Replies to Interactive comment on Ozone Impacts of Gas-Aerosol Uptake in Global Chemistry Transport Models by Scarlet Stadtler et al.

1 Anonymous Referee #2

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1.1 General Comments

This paper presents two global model simulations (EMEP, ECHAM-HAMMOZ) that assess the influence of six heterogeneous reactions on global atmospheric mixing ratios of reactive nitrogen species and ozone. The six reactions (given in Table 1) have been investigated in previous model studies, notably Jacob, Atmos. Environ. 2000, on which this submission appears to be largely based. The influence of heterogeneous chemistry is known to be important in global chemical transport models, but it is also generally difficult to parameterize for a number of reasons. These include the difficulty of accurately simulating aerosol surface areas available for heterogeneous reactions and the large uncertainty in some uptake coefficients, especially N_2O_5, which has the largest effects in the analysis from this paper. For these reasons, further investigations of the details of the heterogeneous reactions in global models are generally valuable contributions to the literature.

Reply: We thank the referee for the positive comments. As noted further below, we believe our article presents material which has not been presented before for CTMs, but we agree about the uncertainties and a constant need to re-evaluate the importance of these reactions.

Before giving the main replies below, we should point out that for the revised manuscript we re-ran all results with an updated version of the EMEP model. This was done following some bug-fixes in the rv4.15 version originally used, including in the deposition of N_2O_5 and radiation schemes. These changes have not affected basic model performance very much, but especially the deposition change affects N_2O_5 levels, and the impact of the noN2O5 scenarios. Indeed, the impacts in the EMEP system now resemble much more those of ECHAM-HAMMOZ. We have added a small Appendix to explain these changes, and modified the manuscript to reflect the updated results.

While the above is a good justification for the present work, it is somewhat difficult to see that this paper advances the subject much beyond what has been presented in previous papers. This deficiency in presentation could likely be addressed, but the authors would do well to review how their results compare to previous model simulations that have investigated this set of reactions previously, as well as explicitly stating how their treatment differs and why their model arrives at different results or corroborates previous analysis. Such a comparison is and critical model evaluation is absent from the discussion section. The paper would be much stronger if it were included.

Reply: To strengthen our results, we included an additional Discussion section (Sect. 5.4) (also following your comment below about 18 lines 4-11). We find, N_2O_5 hydrolysis on ozone and nitrogen oxides is lower compared to previous studies although the other studies used rather high γ values for N_2O_5 and older CTMs, and they neglected the other heterogeneous reactions. Details can be found in the reply below.

There is no discussion of the effects of clouds, which have large surface areas for heterogeneous reactions. Are all simulations showing effects of reactions on aerosols but not in clouds? This should be clarified, together with some estimate of the relative effects of both cloud droplets and aerosols if they are both operative in the models.

Reply: The simulations shown here are not including heterogeneous reactions on cloud surfaces, which can be important especially for HO_2 uptake depending of the presence of transition metal ions. The large surface area provided by clouds would lead to unrealistically high uptake rates, because the current parameterizations in EMEP and ECHAM-HAMMOZ do not include diffusion limitation (Davidovits, 2006). Often global model studies exclude the heterogeneous reactions of nitrogen species on clouds, for N_2O_5 Dentener and Crutzen (1993) included the reaction on cloud droplets, but just found minor changes in NO_x and O_3. Jacob (2000) argues that for O_3, HO_x and NO_x life times are not significantly reduced in clouds and current knowledge is insufficient to include cloud chemistry in O_3 models. Therefore, the current model systems cannot treat heterogeneous cloud chemistry without further development and this is why we decided to not look at them in this study. We added some text on this in the new Sect. 5.4.

The paper identifies N_2O_5 uptake as the most important heterogeneous reaction of the six, but it does not include the production of $ClNO_2$ from N_2O_5 uptake. The authors state this deficiency clearly, but at that same time it is a missed opportunity since it would be one aspect where these model simulations could clearly take advantage of recent advances in field and laboratory work. No real explanation is given as to the technical details that prevent the inclusion of this reaction, but the omission should be better justified. Even a crude estimate of this reaction would be helpful to this analysis.

Reply: Yes, technical details was a little vague we admit! The problem is that neither model handles the treatment of Cl in the aerosol thermodynamics. Nor do they handle the chemistry of $ClNO_2$ and associated precursors and products. This makes it very difficult to come up with even a crude estimate of this reaction. We have made these limitations clearer in the manuscript, and strengthened this need in the text discussing future studies. We added some text on this in the new Sect. 5.4.

