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A multi-model study of the hemispheric transport and deposition of oxidised nitrogen

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[1] Fifteen chemistry-transport models are used to quantify, for the first time, the export of oxidised nitrogen (NO_y) to and from four regions (Europe, North America, South Asia, and East Asia), and to estimate the uncertainty in the results. Between 12 and 24% of the NO_x emitted is exported from each region annually. The strongest impact of each source region on a foreign region is: Europe on East Asia, North America on Europe, South Asia on East Asia, and East Asia on North America. Europe exports the most NO_y, and East Asia the least. East Asia receives the most NO_y from the other regions. Between 8 and 15% of NO_x emitted in each region is transported over distances larger than 1000 km, with 3–10% ultimately deposited over the foreign regions.
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1. Introduction

[2] Oxidised nitrogen compounds, collectively referred to as NO_y (here, NO_y is the sum of the concentrations of NO, NO_2, NO_3, HNO_3, HO_2NO_2, NO_3, $2 \times N_2O_5$, organic nitrates and nitrate aerosols) play a central role in the chemistry of the atmosphere, particularly ozone formation [*Seinfeld and Pandis*, 2006]. Deposition of these compounds to water and soils is an important source of nutrients for many ecosystems. However, human activities, such as the burning of fossil fuels (which produce nitrogen oxides, NO_x, the sum of NO and NO_2), have significantly perturbed the natural nitrogen cycle [*Galloway et al.*, 2004]. The NO_x emitted undergoes rapid reaction to form the various NO_y species. Excessive deposition of nitrogen to ecosystems can cause eutrophication, where the extra nitrogen stimulates rapid plant growth and leads to a change in the species distribution and a loss of biodiversity. For example, *Bergström and Jansson* [2006] showed that inorganic nitrogen levels in lakes in Europe and North America have increased over the past 40 years, resulting in eutrophication and increased phytoplankton biomass. The results of the present work will be useful for other studies such as the International Nitrogen Initiative (http://www.initrogen.org), of whose aims one is to minimise the negative impact of nitrogen on the environment. The focus of the present work is on oxidised nitrogen species; deposition of reduced nitrogen species is also important, but is not considered here.

[3] There have been a few previous multi-model studies of nitrogen deposition. *Holland et al.* [1997] used five models to examine global nitrogen deposition and its impact on carbon uptake by vegetation. The latitudinal distributions and proportions of NO_y deposited to land varied considerably between the models. *Lamarque et al.* [2005] used results from six models to investigate changes in the deposition of NO_y between the years 2000 and 2100, using the IPCC SRES A2 scenario. They found significant increases in the future deposition fluxes, driven by greater emissions. The impact of climate change on regional deposition fluxes (a maximum of 50%) was greater than the modelled interannual variability (about 10%), but smaller than the impact of emissions increases (200–300%). *Dentener et al.* [2006] focused on global and

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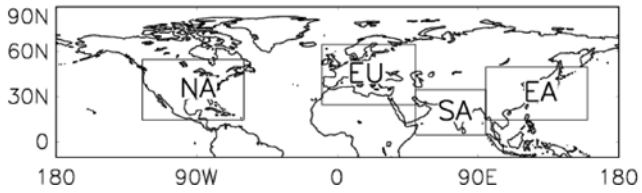

Figure 1. TF HTAP regions, EU (Europe), NA (North America), SA (South Asia) and EA (East Asia).

regional deposition fluxes of both oxidised and reduced nitrogen compounds for the present day and near future (2030), using an ensemble of 23 models. These authors calculated that 11% of the world's natural vegetation receives excess nitrogen through deposition, leading to eutrophication of ecosystems as discussed above. The emissions used in the study of *Dentener et al.* [2006] were prescribed, and so the spread in model deposition fluxes (between 30 and 50%) was mostly caused by differences in NO_y removal mechanisms between the models.

[4] However, it is not clear from these previous studies how much NO_y is exported from a given region, nor where regional emissions are ultimately deposited. The work described here is the first to use results from a series of multi-model experiments to quantify the impact of emissions of NO_x from each of four regions on the others, and estimate the associated uncertainty in the results. The four regions are Europe (EU), North America (NA), South Asia (SA) and East Asia (EA), and are illustrated in Figure 1. This work was carried out as part of a larger study of the intercontinental transport of both gaseous and aerosol species organised by the *Task Force on Hemispheric Transport of Air Pollution* (*TF HTAP*) [2007]. Since previous studies [e.g., *Schulz et al.*, 2006; *Stevenson et al.*, 2006; *Dentener et al.*, 2006] have shown that mean model results compare better with observations than any individual model, the focus in this paper is on the multi-model mean.

