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Sensitivity of a global model to the uptake of N_2O_5 by tropospheric aerosol

H. L. Macintyre and M. J. Evans

Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

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Correspondence to: H. L. Macintyre (h.macintyre@see.leeds.ac.uk)

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Abstract

The uptake of N_2O_5 on aerosol impacts atmospheric concentrations of NO_x and so O_3, OH, and hence CH_4. Laboratory studies show significant variation in the rate of uptake, with a general decline in the value of $\gamma_{N_2O_5}$ over the last decade as increasingly relevant tropospheric proxies have been studied. In order to understand the implication of this decline for tropospheric composition, a global model of tropospheric chemistry and transport (GEOS-Chem) is run with differing values of $\gamma_{N_2O_5}$ (0.0, 10^{-6}, 10^{-4}, 10^{-3}, 5×10^{-3}, 10^{-2}, 2×10^{-2}, 0.1, 0.2, 0.5, and 1.0). We identify three regimes in the model response. At low values of $\gamma_{N_2O_5}$, the model shows reduced sensitivity to the value of $\gamma_{N_2O_5}$ as heterogeneous uptake of N_2O_5 does not provide a significant pathway to perturb NO_x burdens. At high values of $\gamma_{N_2O_5}$ the model again shows reduced sensitivity to the value of $\gamma_{N_2O_5}$, as NO_x loss through heterogeneous removal of N_2O_5 is limited by the rate of production of NO_3, rather than the rate of heterogeneous uptake. At intermediate values of $\gamma_{N_2O_5}$ the model shows significant sensitivity to the value of $\gamma_{N_2O_5}$. We find regional differences in the model's response to changing $\gamma_{N_2O_5}$. Regions with high aerosol surface area and low temperatures show NO_3 production becoming rate limiting at lower $\gamma_{N_2O_5}$ values than regions with lower aerosol surface area and higher temperatures. The northern extra-tropics show significant sensitivity to the value of $\gamma_{N_2O_5}$ at values consistent with current literature (0.001–0.02), thus an accurate description of $\gamma_{N_2O_5}$ is required for adequate simulation of O_3 burdens and long-range transport of pollutants in this region.

Our model simulations also provide insight into model sensitivity to changes in aerosol load through changing surface area for different values of $\gamma_{N_2O_5}$. We find little change in the global sensitivity to $\gamma_{N_2O_5}$ in the range 0.05 to 1.0, but a significant drop in sensitivity below this range. Thus simulations of the coupled impact of both chemistry and aerosol changes will be sensitive to the choice of $\gamma_{N_2O_5}$.

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1 Introduction

Aerosols provide a significant source of uncertainty in our understanding of climate (Solomon et al., 2007). As well as affecting climate through direct and indirect radiative forcings (Lohmann and Feichter, 2005), they can impact photo-chemistry and thus the concentration of climate relevant gases such as methane (CH_4) and ozone (O_3). This impact is achieved both by changing the photolysis rate of species (Wild et al., 2000; Martin et al., 2003) and by providing a surface upon which heterogeneous reactions can occur (Dentener and Crutzen, 1993; Jacob, 2000). The dominant heterogeneous reaction in the troposphere is the reactive uptake of N_2O_5 (Tie et al., 2001; Martin et al., 2003; Liao et al., 2003) producing nitric acid (HNO_3), thus removing oxides of nitrogen from the atmosphere. Laboratory studies show the rate of reactive uptake of N_2O_5 varies with aerosol composition, temperature and relative humidity, with more recent studies tending to give lower values (Hanson and Ravishankara, 1991; Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003; Badger et al., 2006; Brown et al., 2009; Bertram et al., 2009). In this paper the sensitivity of a global composition transport model to the uptake of N_2O_5 is investigated to gauge the impact of this downward trend.

