Atmos. Chem. Phys. Discuss., 8, S8645–S8653, 2008
www.atmos-chem-phys-discuss.net/8/S8645/2008/

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 their valuable comments. We have replied to each of the comments in the order given by the reviewer. In our revision of this manuscript for submission to ACP, we will take these comments into account as discussed in the replies below.

Specific Comments:

Comment 1: Page 12597: Reaction (R4) not balanced - no oxygen is produced in this reaction.

We thank the reviewer for catching this typographical error and will correct it in the revised version.

Comment 2: Page 12599: regional NOx sources near Fairbanks - is there any biogenic contribution that is significant on the scale of anthrpogenic NOx from Fairbanks?

To the best of our knowledge the biogenic NOx contribution has not been characterized in the Fairbanks region. Furthermore, little is known about NO emissions from soils at low temperatures, and even less is known about NO emissions from snow-covered soils. A study by Koponen et al. (2006) indicates that biogenic NO soil emissions are suppressed at low temperatures. When the soil temperature is near -5°C, the reported soil NO flux is $\approx$1.5 micrograms N / $m^2$ / hr. That NO will mix through the snow and into the boundary layer, being oxidized by $O_3$ as it mixes upwards. If we consider the NO mixing into a shallow surface layer (due to its short lifetime with respect to oxidation by ozone) of 1 m and a lifetime of 4 minutes, we derive a steady state NO mixing ratio of about 0.15 ppbv. This level of NO is below the detection limits of our NOx analyzer. Oxidation and slow transport of the NO through the snowpack would probably hold the NO significantly lower than this value in the actual case. Once the NO is oxidized, it will add $NO_2$ to the boundary layer and is likely to mix over a higher height. If we assume a height of 10 meters and a 4 hour timescale for this boundary layer to ventilate, we get about 1 ppbv $NO_2$ in the boundary layer. While this level might contribute to the NOx budget, it is significantly lower than anthropogenic NOx from Fairbanks.

We also note that our data show low levels ($<$1 ppbv) of NO and $NO_2$ at multiple times during the campaign, indicating that biogenic NO and $NO_2$ do not always produce significant NOx levels in our airmasses. The variability in $NO_2$ also argues for a local pollution source as opposed to a broad regional source, as we would probably expect from soil emissions. Overall, we feel it is unlikely that biogenic NOx contributed much of the overall observed NOx. We will add a discussion of possible biogenic sources of NOx to the revised manuscript.

Reference: Koponen, H. T.; Duran, C. E.; Maljanen, M.; Hytonen, J.; Martikainen, P. J., Temperature responses of NO and $N_2O$ emissions from boreal organic soil. Soil Biology & Biochemistry 2006, 38 (7), 1779-1787. DOI: 10.1016/j.soilbio.2005.12.004.

Comment 3: Page 12600: strong temperature inversions - how important is stratification in analysis of the data here? If there is significant up/down transport, it may affect interpretation of steady states.

The mention here of topography and strong temperature inversions was aimed at describing the appropriateness of the selection of our study site. The strong inversions coupled with the local topography resulted in a “channeling” of the Fairbanks pollution plume towards the study site. Furthermore, the strong temperature inversions resulted in suppressed vertical mixing of air masses as the plume moved towards our study site. Up/down transport would only impact the interpretation if it were occurring on a timescale faster than the approach to steady state (which we argue occurs in typically less than 20 minutes). Given the strong stratification of the lower troposphere due to the temperature inversions, it is unlikely that vertical transport was occurring faster than the approach to steady state.

Comment 3 continued: Also, issues of particle volatilization in sampling with the DRUM system, referred to later in the manuscript, should be described in the experimental section.

Volatilization can be a problem for semi-volatiles such as nitric acid. Our aerosol analysis focused solely on sulfate data and sulfate is not volatile. Therefore, the evaporation of ice, discussed later in the manuscript, is not expected to impact the analysis of the sulfate data collected using the DRUM system. We will expand upon these topics in the experimental section.

Comment 4: Page 12601: The assumptions for the kinetic loss equation is not that the system is in steady state but rather that there is an equilibrium between reactions R2 and R3. Steady state is the result of setting the differential in equation (1) to zero. The interesting aspect of this analysis is that if the term, k4[$N_2O_5$] competes with thermal dissociation of $N_2O_5$ (i.e., k3[$N_2O_5$]), then the equilibrium between $NO_3$ and $N_2O_5$ will no longer hold. Some comparison of these two rate coefficients might be useful, either here or later in the paper.

The referee is correct in their statements regarding the equilibrium between reactions R2 and R3. Here, we are not commenting on the equilibrium between reactions R2 and R3, instead we assume that the differential equation (1) is equal to zero (steady state). This assumption allows for the derivation of steady state lifetimes for $N_2O_5$ (equation (2)). Because of the cold temperatures, the thermal dissociation of $N_2O_5$ is greatly slowed, and k3[$N_2O_5$] is much less than the chemical loss of $N_2O_5$ (k4[$N_2O_5$]). We will rework this section to clarify these ideas.

