Past, Present, and Future Atmospheric Nitrogen Deposition

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ABSTRACT

Reactive nitrogen emissions into the atmosphere are increasing as a result of human activities, affecting nitrogen deposition to the surface and impacting the productivity of terrestrial and marine ecosystems. An atmospheric chemistry–transport model [Tracer Model 4 of the Environmental Chemical Processes Laboratory (TM4-ECPL)] is here used to calculate the global distribution of total nitrogen deposition, accounting for the first time for both its inorganic and organic fractions in gaseous and particulate phases and past and projected changes due to anthropogenic activities. The anthropogenic and biomass-burning Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) historical and RCP6.0 and RCP8.5 emissions scenarios are used. Accounting for organic nitrogen (ON) primary emissions, the present-day global nitrogen atmospheric source is about 60% anthropogenic, while total N deposition increases by about 20% relative to simulations without ON primary emissions. About 20%–25% of total deposited N is ON. About 10% of the emitted nitrogen oxides are deposited as ON instead of inorganic nitrogen (IN), as is considered in most global models. Almost a threefold increase over land (twofold over the ocean) has been calculated for soluble N deposition due to human activities from 1850 to present. The investigated projections indicate significant changes in the regional distribution of N deposition and chemical composition, with reduced compounds gaining importance relative to oxidized ones, but very small changes in the global total flux. Sensitivity simulations quantify uncertainties due to the investigated model parameterizations of IN partitioning onto aerosols and of N chemically fixed on organics to be within 10% for the total soluble N deposition and between 25% and 35% for the dissolved ON deposition. Larger uncertainties are associated with N emissions.

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1. Introduction

Nitrogen (N) is an important constituent of any form of life, including plant tissues and proteins. Reactive N availability in the environment together with other nutrients like iron, phosphorus, and silica control ecosystem productivity (Mills et al. 2004). Nitrogen availability is thus linked to the carbon cycle and in particular to carbon dioxide (CO_2) removal from the atmosphere by the terrestrial and marine ecosystems and to food production (Duce et al. 2008; Galloway et al. 2008). Atmospheric deposition of reactive nitrogen (N) compounds fertilizes ecosystems or has negative impacts due to acidification and accumulation of excess nutrients (Driscoll et al. 2003), while reactive nitrogen chemically trapped on pollen particles (Franze et al. 2005) or forming secondary gaseous and particulate pollutants in the atmosphere (Lelieveld et al. 2015) can be harmful for human health. Reactive nitrogen compounds are emitted to the atmosphere in oxidized or reduced inorganic (IN) or organic (ON) forms by natural (e.g., soils, lightning, plants, bacteria, viruses) and anthropogenic sources (e.g., industries, transportation, domestic wood burning) (Neff et al. 2002; Dentener et al. 2006; Galloway et al. 2008; references therein). Recent observations and modeling studies have shown that ON is a significant fraction of total nitrogen (TN) deposition; however, the chemical characterization of this fraction remains a challenge (Cornell 2011; Cape et al. 2011; Altieri et al. 2012; Kanakidou et al. 2012; references therein).

Since the beginning of industrialization, human activities have dramatically increased the amounts of N emitted to the atmosphere and deposited to the surface, modifying the biogeochemical cycle of N (Galloway et al. 2008). Duce et al. (2008) estimated that the human-induced increase in atmospheric N deposition to the oceans may account globally for up to approximately 3% of the annual new oceanic primary productivity. Higher contributions have been estimated for semi-enclosed marine ecosystems such as the Mediterranean Sea, for which atmospheric deposition of N may account for up to 35%–60% of new production (Christodoulaki et al. 2013). Reactive nitrogen is also an important driver of atmospheric chemistry, since ozone production is controlled by nitrogen oxides availability. Nitric acid is a major contributor to the atmospheric acidity, ranking second after sulfuric acid, and NH_3 is the main neutralizing gas for these acidic compounds (Seinfeld and Pandis 2016). Thus, removal of atmospheric N species by deposition also impacts atmospheric chemistry. Consequently, evaluation of the impact of N emissions on the environment and climate requires the estimation of past and future changes in N atmospheric deposition.

Projections for N emissions in the atmosphere are based on different scenarios that assume control of nitrogen oxide emissions but not those of ammonia [Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP); Lamarque et al. (2013a,b)], pointing to expected changes in the chemical composition and thus possibly in the bioavailability of deposited N.

