$ (Beman et al., 2011; Huesemann et al., 2002; Kitidis et al., 2011; Stein et al., 1997; Suzuki et al., 1974; Ward, 2008). This introduces an additional modulation of nitrification by acidification (decrease) and warming (increase) through the pKa of NH$_x$/NH$_3$ (Clegg & Whitfield, 1995). COBALTv2 does not explicitly represent nitrifying organisms, and we set $b = 2$ to represent the adjustment of the biomass of nitrifying organisms to NH$_x$ availability. Tuning of $f_{\text{nurif}}$ is based on surface NH$_x$ observations, and further assessment against a compilation of nitrification rates is currently underway.

The uptake of NH$_x$ by phytoplankton is controlled by the N required to support growth rates achieved under prevailing nutrient and light conditions (Geider et al., 1997; Stock et al., 2020) and their relative preference for NH$_x$ relative to NO$_3$ (Dortch, 1990; Gilbert et al., 2015; Syrett, 1981). COBALTv2 allows for the inhibition of the uptake of NO$_3$ and NH$_x$ in the presence of abundant NH$_x$ and NO$_3$, respectively, following O’Neill et al. (1989):

\[
\frac{j_{\text{NH}_x}}{j_{\text{NO}_3}} = \frac{[\text{NH}_x(\text{sw})]}{[\text{NH}_3(\text{sw})] + \frac{\kappa_{\text{NO}_3}}{\kappa_{\text{NH}_x}}[\text{NO}_3(\text{sw})]} \frac{\kappa_{\text{NO}_3} + [\text{NO}_3(\text{sw})] + \frac{\kappa_{\text{NO}_3}}{\kappa_{\text{NH}_x}}[\text{NH}_x(\text{sw})]}{[\text{NO}_3(\text{sw})]} \tag{6}
\]

where $j_X$ denotes the uptake rate of $X$ and the half-saturation for NO$_3^-$ ($\kappa_{\text{NO}_3}$) and NH$_x$ ($\kappa_{\text{NH}_x}$) are given in Table 1. We note that the O’Neill et al. (1989) parameterization results in less inhibition of NO$_3^-$ uptake by NH$_x$ than the parameterization of Frost and Franzen (1992) that was used in previous versions of the model (ESM2M-COBALT, Paulot et al., 2015; Stock et al., 2014a), particularly in iron-limited high-nutrient low-chlorophyll (HNLC) areas where NO$_3^-$ is found in abundance. The impact of changes in the nitrification and ammonium uptake scheme on the simulation of NH$_x$(sw) will be discussed in section 3.1.

2.2. Atmosphere-Ocean N Exchange

2.2.1. NH$_3$ Exchange

The net exchange of NH$_3$ ($F$) between ocean and atmosphere is calculated following Liss and Slater (1974) as described in Paulot et al. (2015).

\[
F = -K([\text{NH}_3] - H^* [\text{NH}_x(\text{sw})]) \tag{7}
\]

where $H^*$ is the dimensionless effective Henry's law constant for NH$_x$ and $K$ is the transfer velocity between atmosphere and ocean.

\[
H^* = \frac{H}{1 + 10^{\text{pK}_{\text{NH}_3} - \text{pK}_{\text{NH}_x}}} 
\]

\[
K = \left[ \frac{1}{k_T} + \frac{H}{k_{O_2}} \right]^{-1} \tag{9}
\]
where $H$ is the Henry’s law constant for NH$_3$ (Jacobson, 2005), $pK_{aNH_3}$ is the $-\log_{10}$ of the acid dissociation constant of NH$_3$/NH$_4^+$ (Clegg & Whitfield, 1995), and $k_g$ and $k_w$ are the transfer velocities in the gas phase and water, respectively (Johnson, 2010). For NH$_3$, $K \approx k_g$ under environmentally relevant conditions (Beale et al., 2014). $k_g$ is calculated following Johnson (2010):

$$k_g = 10^{-3} + \frac{u*}{13.3 \sqrt{Sc_a} + C_D^{1/2}} - 5 + \frac{\ln(Sc_w)}{2 \kappa}$$

(10)

where $Sc_a$ is the airside Schmidt number, $C_D$ is the drag coefficient, $u*$ is the friction velocity, and $\kappa$ is the von Karman constant ($\kappa = 0.4$).