Comment 5: Page 12603: Conditions for rejection of data for SS analysis. The threshold value for NO seems somewhat arbitrary, unless it is related to an instrumental limit. Data for NO $> 1$ ppbv should actually achieve rapid steady state if $N_2O_5$ is measurable at all for these cases, since there would be a very rapid $NO_3$ sink that should pull the system closer to steady state. Do measurements agree with a steady state predicted by the presence of NO?

As the goal was to analyze an aged pollution plume emanating from the city of Fairbanks, selection of a threshold value for “fresh” emissions (NO) was required. Local and transient sources (cars, snow mobiles) would perturb the steady state between $NO_2$, $NO_3$ and $N_2O_5$ (reactions R2 and R3). When NO is present, it represents a fast loss for $NO_3$, and 1ppbv is a somewhat arbitrary number, that was chosen to be about the detection limit of the commercial NOx analyzer used in the study. Additionally, at 1ppbv NO the rate of NO+$NO_3$ (destroying nocturnal $NO_N$ species) exceeds the rate of $NO_3$+$NO_2$ (which forms $NO_N$ species), so it is a reasonable threshold, chemically.

It is true that a fast loss of $NO_3$ (which is the case at high NO) will speed the approach to steady state, but that steady state has very little $NO_N$ concentration, so we expect very low $NO_N$ to be detected when NO is present. Our data generally shows very low $N_2O_5$ is detected when NO is present. We will clarify this section.

Comment 6: Page 12604: How is it known that wind speeds are uniformly below 3 m

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

$s^{-1}$ throughout the lowest 1200 m? Wind profiler data available?

We made this statement based on a combination our data and a review of the twice-daily radio soundings conducted by the National Weather Service from the Fairbanks International Airport about 20 km from our site. We will clarify the source of this information.

Comment 7: Page 12605: Following source rate as opposed to integrating it. Since it is likely that variations in all measured concentrations are the result of transport of pollution plumes of varying intensity, it would seem that the $N_2O_5$ concentrations would likely follow the source strength regardless of whether they were in steady state or integrating the source. The argument regarding integration of the source could be developed by estimating the total amount of $N_2O_5$ observed against the total amount formed. Such an analysis seems to be possible given the arguments presented to this point that the transport time from the source in Fairbanks is known. Thus, if the production rate coefficients and transport time from source are known, the integral referred to here could be explicitly calculated.

The argument presented was that there was a minimum transport time of 2 hours (based on maximum observed wind speeds for the whole campaign) from the source to the study site. The actual trajectory and transport time from the source in Fairbanks is not known to us and probably difficult to know because of the shallow slowly-flowing boundary layer characteristic of this season and location. Therefore, while the referee's comments are valid, we are unable to conduct the analysis described by the referee. Nevertheless, the representative data presented in Fig. 3 demonstrates that $N_2O_5$ levels do not build at the rate predicted by the source rate, indicating rapid loss and suggesting the system is in steady state. One can observe that the hourly source of $N_2O_5$ is generally greater than the value of $N_2O_5$'s mixing ratio. Therefore, the $N_2O_5$ abundance would be produced in an hour or less. On the other hand, the transport time is more than a couple hours, clearly indicating a greater cumulative production of $N_2O_5$ than is detected, which then indicates a loss of $N_2O_5$ faster than the transport

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

time. We will add to this discussion in the revised manuscript.

Comment 7 continued: Also, not clear where the 1 ppbv hr$^{-1}$ Ox loss rate comes from. The production rates given for reaction R1 at 100 pptv hr$^{-1}$ would not give this Ox loss rate. The Ox loss from the more rapid reaction of NO with $O_3$ could give this Ox loss rate, though this is not the aging that is referred to here.

For each molecule of $N_2O_5$ hydrolysed, three molecules of Ox are lost. Therefore, the loss of Ox is three times the formation rate of $N_2O_5$, converting the 100pptv hr$^{-1}$ in-situ formation of $N_2O_5$ into a 300pptv hr$^{-1}$ loss of Ox. Dilution also limited the loss at our site and the losses were higher at the source region (where $NO_2$ and sometimes $O_3$ were higher). We have measured Ox loss in the source region, and it is often 1ppbv hr$^{-1}$ Ox loss due to generally higher $NO_2$ levels. We will clarify this calculation in the revised version.

Comment 8: Page 12606: RH values above 100% - how far above 100% is reasonable? Is there potential for error in the RH measurement for values to 105 or 108%, which seem very large? The arguments regarding saturation with respect to ice would still be valid, even if many of these data were much closer to 100%.

The RH data were collected independently by the referenced investigators and reported without estimates of error. These super-saturated values could be lower due to small sensor calibration errors. However, it should be noted that ice nucleation can be kinetically difficult and that previous airborne investigations have reported significantly higher supersaturations than observed here (e.g. Curry et al., 1990).

