

Past and future changes of organic and inorganic nitrogen global atmospheric deposition

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Nitrogen is an important nutrient that controls the productivity of terrestrial and marine ecosystems. Emissions of reactive nitrogen into the atmosphere are increasing due to human activities, affecting also nitrogen deposition to the surface. There is also growing evidence that a significant fraction of nitrogen deposition occurs in the form of organic nitrogen, although the chemical characterization of this fraction remains a challenge. The present study uses a global atmospheric chemistry transport model to calculate the global distribution of nitrogen deposition, accounting for both its inorganic and organic fractions in gaseous and particulate phases. Present-day simulations suggest that the global organic nitrogen cycle has a strong anthropogenic component with almost half of the overall atmospheric source (primary and secondary) associated with anthropogenic activities, while about 25% of total N deposition is in the form of organic nitrogen. Almost a 3 fold increase has been calculated by TM4-ECPL for N deposition fluxes due to increase in human activities from 1850 to present. Projections indicate changes in the chemical composition of N deposition and regional changes but not significant changes in the global flux.

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1 Introduction

Terrestrial and marine ecosystem productivity is controlled by the availability of nutrients like nitrogen. Atmospheric deposition of nitrogen (N) compounds can be beneficial for ecosystems (fertilization) or have negative impacts due to acidification and accumulation of excess nutrients (Driscoll et al. 2003). In addition, chemical trapping of reactive nitrogen on pollen particles (Franze et al. 2005) can be harmful for human health. Reactive nitrogen compounds are emitted to the atmosphere both in reduced and oxidized forms by natural (e.g. soils, lightning, plants, bacteria, and viruses) and anthropogenic sources (e.g. industries, transportation, and domestic wood burning). Recent observations and modeling studies have shown that organic nitrogen is a significant fraction of total nitrogen deposition, however the chemical characterization of this fraction remains a challenge (Kanakidou et al. 2012 and references therein).

In the Anthropocene era human activities have significantly increased the amounts of N emitted to the atmosphere, modifying the N biogeochemical cycle in both terrestrial and aquatic ecosystems (Galloway et al. 2008). This human-driven increase in reactive nitrogen emissions into the atmosphere affects nitrogen deposition to the surface. First estimates indicate that the human-induced increase in atmospheric N deposition to the oceans may account globally for up to ~3% of the annual new oceanic primary productivity (Duce et al. 2008). For semi-enclosed marine ecosystems such as the Mediterranean Sea, atmospheric deposition of N may account for up to 35-60% of new production (Christodoulaki et al. 2013). Reactive nitrogen is also involved in atmospheric chemistry, since ozone production is driven by nitrogen oxides availability, and atmospheric acidity is controlled by nitric acid and sulfuric acid formation and NH_3 is the main neutralizing gas for these acidic compounds (Seinfeld and Pandis 2006). Thus, deposition of atmospheric N species also impacts atmospheric chemistry. Estimating the past and future changes in N atmospheric deposition is a prerequisite for the evaluation of N emissions impact on the environment and climate. Projections for N emissions in the atmosphere are based on different scenarios that assume control of nitrogen oxide emissions, but not those of ammonia (Lamarque et al. 2013), pointing to expected changes in the chemical composition and thus possibly in the bioavailability of N deposition.

The present study uses the global atmospheric chemistry/transport model TM4-ECPL to evaluate past and future changes in atmospheric deposition of N that are driven mainly by human activities. It accounts for deposition of reactive nitrogen inorganic and organic compounds both in the gas and the aerosol phases, in particular the organic nitrogen (ON) in the aerosol phase that has been neglected in earlier studies.

2 Methodology- Model description

The global 3-dimensional atmospheric chemistry/transport model TM4-ECPL accounts for all major primary and secondary aerosol components, oxidants, volatile organic compounds chemistry, and secondary organic aerosol formation (Myriokefalitakis et al. 2011, Kanakidou et al. 2012).