In our previous work (Paulot et al., 2015), we used a climatology for [NH$_x$(sw)] derived from ocean biogeochemical models including ESM2M-COBALT. Here, the atmospheric and ocean pools of NH$_3$ are coupled and simulated interactively. In this way, NH$_x$(sw) responds to NH$_3$ outgassing and its impact on ocean biogeochemistry can be quantified.

### 2.2.2. Other Atmospheric Sources of Nitrogen

ESM4.1 includes a detailed representation of the atmospheric chemistry of NH$_x$ and NO$_x$ (Horowitz et al., 2020). Emissions of reactive nitrogen include anthropogenic emissions from the Community Emissions Data System v2017-05-18 (Hoesly et al., 2018) and biomass burning emissions (BB4CMIP, van Marle et al., 2017). Surface natural sources of NH$_3$ and NO are prescribed following Naik et al. (2013) for soil and land-based animals and Riddick et al. (2012) for sea bird NH$_3$ emissions. NO emissions from lightning are calculated following Naik et al. (2013). Ammonia partitioning between aerosol and gas phase is determined using the thermodynamic model ISORROPIA (Fountoukis & Nenes, 2007) as described in Paulot et al. (2016). Removal rates of oxidized and reduced nitrogen by wet and dry deposition are calculated in the atmospheric component of ESM4.1 and passed to COBALTv2 every hour (the ocean coupling time step). This treatment improves the representation of the spatial and temporal variability of N deposition relative to ESM2M-COBALT for which a climatology of N deposition was used (Stock et al., 2014b).

Figure 1a shows the simulated changes in global reactive N emission over the 1850–2014 period, and Figure 1b shows the associated change in marine N deposition. Total emissions increase from 27.4 to 116 TgN yr$^{-1}$ from 1850 to 2014 with comparable contributions from oxidized and reduced nitrogen. Our estimates are $\approx$20 TgN yr$^{-1}$ lower than in the study of Jickells et al. (2017), which is consistent with the incomplete representation of organic nitrogen in ESM4.1. Gross and net marine N deposition increase from 11 to 41 and from 7.5 to 38 TgN yr$^{-1}$, respectively. Table 2 shows that the net total and reduced N deposition to the
oceans have increased by 4.6 and 5.6 times, respectively. Over 50% of present-day N deposition occurs in coastal areas, defined here as large marine ecosystems (LMEs, Sherman & Alexander, 1986), with coastal Asia, Europe, and the United States accounting for more than 30% of all N deposition to the ocean. The largest fractional increase is simulated in North American coastal water (11 times, including 22 times for the Northeast U.S. continental shelf). Approximately 40% of emitted oxidized nitrogen is deposited over the ocean, where it accounts for over 60% of the gross marine N deposition to both coastal and open ocean.

3. Results and Discussion

3.1. Evaluation of NH$_x$(sw) Concentration

There is currently no global database of [NH$_x$(sw)], which complicates model evaluation. Here, we use surface [NH$_x$(sw)] observations (depth < 10 m) summarized by Paulot et al. (2015) supplemented by observations from the Climate and ocean-variability, predictability, and change and Carbon Hydrographic Data Office (CCHDO) and SeaDataNet. We exclude observations exceeding 2 mmol m$^{-3}$ to reduce the influence of coastal hot spots. After filtering, the median [NH$_x$(sw)] is 0.13 mmol m$^{-3}$. We note that the detection threshold for conventional colorimetric techniques ($\simeq$0.08 mmol m$^{-3}$) is higher than the simulated [NH$_x$(sw)] in many oligotrophic regions, which may cause a positive bias.

