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Key Points:
- Soluble secondary reduced ON improves model-observation comparison
- Vertical profile of soluble ON differs between different formation processes
- Human activities increase terrestrial soluble ON input to the oceans

Supporting Information:
- Readme
- Figure S1
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Reconciling modeled and observed atmospheric deposition of soluble organic nitrogen at coastal locations

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Abstract Atmospheric deposition of reactive nitrogen (N) species from air pollutants is a significant source of exogenous nitrogen in marine ecosystems. Here we use an atmospheric chemical transport model to investigate the supply of soluble organic nitrogen (ON) from anthropogenic sources to the ocean. Comparisons of modeled deposition with observations at coastal and marine locations show good overall agreement for inorganic nitrogen and total soluble nitrogen. However, previous modeling approaches result in significant underestimates of the soluble ON deposition if the model only includes the primary soluble ON and the secondary oxidized ON in gases and aerosols. Our model results suggest that including the secondary reduced ON in aerosols as a source of soluble ON contributes to an improved prediction of the deposition rates (g N m^{-2} yr^{-1}). The model results show a clear distinction in the vertical distribution of soluble ON in aerosols between different processes from the primary sources and the secondary formation. The model results (excluding the biomass burning and natural emission changes) suggest an increase in soluble ON outflow from atmospheric pollution, in particular from East Asia, to the oceans in the twentieth century. These results highlight the necessity of improving the process-based quantitative understanding of the chemical reactions of inorganic nitrogen species with organics in aerosol and cloud water.

1. Introduction

Human activities for energy and food production have substantially perturbed the biogeochemical cycle of nitrogen (N) since the industrial revolution [*Galloway et al.*, 2008]. The atmospheric emissions of N-containing compounds from fossil-fuel combustion, intensive agricultural activities, and other anthropogenic processes have substantially increased the supply of reactive N over the oceans downwind of major industrialized regions since 1860 [*Duce et al.*, 2008]. The dominant reactive N species are emitted in the form of nitrogen oxide (NO) and ammonia (NH_3) from fossil fuel combustion and agricultural practices, are transformed to a number of other nitrogen oxides (NO_y) and ammonium (NH_x) during the long-range transport, and then deposited to the oceans [*Reay et al.*, 2008]. Little is known about the chemical composition of organic N (ON) in the atmosphere or its spatial distribution, due to the limitations of available analytical methods [*Cape et al.*, 2011; *Cornell*, 2011; *Jickells et al.*, 2013]. Over the North Atlantic, a significant fraction of the wet deposition of total soluble N has been measured in the form of soluble ON at coastal and marine locations (23 ± 18%) [*Zamora et al.*, 2011]. The effect of atmospheric ON input on marine ecosystems can either be helpful or harmful depending on the deposition rate and chemical form of ON [*Cornell et al.*, 1995; *Peierls and Paerl*, 1997]. Dissolved ON such as urea, amino acids, and humic substances can provide an important nutrient source to marine environments [*Peierls and Paerl*, 1997; *Cornell et al.*, 2001; *Bronk et al.*, 2007]. These studies suggest that atmospheric models need to predict the chemical speciation of reactive N species to accurately predict the effects of changes in N inputs on marine ecosystems and climate.

Atmospheric ON is generally associated with anthropogenic activities, biomass burning, dust, and oceanic sources, but the quantitative contribution of anthropogenic and natural sources to ON deposition is a question that is still wide open [*Cornell*, 2011]. Analyses of specific ON components in the aqueous phase (rain or cloud) led to the identification of amines, amino acids, urea, and oxidized N compounds such as nitrophenols and organic nitrates [*Cape et al.*, 2011]. ON in the atmosphere could be produced by the reactions of volatile organic compounds (VOCs) with NO_x [*Atherton and Penner*, 1990; *Cornell et al.*, 1995; *Goldstein et al.*, 2009] and with reduced N gases (e.g., ammonia (NH_3), monomethylamine (MMA),

dimethylamine (DMA), and diethylamine (DEA)) through a variety of reaction pathways [*Facchini et al.*, 2008; *Ervens et al.*, 2011; *Altieri et al.*, 2012]. Biomass burning is an important source of soluble ON in certain regions of the world's oceans [*Mace et al.*, 2003a; *Sundarambal et al.*, 2010]. Since substituted N-heterocyclic compounds typically undergo minor pyrolytic and oxidative fragmentations at relatively low temperatures (i.e., smoldering fires) [*Laskin et al.*, 2009], organic N-containing compounds can be emitted during the vegetation fires [*Mukai and Ambe*, 1986]. High-soluble ON concentrations associated with dust aerosol samples have also been measured [*Mace et al.*, 2003b; *Nakamura et al.*, 2006; *Lesworth et al.*, 2010; *Gioda et al.*, 2011; *Zamora et al.*, 2011]. The ON could be produced by the chemical reactions of carbon-oxygen complexes with NH_3 or NO at high temperature on carbonaceous aerosols [*Chang and Novakov*, 1975; *Dod et al.*, 1984; *Ge et al.*, 2011] or on dust by biological activity [*Mace et al.*, 2003b]. The oxidation processes of organic matter could act to increase both the nitrogen content and the water solubility of organic aerosols [*Hallquist et al.*, 2009].

In addition to continental sources, ON compounds could be released from the surface ocean, since ON is part of living and dead material in the marine ecosystem [*Milne and Zika*, 1993; *Cornell et al.*, 2001; *Facchini et al.*, 2008; *Miyazaki et al.*, 2011; *Altieri et al.*, 2012]. *Facchini et al.* [2008] observed an oceanic source of amines and related it to secondary biogenic formation. *Kanakidou et al.* [2012] estimated much smaller secondary ON from oceanic amines (0.8 Tg N yr^{-1}) than their primary oceanic source (5.4 Tg N yr^{-1}). Moreover, *Ge et al.* [2011] suggest that the sum of MMA, DMA, and DEA emissions from oceans may contribute up to 0.08 Tg N yr^{-1}. Submicrometer organic carbon from the direct sea spray source was found to be mainly water insoluble [*Facchini et al.*, 2008]. Further, *Miyazaki et al.* [2011] observed that water-insoluble ON was the most abundant N in the marine aerosols. Thus, *Kanakidou et al.* [2012] assumed that the water-soluble organic fraction of oceanic primary ON was zero in fine mode and 0.8 in the coarse mode, with the latter more rapidly removed from the atmosphere.