The present study uses the global atmospheric chemistry–transport model Tracer Model 4 of the Environmental Chemical Processes Laboratory (TM4-ECPL) [Myriokefalitakis et al. (2015) and references therein] to evaluate past and future changes in atmospheric deposition of N that are driven by human activities, accounting for ON in the aerosol phase that has been neglected in most of the earlier studies (e.g., Lamarque et al. 2013b). Thus, the present study accounts for ON primary emissions as well as chemical formation of ON in secondary organic aerosol (SOA). Unlike recent ON global modeling studies (Kanakidou et al. 2012; Ito et al. 2014, 2015) the N-containing SOA formation, when it is not originating from amines, is here considered to occur only when sufficient nitrogen oxides (NO_x) are available. It is also the first time that expected future changes in ON atmospheric deposition based on human-driven emission scenarios are evaluated. A global picture of the changes in the atmospheric deposition of nitrogen and its composition, in particular the ON component, due to changes in anthropogenic emissions, and subsequently atmospheric chemistry, is here provided together with an uncertainty estimate.

2. Methodology—Model description

TM4-ECPL accounts for gas and multiphase oxidants, volatile organic compound (VOC) chemistry in the troposphere, and all major primary and secondary aerosol components, including SOA formation (Tsigaridis and Kanakidou 2003, 2007; Myriokefalitakis et al. 2011; Kanakidou et al. 2012). The present model configuration explicitly considers the atmospheric iron cycle (Myriokefalitakis et al. 2015). It uses the ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes 2007) to calculate the formation of ammonium (NH_4^+) and nitrate (NO_3^-), assuming thermodynamically stable conditions (Karydis et al. 2016) and accounting for the impact of mineral dust and sea-salt elements on nitrate and ammonium partitioning to the aerosol phase (see Myriokefalitakis et al. 2015). In-cloud pH is controlled by strong acids [sulphuric acid (H_2SO_4), methanesulphonic acid (MSA), and nitric acid (HNO_3)] and bases [ammonia (NH_3)] and by the dissociation of hydrated CO_2, SO_2, and oxalic acid (Myriokefalitakis et al. 2011).

The photochemical degradation of VOC in the atmosphere forms secondary products, carbon monoxide, and, ultimately, CO_2. Thus, only part of the emitted organics are ultimately deposited to the surface by dry or wet deposition processes in either the gas or the particulate form. The deposition parameterization in TM4-ECPL uses solubility estimates for the individual compounds (Tsigaridis et al. 2006; Myriokefalitakis et al. 2011; Kanakidou et al. 2012).

The model uses primary emissions of NO_x, ammonia, marine amines (that are two orders of magnitude weaker than ammonia marine emissions; Duce et al. 1983, 1991; Facchini et al. 2008), and emissions of particulate ON from various natural and anthropogenic sources [Table S1; see also Kanakidou et al. (2012)]. These particulate ON emissions contain both oxygenated and reduced nitrogen species although no specific distinction is made in the model between the two categories of ON owing to insufficient knowledge. Moreover, marine amines (ON) in the gas phase are here considered to form amine salts (ON in the particulate phase) consistent with the ON characterization by Altieri et al. (2012) as predominantly containing reduced nitrogen. Amines of continental origin are not considered here because of the uncertainty and the weakness of their sources both of human and natural origin (Schade and Crutzen 1995; Ge et al. 2011; Karl et al. 2014; Sintermann and Neftel 2015). The organic nitrates that are of secondary origin and oxygenated inorganic nitrogen compounds both in the gas and particulate phases are explicitly calculated (Myriokefalitakis et al. 2011). An increasing number of global atmospheric chemistry–transport models account for the formation of organic nitrate during VOC oxidation using chemical schemes of various complexities. However, they do not explicitly account for the production of other forms of ON, particularly those associated with the primary and secondary organic aerosol (OA). Thus, these models underestimate the total atmospheric burden of ON and its deposition to the surface. In this study, to account for particulate ON primary emissions (Table S1), particulate ON concentrations are linked to source-specific OA tracers using varying N:C molar ratios at emission time as measured in the organic matter from different source types and detailed in Kanakidou et al. (2012). Two different N:C molar ratios have been used for fossil fuel and biomass burning sources (0.16 and 0.30) within the range of uncertainty (Kanakidou et al. 2012). Furthermore, it is here assumed that SOA formed under high NO_x-to-VOC conditions [as these are defined in Tsigaridis et al. (2006)] by VOC other than amines contains N, and thus, during this SOA formation, IN is converted into ON. Sensitivity simulations have also been performed neglecting this

NO_x-to-VOC dependence and the mixing with dust and sea-salt aerosol in ISORROPIA II for comparison to the earlier study by Kanakidou et al. (2012). The present model setup differs also from that earlier study in the meteorological fields used (ERA-Interim is used here instead of ECMWF operational data) and the emission datasets as described below. The results of all simulations are provided in Table 1.