In Paulot et al. (2015), we reported that the simulated [NH$_x$(sw)] in the ESM2M-COBALT model was biased high and we increased phytoplankton’s affinity for NH$_x$(sw) to reduce this bias. Figure S1 shows that the resulting configuration (ESM2M-COBALT-HA) exhibits low normalized mean bias (NMB) in all seasons ($|\text{NMB}| \leq 20\%$), where NMB is estimated as $10^\Delta$ with $\Delta$ the difference between the log$_{10}$ of the simulated and observed surface [NH$_x$(sw)]. However, ESM2M-COBALT-HA does not capture the spatial distribution of [NH$_x$(sw)] well with $R$ ranging from 0.17 to 0.4. Figure 2 shows that ESM4.1 captures the spatial distribution of [NH$_x$(sw)] better, with correlations ranging from 0.48 to 0.52 on a seasonal basis, without significant increase in the model bias ($|\text{NMB}| \leq 25\%$). In particular, ESM4.1 better captures the observed elevated [NH$_x$(sw)] in the Southern Ocean in DJF and MAM. This improvement is primarily driven by the reduced

![Figure 2](image-url)

Figure 2. Seasonal mean surface seawater concentration of total ammonium (NH$_x$(sw)) simulated by ESM4.1 (1990–2014 average). Observations are denoted by circles and averaged onto a 7.5 x 7.5° grid for readability. Normalized mean biases (NMBs) and correlation (R) are indicated in the insets.
preference of phytoplankton for NH$_x$(sw) at high [NO$_3^-$ (sw)] (Glibert et al., 2015; as parameterized in O’Neill et al., 1989).

Comparisons against the few available time series of surface [NH$_x$] also show improvements in the seasonality of NH$_x$(sw) at high latitudes relative to ESM2M-COBALT-HA (Figure 3). However ESM4.1 tends to underestimate the post-bloom decrease of NH$_x$(sw) in the Southern Ocean (Figure 3e), suggesting that the decrease of nitrification with temperature (both through $k_T$ and $f_{NH_3}$) needs to be revisited. Figure 3 also shows the simulated surface concentrations of NH$_x$ in five CMIP6 models averaged over 1990 to 2014. Large differences in both the magnitude and the seasonality of NH$_x$(sw) across models highlight continuing challenges in the representation of NH$_x$ in models (Paulot et al., 2015), which are compounded by sparse measurements of patchy NH$_x$ fields. The large difference in the simulated seasonality of NH$_x$ in midlatitudes across CMIP6 models (Figures 3a and 3b) is consistent with that between ESM2M-COBALT-HA and ESM4.1, suggesting that it may be associated with similar differences in the treatment of nitrification and ammonium uptake across CMIP6 models.
3.2. Susceptibility of Ocean Ammonia Outgassing to N Deposition and Climate Change

Figure 4a shows the distribution of ocean outgassing in present-day conditions. The magnitude of NH$_3$ outgassing in ESM4.1 is 3.1 TgN yr$^{-1}$ under present-day conditions, similar to estimates derived by Paulot et al. (2015) (2–5 TgN yr$^{-1}$) but much lower than estimates commonly used in global models (8.2 TgN yr$^{-1}$) (Bouwman et al., 1997; Jickells et al., 2017). The spatial distribution of ocean NH$_3$ outgassing reflects both the distribution of [NH$_x$(sw)], with high emissions from N-rich upwelling regions, iron-limited HNLC regions (e.g., equatorial Pacific, Southern Ocean, and North Pacific), and river outflows (e.g., Amazon, Congo, Indus), as well as the sensitivity of NH$_3$ solubility to sea surface temperature, which results in higher emissions in the equatorial Pacific than in the Southern Ocean. The large outgassing of NH$_3$ in the equatorial Pacific is consistent with recent isotopic measurements (Kamezaki et al., 2019) that suggest that a significant portion of NO$_x$ in this region may be derived from the oxidation of marine N.

