Atmos. Chem. Phys. Discuss., 8, S5027–S5029, 2008
www.atmos-chem-phys-discuss.net/8/S5027/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of ice in N_2O_5 heterogeneous hydrolysis at high latitudes" *by* R. L. Apodaca et al.

Anonymous Referee #2

Received and published: 18 July 2008

Via measurements of N2O5, NO2 and O3, the authors have determined steady state (SS) lifetimes of N2O5 and related this to RH. They suggest that the relatively short steady-state lifetimes of N2O5 ($<$1 to 80 min), which they determine at high latitudes (compared to lower latitudes) is due to heterogeneous loss on icy particulate surfaces. This is based on the anti-correlation between relative humidity and SS-lifetime.

The anti-correlation between the levels of N2O5 and RH is however rather weak and only becomes apparent in a population analysis (Fig 6) which reveals a small (but apparently significant) difference in the peaks of the rather broad distributions. The authors make some assumptions about ice particle surface area densities (not measured) and then derive a rough sticking coefficient for N2O5. This is a rather bold analysis and must be regarded only as tentative evidence for the role of air-borne par-

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

ticles in reducing the lifetime of N2O5 at high latitudes. It does however help explain the need for larger than acceptable values of the sticking coefficient for N2O5 on aerosols to explain the modeling results of Dentener and Crutzen and therein lies its value.

The comments / questions listed below should be addressed by the authors.

P 12598, L 3 Thermal dissociation of N2O5 results in similar abundances of NO3 and N2O5 under warm conditions. This is not really accurate as the relative abundances depend also on the NO2 mixing ratio. N2O5 / NO3 $>$ 10 is common.

P12599, L7 The oa-CRD filter was changed every 3 to 4 hrs. This is not very often if reactive aerosols are present (the conclusion of this study). In latter text it is stated that black spots were observable in the DRUM impactor after just 2 hrs. What were the relative volume flow rates though the two experiments and relative spot / filter sizes ? How do the authors know that 3-4 hrs was sufficient ?

P12600, L11 The measurements were taken just 1 m from a reactive surface; the snow pack. Some calculations of deposition velocities would have been useful to estimate to which extent the snow pack controls the N2O5 lifetime. Indeed, the authors mention this likelihood on P12611, L6. Would measurements at different heights have been possible ? Strong gradients in NO3 vertical profiles are known to exist. Are the N2O5 measurements representative of air masses 30 to 50 m above the ground ? In a similar vein: at what height were the RH data obtained ?

P 12601, L12 The text is rather qualitative. It would be interesting to learn at which NO level the reaction of NO3 with NO competes with NO3 photolysis at high latitudes.

P12605, L22 I am not sure that the anti-correlation between N2O5 and RH is apparent in this Figure. Some of the anti-correlation will be washed out by variable source terms for N2O5 and only the correlation with SS-lifetime is useful. Is this Figure necessary ?

P12606, L4 Is -20 degrees celcius really cold enough that most homogeneous nucleation occurs close to the thermodynamic threshold. Even at much lower temperatures

ACPD

8, S5027–S5029, 2008

Interactive Comment

RH in cold ice clouds has been observed to significantly exceed 100 %.

P12606, L10 Figure 5 indicates a number of data points at very low RH which have short lifetimes. Is this a real effect, or is the selection criterion too loose (these selected data points are in the middle of a set of data that was rejected).

P12608, L5 As mentioned above, the calculations of sticking coefficients seem to be an over-interpretation of the available data, especially as neither the available surface area nor the chemical state of the aerosol surface was known. In this context, mention of the contribution of the snow pack to N2O5 loss rates would be useful. Replace (while not fully quantitative) with (while remaining qualitative).

Typographical / formatting etc

P12597, (R1) to (R4) The listing of k1 to k4 as part of the chemical equations is cumbersome. Why not just mention in the manuscript that ki refers to the rate coefficient for Ri.

P12602, L6 Replace (in their simulations)with (in the simulations of Brown et al (2003)).

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12595, 2008.

ACPD

8, S5027–S5029, 2008

Interactive Comment