Most previous atmospheric modeling studies have focused on deposition of inorganic N (IN) species (i.e., NO_y and NH_x) [e.g., *Holland et al.*, 1997; *Dentener et al.*, 2006; *Lamarque et al.*, 2013]. However, in recent studies, considerable attention has been given to the deposition of organic nitrogen to the oceans [*Duce et al.*, 2008; *Kanakidou et al.*, 2012]. The global estimates of total soluble ON deposition are highly uncertain, due to uncertainties in sources, transformation, and deposition processes. Intensive animal production, biomass burning, and oceans are a source of amines, but the emission of reduced N gases was estimated to make a small contribution (0.3 Tg N yr^{-1}) to overall organic N emissions on a global scale [*Ge et al.*, 2011]. *Neff et al.* [2002] was the first to estimate the global deposition of soluble ON (10 Tg N yr^{-1}). These authors used a chemical transport model and found most soluble ON to be from secondary oxidized ON (9 Tg N yr^{-1}) with a small contribution from reduced ON ($<$1 Tg N yr^{-1}) based on observations. Primary emissions of particulate organic N are not well understood quantitatively.

In a comprehensive modeling study, *Kanakidou et al.* [2012] used an assumed N:C molar ratio for organic aerosols and estimated larger amount of soluble ON deposition than that in the study by *Neff et al.* [2002] (32 Tg N yr^{-1}). However, comparison of the model results with available observational data indicated significant underestimates of the amount of soluble ON deposition [*Neff et al.*, 2002; *Kanakidou et al.*, 2012]. This model deficiency suggests possible other sources or transformation mechanisms for soluble ON, keeping in mind the significant uncertainties in the measurements.

Here we use an atmospheric chemical transport model to investigate the potential source of soluble ON from anthropogenic activities and its deposition to the oceans. The motivation for this study is to explore methods for improving the apparent underestimate in previously modeled ON [*Neff et al.*, 2002; *Kanakidou et al.*, 2012]. Section 2 describes the modeling methods and the numerical experiments that were performed. The sensitivity results of soluble ON deposition in different simulations are shown to explore a possible explanation for apparent underestimates in the modeled ON in section 3. Section 4 presents a summary of the findings and the future outlook.

2. Model Approach

2.1. Model Description

The global chemical transport model used in this study is a coupled gas-phase [*Ito et al.*, 2007a; *Lin et al.*, 2012] and aerosol chemistry version [*Liu et al.*, 2005; *Feng and Penner*, 2007; *Ito and Feng*, 2010; *Lin et al.*, 2012;

Table 1. Annual Emission Rates of NO, NH_3, and the Primary ON (PON)[a]

Species	Preindustrial Era	Present Day	*Kanakidou et al.* [2012]
NO (Tg N yr^{-1})	15	46	52
NH_3 (Tg N yr^{-1})	21	46	48
PON (Tg N yr^{-1})	11 (8.7)[b]	13 (11)[b]	21 (12)[b]

[a]Oceanic emission is not shown.
[b]PON from anthropogenic sources including biomass burning emissions is listed in parentheses.

Xu and Penner, 2012; *Ito and Xu*, 2014] of the Integrated Massively Parallel Atmospheric Chemical Transport (IMPACT) model [*Rotman et al.*, 2004]. The model simulates the emissions, chemistry, transport, and deposition of major aerosol species, including ON, IN, organic carbon (OC), black carbon, sulfate, mineral dust and sea salt aerosols, and their precursor gases. The model is driven by assimilated meteorological fields from the Goddard Earth Observation System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO). Cloud volume fraction (used to determine where aqueous chemistry occurs) and cloud liquid water content (used to compute the aqueous chemistry reaction rates) are taken directly from the assimilated meteorological fields for each grid box [*Fisher et al.*, 2011]. Simulations have been performed with a horizontal resolution of $2.0° \times 2.5°$ and 59 vertical layers using meteorological fields for the year 2005.

We run the model with emissions of precursor gases and aerosols for the preindustrial era and the present day to disentangle the natural and anthropogenically perturbed components. The emission data sets for anthropogenic activities such as fossil fuel use and biofuel combustion (except the combustion-generated aerosols) are taken from the historical emissions for IPCC Fifth Assessment (AR5) report for the preindustrial era and the present day [*Lamarque et al.*, 2010]. Nitrogen oxides are emitted via microbial nitrification and denitrification activities in soils [*Yan et al.*, 2005]. Ammonia is formed in soils from biological degradation of organic compounds and from ammonium yielding synthetic and organic fertilizers [*Beusen et al.*, 2008]. The use of nitrogen fertilizer significantly increases the soil emissions of NO_x and NH_3 from the preindustrial era to the present day [*Lamarque et al.*, 2010]. The emission data sets for biomass burning are taken from our previously published emission inventory [*Ito and Penner*, 2004, 2005; *Ito et al.*, 2007b; *Ito*, 2011]. Briefly, the global biomass burning emissions are based on a synthesis of ground-based measurements, satellite information, and atmospheric chemical transport model for the year 2000 [*Ito and Penner*, 2004, 2005] and scaled to the year 2005 using the MODIS fire product [*Giglio et al.*, 2006] except in southern Africa and the high-latitude Northern Hemisphere ($>30°$N latitude), where regional emissions from open vegetation burning are available [*Ito et al.*, 2007b; *Ito*, 2011]. Natural emissions are obtained from a separate emission inventory or are calculated on line in the model [*Ito et al.*, 2009; *Ito and Kawamiya*, 2010; *Lin et al.*, 2012; *Ito*, 2013; *Ito and Xu*, 2014]. To represent natural sources of NH_3 emissions (11 Tg N yr^{-1}), data sets for wild animals, natural soils, and the ocean are taken from *Bouwman et al.* [1997], independent of the year simulated [*Bellouin et al.*, 2011]. Lightning NO_x emissions are estimated from the cloud mass fluxes in the upper troposphere (at about 430 hPa) [*Allen and Pickering*, 2002]. The annual lightning NO_x production is set to 3 (Tg N yr^{-1}) [*Ito et al.*, 2009]. The present-day emissions of NO (46 Tg N yr^{-1}) and NH_3 (46 Tg N yr^{-1}) are comparable with those (52 and 48 Tg N yr^{-1}) used by *Kanakidou et al.* [2012] (Table 1). In our approach, the effects of climate change, land-use change, and CO_2 increase on open vegetation fires, soil-derived dust, and biogenic emissions are not taken into account. Further research is needed to improve our understanding of the processes that alter the open biomass burning and natural emissions due to climate, land use, and CO_2 changes. We also note that the changes in meteorological conditions that could change aerosol chemistry and deposition are not taken in account.

We treat the following three categories of ON sources separately: (1) primary ON emitted from biomass burning, fossil fuel combustion, and marine sources; (2) secondary oxidized ON in gases and aerosols; and (3) secondary reduced ON in aerosols.