Although the paper does not appear to represent a significant advance (unless the authors provide some further comparisons and details), it does not appear to be incorrect in any obvious way. There are some issues with presentation, detailed below, but these issues do not appear to be serious. With some attention to the comments above and the more specific comments below, it should be suitable for publication in ACP.

Reply: Again, we thank the referee for the constructive remarks. As noted also in our reply to Referee #1, we believe that our paper is novel in using very up-to-date chemical transport models (CTMs) which we show can reproduce well daily variations at sites around the world, and with a demonstration of a fair ability to capture aerosol surface area compared to satellite data. In addition, we also illustrate in detail how seasonal patterns are affected by this reaction. We also believe we are the first to systematically compare the impacts of the different reactions in a harmonized way across two model systems. We have now added also a comparison to previous models studies and also new sensitivity tests on the impact of different assumptions for γ. Details can be found in the new Discussion Section 5.4.

1.2 Specific Comments

Page 2, line 1: Solomon et al., Nature 1986 is a better reference (suggestion only)

Reply: We added this reference.

Page 2, line 3: Ravishankara 1997 is a better reference here (again, suggestion only). Ravishankara, A. R. (1997), Heterogeneous and multiphase chemistry in the troposphere, Science, 276, 1058-1065.

Reply: We added this reference.

Page 2, line 22: Not clear what is meant by technical limitations here that precludes the inclusion of $ClNO_2$.

Reply: Yes, We addressed this issue in our comment above.

Page 4, first paragraph: The term S_a is used to refer to aerosol surface area, but later in the paragraph S is used as total surface area. Is there a distinction between S and S_a, or is this just typographic.

Reply: We corrected the paper to use S_a throughout.

Page 4, line 17: correct grammar in make use

Reply: Corrected.

Page 5, lines 8-13: Does the lack of nitrate aerosol formation artificially reduce aerosol surface area available for heterogeneous chemistry?

Reply: There are several major compounds contributing to S_a, in particular sulphate, organic aerosol, black-carbon, sea-salt and dust, so S_a should not be too sensitive to nitrate. And Figures 2 and 5 suggest that although nitrate aerosol lacks in ECHAM-HAMMOZ, the surface area density is comparable to van Donkelaars estimate based on satellite data and to EMEP surface area. There are even regions where ECHAM-HAMMOZ calculates a higher surface area than EMEP.

Page 6, line 15: The value of 5e-1 (0.5) must be misquoted as the N_2O_5 reaction probability is not this large.

Reply: Corrected; this should have been (0.5- 6) x 10^{-6}. We have made it explicit

Page 7, lines 14-16: The authors make a good point regarding the reliability of the parameterization, especially in light of the absence of atmospheric determinations of gamma values as high as those shown in figure 1. Have the authors made any assessment of the effect of reducing the RH dependence of the parameterization for sulfate?

Reply: Although we suspect the RH dependence is unrealistic, we have no real basis to devise an alternative formulation. Such information would need new laboratory or theoretical suggestions.

Page 7, section 3.2: The literature cited for the gamma value of NO_3 is dated. More recent work by Gross et al. shows substantial reactivity on organics, for example. There is somewhat less active research in this area than for uptake coefficients for N_2O_5, so there is no developed parameterization. It is not realistic for the authors to undertake such a review in the context of this paper, but some reference to the more recent studies together with a statement that NO_3 uptake may be larger if organic aerosol is considered is needed in this section.

Reply: The missing literature has now been included in the manuscripts small literature overview, Sect. 3.2, see following paragraph.

The nitrate radical NO_3 undergoes hydrolysis in wet aerosols, but was also observed to react with organic compounds on the aerosol surface. Hydrolysis of the nitrate radical NO_3 happens on various aerosol types depending on the water content. NO_3 heterogeneous reaction produces HNO_3 and OH in the aqueous particle phase and can be counted as a NO_x sink (Rudich et al. 1998). Several laboratory studies shown γ ranging between 10^{-4} and 10^{-3} (Rudich et al. 1996, Moise et al. 2002). Jacob (2000) recommended to use $\gamma = 10^{-3}$ for atmospheric chemistry model simulations.

