

Interactive comment on “Parameterization of N₂O₅ reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate” by J. M. Davis et al.

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This is a nicely written paper that provides a very important contribution to the representation of N₂O₅ heterogeneous uptake coefficients in atmospheric models. Although there have been parameterizations of this coefficient in the recent literature, most notably those of Evans & Jacob, and Riemer et al., the parameterization developed here is the most comprehensive for the ammonium / sulfate / nitrate system. Although there is certainly room for discussion of the author’s assumptions in choosing and fitting the available laboratory data, the reasoning behind the parameterization is clear, and it should be straightforward to implement in models.

Because my coworkers and I have been involved in the measurement of N_2O_5 in the atmosphere and in determining heterogeneous uptake coefficients from these measurements, I felt that it would be useful to add a few comments regarding the comparison between this parameterization and some (rather limited) determinations from field observations.

1. Role of organics. As noted by reviewer #1, a large fraction of actual ambient aerosol consists of organic constituents. Whereas the available laboratory data on pure inorganic salts may be interpreted and fit within certain ranges as a function of temperature and RH, the data for pure organics or mixed organic / inorganic aerosol depends on additional factors, including the choice of organic proxy and the homogeneity of the particles (i.e., coatings, surfactants, etc.). As the authors note on page 16138, there is laboratory and field evidence suggesting a large influence for organics. The field determinations that we have published thus far for aerosol with a large organic content (Brown et al., Science, 311, 67-70 (2006)) show uptake coefficients <0.002 over an RH range from 44-63% and temperatures from 285 - 291 K. Application of the current parameterization to this aerosol type, whose inorganic component consisted mainly of $(\text{NH}_4)_2\text{SO}_4$, would give an uptake coefficients of 0.016 - 0.042, or about 10 times larger than derived from the field measurements. While there are significant uncertainties in the derivations of uptake coefficients from field observations, and while the organic component of the aerosol may not be the only factor that suppresses the uptake coefficients, our observations suggest that any parameterization of N_2O_5 uptake coefficients based solely on inorganic salts would provide only an upper limit to the actual uptake coefficient on ambient aerosol. The exception would be aerosol that are mainly derived from sulfate or nitrate - e.g., in regions such as the Ohio River Valley parts of the western U. S. in winter. The authors are clearly aware of the limitation imposed by excluding organics, but they would perhaps do well to further emphasize it in the abstract and conclusions.

2. Relative humidity dependence. Both reviewers questioned the assumptions behind

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the RH dependence of this parameterization, particularly at high RH. It does seem that the RH dependence is determined mainly by the study of Kane et al., which provides a large number of data points but differs from the RH dependences of Hallquist, Folkers and Badger. Our published field data on aerosol with a large inorganic component (mainly NH_4HSO_4) give an uptake coefficient near 0.02 with no clear dependence on RH between 62 - 82%, in agreement with the laboratory data of (for example) Hallquist, but smaller than the laboratory data of Kane.

3. Effect of inorganic aerosol composition. Within the ammonium / sulfate / nitrate system, the two most important variables appear to be the nitrate content and the ammonium to sulfate ratio (aerosol acidity). We have little definitive field data on the effect of aerosol nitrate, although our measurements are consistent with the conclusion reached here that uptake coefficients are larger on acidic than on fully neutralized aerosol.

4. Sea salt aerosol. This is likely of lesser relevance for the modeling domain considered here, but it is worth noting that N_2O_5 hydrolysis on chloride aerosol gives different products ($\text{HNO}_3 + \text{ClNO}_2$ rather than $2x \text{HNO}_3$). See, for example, Behnke et al. *J. Geophys. Res.*, 102, 3795-3804 (1997).

5. Temperature dependence and winter measurements. Hydrolysis of N_2O_5 is most important in winter, both because of the longer hours of darkness and also because of reduced photochemical (i.e., OH driven) conversion of NO_x to soluble nitrate. The authors have highlighted the critical need for further laboratory work as a function of RH at low temperature. Winter field data is currently very sparse but would also be helpful in addressing this issue, and we hope to be able to offer such results in the near future.

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