Primary emissions of ON are not well understood quantitatively, and much of what is measured as atmospheric ON may have arisen from atmospheric reactions of VOCs with ammonia or oxidized N [*Hertel et al.*, 2012]. Here, the historical emission data sets for primary organic matter (POM) aerosols from combustion sources were taken from our emission inventory [*Ito and Penner*, 2005; *Ito*, 2013]. A mean N:C molar ratio of 0.3 was assumed for these emissions [*Kanakidou et al.*, 2012]. Our present-day emission of the

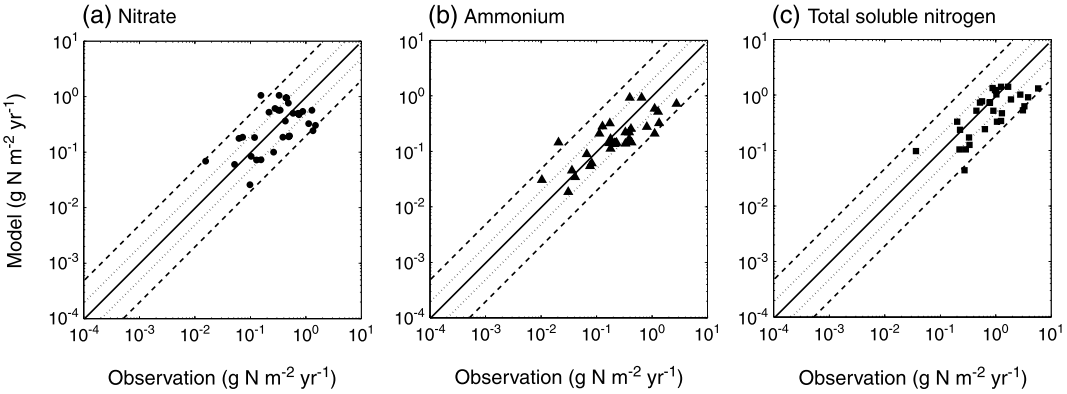

Figure 1. Comparison of simulated (Experiment 1) and observed deposition rates (g N m^{-2} yr^{-1}) for (a) inorganic nitrate, (b) ammonium, and (c) total soluble nitrogen at coastal and marine locations. The annual average model results were calculated from the sum of wet and dry deposition at the observation sites. The solid line represents a 1-to-1 ratio. The dashed lines show deviations from the solid line by a factor of ±5. The dotted lines show deviations from the solid line by a factor of ±2.

primary ON from anthropogenic sources (including all biomass burning emissions for the comparison) (11 Tg N yr^{-1}) is consistent with that used by *Kanakidou et al.* [2012] (12 Tg N yr^{-1}) (Table 1) who also included emissions of natural sources from primary biogenic particles (8.7 Tg N yr^{-1}), soil organic matter on dust (0.2 Tg N yr^{-1}), and oceanic ON (5.4 Tg N yr^{-1}).

Natural ON sources over land areas are not directly emitted in our model, but atmospheric ON is formed in gas and aerosol phases through chemical reactions and thereby become secondary ON whose origin is mixed with that from anthropogenic sources. We derive the emitted organic sea spray contribution in fine and coarse modes (radius: 0.63–1.25 and 1.25–2.5 μm) from bubble bursting experiments and field observations (3%) [*Facchini et al.*, 2008], independent of the chlorophyll concentration in sea surface water [*Vignati et al.*, 2010]. Recent cruise measurements also showed that the organic mass fraction from nascent sea salt aerosols produced by an in situ particle generator was not correlated with surface seawater chlorophyll [*Bates et al.*, 2012]. The super-micron mass emission rate of marine primary OC was calculated using an estimated OC to OM conversion factor of 1.52 [*Gantt et al.*, 2009]. The C:N Redfield molar ratio of 106:16 was used for the marine OC to estimate the primary ON emissions from the ocean [*Arrigo*, 2005]. Our total oceanic primary ON emission is 2.1 Tg yr^{-1} on a global basis, which is lower than that derived by *Kanakidou et al.* [2012] (5.4 Tg yr^{-1}).

Atmospheric VOCs such as isoprene, monoterpenes, and aromatic compounds including phenols are emitted from the anthropogenic and natural sources [*Ito et al.*, 2007a, 2009; *Lin et al.*, 2012]. The photochemical oxidation of VOCs and their subsequent reaction with NO_x in the atmosphere forms alkyl nitrates (Table S1). Subsequently, the semivolatile and low-volatility organic N-containing products are transferred to the particulate phase in the atmosphere (Table S1). The heterogeneous uptake of nitrate (NO_3^-) and ammonium (NH_4^+) on existing particles is interactively simulated in the model following a hybrid dynamical approach [*Feng and Penner*, 2007]. Five types of aerosols (i.e., dust, sulfate, carbonaceous aerosols from fossil fuel combustion, carbonaceous aerosols from biomass burning, and sea salt) were assumed to be externally mixed in each size bin for the computation of aerosol chemistry, while nitrate and ammonium were internally mixed within each aerosol type [*Xu and Penner*, 2012]. The reactions to calculate the aerosol pH involve gas-phase CO_2 (i.e., 285 ppmv in preindustrial era and 369 ppmv in present day), aqueous-phase carbonates, and soil-phase carbonates [*Ito and Feng*, 2010]. The spatial heterogeneity in the mineralogy of the soil particles is accounted for the alkaline carbonates in dust aerosols [*Ito and Xu*, 2014].

Dry deposition of aerosol particles uses a resistance-in-series parameterization following *Zhang et al.* [2001]. For the dry deposition of gaseous species (e.g., PAN-like organic nitrates, alkyl and hydroxyalkyl nitrates) [*Rotman et al.*, 2004; *Ito et al.*, 2007a], the *Wang et al.* [1998] resistance-in-series scheme has been used, which is based on the formulation developed by *Wesely* [1989]. The wet deposition scavenging parameterization is based on the wet scavenging scheme described by *Mari et al.* [2000] and *Liu et al.* [2001]. The wet deposition scavenging parameterization includes contributions from scavenging in convective updrafts, rainout,

