

Interactive comment on “Sensitivity of a global model to the uptake of N₂O₅ by tropospheric aerosol” by H. L. Macintyre and M. J. Evans

H. L. Macintyre and M. J. Evans

h.macintyre@see.leeds.ac.uk

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The authors wish to thank the referees for their useful comments on the paper. Issues raised by both referees are addressed together first (numbered 1 - 3), with more specific comments answered afterwards (4). Technical corrections are addressed at the end (5 - 10).

Issues raised by both referees #1 and #2.

1) ClNO₂ as alternative product.

Referee 1 comment: “...in light of recent findings the descriptions of products from this reaction should be amended to include nitryl chloride (ClNO₂), though it is apparent

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that the modeling studies presented herein do not include it...”

Referee 2 comment: “A related issue is the branching between HNO₃ and ClNO₂ formation in N₂O₅ hydrolysis. The latter is a relatively recent discovery at least in terms of its potential importance in the troposphere. It is clear that this branching has not been considered in this paper. The authors should explicitly state this assumption.”

We have added a couple of sentences about this into the paper (at line 19, p 13561): “Recent studies have shown that ClNO₂ may also be produced by reaction of N₂O₅ on chloride-containing aerosol (Osthoff et al., 2008; Roberts et al., 2009). This would act to reduce the nitrate source from the heterogeneous reaction, as well as reducing the NO_x sink (ClNO₂ may photolyse producing NO₂ and a Cl radical). This could also be viewed as a lowering of the gamma value for reaction R4, as it similarly results in a smaller NO_x sink and lower nitrate production.”

We have also explicitly stated in the ‘model simulations’ section that the reaction proceeds via N₂O₅ → 2HNO₃

2) Model resolution.

Referee 1 comment: “The role of model resolution in biasing the conclusions should be discussed. The simulations were conducted at 4x5 degree resolution, which is rather coarse. N₂O₅ formation (NO₂+ O₃), thermal and photochemical stability via the N₂O₅/NO₃ ratio depend strongly on the NO_x concentration. Moreover, as noted, the N₂O₅ loss rate depends as much on aerosol surface area as on the gamma NO_x and aerosol plumes will not be well mixed on the 4x5 degree scale. To what extent would or could the conclusions drawn about the sensitivity to gamma change if the model had been run at higher resolution? Perhaps this question is more appropriate for regional air quality models, but global models running simulations of past and future conditions are even moving to higher resolution.”

Referee 2 comment: “Lastly, the effect of model resolution is not considered in this

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global-scale model study. Anthropogenic NO_x emissions tend to be highly localized, and the chemistry that leads to N_2O_5 formation is quadratic in NO_2 (i.e., two NO_2 required to form each N_2O_5). Therefore, inputs of average NO_x into a model grid cell may not represent how NO_x and N_2O_5 actually evolve overnight in the near source regions where this chemistry is likely to have the greatest impact. Such fine-scale interactions are clearly not the goal of this paper, which is intended to simulate global scale effects. However, some comment on the potential for these kinds of interactions to affect the larger scale conclusions would be appropriate.”

Due to the number of simulations performed (eleven 2-year simulations), the resolution was chosen for computational expedience. A short comment on how the resolution may impact the chemistry has been added (line 17, p 13562): “At the resolution used here, correlations between tracers, (e.g. aerosol and NO_x) in plumes, may not be fully resolved, with subsequent impacts on chemistry.”

3) NO_3 chemistry.

Referee 1 comment: “The importance of NO_3 was mentioned only to note that N_2O_5 chemistry was confined to nighttime. However, NO_3 -VOC reactions at night likely influence the sensitivity of the model to the value of gamma, especially in summer but also year round in the tropics. This issue should be briefly discussed in the context of the completeness of the NO_3 mechanism in GEOS-Chem.”

Referee 2 comment: “The paper considers competition between daytime photochemical conversion of NO_x to HNO_3 via OH and nighttime oxidation of NO_x in O_3 to produce N_2O_5 . While this competition is certainly relevant and likely an important metric in a global scale model it neglects competition between nighttime heterogeneous reactions of N_2O_5 and those of the nitrate radical, NO_3 . In fact, no details are actually given about how NO_3 chemistry is handled here. One obvious impact, for example, of changing N_2O_5 heterogeneous uptake would be the change in formation of other NO_x species, such as organic nitrates, from NO_3 oxidation reactions. Such chemistry would be less

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important in winter, when the largest effects due to N_2O_5 heterogeneous reaction are inferred. The authors should include some comment about variability in NO_3 chemistry and how this is handled in their model.”