Tropospheric NO_x (=NO+NO_2) sources are dominated by anthropogenic combustion processes, with significant natural sources including lightning and soils (Solomon et al., 2007). The conversion of NO_x to HNO_3 is the most significant sink for NO_x. During the day this is achieved by the reaction of NO_2 with OH (Reaction R1). At night NO_2 can react with O_3 to produce NO_3, and then NO_3 can react with NO_2 to produce N_2O_5, which subsequently reacts on aerosol (Reactions R2–R4) to produce aerosol nitrate. This channel is only significant at night as NO_3 concentrations are low during the day due to its photolysis.

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$$NO_2 + OH \rightarrow HNO_3 \quad \text{(R1)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R2)}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \quad \text{(R3)}$$

$$N_2O_5 \xrightarrow{\text{aerosol}} 2HNO_3 \quad \text{(R4)}$$

The significance of N_2O_5 uptake as a NO_x sink is shown both by modelling studies (Dentener and Crutzen, 1993; Tie et al., 2001; Evans and Jacob, 2005), and field evidence, (Platt et al., 1984; Munger et al., 1998; Brown et al., 2006). NO_x concentrations impact the production of O_3 and thus the concentration of OH, one of the most important tropospheric oxidants (Logan et al., 1981). Thus understanding the sources and sinks of NO_x is important for climate, as they impact the global O_3 and CH_4 burdens (the dominant sink for CH_4 is reaction with OH), and hence radiative forcing.

Model representation of the heterogeneous process is achieved by an uptake parameter, gamma (γ), defined as the probability that a molecule impacting the surface of an aerosol undergoes irreversible reaction (Schwartz, 1986; Dentener and Crutzen, 1993). Initial laboratory studies to determine $\gamma_{N_2O_5}$ were performed on cold sulfuric acid aerosol as a proxy for stratospheric conditions (Mozurkewich and Calvert, 1988; Hanson and Ravishankara, 1991; Van Doren et al., 1991). Relatively high values of $\gamma_{N_2O_5}$ (~0.1) were found. Given the lack of measurements of $\gamma_{N_2O_5}$ for tropospherically-relevant temperatures, humidities and aerosol compositions, this value was adopted for global tropospheric modelling. Dentener and Crutzen (1993) included reactive uptake in a global chemistry-transport model with a $\gamma_{N_2O_5}$ value of 0.1, and found a global reduction in NO_x of 49%, with a corresponding drop in O_3 and OH of 9% each (examining only the winter Northern Hemisphere yields a reduction in NO_x of 75%, with corresponding drops in O_3 and OH of 20% and 25%, respectively). Other modelling studies examining the effect of aerosol on tropospheric oxidants found surface reductions in NO_x and O_3 of 80% and 10–30%, respectively, for winter northern latitudes (Tie et al., 2001, 2003; Liao et al., 2003).

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As laboratory studies were performed for more tropospherically relevant aerosol, it was apparent that the value of $\gamma_{N_2O_5}$ from the early lab studies (~0.1) was too high for the troposphere. Evans and Jacob (2005) used more appropriate laboratory studies to develop a new scheme for uptake more suited to the troposphere. This used data from studies on single component aerosol (neutralised sulfate, dust, organics and sea-salt). A global average $\gamma_{N_2O_5}$ of 0.02 was calculated, increasing the mass weighted global NO_x, O_3 and OH burdens by 7%, 4% and 8%, respectively, compared to values simulated using the previous $\gamma_{N_2O_5}$ value of 0.1.

Recent studies suggest that $\gamma_{N_2O_5}$ values may be smaller still than those used in Evans and Jacob (2005). Brown et al. (2009) estimate the value on ambient aerosol to be in the range 5×10^{-4}–6×10^{-3}, and Bertram et al. (2009) in the range 3×10^{-3}–9×10^{-3}, both roughly a factor of ten lower than the mean value of 0.02 found by Evans and Jacob (2005). Both studies also characterise the aerosol and find up to 60% (Brown et al., 2009) and 75% (Bertram et al., 2009) consists of organic material. It has been shown that additional organic material can significantly reduce the uptake coefficient on sulfate aerosol, in some cases by several orders of magnitude (Folkers et al., 2003; Badger et al., 2006; Anttila et al., 2006; Brown et al., 2009), therefore the estimates for ambient aerosol from single-component studies made by Evans and Jacob (2005) may be too large.