Natural emissions of reactive gases and aerosols from both terrestrial and oceanic sources as well as lightning used in the model are as reported in Myriokefalitakis et al. (2015) but for the year 2005. Primary biogenic particle emissions are distributed according to the leaf area index spatial and temporal distribution with 25% in the fine and 75% in the coarse mode [as in Kanakidou et al. (2012)]. Anthropogenic and biomass burning emissions of NO_x, carbonaceous aerosols, SO_2, and organics come from the ACCMIP database: for 1850 (past), the historical ACCMIP inventories, for 2005 (present day), first scenario year of the representative concentration pathway 6.0 (RCP6.0) inventory, and for 2050 (future) both RCP6.0 and RCP8.5 inventories (Lamarque et al. 2013a) (Fig. 1, columns marked with "xx_emi").

While past ON emissions are estimated to be of the same magnitude as alkaline (NH_x) and acidic (NO_x) compounds emissions (Fig. 1), projections (van Vuuren et al. 2011) show that NH_x emissions will gain importance compared to NO_x emissions, overall reducing atmospheric acidity. There is no clear trend in future estimates of ON emissions. All simulations presented here have been performed using present-day ERA-Interim meteorology (Dee et al. 2011) and natural emissions of the year 2005. Thus, the calculated changes are only due to anthropogenic emission changes. Henry's law coefficients for organic nitrates are taken from Sander (1999) and the soluble fractions of primary particulate ON by Kanakidou et al. (2012) are used. Simulations are performed with the model horizontal resolution of $3°$ longitude $\times$ $2°$ latitude and 34 vertical layers. Atmospheric deposition fluxes are computed in this horizontal resolution and have been further interpolated to $1° \times 1°$ grid for further analysis.

3. Results

The global distributions of ON and IN fractions of nitrogen atmospheric deposition are computed as the sum of the corresponding terms of the individual ON and IN model tracers calculated by TM4-ECPL. The results are summarized in Table 1 and Fig. 1 (columns marked with "XX_dep") that show the global changes in atmospheric N deposition due to human activities computed using different parameterizations and emission

TABLE 1. Atmospheric total deposition of reactive N (TgN yr^{-1}) calculated by TM4-ECPL based on different anthropogenic emission inventories. The respective deposition fluxes over the oceans are provided in parentheses. The estimate from the ACCMIP multimodel simulations (Lamarque et al. 2013a,b), from the PhotoComp simulations (Dentener et al. 2006), and from Vet et al. (2014) for the year 2000 are provided for comparison. For the Vet et al. (2014) estimates, the number in parenthesis provides deposition on coastal and ocean systems. Regular font indicates base-case simulations done with an N:C ratio of 0.16 for combustion sources and sea-salt and dust components taken into account in ISORROPIA II. Italics indicate simulations as base case but with an N:C ratio of 0.3. Boldface indicates simulations as base case but without NO$_x$-to-VOC dependence of N-SOA formation and neglecting sea-salt and dust aerosol components in the ISORROPIA II thermodynamic equilibrium model. NO$_y$ is the sum of NO$_x$, HNO$_3$, and NO$_3$p; NH$_x$ is the sum of NH$_3$ and NH$_4^+$.

Deposition	ACCMIP			RCP6.0						RCP8.5	ACCMIP	PhotoComp	Vet et al. (2014)
	1850	*1850*	**1850**	2005	*2005*	**2005**	2050	*2050*	**2050**	**2050**	2000	2000	2000
NH$_x$	17 (10)	*17 (10)*	**17 (10)**	53 (19)	*53 (19)*	**53 (20)**	68 (21)	*68 (21)*	**64 (22)**	70 (21)	49 ± 1	63	—
NO$_y$	12 (6)	*12 (5)*	**6 (3)**	46 (22)	*46 (22)*	**40 (20)**	37 (18)	*37 (18)*	**30 (15)**	39 (20)	51 ± 4	51	—
DON	14 (9)	*13 (8)*	**21 (10)**	22 (12)	*28 (14)*	**29 (13)**	22 (12)	*28 (14)*	**29 (13)**	21 (12)	—	—	—
ON insoluble	5 (2)	*7 (2)*	**7 (1)**	5 (2)	*5 (2)*	**7 (1)**	5 (2)	*5 (2)*	**7 (1)**	5 (2)	—	—	—
Total N	48 (27)	*49 (23)*	**51 (24)**	126 (55)	*132 (58)*	**129 (54)**	132 (53)	*138 (55)*	**129 (50)**	135 (55)	101 ± 2	114	122.2 (39)