[5] The results have been used to calculate source-receptor relationships, defined as the response of the deposition of NO_y in a receptor region to a perturbation in the NO_x emission from a source region. Such source-receptor relationships provide useful information for policy makers [*Tarrasón et al.*, 2003]. These relationships imply that a change in emission in a given source region will result in a particular response at a receptor. The exact response in the receptor region will be dependent on the size of the perturbation in the source region. The areas of the four regions used here are large; use of emission perturbations in smaller areas may produce different source-receptor relationships. It should also be noted that the source-receptor relationships are calculated using a particular background state of the atmosphere, and that the relationships may be sensitive to changes in atmospheric composition.

[6] In this study, a 20% decrease in anthropogenic emissions was used, as it lies within the range of possible future regional emission reductions [*Cofala et al.*, 2007]. Previous results indicate that model responses to this size of emission change are close to linear [*TF HTAP*, 2007].

2. Models and Simulations

[7] Many different models have been used in the TF HTAP assessment of the hemispheric transport of pollutants; the subset of 15 models used in the present work are described briefly in Table S1[1] (further details are at http://www.htap.org). Many of the models have been used in previous assessments of deposition fluxes [*Dentener et al.*, 2006]. Emissions of precursor gases (NO_x, CO, volatile organic compounds excluding methane, referred to as NMVOC and SO_2) were not prescribed for this assessment; instead, each modelling group used their own best estimate of emissions for 2001. This course was followed because differences in emissions of both natural and anthropogenic precursor gases are an important source of uncertainty which we wished to include in our results (although the source-receptor relationships should be independent of the magnitude of the emissions). The global NO_x emissions and anthropogenic components in each HTAP region are listed in Table S2 for each model. The NO_x emissions show much less variation between models than those of CO or NMVOC. Global methane levels were fixed at 1760 ppb in all simulations, as this value is representative of the early 2000s [*Stevenson et al.*, 2006].

[8] All models used meteorology for 2001, and with two exceptions used either NCEP reanalyses, ECMWF analyses, NASA GEOS meteorological fields, or internally generated meteorology relaxed toward a reanalysis. Two models used monthly varying sea surface temperature and sea ice fields to drive their meteorology (Table S1). Each simulation was 1 year long, but all models were executed for a minimum of 6 months beforehand to bring the concentrations of reactive species into balance with the particular meteorology, emissions and chemical mechanisms used.

[9] The simulations consist of a control run, using the best estimate emissions for 2001, and a series of experiments where the anthropogenic emissions of NO_x were decreased by 20% in one of the four source regions (EU, NA, SA and EA; see Figure 1). For each experiment, the changes in NO_y deposition in each of these regions were examined. Previous work indicates that NO_y deposition fluxes are principally controlled by the location and magnitude of NO_x emissions [*Lamarque et al.*, 2005; *Sanderson et al.*, 2006]. To check this, results from a second series of experiments, in which anthropogenic emissions of all precursor gases (SO_2, CO, NMVOC and NO_x) were reduced by 20% in each of the four source regions were also analysed. A comparison of these two series of experiments will illustrate the impact of any non-linearities in the chemistry of the different models. The ratio of the concentrations of NO_x to VOCs will clearly be different in the source region between the two sets of experiments, which in turn might impact on the proportions of the different NO_y species produced, and hence the amounts exported.

3. Results and Discussion

[10] A comparison of the multi-model mean wet deposition fluxes of NO_y with measured values are shown in Figure S1, using the same measurement data as *Dentener et al.* [2006]. Summary statistics for this comparison are presented in Table S3. Briefly, the mean model fluxes reproduce observed wet deposition fluxes well over NA and EU, but with more scatter for EA. The models under-

[1] Auxiliary materials are available in the HTML. doi:10.1029/2008GL035389.

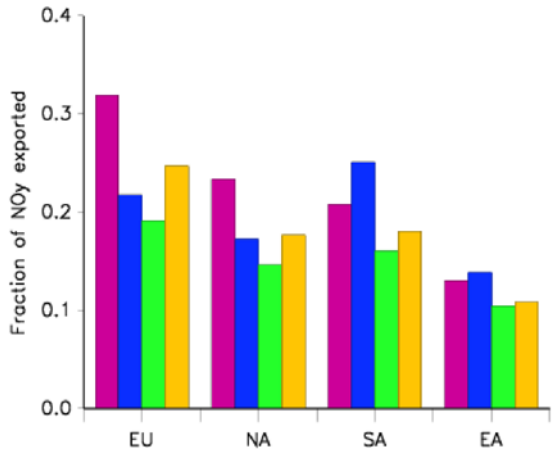

Figure 2. Export fractions of NO_y from each HTAP region, for each season, Winter (pink), Spring (blue), Summer (green) and Autumn (yellow). The values shown are ensemble (15-model) means; see text for details.

estimate observed deposition fluxes over SA, by up to a factor of 4; it is likely that the emissions of NO_x in this region used by the models are too low.