ESM4.1 simulates a small decrease (≈7%; Table 3 and Figure 4b) in NH$_3$ outgassing from preindustrial conditions to 1990–2014 conditions, with contrasting changes in coastal regions (increase) and open ocean (decrease). Figure 4c shows that changes in CO$_2$ alone (estimated from the 1pctCO2 simulation averaged from years 24 to 34 to match CO$_2$ concentrations over the 1990–2014 period) would result in a stronger decline in NH$_3$ outgassing (−16%, Table 3). This change is consistent with the decrease in the NH$_3$(sw):NH$_x$(sw) ratio (≈−17%) associated with the change in surface pH from 8.17 in 1850 to 8.09 over the 1990–2014 period. The difference between the CO$_2$-alone response and the historical response can be well explained by changes in [NH$_x$(sw)], particularly in coastal areas strongly impacted by increasing deposition, which has led to an increase in NH$_3$ outgassing of 0.3 TgN yr$^{-1}$, thus offsetting more than half of the changes induced by acidification (Figure 4). The decrease of ocean outgassing in the subtropical South Pacific is due to changes in both CO$_2$ and [NH$_x$(sw)] consistent with a reduction in [NH$_3$(sw)] from increased stratification (Capotondi et al., 2012).

Figure 4. 1990–2014 average simulated ocean NH$_3$ outgassing (a) and its relative change from preindustrial conditions (b). Relative changes in ocean NH$_3$ outgassing due to changes in CO$_2$ and NH$_x$(sw) between preindustrial and present-day conditions are shown in panels (c) and (d), respectively. The magnitude of NH$_3$ outgassing (a) and its change (b–d) are indicated in inset.
The opposing responses of NH$_3$ outgassing to N deposition and acidification help explain the contrasting response of NH$_3$ outgassing in coastal regions and in the open ocean. In the open ocean, ESM4.1 simulates a 13% decrease in NH$_3$ outgassing. This is consistent with the impact of CO$_2$ alone (−16%) and the small impact of N deposition on open ocean [NH$_3$(sw)] (Table 3). In contrast, coastal NH$_3$ outgassing has increased by 15% from preindustrial conditions to present day, as the increase in NH$_3$(sw) outweighs the impact of acidification. The increase in coastal NH$_3$ outgassing is likely to be underestimated in ESM4.1, as riverine N concentrations are held at constant contemporary values (Seitzinger et al., 2005) throughout the simulation. The relative change in outgassing ranges from +6.5% off the coast of the contiguous United States to 62% off the coast of Asia, which is consistent with changes in absolute N deposition to these regions. The compensation between acidification and N deposition also has implications for future NH$_3$ outgassing. At CO$_2$ doubling, the simulated NH$_3$ outgassing is 2.78 TgN yr$^{-1}$ under the Shared Socioeconomic Pathways scenario 3-7.0 (Fujimori et al., 2017) but 1.86 TgN yr$^{-1}$ with CO$_2$ increase alone (Figure S2). This suggests that N deposition can offset almost two thirds of the impact of CO$_2$ on ocean NH$_3$ outgassing.

Differences between the responses of coastal and open-ocean NH$_3$ outgassing in ESM4.1 are also useful to understand differences between ESM2M-COBALT-HA and ESM4.1 (+35%, Table 3). Open-ocean outgassing is 20% greater in ESM4.1, which reflects changes in [NH$_3$(sw)] associated with the updated treatment of ammonium uptake and nitrification (Figures 2 and S1). The difference is much larger for coastal outgassing (+60%) and similar to the simulated change in outgassing due to NH$_3$(sw) between preindustrial and present day in ESM4.1 (+38%). This is consistent with the fact that ESM2M-COBALT-HA does not consider the increase of N deposition between preindustrial and present day. We note that there remain important uncertainties in the simulated response to increasing N deposition. For instance, higher outgassing in the Arabian Sea, Bay of Bengal, Northwest Pacific, and North Atlantic is stimulated by a simulated shift toward phosphate limitation in these regions in response to increasing anthropogenic N inputs. While there is evidence for growing phosphate limitations in these regions (e.g., Kim, Lee, Gruber, et al., 2014; Martiny et al., 2019 and references therein), it is likely overexpressed in ESM4.1 (Stock et al., 2020).