In TM4-ECPL, the photochemical degradation of volatile organic compounds in the atmosphere forms secondary organic products, carbon monoxide, and, ultimately, carbon dioxide. Semi-volatile and low volatility organic compound products are also produced, which are subsequently partition between the gas and particulate phase in the atmosphere. Thus, only part of the emitted organics is ultimately deposited to the surface by dry or wet deposition processes in either the gas or particulate form. The deposition parameterization in TM4-ECPL uses solubility estimates for the individual compounds (Myriokefalitakis et al. 2011). Organic aerosol (OA) is simulated by using 20 tracers linked to various origins, which can be grouped as: i) primary OA from fossil fuel, biofuel and biomass burning; ii) primary OA from the ocean (Myriokefalitakis et al. 2010); iii) secondary OA from semi-volatile

organics formed by anthropogenic and natural gaseous volatile organics oxidation (Tsigaridis and Kanakidou 2007) or formed by multiphase chemistry (Myriokefalitakis et al. 2011); and iv) aged primary and secondary OA (Tsigaridis and Kanakidou 2003). TM4-ECPL has been further improved to account for primary biogenic particles of terrestrial origin and for organic matter associated with dust particles (Kanakidou et al. 2012).

The model uses primary emissions of N oxides, ammonia and a small amount of amines emitted from the oceans (Facchini et al. 2008) that form amine salts. The chemically-produced organic nitrates and oxygenated inorganic nitrogen compounds both in the gas and particulate phases are explicitly calculated (Myriokefalitakis et al. 2011). Most global atmospheric chemistry transport models account for the formation of organic nitrate during oxidation of volatile organic compounds using chemical schemes of various complexity. However, they do not explicitly account for the production of other forms of ON, particularly those associated with the primary and secondary particulate organic matter, thus underestimating the atmospheric burden of ON and its deposition to the surface. In this study, N concentrations were linked to source-specific OA tracers using varying N:C molar ratios as measured in the organic matter from different source types, following the methodology described in detail by Kanakidou et al. (2012) (Fig. 1).

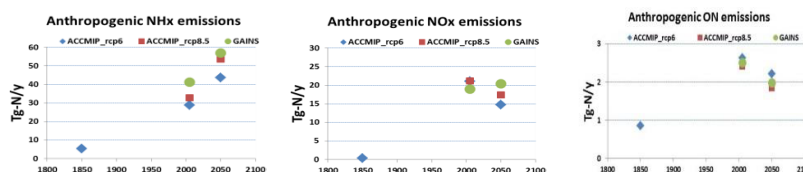


Fig. 1. Anthropogenic emissions of NH₃ and NO_x and those of particulate ON used for this study for 1850, 2005 and 2050. Blue diamonds show emissions from historical ACCMIP database and RCP6.0, red squares RCP8.5 emissions and green circles GAINSv4a emissions developed in the frame of PEGASOS EU project. 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).

For the present study, NO_x from lightning is calculated online. Biogenic emissions of volatile organic compounds are taken from MEGAN emission inventory. Sea-salt emissions are calculated online as described by Vignati et al (2010). Dust emissions are offline, taken from the AeroCom emissions inventory but for the year 2005 (Dentener et al. 2006). Primary biogenic particles are distributed according to the Leaf Area Index spatial and temporal distribution. Anthropogenic and biomass burning emissions of nitrogen oxides, carbonaceous aerosols, sulfur dioxide and organics come from different databases since several simulations have been performed with different anthropogenic emission inventories: for 1850 (past) the historical ACCMIP (Lamarque et al. 2013) inventories; for 2005 (present day) both GAINSv4a (Klimont et al. 2013) and RCP6.0 inventories; for 2050 (future) GAINS v4a, RCP6 and RCP8.5 inventories have been used. As seen in Fig.1, RCPs and GAINSv4a do not show similar tendencies for the NO_x emissions. All projections show that while NO_x emissions are reduced by 2050, NH₃ emissions still increase. Thus, reduced N emissions (alkaline compounds) are gaining importance compared to NO_x emissions, which tend to acidify the atmosphere.

TM4-ECPL is driven by ECMWF ERA-interim meteorological fields. All simulations presented here have been performed using present-day meteorology, that of the year 2005. Natural emissions have been kept constant to those of the year 2005. Thus, the calculated changes are only due to anthropogenic emission changes.

3 Results

The global distributions of organic and inorganic fractions of nitrogen deposition are computed as the sum of the corresponding terms of the individual organic and inorganic nitrogen model tracers calculated by TM4-ECPL. Simulated particulate PM_{2.5} OC

concentrations have been evaluated against observations (Tsigaridis et al. 2014), and nitrogen deposition fluxes in Kanakidou et al. (2012). Modeled values fall within a factor of ten of the measured values, although the model tends to be biased low.