Thus, heterogeneous uptake of N_2O_5 is a significant driver of tropospheric composition. However there are a wide range of $\gamma_{N_2O_5}$ within the literature (10^{-4} to >0.1), with recent assessments using real atmospheric aerosols suggesting even lower values than previously considered. Conceptually, below some value of $\gamma_{N_2O_5}$, the heterogeneous uptake of N_2O_5 becomes an insignificant process for the loss of NO_x and therefore an precise definition of $\gamma_{N_2O_5}$ is not necessary. In this paper we investigate the sensitivity of a model of tropospheric chemistry and transport to a wide range of $\gamma_{N_2O_5}$ in order to investigate model response to different values of $\gamma_{N_2O_5}$.

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2 Model simulations

We use the GEOS-Chem global chemical-transport model version v8-01-04 (http://acmg.seas.harvard.edu/geos/) (Bey et al., 2001), driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Global Modelling Assimilation Office (GMAO). Simulations are run at 4° latitude by 5° longitude, with 30 vertical layers. The model carries five externally-mixed aerosol types (sulfate, black carbon, organic carbon, dust, and sea-salt), with a relative humidity dependent size distribution based on Martin et al. (2003) and references therein. In order to simplify the analysis, the value of $\gamma_{N_2O_5}$ is set to a single value across all aerosol types and ambient conditions for each simulation. $\gamma_{N_2O_5}$ values of 0.0, 10^{-6}, 10^{-4}, 10^{-3}, 5×10^{-3}, 10^{-2}, 2×10^{-2}, 0.1, 0.2, 0.5, and 1.0 are chosen to fill the range of possible values. First order loss rate coefficients are calculated using the equation of Schwartz (1986). Each simulation is run for two years. The analysis is performed on the second year of output, and the first year discarded as spin-up.

The GEOS-Chem model has been extensively used and has previously been evaluated against observations for many locations (Bey et al., 2001; Martin et al., 2003; Evans and Jacob, 2005; Zhang et al., 2008; Nassar et al., 2009).

3 Impact on concentrations

Figure 1 shows the impact that changing $\gamma_{N_2O_5}$ has on the monthly mean mass averaged burden of tropospheric NO_x in various latitude bands, integrated up to the tropopause. The greatest impact is seen on concentrations in the northern extra-tropics during the winter months. This can be explained by the large NO_x and aerosol sources in this region, coupled to the longer nights during the Northern Hemisphere winter. The low solar insolation in the northern extra-tropics winter leads to lower OH concentrations, and hence reduced rates of OH loss through the reaction of NO_2 with OH (R1). The long nights enhance NO_3 persistence and hence NO_x loss through N_2O_5 hydrol-

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ysis. Tropical regions do not exhibit this strong seasonality, but rather show a steady shift from the baseline concentration, due to the more consistent solar insolation year round. Considerable aerosol loadings in the tropical regions, mainly from biomass and biogenic sources, provide a potentially large sink for NO_x. However, the persistence of NO_3 is inhibited by its photolysis, causing a much smaller overall impact on NO_x concentrations compared to the winter northern extra-tropics. Despite the long nights in the southern extra-tropics, aerosol and NO_x loadings are low here, hence little impact is seen.