We agree with the suggestion made by both referees for more information on the NO_3 chemistry. This has been duly added (line 8, p 13562): “The model contains a detailed representation of NO_x - O_x -hydrocarbon chemistry, including reactions of NO_3 with the organic compounds isoprene, propene, dimethyl sulfide, formaldehyde, acetaldehyde, $\text{C}>4$ alkanes, $\text{C}>2$ aldehydes, $\text{C}>3$ ketones, glyoxal, methylglyoxal, methylvinylketone, methacrolein and ethane, and their subsequent degradation chemistry.”

Specific comments from referee #1

4) Justification for the large range in gamma values and regional variations.

Referee 1 comment: “I accept the need to simplify the situation by spanning a range in gamma values that are constant across aerosol types. However, the authors should discuss how such a choice impacts their interpretations of the regional sensitivities where possible, as certain regions might be more heavily affected by one of the aerosol types for which the large range in gammas may not be appropriate. It should be noted that much of the justification for the large range in gammas (especially the very low values) used in the study comes partly from some field observations limited exclusively to NH summer time. That is, very little observational constraints exist during the period and region for which the model is most sensitive to the value of gamma (NH winter). Laboratory studies at lower temperatures on relevant aerosol compositions are even fewer. There are some constraints from isotopic studies in the field that did not get mentioned here, e.g. Alexander, et al ACP 2010.”

The referee makes a very valid point that we have not addressed this issue. However, we believe the large range in gammas cannot be completely ruled out. The focus of this paper is to investigate model sensitivity across the range of gamma values to

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assess which regions are sensitive and under what conditions (i.e. what time of year). Having discerned these sensitivities, this paper will hopefully galvanise further lab and field measurements of uptake under conditions relevant to the regions showing highest sensitivity (which the referee correctly identifies as lacking) to further our understanding of the significance of this complex process. The text is adjusted as follows, with the isotope study included also:

(altered, from line 14, p 13561): "Throughout the troposphere, organic material makes up a significant and sometimes dominant fraction of aerosol mass (Zhang et al., 2007). Evidence from both field and lab studies suggests this organic material may form a coating (Pósfai et al., 1998; Tervahattu et al., 2002; Vaden et al., 2010). 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), and that this coating need not be complete to suppress gammaN₂O₅ (Cosman and Bertram, 2008). Therefore the estimates for ambient aerosol from single-component studies made by Evans and Jacob (2005) may be too large. A study by Alexander et al (2009) looked at modelled and observed $\Delta^{17}\text{O}$ to constrain nitrate formation pathways, and found that the model overestimated production through N₂O₅ hydrolysis at winter northern latitudes, lending further support to the fact that gammaN₂O₅ may be lower than previously thought."

(at line 8, p 13563): "It is noted that for the region which displays the highest sensitivity (i.e. winter northern latitudes), there exist very few appropriate lab or field determinations of gammaN₂O₅. It is likely that additional organic material in the aerosol (which lowers gammaN₂O₅) may not be as prevalent during this time (due to low productivity), therefore further determinations of the true value of gammaN₂O₅ for aerosol types that dominate this region would be beneficial."

Technical corrections

5) Referee 1 comment: *"Abstract: Line 23, This sentence is a little awkward. I came C5005*

to understand it only after having read the paper and inspected Figure 3. Perhaps just note the main conclusion of this section which was that for studies of coupled aerosol and chemistry changes over time, the results may be sensitive to the choice of gamma."

Agreed, changed accordingly.

6) Referee 1 comment: *"Pg 13560, Reaction R2 in light of recent findings the descriptions of products from this reaction should be amended to include nitryl chloride (ClNO₂), though it is apparent that the modeling studies presented herein do not include it. Presumably its effects could be inferred as the yield of ClNO₂ is to first order a lowering of the gamma to form 2HNO₃."*

We assume that the referee is referring to R4 and not R2. This has been addressed in issue 1 (see above).

7) Referee 1 comment: *"Pg 13560 line 16 To my knowledge, Mozurkewich and Calvert, while the first aerosol flow tube measurement, did not specifically focused on cold sulfuric acid aerosol. Fried, et al 1994 is probably a better reference for that statement. That said Mozurkewich and Calvert should still be referenced as it is relevant to the overall argument."*

Reference added accordingly.

8) Referee 1 comment: *"Pg 13564 line 21 Please clarify that the curves shown in Figure 3 are derived from error function fits to the model output shown in Figure 2, and not from additional model runs."*

Agreed, clarified in the text.

9) Referee 1 comment: *"Pg 13564 last line going onto next page I agree with this statement for global O₃ and OH, but the sensitivity of global tropospheric NO_x seems*

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change at most by a factor of 2 or so from $\gamma = 0.1$ to 0.001 (in fact it changes very little between those two end points)."

Agreed. The text has been amended to make clearer the different behaviour of the sensitivity for different regions and tracers.

10) Referee 1 comment: "Figure 3 caption: change to, "Impact of a 10% reduction in the product $\gamma_{N_2O_5} A$, where A is aerosol surface area density."

Changed.

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