Reactions with different organic compounds were explored in laboratory experiments. Gross and Bertram (2008) measured the reaction probabilities between 0.059 and 0.79 of NO_3 with different polycyclic aromatic hydrocarbons leading to NO_2 and HNO_3 formation. Two following studies also found high reaction probabilities of NO_3 with alkenoic acid (>0.07) (Gross et al. 2009) and alkene monolayers (0.034) (Gross and Bertram 2009). Organic coatings could enhance NO_3 reactive uptake, nevertheless knowledge of explicit organic compounds in the organic fraction of aerosol is unknown in both model systems, therefore the recommended of $\gamma = 10^{-3}$ for NO_3 hydrolysis value was adopted for EMEP and ECHAM-HAMMOZ.

Page 7, section 3.3: Again, the authors are justified in the use of the simple uptake coefficient for NO_2 based on what is currently available in the literature, but the system is at least as complex as that for N_2O_5. Some model studies have assumed effectively very large uptake coefficients for NO_2 or at the very least rapid conversion of NO_2 to HONO. This body of literature should be represented here via referencing. One example of a recent modeling study: Elshorbany, Y. F., P. J. Crutzen, B. Steil, A. Pozzer, H. Tost, and J. Lelieveld (2014), Global and regional impacts of HONO on the chemical composition of clouds and aerosols, Atmos. Chem. Phys., 14(3), 1167-1184, 10.5194/acp-14-1167-2014.

Reply: We did not see a good way of including the results of the Elshorbany paper in our study. Elshorbany et al. 2014 looked at the impacts of a non-mechanistic and instantaneous gas-phase conversion of NO_2 to HONO (2 % yield) on the composition of aerosols and clouds, so they were not dealing with heterogeneous reactions as in our study. Such changes have been simulated by an enhanced gas-phase H_2SO_4 production caused by OH from HONO photolysis.

Page 13, section 5.1 and Figure 2: What altitude range is shown in Figure 2? Is this for some distance above the surface, boundary layer only, column average, etc?

Reply: All figures and tables refer to the lowest model layers, therefore the description ground level was added to the figures. In the model descriptions lowest layer thicknesses are mentioned. ECHAM-HAMMOZ lowest level has a thickness of 50 m, EMEP has 90 m, but EMEPs ground level refers to the value at 3 m height.

Second, is the displayed quantity a dry aerosol surface area or does it include water? If the latter (presumably), to what extent are the regional variations due to RH and to what extent to dry aerosol mass?

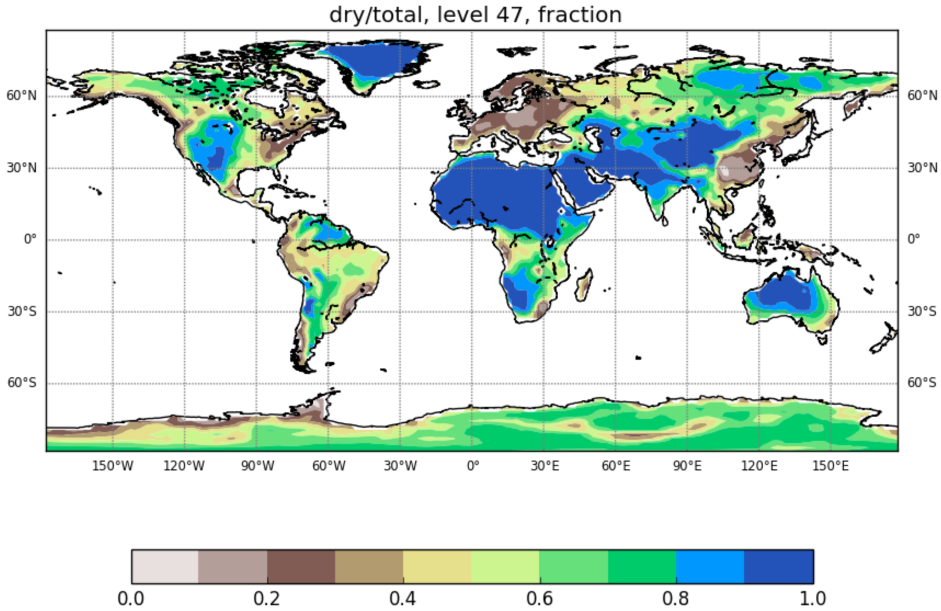

Figure 1: Fraction of dry aerosol over total aerosol mass containing water for the lowest model layer at ~50 m over ground. If aerosol is wet in HAMMOZ the surface area is calculated based on the wet radius caused by the water content.