inventories (Fig. 1). Figure 2 compares the computed TN and dissolved ON (DON) deposition fluxes for the base simulation (see Table 1) with observationally derived fluxes [compilation in Kanakidou et al. (2012)]. Modeled TN deposition fluxes are in good agreement with observations [see also supplementary Figs. S2 and S3 using observations from Vet et al. (2014)]. The highest observed DON fluxes seem to be underestimated by the model by less than an order of magnitude, indicating a potential underestimate of the contribution of DON, relative to IN, in TN deposition fluxes. According to our model estimates, primary sources dominate DON emissions, increasing the total present-day N sources commonly taken into account in global models by about 20%. Thus, no direct link is expected between ON and NO$_y$ deposition. Secondary sources of ON (both gases and aerosols) are

estimated to be low, ranging from 4 to 13 TgN yr^{-1}—that is, about 15%–35% of the global present-day sources of ON and converting about 10% of primary NO$_x$ emissions to ON. From this secondary source of ON, most global models account only for the gaseous organic nitrate and peroxyacytyl nitrate (PAN) formation (Lamarque et al. 2013b) that in our model amounts to between 0.9 and 2.9 TgN yr^{-1}—that is, 3%–10% of the total ON source.

Additional comparisons between model results and observations are provided in the supplement (Figs. S1–S4). Comparisons of model results with atmospheric concentrations of N-containing species from the EBAS database indicate an overestimate by the base-case simulation of NO$_3^-$ [normalized mean bias (NMB) = 115%; see supplement] and NH$_4^+$ (NMB = 54%) concentrations in PM$_{10}$, while HNO$_3$ and NO$_2$
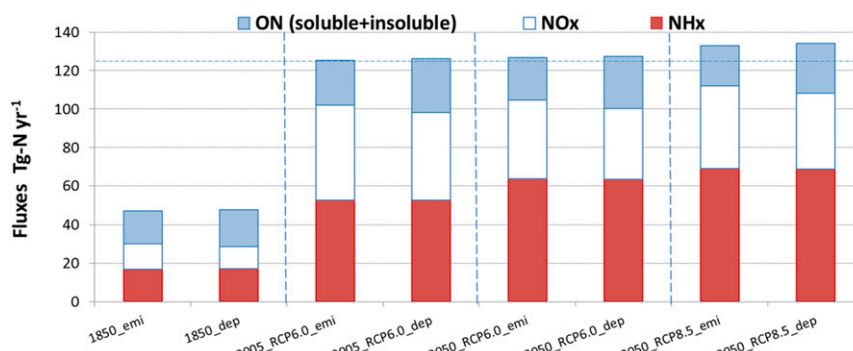

FIG. 1. Anthropogenic emissions of NH$_3$ and NO$_x$ and those of particulate ON used for this study for 1850, 2005, and 2050 from historical ACCMIP database and RCP6.0 and RCP8.5 emissions (marked by "year"_emi). Particulate ON emissions are derived in the present study from the particulate OC corresponding emissions based on the methodology developed by Kanakidou et al. (2012). Atmospheric deposition of reactive nitrogen as computed by TM4-ECPL based on these emissions (marked by "year"_dep). N flux as inorganic reduced N (NH$_x$) (red), as inorganic oxygenated N (NO$_y$ for deposition and NO$_x$ for emissions) (white), and as ON (blue). Noticeable are differences in the projections between RCPs. NO$_y$ is calculated as the sum of NO$_x$, HNO$_3$, NO$_3^-$, HONO, HNO$_4$, and N$_2$O$_5$.
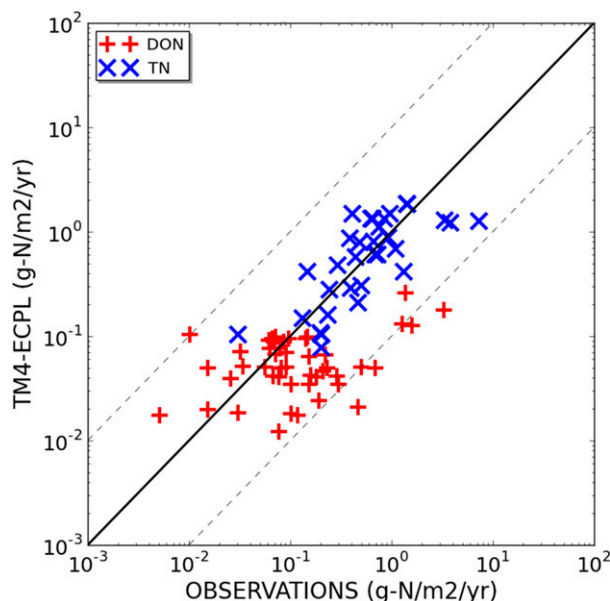
FIG. 2. Comparison between modeled (TM4-ECPL) and observationally derived (OBSERVATIONS) atmospheric deposition annual fluxes of total nitrogen (×) and DON (+) [gN m^{-2} yr^{-1}; compilation of data by Kanakidou et al. (2012) and references therein]. Solid line indicates the 1:1 and dashed lines indicate the 10:1 and 1:10 model-to-observation ratios.