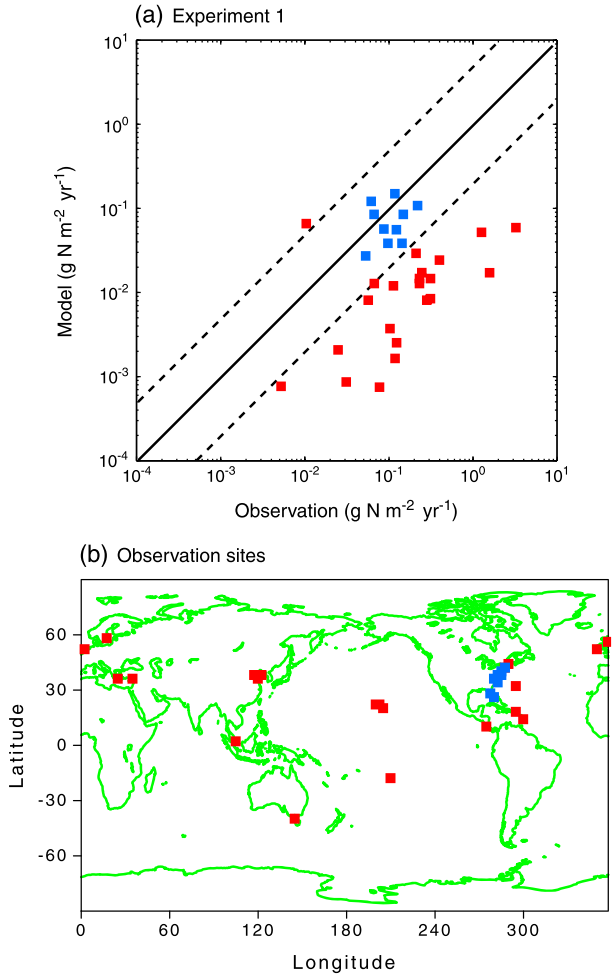

Figure 2. (a) Comparison of simulated (Experiment 1) and observed deposition rates (g N m^{-2} yr^{-1}) for soluble ON at (b) the coastal and marine locations. Experiment 1 includes the secondary ON gases and aerosols formed from oxidized N species. The solid line represents a 1-to-1 ratio. The dashed lines show deviations from the solid line by a factor of ±5. The colors in the scatter plot Figure 2a correspond to the colors of the locations of the observation sites in Figure 2b. The blue colors represent the modeled values that fall within a factor of 5 of the measured values. The standard deviation for the measurements at each site is shown in Table S2 when available.

washout, and reevaporation for stratiform and convective precipitation [*Liu et al.*, 2001]. The aging of carbonaceous aerosols and dust particles from hydrophobic to hydrophilic particles enhances their dry and wet deposition [*Liu et al.*, 2005; *Xu and Penner*, 2012]. The wet removal of gas-phase compounds (e.g., hydroxyalkyl nitrates) is calculated based on the solubility estimates for the compounds [*Ito et al.*, 2007a]. Gaseous NH_3 in the model is efficiently scavenged in warm clouds but has a retention efficiency of only 0.05 during riming (which drives precipitation in mixed-phase clouds) and is not scavenged at all in cold clouds [*Wang et al.*, 2008]. The modeled deposition is sensitive to the meteorological fields and the wet deposition treatment [*Zhou et al.*, 2012]. However, the uncertainties in deposition modeling are unlikely to be the major reasons for the underestimates of the soluble ON deposition, because the predicted nitrate and ammonium deposition are in much better agreement with the observations than is the ON deposition. This is true for both our model (Figures 1 and 2) and previous model comparisons with deposition data [e.g., *Kanakidou et al.*, 2012; *Lamarque et al.*, 2013]. There are also significant uncertainties in the soluble ON measurements [e.g., *Cornell et al.*, 2003], which are briefly described in section 2.3.

2.2. Sensitivity Experiments

In our model (Experiment 1), secondary ON gases in the atmosphere (i.e., PAN-like organic nitrates, alkyl, and hydroxyalkyl nitrates) and secondary ON aerosols formed from the gaseous ON species are explicitly simulated, as in *Lin et al.* [2012], and are treated as separate tracers for this study. A detailed gas-phase mechanism is used to predict the formation of semivolatile products, with gas-particle partitioning estimated from an explicit calculation using an equilibrium partitioning coefficient for each semivolatile compound [*Ito et al.*, 2007a; *Lin et al.*, 2012]. It should be emphasized that our model explicitly calculates N:C molar ratios for secondary ON formed from oxidized N and VOCs, as opposed to assuming a fixed value (0.1) as in *Kanakidou et al.* [2012].

In addition to the standard simulation (Experiment 1), three experiments were performed with different assumptions for the solubility of ON in aerosols at emission and/or the transformation from reduced N on preexisting aerosols (Table 2). Primary carbonaceous aerosols from combustion processes contain nitrogen that may contribute to soluble ON, because the organic compounds within the aerosol are subject to photochemical reactions in the atmosphere that transform them to soluble compounds [*Robinson et al.*, 2007]. However, the solubility of ON in these particles when deposited into the ocean is not known

Table 2. Summary of Sensitivity Simulations Performed in This Study

Experiment	Primary ON[a]	Secondary Reduced ON[b]
Experiment 1	0.0	0.0
Experiment 2	0.5 and 0.8	0.0
Experiment 3	0.0	0.5
Experiment 4	0.5 and 0.8	0.5

[a]Soluble fractions of the primary ON (0.5 for the combustion aerosols and 0.8 for the sea spray aerosols in fine and coarse modes) emitted from combustion and marine sources follow choices made by *Kanakidou et al.* [2012].
[b]We assume that half of the mass fraction of the ammonium that is partitioned to the aerosols is soluble ON. This fraction is chosen to obtain a reasonable agreement between the predicted soluble ON deposition and a compilation of observations at coastal and marine locations.

quantitatively. In a second sensitivity test (Experiment 2), we prescribe the solubility of 50% and 80% of ON emitted from combustion and marine sources, respectively, following *Kanakidou et al.* [2012].

