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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate" *by* J. M. Davis et al.

J. M. Davis et al.

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We appreciate the comments provided by Anonymous Referee #2 (2007). We have given all of the suggestions careful consideration and revised our manuscript accordingly, as described in detail below.

1. *Is some of the dependence on RH and/or T introduced by combining data based on different laboratory procedures?*
Due to the small size of the dataset, it is difficult to answer this question in a statistically rigorous manner. If we treated the data from each lab separately, for example, the individual data sets would be very small and this would complicate any assessment of uncertainty. However, a close inspection of Fig. 1 provides qualitative indications

that the combination of data from multiple laboratories has not introduced a spurious dependence on RH or T. Both studies which tested for a temperature dependence on aqueous NH_4HSO_4 particles (HAL03 and MOZ88) found that γ increases with decreasing T. That trend is captured in our parameterization, as discussed in Section 4.1. With respect to RH, data from different laboratories show RH dependencies that differ in both magnitude and sign. Thus, pooling data from multiple sources more likely dampens the RH dependence rather than amplifying it. Anonymous Referee #1 (2007) raised the possibility that the KAN01 data alone may have caused an artificial enhancement in the RH dependence above 50% RH. In response, we have appended the revised manuscript with an alternative parameterization that considers all data except for KAN01. Indeed, removal of the KAN01 data results in a very different statistical parameterization (see Appendix A).

2. *RH dependence for dry particles ought to be removed.*
The statistical significance of the RH term in Eq. (9) puzzled us initially, because we expected the heterogeneous uptake of N_2O_5 on dry particles to be independent of RH. We later learned that the heterogeneous uptake of HNO_3 on crystalline salts has been shown to increase with RH due to increases in surface-adsorbed water before deliquescence (Goodman et al., 2000; Ghosal and Hemminger, 2004). It is possible that the reactivity of N_2O_5 on solid ammoniated sulfate particles is influenced by a similar process. This text has been added to Section 4.1 of the revised manuscript, providing mechanistic support for the RH dependence in Eq. (9).
Another possibility is that homogeneous gas-phase reactions between N_2O_5 and water vapor were taking place during the laboratory experiments, leading to an apparent enhancement of γ_d. This possibility was discussed in our original manuscript, and we have retained it in the revised manuscript. Though a detailed exploration of this possibility is beyond the scope of our study, it is instructive to repeat the statistical analysis described in Section 3.2 without considering RH in the variable selection procedure (as recommended by Anonymous Referee #2, 2007). In this case, we obtain the following alternative to Eq. (9).

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$\lambda_d = \beta_{d0} + \beta_{d2} T_{288} + \epsilon_d$

The best-fit values and standard errors of each coefficient are $\beta_{d0} = -4.42440 \pm 0.22424$ and $\beta_{d2} = -0.11618 \pm 0.03298$. The multiple R^2 (0.4884) and adjusted R^2 (0.4491) are much lower than the original parameterization (see Table 3c), indicating that an RH-dependent term is necessary to explain much of the variability in the dry particle data. Given the low frequency of events when the ambient RH falls below the CRH at the altitudes where N_2O_5 is most abundant (see Section 5.2), we expect this alternative parameterization for dry particles to have a minor impact on model predictions of pollutant concentrations.

3. *Authors could show the impact of different formulations on aerosol nitrate using their CMAQ simulations.*

Anonymous Referee #2 is under the impression that we had already carried out CMAQ simulations using the new parameterizations of $\gamma_{ambient}$, but this is not the case. The intent of this manuscript is to establish our parameterization in the peer-reviewed literature before we incorporate it in a three-dimensional air quality model. In a follow up to this study, we plan to implement the final parameterization in CMAQ and evaluate the effect of a few alternative parameterizations on the air quality model performance for various pollutants. We have revised our abstract and Section 4.3 so that other readers do not get the false impression that our new parameterization has been implemented in CMAQ already.

4. *Figure labels are small.* We have increased the font size on the contour line labels in Figure 2.

References

Anonymous Referee #1: Interactive comment on "Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate" by J. M. Davis et al., Atmos. Chem. Phys. Discuss., 7, S8004–S8008, 2007.

Anonymous Referee #2: Interactive comment on "Parameterization of N_2O_5 reaction

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