### 3.3. Impact of NH$_3$ Exchange Under Present-Day Conditions

To quantify the impact of changes in ocean NH$_3$ outgassing, we perform a sensitivity experiment, in which the outgassing of NH$_3$ is suppressed. Three ensemble members were branched from the historical simulations starting in 1970 and analyzed over the 1990–2014 period. Comparison of the deposition with bidirectional exchange suppressed to deposition when included quantifies the relative importance of marine-derived NH$_3$ deposition to the total deposition for the whole ocean and for each region. Figure 5 shows that NH$_3$ outgassing accounts for ≃17% and 7% of the total gross marine deposition of NH$_4$ and N, respectively, over the 1990–2014 period (Figure 5). The contribution of marine NH$_3$ emissions exceeds 50% in remote regions such as the equatorial Pacific and Southern Ocean. The ocean contributes little to N deposition in the outflow of
North America, Asia, and Europe. For instance, the ocean is simulated to contribute 20–35% of the annual NH₃ deposition at Bermuda (32.3°N, 64.9°W). This disagrees with isotopic constraints, which suggest that most NH₃ deposited at this location is of marine origin (Altieri et al., 2014). Part of the discrepancy may reflect the release of ammonia from the photochemical degradation of organic nitrogen (Paulot et al., 2015; Zhang & Anastasio, 2003); marine emissions of which are not included in our calculations but may exceed direct marine NH₃ emissions (Jickells et al., 2017; Kanakidou et al., 2012).

Figure 6a shows that NH₃ outgassing tends to transport marine nitrogen away from N-rich regions (ΔNdep < 0), such as upwelling regions, HNLC regions, and river outflows (e.g., Amazon, Congo, Indus), to regions with low NH₃ partial pressures. The atmospheric redistribution of marine nitrogen via NH₃ outgassing results in statistically significant increases in carbon export at 100 m (p < 0.1) in much of the South Pacific and South Atlantic gyres, where changes can exceed 5% (Figure 6b). Overall, we find that the carbon export at 100 m in regions of low NO₃⁻ concentration (annual mean NO₃⁻ < 2 mmol m⁻³) increases significantly (+0.5%, p < 0.1). Changes in N deposition associated with the atmospheric redistribution of outgassed NH₃ are accompanied by opposite changes in N fixation in the Southern Pacific, Indian Ocean, and Southern Ocean (Figure S3). This change in N fixation may partly reduce the impact of the redistribution of outgassed NH₃ on ocean biogeochemistry, as previously noted for anthropogenic N deposition (Krishnamurthy et al., 2007, 2009).

### 3.4. Implication for the Remote Budget of NH₃

Figure 7a shows the response of ocean NH₃ outgassing to a doubling of CO₂. The global outgassing is reduced more (−42%) than expected from changes in surface pH alone (−33%). This can be attributed to increasing stratification and accompanying primary production declines (Stock et al., 2020), which exacerbates the decline of NH₃ outgassing. In contrast, NH₃ outgassing increases in boreal regions, which reflects the reduction in sea ice cover. The overall reduction in NH₃ outgassing is accompanied by a decrease in the concentration of near-surface atmosphere NH₃ (Figure 7b). This reduction is especially large in the equatorial Pacific, where preindustrial NH₃ emissions are sufficient to neutralize non-sea salt sulfate (nss-SO₄²⁻). In contrast, little change is simulated in polar regions, as the increase in NH₃ emissions remains insufficient to neutralize nss-SO₄²⁻. Regional differences in the gas/aerosol partitioning of NH₃ remain challenging to verify because of limited observations of atmospheric NH₃ in remote regions (Paulot et al., 2015). In addition, changes in Dimethyl sulfate (DMS) emissions, the primary source of non-sea salt sulfate in the remote marine atmosphere, with global warming and acidification (Hopkins et al., 2020), may further modulate the response of atmospheric NH₃ to climate change. Such changes are not considered in ESM4.1.