Our model explicitly calculates the formation of oxidized ON compounds (Table S1) but reduced ON compounds are estimated based on the calculated NH_4^+ as explained here. Particulate C–N compounds have been identified in laboratory studies via reactions of glyoxal, methylglyoxal, and isoprene epoxydiols with ammonium sulfate, amino acids, and amines [*De Haan et al.,* 2009a, 2009b, 2010; *Galloway et al.*, 2009; *Noziére et al.*, 2009; *Shapiro et al.*, 2009; *Sedehi et al.*, 2013; *Nguyen et al.,* 2014]. Organic aerosol particles and rainwater sampled in urban and rural sites contain nitrogen-containing oligomers (e.g., alkyl amines and amino acids) [*Altieri et al.*, 2009; *Wang et al.*, 2010]. The positive correlation between soluble ON and NH_4^+ from the compiled observation data at coastal and marine locations ([Soluble ON] = 0.98 × [Ammonium] − 0.12, $R^2 = 0.77$, $N = 30$ in Figure S1) suggests that atmospheric soluble ON originates from net fluxes that have a similar spatial/temporal distribution as those of NH_3 (e.g., MMA, DMA, and DEA) or from a common dominant formation pathway in atmospheric processing, or both [*Zhang et al.*, 2008; *Jickells et al.*, 2013]. At the same time, the major portion of soluble ON in polluted air is observed in the form of gases in the atmosphere or volatilizable aerosols [*Zamora et al.*, 2011]. Clearly, the most fundamental problem with regard to modeling of secondary ON is a lack of experimental data for the main formation mechanisms from ammonia and amines in aerosol water [*Waxman et al.*, 2013; *Nguyen et al.,* 2014]. Therefore, in a third sensitivity test (Experiment 3), we assume that the mass of reduced ON in aerosols is directly proportional to that of ammonium that is partitioned to aerosols in the model. We further assume that half of the mass fraction of NH_4^+ is equal to the soluble ON. This fraction is chosen to obtain a reasonable agreement between the predicted soluble ON deposition and a compilation of observations at coastal and marine locations. Our focus in this paper is to assess whether and where the soluble secondary reduced ON is a potentially important source of soluble ON to explain the large underestimates in ON deposition. Although the formation mechanisms of ON in the form of semivolatile ON and nonevaporative ON from reduced N are not characterized specifically, our simulations provide the first estimate of the secondary reduced ON, which is constrained by available observations of soluble ON deposition at coastal and marine locations. It should be noted that the atmospheric reaction time scales will depend on the acidity, temperature, and availability of organics and reactants (oxidants) in aerosol and cloud water. A more detailed comparison of the importance of different pathways will be obtained by using a multiphase process model that predicts aqueous SOA formation in a future version of our model. In the fourth experiment (Experiment 4), we combine all the soluble ON sources at emission and through chemistry.

2.3. Observational Data for Organic and Inorganic Nitrogen

It is problematic to validate model results with observations for soluble ON concentration, because there is a large diversity in sampling and analysis methods for aerosols [*Cornell*, 2011]. Measuring total soluble nitrogen (the inorganic and organic components together) involves releasing the nitrogen from the organic compounds. Rainwater and aerosol extracts are commonly filtrated to measure soluble material. Ion chromatography has been used for measuring IN in precipitation and aerosol samples. Indirectly, soluble ON is determined by subtracting IN from the total soluble N. Since IN concentrations are generally higher than ON concentrations, ON is subject to relatively large and variable analytical uncertainties [*Cornell et al.*, 2003; *Lesworth et al.*, 2010; *Zamora et al.*, 2011]. When the measurements of soluble ON in precipitation are made with "bulk" precipitation collectors which are continuously exposed to the atmosphere, there could also be a sampling artifact caused by dry deposition of gaseous and particulate soluble ON on collector surfaces [*González Benítez et al.*, 2009].

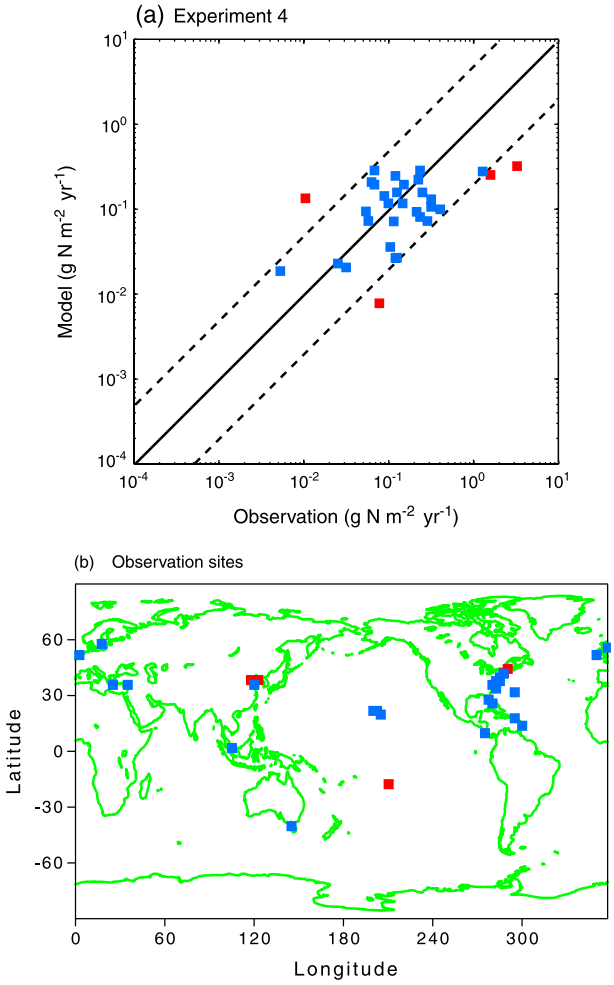

Figure 3. (a) Comparison of simulated (Experiment 4) and observed deposition rates (g N m^{-2} yr^{-1}) for soluble ON at (b) the coastal and marine location. In addition to soluble ON in Experiment 1, Experiment 4 also includes the primary soluble ON emitted from biomass burning, biofuel and fossil fuel combustion, and marine sources and the secondary soluble ON transformed from reduced N on preexisting particles. The solid line represents a 1-to-1 ratio. The dashed lines show deviations from the solid line by a factor of ±5. The colors in the scatter plot Figure 3a correspond to the colors of the locations of the observation sites in Figure 3b.The blue colors represent the modeled values that fall within a factor of 5 of the measured values. The standard deviation for the measurements at each site is shown in Table S2 when available.

We compare our model results for soluble ON in total (i.e., dry + wet) deposition with a compilation of observations at coastal and marine locations (Table S2) [*Rendell et al.*, 1993; *Cornell et al.*, 1998, 2001; *Eklund et al.*, 1997; *Peierls and Paerl*, 1997; *Russell et al.*, 1998; *Scudlark et al.*, 1998; *Spokes et al.*, 2000; *Carrillo et al.*, 2002; *Keene et al.*, 2002; *Luo et al.*, 2002; *Mace et al.*, 2003a, 2003b; *Seitzinger et al.*, 2003; *Kieber et al.*, 2005; *Calderón et al.*, 2007; *Rolff et al.*, 2008; *Zhang et al.*, 2008; *Bencs et al.*, 2009; *González Benítez et al.*, 2009; *Karthikeyan et al.*, 2009; *Violaki et al.*, 2010; *Gioda et al.*, 2011; *Zamora et al.*, 2011]. Deposition in these measurements is estimated from either the sum of the dry and wet deposition or from the concentrations in rainwater [*Zamora et al.*, 2011]. The dry deposition values for the measurements are calculated using the mean aerosol concentration and deposition velocities (e.g., 0.02, 0.006 and 0.012 m s^{-1} for nitrate, ammonium, and soluble ON, respectively in *Zamora et al.* [2011]).

