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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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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 difficultly of accurately simulating aerosol surface areas available for heterogeneous reactions and the large uncertainty in some uptake coefficients, especially N2O5, 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.

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.

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 aerososls if they are both operative in the models.

The paper identifies N2O5 uptake as the most important heterogeneous reaction of the six, but it does not include the production of ClNO2 from N2O5 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.

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.

Specific Comments:

Page 2, line 1: Solomon et al., Nature 1986 is a better reference (suggestion only) Âă 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. Âă Page 2, line 22: Not clear what is meant by "technical limitations" here that precludes the inclusion of ClNO2.Âă Âă Page 4, first paragraph: The term "Sa" 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 Sa, or is this just typographic.

Page 4, line 17: correct grammar in "make use"

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

Page 6, line 15: The value of 5e-1 (0.5) must be misquoted as the N2O5 reaction probability is not this large.

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?

Page 7, section 3.2: The literature cited for the gamma value of NO3 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 N2O5, 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 NO3 uptake may be larger if organic aerosol is considered is needed in this section.

Gross, S., and A. K. Bertram (2008), Reactive Uptake of NO3, N2O5, NO2, HNO3, and O3 on Three Types of Polycyclic Aromatic Hydrocarbon Surfaces, The Journal

of Physical Chemistry A, 112(14), 3104-3113, 10.1021/jp7107544. Gross, S., and A. K. Bertram (2009), Products and kinetics of the reaction of an alkane monolayer and a terminal alkene monolayer with NO3 radicals, J. Geophys. Res., 114, D02307, doi:10.1029/2008JD010987. Gross, S., R. Q. Iannone, S. Xiao, and A. K. Bertram (2009), Reactive uptake studies of NO3 and N2O5 on alkenoic acid, alkanoate and polyalcohol substrates to probe nighttime aerosol chemistry, Phys. Chem. Chem. Phys., 11, 7792-7803.

Page 7, section 3.3: Again, the authors are justified in the use of the simple uptake coefficient for NO2 based on what is currently available in the literature, but the system is at least as complex as that for N2O5. Some model studies have assumed effectively very large uptake coefficients for NO2 or at the very least rapid conversion of NO2 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.

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? 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?

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 refer-

ence 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 O3 uptake should increase O3 in the sensitivity run, leading to sensitivity > reference, or reference – sensitivity < 0, as shown for "no O3").

It is also notable in this table that the change in N2O5 are larger than the "total" or average. How can this be?

The tables are somewhat difficult to interpret since they are in absolute units. Relative changes (e.g., -10%, +20%) would be easier to understand. Relative changes should at 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.

Page 17, line 25: The meaning if the sentence is not clear. "NO3 rapidly photolyses, and resulting NO2 likewise, so has a high ozone-formation potential."

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

Page 18, lines 4-11: How do the reductions in O3 and NOx 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.

As with Tables 4 and 5, these figures would be more easily interpreted in relative units (% change in O3) rather than absolute units (ppbv) as shown.

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

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

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.

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