Table 1 below summarizes the changes in N atmospheric deposition due to human activities computed using different emission inventories on the global scale. While in the past NH_x and NO_x emissions have both increased leading to a similar increase in N atmospheric deposition, in the future NO_x is expected to be limited while NH_3 emissions will continue to grow. These changes are reflected to the simulated deposition fluxes.

Table 1. Atmospheric total deposition of reactive N calculated by the TM4-ECPL model in Tg-N/y calculated based on different anthropogenic emission inventories.

	1850	2005	2005	2050	2050	2050
	ACCMIP	GAINS	RCP6	GAINS	RCP6	RCP8.5
NH_x ($\text{NH}_3/\text{NH}_4^+$)	18	65	53	84	63	64
NO_y ($\text{NO}_x, \text{HNO}_3, \text{NO}_3\text{p}$)	6	51	38	53	29	26
ON	32	38	41	37	42	38
Total N deposition	56	154	132	173	134	128

Figure 2 shows the computed spatial distribution of inorganic and organic N atmospheric deposition for the three studied cases. Inorganic N deposition shows the highest fluxes over industrial areas of the NH and tropical biomass burning regions. The ON deposition flux maximizes in the tropics indicating the large contribution by primary biogenic particles and biomass burning and secondary OA formation. The atmospheric N deposition increased since the preindustrial period and is expected to further increase for 2050. The range in the computed deposition fluxes in RCPs due to emission scenarios indicates the degree of uncertainties. Fig. 3 clearly depicts the large changes that occurred over the heavily industrialized areas of the NH and those that expected to happen mainly in Asia. The global deposition flux changes calculated are based on two different emission inventories (RCPs and GAINS) and are summarized in Figure 3.

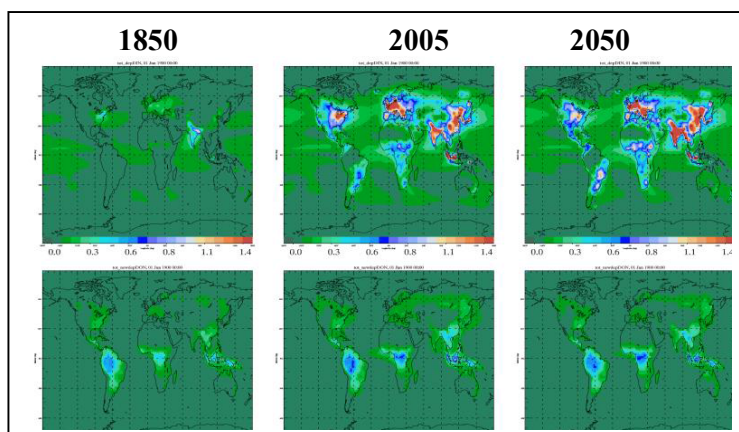


Fig. 2. Atmospheric deposition of N in g-N/m²/y computed by TM4-ECPL for 1850 (left-ACCMIP), 2005 (middle-ACCMIP), 2050 (right RCP8.5). Top inorganic N, bottom organic N.

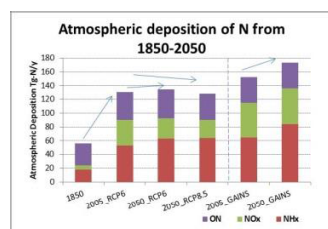


Fig. 3. Atmospheric deposition of reactive nitrogen as computed by TM4-ECPL based on ACCMIP and RCPs (left 3 columns) and based on GAINsv4a (right 2 columns). N deposition as inorganic reduced N (NH_3) in red, as inorganic oxygenated N (NO_x) in green and as ON in blue. Noticeable are differences in the projections (increase vs decrease) between RCPs and the GAINS emissions..

4 Conclusions

Present day global total reactive N deposition is estimated between 125 and 150 Tg-N/yr. ON deposition is about 25% of the total nitrogen deposition and by about half is associated with human activities. However, targeted observational experiments are needed to improve parameterization of the chemical bounding of N on organic aerosol under clean and polluted atmosphere. Large areas in the northern hemisphere are subject to total N deposition higher than the phytotoxicity threshold for vegetation. Total atmospheric N deposition has increased by a factor of about 3 since 1850, mainly due to the large increase of inorganic nitrogen. For the future, the reduction in NO_x emissions is compensated by the continuing increase in NH₃ emissions, and as a result the total N deposition is not expected to change much globally. However, regionally significant changes are expected, in particular over Asia. These results do not account for future changes in biogenic emissions due to climate change.

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