3. Atmospheric Organic Nitrogen Input to Ocean Ecosystems

Atmospheric budgets of nitrate and ammonium have been studied extensively on global and regional scales, and the emission rates and chemistry of their gaseous precursors are reasonably well constrained in our model [*Feng and Penner*, 2007; *Ito and Feng*, 2010; *Xu and Penner*, 2012]. Here, we compare our model results for nitrate, ammonium, and total soluble nitrogen in total (i.e., dry + wet) deposition with the compilation of observations at

Table 3. Soluble ON Budget for the Major Source Categories (Tg N yr^{-1})

Primary Soluble ON	Emission	Dry Deposition	Wet Deposition	Burden
Anthropogenic sources[a]	5.5	0.7	4.9	0.050
Marine sources	1.7	0.5	1.2	0.003
Secondary soluble ON	Chemistry	Dry deposition	Wet deposition	Burden
Oxidized ON[b]	4.9	2.8	2.8	0.48
Reduced ON[c]	13	2.4	10	0.05

[a]Primary anthropogenic sources include fossil fuel combustion and biomass burning.
[b]Secondary oxidized ON includes PAN-like organic nitrates, alkyl, and hydroxyalkyl nitrates in gases and aerosols. The full species and chemical formulas can be found in Table S1 in the supporting information.
[c]Secondary reduced ON is not treated explicitly but is assumed to include imidazole, N-oligomers, and reversible ON in the form of amides, amines, and ammonium salt-like compounds associated with oxygen-containing functional groups in organics.

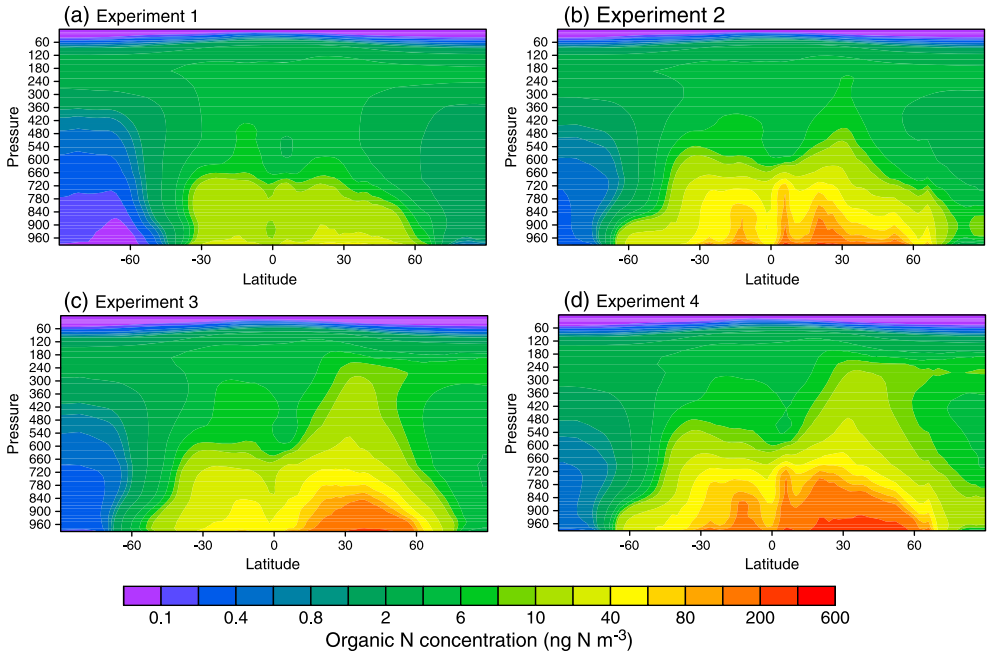

Figure 4. Annual zonal mean simulated soluble ON concentrations (ng N m^{-3}) in aerosols from (a) Experiment 1, (b) Experiment 2, (c) Experiment 3, and (d) Experiment 4.

coastal and marine locations (Figure 1). The comparison of the calculated and measured IN (i.e., nitrate and ammonium) and the total soluble N deposition fluxes indicates that the model captures the observations reasonably well.

The effects of PAN, isoprene nitrates, and SOA on tropospheric ozone and climate have been studied extensively in our model [*Ito et al.*, 2007a, 2009; *Lin et al.*, 2012]. In the case of organic nitrogen, we focus here on the total deposition of soluble ON as a key issue because of increasing concerns over the supply of anthropogenic nitrogen to marine ecosystems. Good agreement for the deposition of soluble ON between our model and observations is obtained over the eastern USA (Figure 2). The colors in the scatter plot (Figure 2a) correspond to the color of the locations of the observation sites in (Figure 2b). The blue colors represent that the modeled values fall within a factor of five of the measured values. However, Experiment 1 significantly underestimates the deposition of soluble ON at most locations. This model deficiency suggests possible other sources or transformation mechanisms for ON, keeping in mind the significant uncertainties and ranges in the annual estimates from both the model simulations and measurements. The model results from Experiment 2 are slightly improved, but significantly underestimate the deposition at most locations (Figure S2), suggesting that there might be missing ON sources in the model. The model results from Experiment 3 (Figure S3) and Experiment 4 (Figure 3) are quite successful in simulating the soluble ON deposition within a factor of 5 in most coastal locations. These results demonstrate that the soluble reduced ON can play an important role in controlling the predictive capability of the deposition rates in the model.

Table 4. Annual Deposition Rates of Soluble ON (Tg N yr^{-1}) to the Ocean[a]

Study	Preindustrial Era	Present Day
Experiment 1	0.7	1.1
Experiment 2	3.8	4.5
Experiment 3	3.5	6.8
Experiment 4	6.7	10
Kanakidou et al. [2012]		11 (6.0)[b]

[a]The sum of biomass burning (1.2 Tg N yr^{-1}) and differences between present day and preindustrial era (i.e., 0.4, 0.7, 3.2, and 3.5 for Experiments 1, 2, 3, and 4, respectively) can be compared to the estimates by *Kanakidou et al.* [2012] for the fraction of ON deposition that is associated with anthropogenic emissions.

[b]Soluble ON from anthropogenic sources including biomass burning emissions is listed in parentheses.