concentrations compare well (Fig. S4). Simulated atmospheric deposition fluxes are compared with data compiled by A. R. Baker et al. (2016, unpublished manuscript) from oceanographic cruises (Fig. S1: dry deposition fluxes) and by Vet et al. (2014) from continental networks (Fig. S2: wet deposition fluxes; Fig. S3: sum of wet and dry deposition fluxes). Fluxes of NO$_y$ are biased high for the base-case simulation (NMB = 17%) and low for the simulations without NO$_x$-to-VOC dependence (in boldface in Table 1) (NMB = −28%) compared to deposition fluxes derived from observations over land (Figs. S2 and S3) and over the ocean (Fig. S1). NH$_x$ deposition fluxes seem to be overestimated by the model (NMB = 17%, Fig. S3a) while for NH$_4^+$ wet deposition, no systematic bias has been found. This difference in the model performance between NH$_x$ and NH$_4^+$ deposition indicates a potential overestimate in NH$_3$ deposition (Figs. S1 and S3). The here-computed deposition fluxes have been also compared with those of the ACCMIP multimodel simulations in Figs. S5 and S6. These comparisons show that the base-case simulation is very close to the 1:1 line with the mean of ACCMIP models, although an underestimate of the low NO$_y$ and NH$_x$ deposition fluxes can be seen.

As seen in Table 1 and Fig. 1b, NH$_3$ and NO$_x$ emissions increased from 1850 to the present leading to

similar (two- to threefold) increases in their respective N atmospheric deposition. In the future (2050), however, NO$_x$ emissions are projected to decline while NH$_3$ emissions will continue to grow. These changes are reflected in the simulated deposition fluxes that are projected to become less acidic (owing to 22% increase in NH$_x$ and 20% decrease in NO$_y$ deposition fluxes). Overall, projected changes in global TN deposition fluxes are small, indicating a 5%–10% increase for RCP6.0 and RCP8.5, respectively.

a. Past–present–future changes of atmospheric nitrogen deposition

Figures 3a–d show the computed spatial distribution of atmospheric deposition NO$_y$ (oxidized IN), NH$_x$ (reduced IN), DON, and TN, respectively, for the year 2005. TN atmospheric deposition (Fig. 3d) is the sum of IN, DON, and insoluble ON (Kanakidou et al. 2012) as seen in Table 1. NO$_y$ deposition (Fig. 3a) shows the highest fluxes over industrial areas of the Northern Hemisphere and tropical biomass burning regions, while NH$_x$ deposition (Fig. 3b) maximizes over Europe, China, and Indonesia reflecting the important NH$_3$ emissions in these regions. Smaller deposition fluxes are computed over oceanic regions, most of them related to recycling of NH$_3$ oceanic emissions that in our model amount to 8.15 TgN yr^{-1} (Bouwman et al. 1997). The here-computed global annual present-day NO$_y$ and NH$_x$ deposition fluxes are well within the range of multimodel estimates that neglect the presence of ON originating from primary ON emissions and SOA formation (Table 1 and references therein). As seen in Fig. 3d, TN deposition exceeds the 1 gN m^{-2} yr^{-1} critical load for vegetation at several locations over the eastern United States, Europe, India, China, and Indonesia. High DON deposition flux (Fig. 3c) in the tropics is due to the large contribution by primary biogenic particles, biomass burning, and SOA formation. The DON maxima computed for China and Southeast Asia indicate, in addition to these sources, the importance of anthropogenic emissions in Asia. According to our calculations the contribution of DON to the global soluble N deposition amounts to 15%–20% globally and to 20%–35% over the ocean. The overall estimated range, including previous studies, in present-day DON atmospheric deposition is 20–32 TgN yr^{-1} globally and 10–20 TgN yr^{-1} over the ocean (Table 2), with about 30%–50% of this amount associated with human activities. This range reflects the uncertainties in the sources and chemical characterization of ON and indicates that further studies are required to improve the understanding of ON in the atmosphere.