Figure 2 shows the mean annual tropospheric burdens of NO_x, O_3 and OH as a function of $\gamma_{N_2O_5}$ (shown on a log scale), for the northern extra-tropics, southern extra-tropics, tropical regions, and the whole globe. Examining the NO_x burden in the northern extra-tropics, there are three obvious regimes. At high and low values of $\gamma_{N_2O_5}$ the model shows reduced sensitivity to the value of $\gamma_{N_2O_5}$ (perturbations in $\gamma_{N_2O_5}$ lead to very small changes in burdens) with a transitional regime where changes in $\gamma_{N_2O_5}$ lead to significant changes in the simulated burdens. The other regions and species show a similar response but shifted towards higher values of $\gamma_{N_2O_5}$. At low values of $\gamma_{N_2O_5}$ the heterogeneous uptake of N_2O_5 plays a negligible role in determining the NO_x budget, thus in this regime, changes in $\gamma_{N_2O_5}$ have a small impact on burdens. At high values of $\gamma_{N_2O_5}$, the rate limiting step for NO_x loss switches from the heterogeneous uptake step (R4) to the production of NO_3 (R2) (which goes on to form N_2O_5). Thus the model is again insensitive to the value of $\gamma_{N_2O_5}$. It is only in the intermediate regime that the model shows sensitivity to the value of $\gamma_{N_2O_5}$. The differing regional response is due to the aerosol loading being much higher in the northern extra-tropics, and temperatures are lower so the NO_3 production limitation occurs at lower values of $\gamma_{N_2O_5}$.

Globally the peak sensitivity for NO_x is at a $\gamma_{N_2O_5}$ of 0.013, not far from the value of 0.02 found by Evans and Jacob (2005), whereas the peak sensitivities for O_3 and OH are at much higher $\gamma_{N_2O_5}$ of 0.16 and 0.2, respectively. Within the northern mid-latitudes the peak sensitivity lies at $\gamma_{N_2O_5}$ of 0.002 for NO_x and at 0.03 for O_3 and OH.

The differing responses of the tropics, extra-tropics and globally leads to different

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conclusions about the importance of a precise description of $\gamma_{N_2O_5}$. If we assume the true atmospheric value lies between 0.02 and 0.001 (as found by Evans and Jacob, 2005 and Brown et al., 2009; Bertram et al., 2009) we find that the northern extra-tropics show a significant sensitivity to our choice of $\gamma_{N_2O_5}$. Moving from 0.02 to 0.001 leads to NO_x, O_3 and OH burdens in this region increasing by 29%, 7% and 8%, respectively. Thus, having a good definition of $\gamma_{N_2O_5}$ is important for defining the composition in this region. Globally the model is less sensitive with a change in $\gamma_{N_2O_5}$ from 0.02 to 0.001 leading to NO_x, O_3 and OH burden changes of 11%, 3% and 4%, respectively. From our simulations we conclude that although an accurate definition of $\gamma_{N_2O_5}$ is significant for determining climate relevant parameters such as the global O_3 and OH burdens, it plays a much more significant role for the northern extra-tropics than the tropical regions. Thus for issues such as the long range transport of pollution, which is mostly a mid-latitude issue, conclusions drawn will be significantly impacted by the description of $\gamma_{N_2O_5}$ used.

4 Impact of aerosol loading on heterogeneous NO_x loss

To a good approximation the rate of N_2O_5 uptake is described by $k = \frac{A\omega\gamma}{4}$, where A is the aerosol surface area concentration, and ω is mean molecular speed. Therefore, the response of the model to a fractional perturbation in surface area, A, will be the same as a fractional perturbation in γ. Thus, our simulations provide insight into the impact of the choices of $\gamma_{N_2O_5}$ on model simulations where aerosol loading is changed (such as that between the pre-industrial and the present day). Figure 3 shows the percent change in burdens of NO_x, O_3 and OH for a 10% reduction in aerosol surface area, (represented here by a 10% reduction in $\gamma_{N_2O_5}$) at different values of $\gamma_{N_2O_5}$. Globally from our simulations we find very little variation in model sensitivity to aerosol perturbations in the range of $\gamma_{N_2O_5}$ 1.0 down to 0.05, with sensitivity then dropping significantly below this value. At a $\gamma_{N_2O_5}$ of 0.001 as suggested by some studies, the global troposphere is significantly (an order of magnitude) less sensitive to perturba-

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tion in aerosol surface area than is the case at $\gamma_{N_2O_5}$ of 0.1. The northern extra-tropics again show a significantly different behaviour with peak sensitivity to an aerosol perturbation at around 0.05 for O_3 and OH. Thus for studies investigating the coupled impact of aerosol and chemistry changes (e.g., Bell et al., 2005; Lamarque et al., 2005; Liao et al., 2009), the conclusions are likely to be sensitive to the choice of $\gamma_{N_2O_5}$.