Our global total deposition flux of soluble ON (26 Tg N yr^{-1}) is between that estimated by *Neff et al.* [2002] (10 Tg N yr^{-1}) and *Kanakidou et al.* [2012] (32 Tg N yr^{-1}) (Table 3). In our model, the major source of the soluble ON

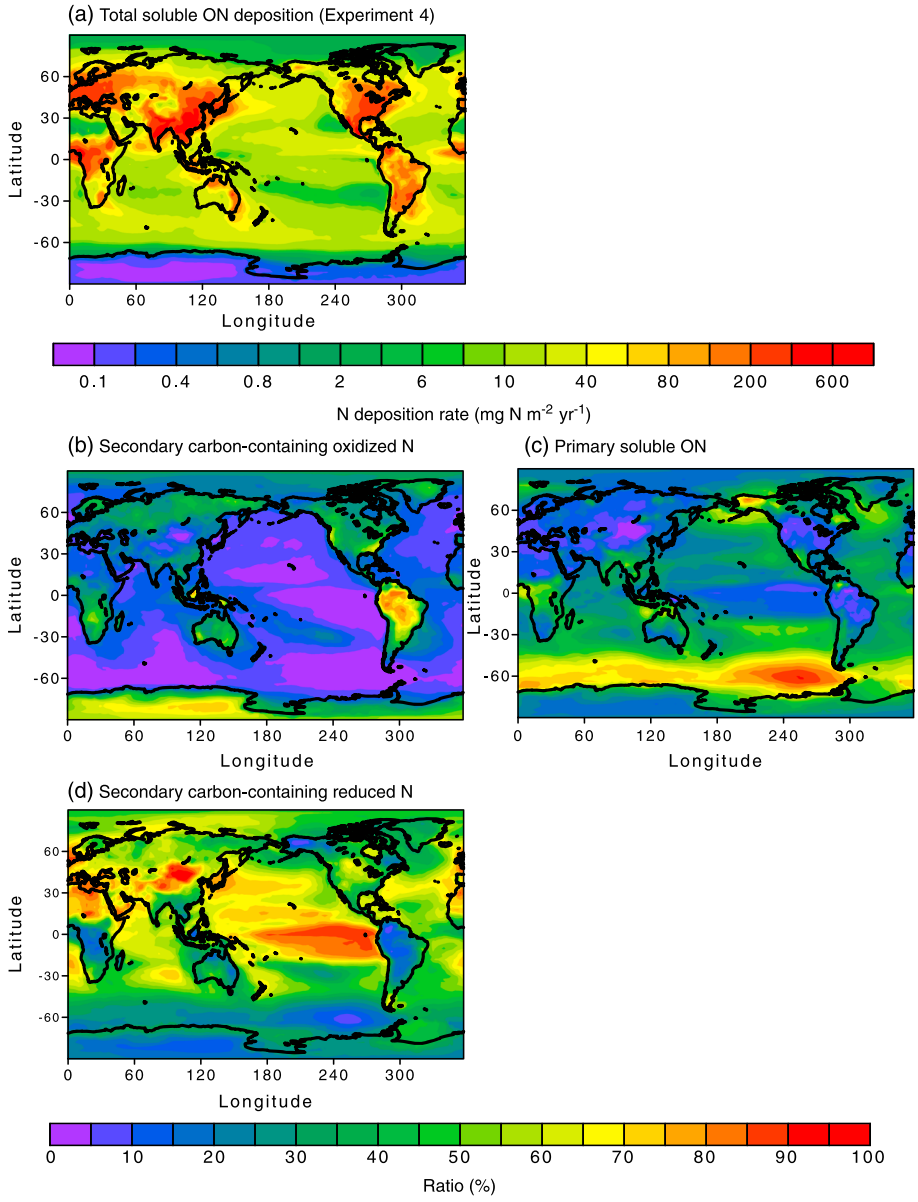

Figure 5. (a) Deposition of soluble ON (mg N m^{-2} yr^{-1}) to the oceans in Experiment 4 (total to the ocean 10 Tg N yr^{-1}), (b) ratio of explicitly calculated soluble ON from oxidized N (Experiment 1) to total soluble ON (Experiment 4) (11%), (c) ratio of soluble ON emitted from biomass burning, fossil fuel combustion, and marine sources (Experiment 2–Experiment 1) to total soluble ON (Experiment 4) (33%), and (d) ratio of soluble ON transformed from reduced N on preexisting aerosols (Experiment 3–Experiment 1) to total soluble ON (Experiment 4) (56%).

originates as chemically produced reduced ON (52%). For comparison, *Kanakidou et al.* [2012] estimated about 70% of the global ON atmospheric source was derived from primary emissions sources.

The comparison of the total deposition with the observations does not offer any information on the adequacy of the vertical distribution of soluble ON. A clear distinction can be seen in the zonal average vertical distribution of soluble ON in aerosols between different experiments (Figure 4). The model predicts a sustained secondary ON production in the free troposphere due to the relatively long lifetimes of the precursors and the colder temperatures there compared to those at the surface. The high concentrations of soluble ON near the surface (below 700 hPa) reflect the primary emissions from biomass burning, fossil fuel combustion, and marine sources (Experiment 2 and Experiment 4). Thus, vertical profiles of observed soluble ON may help to differentiate the relative importance of primary and secondary formation of soluble ON.

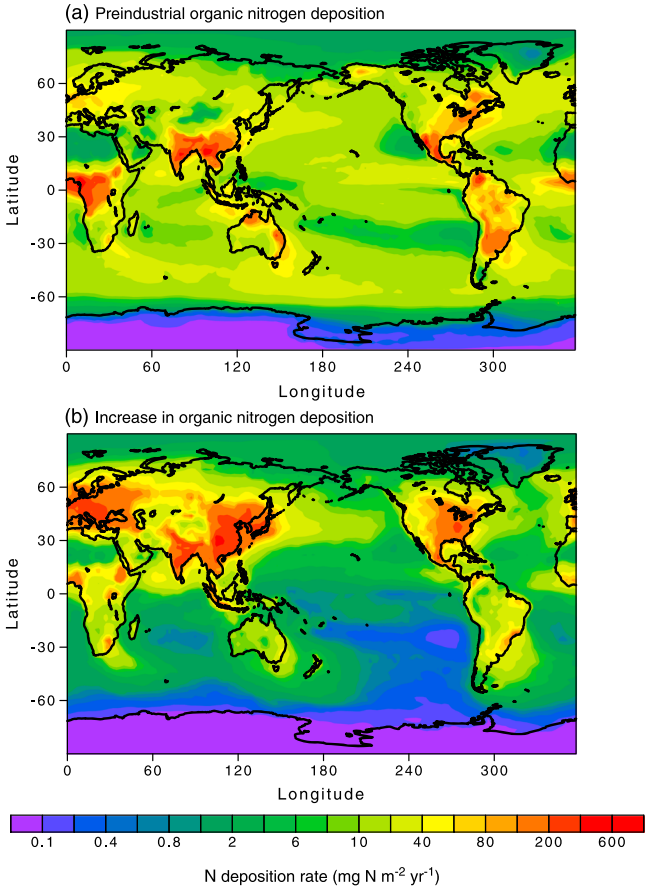

Figure 6. (a) Deposition of soluble ON (mg N m^{-2} yr^{-1}) to the oceans in preindustrial era (total to the ocean 6.7 Tg N yr^{-1}) and (b) increase from preindustrial to present (total +3.5 Tg N yr^{-1}) in Experiment 4.

