Atmos. Chem. Phys. Discuss., 8, S8640–S8644, 2008
www.atmos-chem-phys-discuss.net/8/S8640/2008/

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.

R. L. Apodaca et al.

Received and published: 30 October 2008

We thank the reviewer for the valuable comments. We have addressed these concerns in this reply and will make changes to the revised manuscript as described in the replies below.

Comment 1: P 12598, L 3 Thermal dissociation of N_2O_5 results in similar abundances of NO_3 and N_2O_5 under warm conditions. This is not really accurate as the relative abundances depend also on the NO_2 mixing ratio. N_2O_5 / $NO_3 > 10$ is common.

We will reword this section to reflect the comment. We were simply trying to indicate that NO_3 and N_2O_5 can be of the same order of magnitude (or only 1 order of magnitude different) when warm, but N_2O_5 levels are typically significantly more enriched at colder temperatures.

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Comment 2: 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 ?

The oa-CRDS flow rate was maintained at 8 lpm and the DRUM flow rate was maintained at 3.3 lpm. The oa-CRDS filters have a 47 mm nominal diameter and after 3-4 hours of sampling there was no visible “spotting” or discoloration of the filter surface. The spots on the DRUM sampler result from focusing the aerosol particles to a very small spot (0.75 mm diameter).

Comment 2 continued: How do the authors know that 3-4 hrs was sufficient ?

The filter change frequency was determined using sample loss vs. aerosol mass loading estimates that are presented in reference 2 (Apodaca et al., in preparation). It was also standard practice to examine the data pre- and post-filter change, looking for improved transmission of N_2O_5 following a filter change. If an aerosol-loaded filter was producing significant sample loss, we would expect to see higher N_2O_5 mixing ratios following filter changes than just prior to changing a filter. We did not observe increases in N_2O_5 upon insertion of clean filters. We will expand the discussion of filter changing and tests for filter losses in the revised manuscript.

Comment 3: 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 N_2O_5 lifetime. Indeed, the authors mention this likelihood on P12611, L6.

We have discussed deposition to the snow in the replies to reviewer 1, and will make extensive revisions to the manuscript for resubmission in this regard.

Comment 3 continued: Would measurements at different heights have been possible?

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Vertical profiling is possible using the compact and light-weight N_2O_5 sensor that we developed, but gradient measurements are not available from this particular study.

Comment 3 continued: Strong gradients in NO_3 vertical profiles are known to exist. Are the N_2O_5 measurements representative of air masses 30 to 50 m above the ground?

Our group has previously measured N_2O_5 at different elevations near Fairbanks under similar meteorological conditions (Ayers and Simpson, 2006). The N_2O_5 measurements from the present study are consistent with the N_2O_5 measurements reported by Ayers and Simpson (2006) which were made from buildings with inlet heights approximately 60 to 85 m higher than our surface site. However, strong meteorological inversions inhibit vertical mixing, and thus we cannot say what was happening 30-50 meters above this sampling site.

Ayers, J. D.; Simpson, W. R., Measurements of N_2O_5 near Fairbanks, Alaska. Journal of Geophysical Research-Atmospheres 2006, 111, D14309, doi:10.1029/2006JD007070.

Comment 3 continued: In a similar vein: at what height were the RH data obtained?

The RH sensors are fixed at 1.5 m from ground.

Comment 4: P 12601, L12 The text is rather qualitative. It would be interesting to learn at which NO level the reaction of NO_3 with NO competes with NO_3 photolysis at high latitudes.

The lifetime of NO_3 with respect to photolysis (j-NO_3 = 0.2 s^{-1}) is 5 s with overhead sun (Finlayson-Pitts and Pitts, 2000). 0.3 ppbv of NO is required to produce a 5 s lifetime for NO_3 with respect to reaction with NO. The key point in this discussion is that rapid sinks of NO_3, such as photolysis or reaction with NO, would prevent the formation of N_2O_5 and subsequently prevent our examination of the nocturnal NOx oxidation process. Therefore, as described later in the text, we only consider nighttime N_2O_5 data at low NO levels (1 ppbv or less). We will revise this section to make it more quantitative in

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the revised manuscript.

Finlayson-Pitts, B. J. and Pitts, Jr., J. N.: Chemistry of the Upper and Lower Atmosphere, Academic Press, 269 pp., San Diego, 2000.

Comment 5: P12605, L22 I am not sure that the anti-correlation between N_2O_5 and RH is apparent in this Figure. Some of the anti-correlation will be washed out by variable source terms for N_2O_5 and only the correlation with SS-lifetime is useful. Is this Figure necessary ?

We feel Figure 4 is necessary, not only for demonstrating the anti-correlation between N_2O_5 and RH, but also to present the time series RH data to the reader. This figure provides the reader with a visual representation of the amount of time that the atmosphere is saturated with respect to ice. Furthermore, Figure 4 compares well visually with Figure 7, which is necessary for showing the lack of correlation between N_2O_5 and aerosol particles.

Comment 6: P12606, L4 Is -20 degrees celcius really cold enough that most homogeneous nucleation occurs close to the thermodynamic threshold. Even at much lower temperatures RH in cold ice clouds has been observed to significantly exceed 100 %.

It is true that the RH in ice clouds can exceed the thermodynamic threshold (100% RH with respect to ice) and it is commonly observed to exceed the threshold significantly in aircraft data observations of both mixed-phase and ice clouds. Therefore, we have explicitly discussed that the thermodynamic threshold means that ice could exist and would not sublime under these thermodynamic conditions. The question of how many ice particles might form depends upon the number of active ice nuclei. Work in Fairbanks on ice fog has shown that pollution can nucleate ice, and thus the polluted nature of these airmasses may help to provide ice nuclei. In response to this comment and that of the other reviewer, we are expanding upon this section in the revised manuscript.

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Comment 7: 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).

These periods are at low source rates comparable to the source-rate threshold and should not be considered as a large fraction of the data.

Comment 8: 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 N_2O_5 loss rates would be useful. Replace (while not fully quantitative) with (while remaining qualitative).

We agree with this comment and will make the calculations more of a discussion. We are also expanding upon the discussion of deposition to the snow surface, which provides an alternative interpretation of the data.

Comment 9: Typographical / formatting etc.

We thank the reviewer for noting these typographical issues and will make these changes in the revised manuscript.

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

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