5 Conclusions

Our model simulations show a non-linear tropospheric response to changes in $\gamma_{N_2O_5}$ with very small sensitivity at low values, and significant sensitivity at moderate values of $\gamma_{N_2O_5}$ (0.001–0.02). This response is regional due to differing aerosol loadings, temperature and photolysis. Within the likely range of $\gamma_{N_2O_5}$ (0.02 to 0.001) the northern extra-tropics show significant and enhanced sensitivity to the value of $\gamma_{N_2O_5}$ compared to the tropics and southern extra-tropics.

Models that use high values of $\gamma_{N_2O_5}$ (~0.1) will overestimate the impact of changing aerosol loadings on composition through heterogeneous uptake. Thus a better understanding of the value of $\gamma_{N_2O_5}$ is needed to both understand current composition but also the combined impact of changing gas- and aerosol-phase composition.

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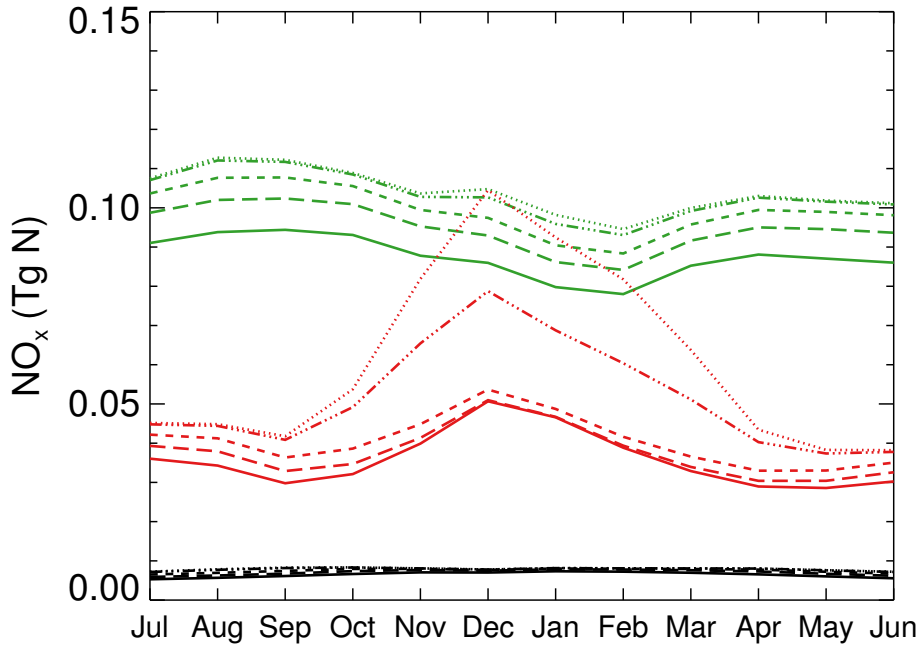

Fig. 1. Impact of $\gamma_{N_2O_5}$ on the NO_x burden in the northern extra-tropics (90° N–30° N, red lines), southern extra-tropics, (30° S–90° S, black), and tropics (30° N–30° S, green) for five of the simulations. Different $\gamma_{N_2O_5}$ values are represented by the line-style as follows: Dotted γ=0.0; dot-dash γ=0.001; dashes γ=0.02; long dashes γ=0.1; solid γ=1.0.