The estimated annual deposition rates of soluble ON to the oceans from Experiment 4 is 10 Tg N yr^{-1} (Table 4, Figure 5a). Next, we discuss how much soluble ON deposition is contributed from the secondary oxidized ON, the primary soluble ON, or the secondary reduced ON for present day (Figure 5). We compared the simulated annual global deposition of soluble ON to the oceans in Experiment 1 with the deposition of soluble ON from Experiment 4 (Figure 5b). Notably, the soluble ON from the secondary oxidized ON (Experiment 1) could contribute 40–70% of the total soluble ON deposition (Experiment 4) over the eastern USA where good agreement for the soluble ON deposition with observations is obtained for all experiments. However, the model results suggest that soluble ON from the secondary oxidized ON in the gas and particulate phases (Experiment 1) might contribute less than 20% of the total ON deposition to the Northern Hemisphere (NH) oceans (10–70°N) (total to the global ocean is 1.1 Tg N yr^{-1} in Table 4). We also examined the fraction of total soluble ON that is emitted from biomass burning, fossil fuel combustion, and marine sources (Figure 5c) and that is transformed from reduced N on preexisting aerosols (Figure 5d). The differences between Experiment 1 and Experiment 2 (Experiment 3) can isolate the effect of the primary soluble ON (the secondary reduced ON). These figures demonstrate that the type of soluble ON present in the model is clearly different between different regions over the land and ocean areas, particularly in the regions downwind of major industrialized countries. The soluble ON emitted from biomass burning, fossil fuel combustion, and marine sources (Experiment 2–Experiment 1) could contribute 30–60% of the total soluble ON deposition over the oceans downwind from tropical Africa, Australia, South America, Alaska, and Canada (total to the ocean 3.4 Tg N yr^{-1}). The soluble ON transformed from reduced N on preexisting aerosols (Experiment 3–Experiment 1) could contribute 50–90% of the total soluble ON deposition over a large portion of the NH oceans downwind of East Asia, Eastern USA, and Europe (total to the ocean 5.7 Tg N yr^{-1}). The model results imply that a significant amount of soluble ON may be formed in the presence of ammonium sulfate in aerosol water. In particular, the soluble ON observed over the oceans downwind of East Asia and Europe could mainly be associated with the terrestrial anthropogenic sources [*Nakamura et al.*, 2006; *Lesworth et al.*, 2010].

The estimated annual total deposition rates of soluble ON to the ocean increase from 6.7 Tg N yr^{-1} in preindustrial era to 10 Tg N yr^{-1} in present day (Experiment 4). Figure 6a shows the annual distribution of soluble ON deposited to the ocean in preindustrial era. The differences in soluble ON deposition due to the differences in anthropogenic emissions between preindustrial era and present day might represent additional ON nutrients to marine ecosystems due to human activities (Figure 6b). These differences, however, do not include changes that result from changes in meteorological fields over this time period nor feedbacks in natural sources. The model results suggest that the anthropogenic activities have significantly increased the terrestrial soluble ON input from major industrialized regions to the oceans (total +3.5 Tg N yr^{-1}

from 6.7 to 10 Tg N yr^{-1}). Especially, the supply of soluble ON to the western Pacific increases from 10–60 to 20–200 mg N m^{-2} yr^{-1} (up to a factor of 5.5 increase). The sum of biomass burning ON (i.e., 1.2 Tg N yr^{-1}) and differences between present day and preindustrial era (e.g., 3.5 Tg N yr^{-1} for Experiments 4) can be compared to the estimates by *Kanakidou et al.* [2012] for the fraction of ON deposition that is associated with anthropogenic emissions (6.0 Tg N yr^{-1}).

4. Conclusions

Atmospheric deposition of anthropogenic reactive nitrogen species may play a key role in altering marine biological activity. We have presented a simulation of the global deposition of soluble ON using a coupled gas-phase and aerosol chemistry version of the IMPACT model. The model includes a detailed representation of a gas-phase mechanism to predict the formation of volatile ON and particulate ON from oxidized N. Modeled total (i.e., dry + wet) deposition of soluble ON from oxidized N only was in good agreement with observation over the eastern USA but significantly underestimated in most locations. We investigated two possible candidates for reducing the model-measurement difference: addition of (a) the primary soluble ON emitted with carbonaceous aerosols and (b) the secondary reduced ON on aerosols. These two significantly increased the deposition of soluble ON, but the latter substantially improved the model-measurement agreement.

The model-derived present-day soluble ON to the ocean (to the land) was estimated to be 10 Tg N yr^{-1} (16 Tg N yr^{-1}), which included both the natural and anthropogenic components. We examined the different types of soluble ON deposition to the global ocean. Of the total deposition to the ocean, 11% was from the secondary oxidized ON (1.1 Tg N yr^{-1}), 33% from the primary ON (3.4 Tg N yr^{-1}), and 56% from the secondary reduced ON (5.7 Tg N yr^{-1}). The additional ON nutrients to the ecosystems due to human activities were estimated from the differences in soluble ON deposition due to the differences in anthropogenic emissions between preindustrial era and present day. The model results suggest that the global supply of atmospheric soluble ON to the ocean (to the land) has a significant anthropogenic component with 34% (54%) of the overall atmospheric source.

The chemical composition of ON is highly variable, and the formation mechanisms of the soluble reduced ON are not well characterized quantitatively. It should be noted that the comparison of the annual averages to validate the modeled deposition is inherently difficult, because the concentrations of biomass burning and dust events are highly variable. Few measurements are available in tropical regions where significant biomass burning occurs. Over such regions, nitrogen and sulfate deposition observational systems could be extended and used to measure organic nitrogen and to distribute the evaluated datasets. The complex emission and formation processes for soluble ON result in predicted burdens that have high spatial and temporal variability. Moreover, the type of soluble ON predicted over the industrialized countries and the open ocean is substantially different. Further observations to evaluate the variability of ON and its solubility under a variety of conditions over the oceans are desirable. The model results highlight the need for more field measurements of the source of ON (i.e., primary emission versus secondary formation) and the chemical characteristics of organic aerosols (i.e., oxidized ON versus reduced ON). Vertical profiles of soluble ON within the atmosphere would be beneficial for a better understanding of its origin and/or transformation in the atmosphere. The emission sources of nitrogen oxide, ammonia, and carbonaceous aerosols are different between different locations and times. Continuous monitoring of soluble ON together with monitoring NO_x, NH_3, and carbonaceous aerosols may be used to constrain the contribution from a particular source.

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