According to our calculations, the anthropogenic contribution to TN emissions increased from 15% in
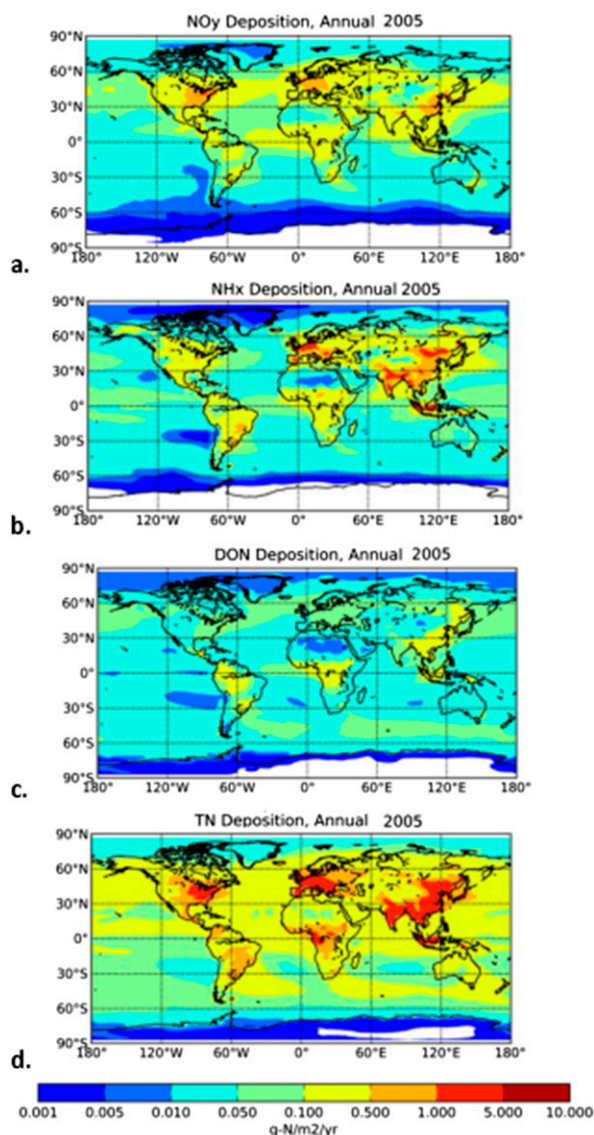
FIG. 3. Atmospheric deposition of N $(gN\,m^{-2}\,yr^{-1})$ computed by TM4-ECPL for (a) NO_y, (b) NH_x, (c) DON, and (d) TN for 2005.

TABLE 2. DON annual deposition flux estimates $(TgN\,yr^{-1})$ for present day.

DON deposition global	DON deposition ocean	Reference
9 (up to 50)	—	Neff et al. (2002)
—	20	Duce et al. (2008)
32	16	Kanakidou et al. (2012)
26	1.1–10	Ito et al. (2014)
19–30	9–14	Ito et al. (2015)
20–29	10–13	This work

globally since 1850 emissions (except for a few locations over the eastern United States, southern India, the Bengal Bay, the Arabian Sea, and southeastern Australia, where significant land-use changes have occurred) and is expected to further increase over densely populated regions (Fig. 4d). Large increases have occurred over the heavily industrialized areas of the Northern Hemisphere for all soluble reactive N fractions as depicted in Figs. 4a–c and are projected to occur in the future mainly in Asia (Figs. 4b–f), while NO_y deposition will be reduced everywhere except over Asia (Fig. 4b). Projected DON deposition changes show similar patterns with those of NO_y, with significant reductions over Europe and increases over Asia.

The comprehensive inclusion of ON in the model increases the total soluble N deposition [since additional primary (ON) sources are taken into account] but also converts NO_x to ON, thus changing the chemical composition of TN deposition. However, the amount of ON originating from NO_x chemistry remains uncertain. According to the present-day estimates, it can vary between 4 and 13 $TgN\,yr^{-1}$.