Finally, we note that changes in marine NH₃ outgassing with CO₂ may also help interpret changes in ice core NH₄⁺ in Antarctica. In this region, 50–70% of NH₄⁺ deposition is simulated to originate from the ocean, which agrees well with limited in situ constraints (Kaufmann et al., 2010; Legrand et al., 1998). Figure 7c shows that the decrease in NH₃ outgassing associated with a doubling of CO₂ leads to a 20–35% decline in NH₄⁺ concentration in precipitation over most of Antarctica. The decrease of NH₃ outgassing with ocean acidification may thus be an important driver for the 70% lower NH₄⁺ concentration in the ice cores collected by European Project for Ice Coring in Antarctica (Kaufmann et al., 2010) at the beginning of the last glacial period (CO₂ ≃ 253 ppmv) relative to the last glacial maximum (CO₂ ≃ 188 ppmv). We further note that our simulations do not support a correlation between NH₄⁺ in ice cores and the productivity of the Southern Ocean as hypothesized by Kaufmann et al. (2010).
4. Conclusions

ESM4.1 implements a comprehensive representation of N exchange between the ocean and atmosphere. Our estimate of global marine NH₃ emissions (3.1 TgN yr⁻¹) falls within the range estimated by Paulot et al. (2015) (2–5 TgN yr⁻¹) using a previous version of the model, despite large changes in the model physics and treatment of NH₄(sw). Small changes in ocean NH₃ outgassing simulated over the historical period (−7%) reflect the competition between ocean acidification (−16%) and N deposition (+9%). The impact of N deposition on ocean outgassing is most important in coastal regions, where a 15% increase in NH₃ outgassing is simulated. Ammonia outgassing contributes to the supply of N to N-poor area, where it promotes carbon export at 100 m (≃+0.5%).

Ammonia outgassing is projected to decrease by 42% in response to a doubling of CO₂ primarily due to acidification, with a greater decrease in subtropical regions due to lower primary production associated with higher stratification. This reduction in ocean ammonia outgassing results in a large decrease (70%) in near-surface atmospheric NH₃ in the equatorial and subtropical Pacific, which may impact aerosol pH and aerosol nucleation (Dunne et al., 2016; Jokinen et al., 2018; Kirkby et al., 2011). We further suggest that the decrease of NH₃ ocean outgassing with increasing CO₂ can also explain most of the increase in the concentration of NH₄ in Antarctic ice cores between 125 and 22.5 kyr BP (Kaufmann et al., 2010).

Finally, we suggest that the following items should be prioritized to help reduce the uncertainty in the magnitude and sensitivity of NH₃ outgassing that is reflected in the considerable range of estimates for NH₃ outgassing (2–23 TgN yr⁻¹).

1. Development of a global database of quality-controlled surface NH₄(sw) observations. This is especially important in oligotrophic regions, where NH₄(sw) concentrations are often below detection limit for conventional colorimetric techniques. Such a database was recently developed by Yasunaka et al. (2017) using observations from Japanese research institutes in the Pacific.
2. Evaluation of NH₄(sw) sinks, i.e., nitrification, and uptake by plankton, against field observations. Critical uncertainties include the level of ammonium inhibition on nitrate uptake (Glibert et al., 2015) and the sensitivity of nitrification to the speciation of NH₄(sw) (Beman et al., 2011; Ward, 2008).
3. Spatial pattern and sensitivity of nutrient limitation (Moore et al., 2013). In ESM4.1, increasing P limitation results in a large increase in NH₃ outgassing in coastal regions (+38%) and in the North Atlantic over the historical period.
4. Observations of gas-phase NH$_3$ in remote regions, which are needed to constrain the partitioning of NH$_x$ between gas and aerosol phases. The impact of uncertainties in DMS emission and its response to climate change on the net outgassing of NH$_3$ also need to be better characterized.

5. Parameterization of NH$_3$ exchange ($k_a$) under extreme wind conditions (Johnson, 2010).

6. Quantification of the role of marine organic nitrogen as a source of marine NH$_3$. In particular, ESM4.1 remains unable to explain the large source of marine NH$_3$ reported by Altieri et al. (2014) in the outflow of North America, which suggests an important missing source of marine N.

Data Availability Statement

Observed NH$_x^+$ concentrations can be obtained at the CLIVAR and Carbon Hydrographic Data Office (https://cchdo.ucsd.edu/, last retrieved on 10 June 2019) and SeaDataNet (https://www.seadatanet.org/, last retrieved on 28 August 2019). ESM4.1 model outputs are available on the ESGF portal (John et al., 2018; Krasting et al., 2018).

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