[11] We examine the change in the deposition flux of NO_y in the receptor region divided by the size of the perturbation of NO_x emissions in the source region, which we define to be the "sensitivity". Although the absolute change in the deposition of NO_y in a receptor region will depend on the size of the emission perturbation, the sensitivity will be independent of the emission perturbation, assuming a linear response from the models. The annual and seasonal mean sensitivities for each receptor region were calculated for each model; these individual results were then used to calculate the multi-model mean sensitivity and standard deviations.

[12] When the source and receptor regions are the same, subtracting the sensitivity from 1 gives the fraction of NO_y that is exported; these export fractions are shown in Figure 2 for each season, using multi-model mean values. In the four regions shown in Figure 1, almost all of the NO_x emissions result from anthropogenic activities, even with a 20% reduction. Many NO_y species (e.g. HNO_3 and N_2O_5) are readily removed by dry and wet deposition, and so the lifetime of NO_y is short. Hence, the majority of the NO_x emitted is deposited within the continental-scale source regions. Between 12 and 24% of emitted NO_x is exported out of the source regions as NO_y. Of the four source regions, EA exports the least NO_y, with little seasonality (between 0.10 and 0.15). The most NO_y is exported from NA during winter and for SA during spring, although the difference between the seasons for each of these two regions is fairly small. EU exports more NO_y than the other regions (0.24), and exports the most in winter (0.32). There is a greater spread of model results for winter than the other seasons.

[13] The annual mean sensitivities for each region to a 20% reduction in anthropogenic NO_x emissions in each of the source regions are summarised in Table 1. The associated standard deviations (given in brackets after each value) give an indication of the spread in model results. The largest impacts of each region on another are EU on EA (2.4%), NA on EU (2.1%), SA on EA (6.4%) and EA on NA (1.3%). These proportions should be compared with the amounts of NO_y exported. For example, SA exports 20% of the NO_x emitted, of which 32% is deposited in EA. The scatter in the model results is most likely to be due to differences in the boundary layer and convection schemes used to mix and transport the NO_y species, and the associated wet removal processes. Overall, between 3 and 10% of NO_x emitted in a HTAP region is deposited as NO_y in the other three regions (assuming individual sensitivities combine linearly). Using the mean model results, between 51 and 66% of the exported NO_y (or between 8 and 15% of NO_x emitted) is transported over 1000 km from the boundaries of the source regions.

[14] The influence of the anthropogenic emissions of NO_x from each of the four source regions on global NO_y deposition is illustrated in Figure 3. Here, each panel shows the percentage reduction in the annual total NO_y deposition fluxes in each of the NO_x emission perturbation experiments, as compared with the control simulation, using multi-model mean values from each simulation. The emissions from NA and especially EU are clearly transported significant distances from the source regions and deposited over a wide area. EA emissions are transported across the Pacific to the west coast of NA, but no further. Conversely, the majority of the emissions from SA are deposited within the same region, or adjacent to it. In this latter case, a significant amount of the NO_y will be removed by convective rainout; the high temperatures associated with SA promote thermal decomposition of insoluble PAN, and hence more wet deposition and less export of NO_y.

[15] The sensitivities of the NO_y deposition fluxes in the receptor regions when all anthropogenic emissions (CO, NMVOC, and SO_2, as well as NO_x) are reduced by 20% in each source region were also calculated (data not shown). A comparison with the previous results shows that the mean responses and uncertainties are generally similar, but not identical to those given in Table 1. For most source-receptor pairs the majority (10 or more) of the models gave a similar result, but there were instances where the sensitivities were different. This latter result suggests that there are some non-linear chemical effects on the formation and deposition of NO_y, but the spread of results amongst the models is too large to allow a more definitive statement to be made.

[16] Deposition of NO_y species occurs via both wet and dry processes, and the former is generally a more efficient removal process. The fraction of the NO_y which is wet deposited may indicate one reason for the spread in the

Table 1. Source-Receptor Relationships for Each HTAP Region, When the Anthropogenic NO_x Emissions are Reduced by 20% in the Source Region[a]

Source Region	Receptor Region			
	EU	NA	SA	EA
EU	76.2 (7.0)	0.7 (0.6)	2.2 (1.2)	2.4 (1.5)
NA	2.1 (0.8)	82.0 (5.4)	0.5 (0.3)	0.9 (0.5)
SA	1.3 (1.1)	0.8 (0.6)	80.6 (7.6)	6.4 (2.4)
EA	0.5 (0.3)	1.3 (0.8)	1.0 (0.4)	88.1 (5.7)

[a]Sensitivities are expressed as percentages; see text for definition. The values given here were calculated using annual mean results from 15 models. The standard deviations are given in brackets.