b. Uncertainties

In the present study the fraction of ON secondary formation from nonamine VOC that is driven by NO_x chemistry leads to about 3 $TgN\,yr^{-1}$ of organic nitrates and 2 $TgN\,yr^{-1}$ of N-SOA formation in the present day. This present-day N-SOA flux estimate $(2\,TgN\,yr^{-1})$ is from five- to eightfold lower than earlier estimates, which neglect the NO_x dependence [10 $TgN\,yr^{-1}$ (Kanakidou et al. 2012) and 17.6 $TgN\,yr^{-1}$ (Ito et al. 2014)]. This indicates the large uncertainty associated with the chemistry of ON aerosols, and this introduces an uncertainty of at least 25%–35% in the global deposition fluxes of soluble ON and about 10% in the global TN deposition. Significantly larger uncertainties exist also in the primary emission of ON, as is the case for other pollutant primary emissions (Granier et al. 2011). For instance, when using an N:C ratio for anthropogenic aerosol varying from 0.16 (base case) to 0.3 (simulations in boldface in Table 1), the primary ON
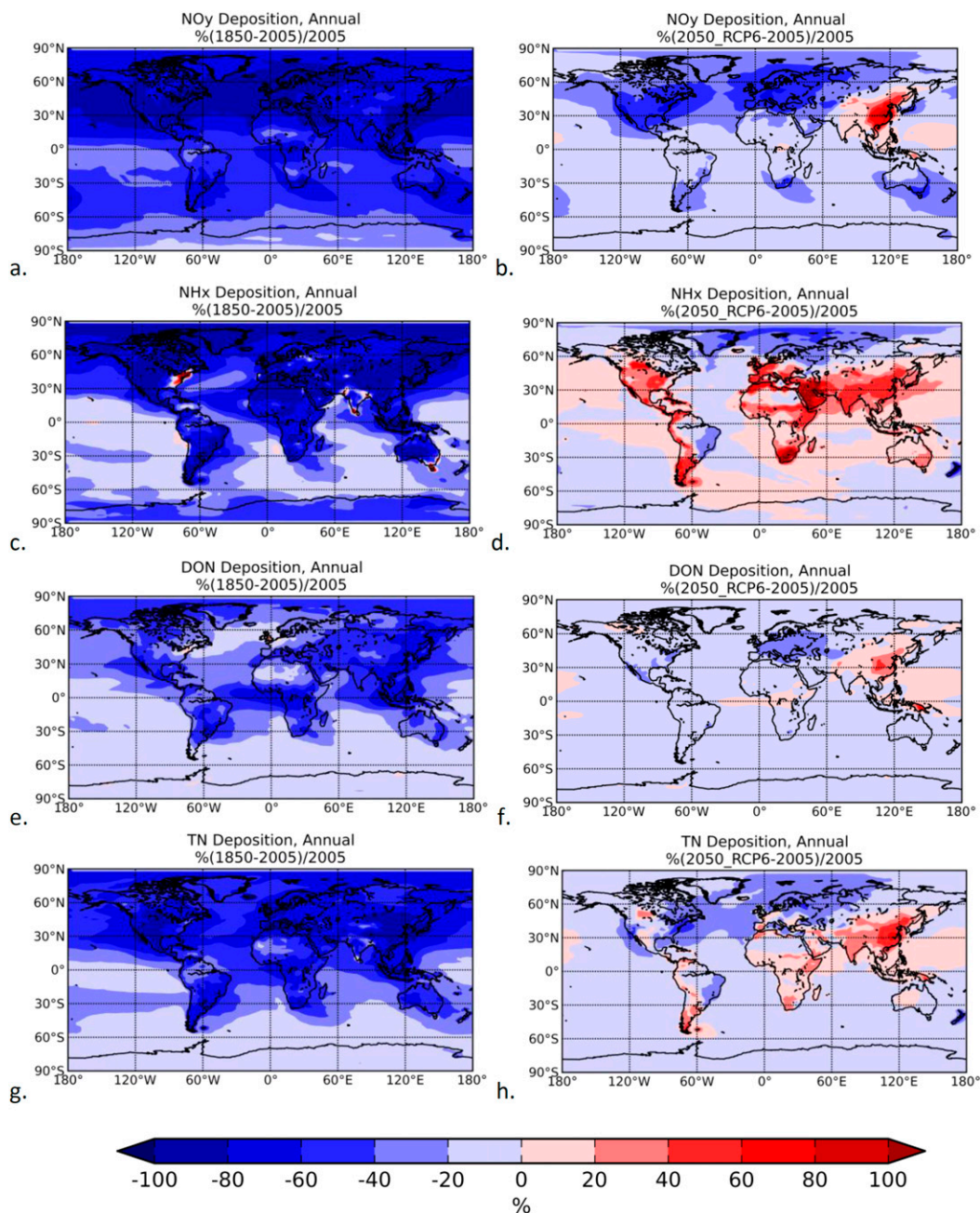
1850 (mainly in the form of NH_x) to 60% at present (2005; in the form of NH_x: 50%; NO_x: 40%; and ON: 10%) and in the future (2050; in the form of NH_x: 60%; NO_x: 30%; and ON: 10%), with similar changes in deposition fluxes. The atmospheric soluble N deposition increased since the preindustrial period (Table 1) by a factor of 3 mainly owing to a larger (3.5-fold) increase in IN deposition (Figs. 4a,c) and is expected to further change for 2050 (Figs. 4b,d), although this estimated change is smaller than 15%. These changes are from 15% to about 150% larger over land where most anthropogenic N sources are located than over the ocean. NH_x deposition (Fig. 4b) is calculated to have increased