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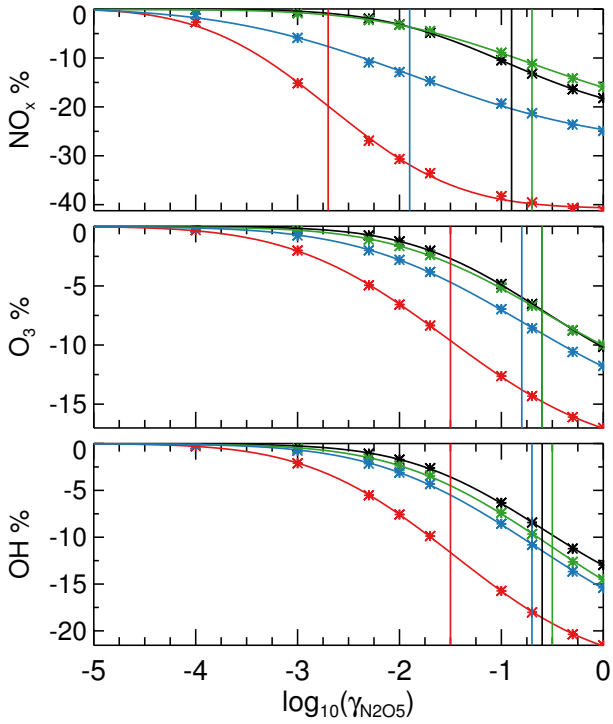

Fig. 2. Impact of $\gamma_{N_2O_5}$ on mean annual burdens of NO_x, O_3, and OH. The curves are plotted using an error function fit to the points, which are taken from the mass weighted annual mean model diagnostics. Northern extra-tropics (90° N–30° N) are in red, tropics (30° N–30° S) are in green, southern extra-tropics (30° S–90° S) are in black, and global values are shown in blue. The vertical bar indicates the point of maximum gradient on the curve (the vertical black bar is not visible on the O_3 plot as it is overlain exactly by the green bar).

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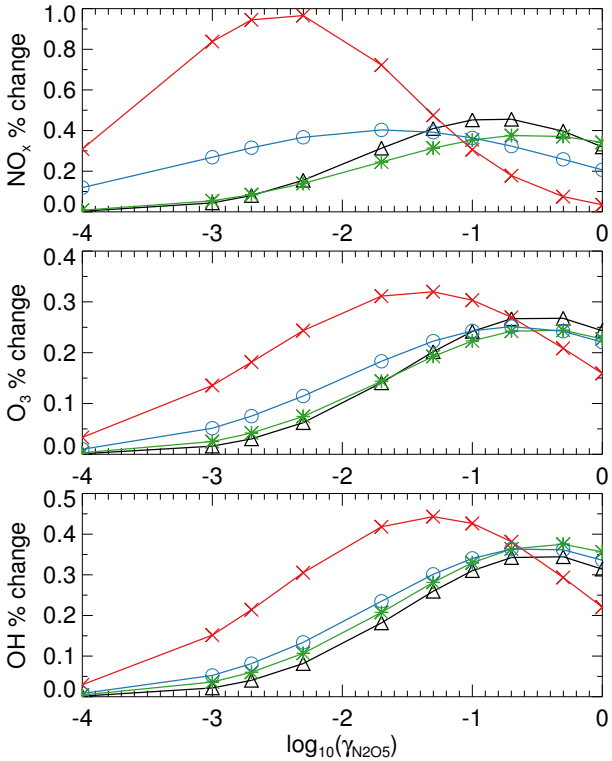

Fig. 3. Impact of a 10% reduction in $\gamma_{N_2O_5}$ (derived from the fits to the curves shown in Fig. 2) on mean annual burdens of NO_x, O_3, and OH for various $\gamma_{N_2O_5}$ values (shown on a log scale). Northern extra-tropics (90° N–30° N) are the red crosses, tropics (30° N–30° S) are green stars, southern extra-tropics (30° S–90° S) are black triangles, and global values are shown in blue circles.

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