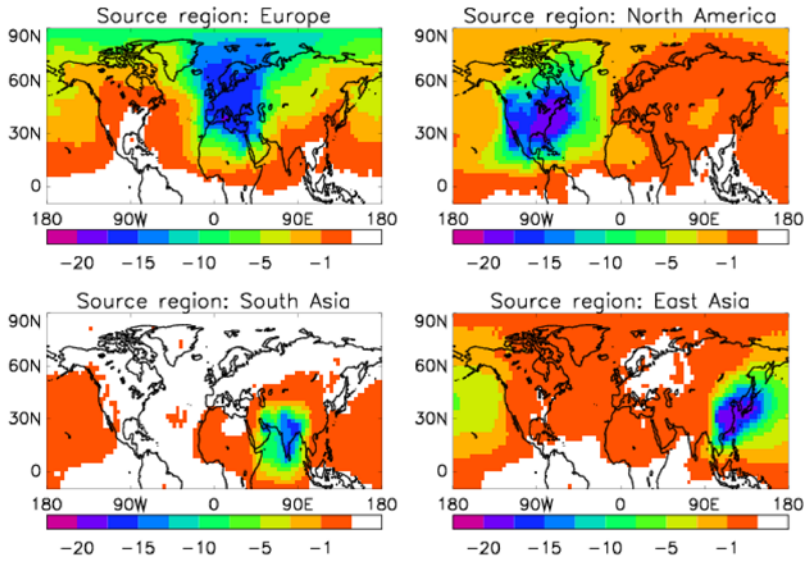

Figure 3. Percentage change in deposition of NO_y in each NO_x emission perturbation experiment relative to the control run, using multi-model annual mean deposition fluxes. The annual total deposition fluxes from each model were interpolated onto a $2.5^\circ \times 2.5^\circ$ grid, from which the multi-model mean values were calculated; the data above are differences in the multi-model means. The white areas indicate a change in deposition of less than 0.1%.

model deposition fluxes, and hence in the fractions of NO_y exported from a given region. For deposition to EU and NA, wet deposition accounts for about 0.3–0.6 of the total. For the two Asian regions (SA and EA), the wet deposition fraction lies between 0.4 and 0.7, similar to the estimates obtained by *Lamarque et al.* [2005]. The modelled deposition fluxes were found to be independent of the methane lifetime, suggesting that modelled OH abundances (which control the methane lifetime) do not control the NO_y lifetimes. Another factor could be the efficiency of uptake of NO_y by aerosols; an efficient uptake will reduce the NO_y lifetime and hence the amounts available for long range transport.

4. Conclusions

[17] Fifteen global chemistry-transport models have been used to assess the transport and deposition of NO_y between four regions representing the major source areas. A source-receptor matrix was created using annual deposition totals. This matrix indicated that the largest impacts of Europe are on East Asia, North America on Europe, South Asia on East Asia, and East Asia on North America. 8–15% of NO_x emitted from each region is transported over distances larger than 1000 km, and between 34 and 49% of the exported NO_y is deposited within 1000 km. Between 3 and 10% of the NO_x emitted from each region was deposited as NO_y in the other three. These results, particularly the latter, suggest that the impact of intercontinental transport on regional NO_y deposition is small. A continental scale focus on NO_x emission controls might be the most effective policy to reduce nitrogen deposition fluxes.

[18] The differences between the deposition fluxes from the models will originate from many areas, including differing resolutions and the complexity of their chemical mechanisms. The fraction of NO_y removed by wet deposition differs considerably between the models (see Table S2), and is likely to be a principal source of uncertainty in the source-receptor relationships; this process is more efficient at removing NO_y than dry deposition. Some models do not include uptake of NO_y by aerosols. Only one model simulates the formation, transport and deposition of ammonium nitrate. Some of the scatter in the sensitivities will be due to the different sources of meteorology, despite the same year being used. Some very recent work suggests that the formation of HNO_3 from the reaction between HO_2 and NO may have a significant impact on modelled NO_y concentrations, and hence deposition fluxes [*Cariolle et al.*, 2008].

[19] The simulations used were only 1 year long, and so the influence of interannual variability on the derived source-receptor relationships via changes in the transport pathways cannot be assessed. Further experiments are currently underway, which use prescribed emissions and idealised species with fixed lifetimes and production rates to understand the impact of the different model transport processes on the results.

[20] **Acknowledgments.** This modelling exercise was organised under the Task Force for Hemispheric Transport of Air Pollution, which was set up by the Executive Body of the Convention on Long-Range Transboundary Air Pollution. MGS and KJP acknowledge funding from the UK Defra under contract AQ0409 and the Joint Defra and MoD Programme (Defra) GA01101 (MoD) CBC/2B/0417_Annex C5. Work by CSA and DJB was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27.

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