FIG. 4. Percentage change relative to 2005 annual deposition flux computed by TM4-ECPL for (a),(b) NO$_y$; (c),(d) NH$_x$; (e),(f) DON; and (g),(h) TN due to (left) preindustrial emissions and (right) anthropogenic RCP6.0 emissions.

emissions are evaluated between 23 and 30 TgN yr^{-1}, respectively—that is, about a 30% difference. Thus, the largest uncertainties in the deposition fluxes are found to be associated with the primary and secondary sources of ON (that can vary by at least a factor of 2) and to the projected anthropogenic emissions. The latter vary in magnitude by about 50% and can even show different trends [Stohl et al. (2015) and references therein]. Kanakidou et al. (2014) investigated the impact of the

use of different anthropogenic emission inventories [Greenhouse Gas and Air Pollution Interactions and Synergies, version 4a (GAINSv4a; Klimont et al. 2013), vs RCPs (Lamarque et al. 2013a)] on the calculated global annual deposition fluxes of N. They found higher N-deposition fluxes by 17% for present day and 30% for 2050 when using GAINSv4a emissions compared with RCP6.0 emissions. In addition, the higher increase in N deposition computed for the year 2050 using

GAINSv4a emission inventories is mainly associated with the stronger projected increase in NH_3 emissions in GAINSv4a than in RCPs. Thus, while using RCP6.0 or RCP8.5 projections, the calculated N-deposition future change is small ($<3\%$), but when using GAINS projections, N deposition is calculated to further increase in the future ($+12\%$). In addition, natural emissions have significant natural variability that has been neglected here. The deposition fluxes to the ocean have also been found to be sensitive to the model horizontal resolution, most probably because increasing resolution leads to better separation between ocean and land grid boxes. Thus, a 4-times-higher horizontal resolution (smaller grid) leads to about a 20% increase in atmospheric deposition of reactive nitrogen over the oceans, while, as expected, global deposition fluxes remain practically unchanged. This uncertainty associated with the limitations of numerical models in separating coastal and ocean regions has to be taken into account when studying the impact of atmospheric deposition to marine ecosystems.

4. Conclusions

For the present study, anthropogenic and biomass burning emissions were taken from the RCP6.0 database for the year 2005, from ACCMIP historical emissions for the year 1850, and from RCP6.0 and RCP8.5 projections for the year 2050. Present-day global TN deposition is estimated between 125 and 132 TgN yr^{-1}. ON deposition (27–36 TgN yr^{-1}) is about 20%–30% of the TN deposition (Fig. S6), about 30%–50% of which is associated with human activities. From this ON deposition, only 25%–35% that is associated with the secondary ON source has been accounted for in earlier studies as gaseous organic nitrates or IN deposition. However, targeted observational experiments are needed to improve the parameterization of the chemical bonding of N on OA under clean and polluted atmospheric conditions as well as the estimate of the primary emissions of ON. Large areas in the Northern Hemisphere are subject to TN deposition higher than the critical load for vegetation. Atmospheric TN deposition has increased by a factor of about 3 since 1850 (calculated using ACCMIP historical emissions), mainly owing to the large increase of IN. This also led to a decrease in the ratio of dissolved ON to dissolved TN from 0.77 in 1850 to 0.30 nowadays [in agreement with Duce et al.'s (2008) estimate] on an annual global-mean basis while regionally significant deviations from these mean ratios are computed (Fig. S6). For the future, using RCP6.0 and RCP8.5 scenarios, the reduction in NO_x emissions is projected to be compensated by the continuing increase in NH_3 emissions, and as a result the global TN deposition is not

expected to change much while its acidity will be significantly reduced. Regionally significant changes are projected, in particular over Asia. These results neglect future changes in biogenic emissions driven by climate. However, changes in natural emissions are expected to have much smaller impact on N deposition than changes in anthropogenic N emissions. The evaluation of the impact of the estimated changes in TN fluxes on the ecosystems requires dedicated biogeochemical ecosystem studies.

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