Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-693-RC2, 2016

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimating N_2O_5 uptake coefficients using ambient measurements of NO_3, N_2O_5, $ClNO_2$ and particle-phase nitrate" *by* G. J. Phillips et al.

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Received and published: 7 September 2016

The paper describes a study involving field measurements of nitrogen oxides and atmospheric particulate matter, and analysis aimed at estimating the uptake coefficient (gamma) and yield of nitryl chloride (f) in the heterogeneous processing of dinitrogen pentoxide in the reaction: N2O5 + Cl- = ClNO2 + NO3-. The measurement site is at 800m altitude in a rural location in Western Germany, which is influenced by pollution from the adjacent Rhein-Main conurbation, and by long range transport of air of marine origin containing sea salt aerosol. This is the latest of several papers appearing in the literature reporting estimates of N2O5 uptake coefficients and reaction paths on ambient atmospheric aerosol of more or less defined composition. It is known from lab-

oratory studies that the rates of these heterogenous reactions are highly dependent on atmospheric conditions as well as the chemical nature of the aerosol. Measurements under 'real world' conditions are necessary to provide confidence that the correct parameters are used. This is a timely study and the measurements have been conducted with a well conceived strategy for advancement of knowledge of this potentially important atmospheric process. Two different methods were used to obtain estimates of gamma and f from the observational data. In the first methodology (discussed in section 4.1) involved determination of the formation rates of ClNO2 and NO3- products for known [N2O5] and aerosol surface area. A total of 12 values of gamma were obtained during the field campaign. The second methodology used for estimating gamma is the so called steady state method, (discussed in section 4.2), which assumes that during nighttime the loss of NO3 and N2O5 is in balance with production from NO2 +O3. The gamma values can be evaluated from the expressions for inverse steady state lifetimes of NO3 and N2O5 Periods were selected so that air mass characteristics were consistent with assumptions made for a tractable analysis to obtain the target parameters. Only 3 values of gamma were obtained using the steady state method. As in previous studies in which uptake coefficient have been derived from ambient data sets there is large variability in the results over the time period of the observations: (0.004<gamma<0.11; gamma(av) =0.028 $\pm$ 0.027). Overall the results were consistent with those derived from earlier field studies, as discussed in section 4.4. The factors affecting the gamma values derived in this study were are discussed in section 4.6 in terms of parameterisations of IUPAC panel (RH), Bertram and Thornton (2009; particulate NO3-, Cl- and H2O), and Antilla (2006; organic content) derived from the body of information based on laboratory studies. The predictions and the measurements are again in reasonable agreement. However the apparent influence of particulate [NO3-] is less than predicted by the models and the predicted suppression of uptake by organics is much less if it is assumed that the organic content exists as a hydrophobic coating. There was also a high variability in the values of f (range 0.035 $\pm$ 0.027 to 1.38 $\pm$ 0.60). The large spread of values is expected from the variability in particulate Cl-

as a result of differing air mass origins (discussed in section 4.5). The observation of ClNO2 is an unambiguous indication that the particles at the measurement site contain Cl-, which will influence the overall uptake rate in the field situation. In summary the study provides further evidence for a role of active heterogeneous chemical processing of N2O5 in the lower atmosphere at nighttime, which is strongly influenced by the local physical conditions and chemical composition of the particles. The rates are as a result very variable but current mechanisms based on laboratory studies give a reasonable rationale of the parameters observed.

Other comments The presentation of the work is of a high standard of accuracy and completeness. For such complex data set and depth of analysis it is reasonably easy to read and the diagrams are informative and not excessively detailed. The conclusions are justified in the context of the body of knowledge on this topic.

Minor queries P 3, l. 20 insert 'a' after 'in' p 5, l. 1 please use metric units of length paragraph starting l.28 and Fig 2. Please reorder the 3 plots to be consistent with the order they are discussed in the text p 8, l. 1 Please indicate here that the covariance is illustrated in Fig 5 p 17, l. 14 please indicate the direction of the dependence of gamma suppression on RH; does it increase or decrease? Table 1, last row, col. 1 Were the observations made at 650 m or at 825 m, the altitude referred to on p3, l.27?

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-693/acp-2016-693-RC2-supplement.pdf

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