Reply: Indeed, the displayed aerosol surface area includes water, consistent with the satellite observation. Figure 1 shows the fraction of dry aerosol over total aerosol, the blue color shows areas where the dry aerosol mass equals the total mass, while brown colors indicate that the majority of the aerosol mass is made of water. Especially in Europe and East Asia 70-80 % of aerosol mass are water, so the large surface area is also caused by water. Nevertheless, in East Asia also dry aerosol mass concentrations are high. Most heterogeneous reactions implemented into EMEP and ECHAM-HAMMOZ are hydrolysis reactions and need aerosol water, therefore our comparison including aerosol water to water containing observed aerosol fits the purpose well.

Table 4: Caption states that reference runs values are given in total mixing ratios. This term is not clear. Do the authors mean average? Once again, over what altitude range do these values apply? Was this information given elsewhere? If so, it should be repeated here as it is not clear when reading the table or figure 2. The caption also appears to be logically in error: Since the sensitivity runs were subtracted from the reference run, positive values mean higher mixing ratios in the reference run than in the sensitivity runs and vice versa. By this logic, a higher value in the reference run would lead to a negative displayed value, consistent with what is shown in the table (e.g., removing O_3 uptake should increase O_3 in the sensitivity run, leading to sensitivity $>$ reference, or reference sensitivity < 0, as shown for no O_3). It is also notable in this table that the change in N_2O_5 are larger than the total or average. How can this be?

Reply: We should have used the term regional average near-surface mixing ratios, and will do this in the revised manuscript. We do not think the original results were logically in error (we used REF-TEST there), but to further increase clarity we have now used percentage changes in Tables 4 and 5, and provided values of TEST - REF so that positive values show the increase in mixing ratios caused by turning off the individual reactions. With this we hope to make it easier for the reader to get a quick impression of the results. From the percentages it is visible that sometimes the changes are higher than the annual field average surface mixing ratio, like in the ECHAM-HAMMOZ case of Europe N_2O_5 mixing ratio changing by 177 %. Some examples of this can also be seen in Fig. 5, where e.g. the change in European or East Asian N_2O_5 are bigger than the base-case values.

The tables are somewhat difficult to interpret since they are in absolute units. Relative changes (e.g., -10at least be given in addition to the absolute changes, and could be substituted for them easily since the absolute value is given in each case for the reference run.

Reply: We changed the Tables and text accordingly - the revised style of Table is given as Tables 1-4 in the reply to Ref #1. The current tables have been moved to the supplement, because we think they still include valuable information.

Page 17, line 25: The meaning if the sentence is not clear. NO_3 rapidly photolyses, and resulting NO_2 likewise, so has a high ozone-formation potential.

Reply: In order to clarify the meaning of this sentence following lines were added to the manuscript:

NO_3 rapidly photolyses and produces NO_2 and atomic oxygen $O_3(^3P)$. NO_2 subsequently photolyses and results in NO and a second $O_3(^3P)$. From these two reactions two ozone molecules can be formed, therefore NO_3 has a high ozone-formation potential.

Figure 3,4: Again, please specify the altitude range in the captions and text.

Reply: Added.

Page 18, lines 4-11: How do the reductions in O_3 and NO_x compare with those determined from other model studies, e.g., Dentener and Crutzen (1993), Tie et al. (2001, 2003), Alexander et al. (2009), Macintyre and Evans (2010) etc. Critical comparisons of these results to these and other literature studies are missing, but extremely important to place the current work in context and understand what advances have been made in this model analysis.

Reply: We have added text on such comparisons into a new section (5.4), focussing on NO_x and O_3 % reductions, which will include the following points among other items of discussion:

The results from this study, suggesting that the N_2O_5 reactions is generally the most important among the heterogeneous reactions implemented tested into ECHAM-HAMMOZ and EMEP models are loosely consistent with results from previous studies (e.g. Dentener and Crutzen 1993, Tie et al. 2001, 2003, Alexander et al. 2009, Macintyre and Evans 2010), although the magnitude of the changes seems to be somewhat less with our models. Direct comparison is difficult since all studies report different metrics, domains, seasons, and years, usually underlining the higher importance of heterogeneous reactions in the aerosol loaded northern hemisphere. As shown before, the impact of N_2O_5 hydrolysis is higher during winter and Dentener and Crutzen (1993) report about a 75 % NO_x and 20 % O_3 reduction in their winter (November-April) period. Similar NO_x reductions are found by Tie et al. (2001) and Tie et al. (2003) with 73 % and up to 90 % in December (although Tie et al. (2003) reports maximum reductions, whilst Tie et al. (2001) reports averages). In contrast, our models produce much smaller changes, for example ECHAM-HAMMOZ simulates a NO_x reduction due to N_2O_5 hydrolysis of 16 % in winter (December-February). Also, O_3 reductions with our models are somewhat lower compared to these other models: e.g. 8 % in ECHAM-HAMMOZ compare to 11 % to 20 % in the other three model studies.

There are many possible reasons for these differences. Firstly, there have been many changes in models, emissions, and indeed the atmosphere since these early studies. For example, Dentener and Crutzen (1993) provided one of the first quantifications of the importance of N_2O_5 reactions, but the model used had a horizontal resolution of $10 \times 10°$, giving grid cells with 100 times the area of the $1\times1°$ grid used in EMEP or almost 30 times that of ECHAM-HAMMOZs $1.85\times1.85°$ grid. This alone will lead to different regimes of ozone productivity. For example, the collectio of earlier models included in the multi-model comparison of Wild et al. (2012) showed a very wide-spead of ozone results for the Mace Head site. Our comparisons (Fig. 7 in manuscript) suggest significant progress in model performance. Emissions have also changed enormously over this period, especially in Asia (Granier et al. 2011); again with implications for the atmospheric oxidation capacity.

The $\gamma_{\mathrm{N_2O_5}}$ values used by Dentener and Crutzen 1993 and Tie et al. (=0.1) are significantly larger than the mean value of 0.02 calculated globally by the parametrizations used here, or than atmospheric observations (Brown et al. 2009)). Macintyre and Evans (2010) tested the model sensitivity to uniform $\gamma_{\mathrm{N_2O_5}}$ values and report the highest sensitivity between 0.001 and 0.02. This is exactly the range of values given by the $\gamma_{\mathrm{N_2O_5}}$ parametrization used here. As discussed below, and illustrated in Table 3 of the reply to Ref #1, the impact of the hydrolysis reaction on ozone is indeed stronger with higher γ, but our main results are relatively insensitive to these necessarily very uncertain choices. The ECHAM-HAMMOZ and EMEP models also have a set of other heterogeneous reactions competing with N_2O_5 hydrolysis, which again lowers the possible impact of this hydrolysis reaction.

As noted above, chemical transport models have developed in many ways over the last 20-30 years, and in this paper we show that both ECHAM-HAMMOZ and EMEP can reproduce even daily ozone variations at sites across the globe. We have also demonstrated that both models do a fair job of reproducing surface area density, so we believe our new estimates provide a valuable up-to-date revision of these earlier calculations.

As with Tables 4 and 5, these figures would be more easily interpreted in relative units (% change in O_3) rather than absolute units (ppbv) as shown.

Reply: Tables 4 and 5 were updated showing annual mean surface mixing ratios in ppb (or ppt) for the reference runs and percentage changes between the reference run and the sensitivity runs - the revised style of Table is given as Tables 1-4 in the reply to Ref #1. However, we have retained the absolute numbers for maps since otherwise division by small numbers can produce rather confusing effects. With NO_x especially some of the absolute values can be very low, but percentage changes very high.

Page 18, line 25: Suggest a change in the phrase therefore the sun is less favorable to something more like therefore photochemistry is inactive.

Reply: Changed.

Page 18, line 28: The statement is that less ozone production reduction occurs (awkward phrasing).

Reply: For clarification the text was adjusted with the following lines:

During winter, nights are longer leading to inactive photochemistry. Therefore, heterogeneous chemistry is efficient. Nevertheless, a rather inactive photochemistry also leads to less ozone production. Comparing to spring, the impact seen here is lower because of already low ozone formation rate.

Is this a statement about absolute or relative ozone production? The latter would be more relevant, since it is already understood that ozone photochemistry is weaker in winter.

Reply: This statement is about absolute and relative ozone production,although the differences are actually quite modest, eg. 7.7% O3 reductionfor HAMMOZ in winter (DJF) compared to 9.2% reduction in spring (MAM). We added this information to the text.

Page 22, line 9: The comma should be after ground stations. Having it before ground stations changes the meaning of the sentence in a way that the authors probably do not intend.

Reply: Changed.

Extra references

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