Comment 9: Page 12608: For large diameter particles inferred here, it would be more appropriate to use the uptake rate coefficient expression of Fuchs & Stugnin (Fuchs, N. A., and A. G. Stugnin (1970), Highly Dispersed Aerosols, Ann Arbor Science, Ann Arbor, MI.) rather than equation 3.

k = c*gam*N*pi*r710;2[1+gam*(0.75 + 0.283*Kn(r))/(Kn(r)[Kn(r)+1])

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Kn(r) = 3*D/(r*c)

Where N is the particle number density (monodisperse) and D is the $N_2O_5$ gas phase diffusion coefficient. The correction term (in brackets) should make a difference for particles of this size.

The uptake rate coefficient for ice particles presented in this section was estimated assuming that the ice particles were near the micron threshold because actual particle size and surface area density were not measured. Using the mean modal radius of 10 microns, a particle density of 1 particle per cubic centimeter, and the Fuchs and Stugnin expression would give a gamma approximately 3 times smaller, yet on the same order of magnitude. Given the fact that the particle number density and size distribution is unknown during the period of our study, we feel that an order of magnitude approximation for gamma (given by equation 3) is appropriate. Being so near the micron threshold of the mass transport limitation highlights the importance of including ice particle measurements in future studies. We will enhance this discussion in the revised version but make it more of a discussion than a derivation (based upon input from the other reviewer).

Comment 10: Page 12609: Discussion of Figure 7. The measured particle number densities show concentrations of $10^3$ $cm^3$, which is much larger than the values of 1 $cm^3$ quoted earlier in the paper. The authors should use consistent numbers or explain if different assumptions / measurements apply to different air masses. The presence of larger particle number densities bolsters the argument for large surface areas near ice saturation, though it changes the calculation of the actual surface area.

The value of 1 $cm^3$ was given for estimates of supermicron ice particle densities reported in the literature and should not be confused with the aerosol particle number densities (predominantly submicron particles) measured during our study and reported in the middle panel of figure 7. We are not able to use the argument that a “presence of larger particle number densities bolsters the argument for large surface area near

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ice saturation” as we did not explicitly measure ice particle number densities. It is likely that only a few of the detected aerosol particles (a few of the thousand particles per cm$^3$) were actually ice nuclei.

Comment 10 continued: If 20% of the aerosol mass in Fairbanks is sulfate, what is the rest? How much nitrate is in the aerosol? The presence of nitrate in the aerosol is known to suppress $N_2O_5$ hydrolysis (Hallquist, M., D. J. Stewart, S. K. Stephenson, and R. A. Cox (2003), Phys. Chem. Chem. Phys., 5, 3453-3463; Mentel, T. F., M. Sohn, and A. Wahner (1999), Physical Chemistry Chemical Physics, 1, 5451-5457), but would not do so at very high RH, where particle growth would reduce the nitrate concentration (activity). This mechanism would also be consistent with the observations of short lifetimes at high RH.

The report by Di Genova and Dull (2007) indicates that less than 10% of the total aerosol mass in Fairbanks is from nitrate. In addition to sulfate and nitrate, the remaining mass of Fairbanks aerosol consists of black carbon, mineral and soil dust, and traces of metals and sea salt. The Di Genova and Dull (2007) methods were based upon filter sampling, which could under-sample nitrate due to revolatalization, and thus there could be more nitrate in the actual aerosol. However, it is difficult to attribute the short $N_2O_5$ lifetimes observed during our study to suppression of the nitrate effect at high RH. Given the cold conditions of our study (typically -10 to -30°C) and RH with respect to ice (fig. 4), it is likely that the majority of the water associated with the aerosol particle was frozen, and similarly to the discussion on P12608 for sulfate and ice particles, aerosol particles are likely to have surfaces coated with concentrated nitrate solutions, potentially increasing the nitrate effect on $N_2O_5$ hydrolysis. This area needs further laboratory study, and we will make mention of the topic and need for study in the revised manuscript.

Comment 11: Page 12611: Some further detail on deposition loss to the snow surface would be helpful here - is it possible, for example, to estimate a deposition velocity? Is the depth of the mixed layer known?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

We unfortunately did not constrain the deposition loss to the snow surface nor the depth of the mixed layer in this study. The highly stable boundary layer makes the situation even more complex, and thus it is not simple to estimate loss to the surface. However, we do realize that loss to the surface is a real possibility to be a major loss for $N_2O_5$. In fact, we would expect that airmasses that had been in recent contact with the snow surface would be saturated with respect to ice (because if it were drier, snow would sublime until the airmass was saturated). Therefore, it is possible that saturation with respect to ice is an indicator of turbulent contact with the surface and the observed relationship between $N_2O_5$ loss rate and saturation with respect to ice is due to surface deposition of $N_2O_5$. We have added a section to the revised manuscript describing these ideas and discussing the possible implications. In either case, loss of $N_2O_5$ to ice particles or loss of $N_2O_5$ to snowpack, ice is the relevant surface for $N_2O_5$ heterogeneous hydrolysis at high latitudes.

Page 12612: To my understanding, the Dentener and Crutzen model study did not fit a value of 0.1 for gamma to observations, but rather applied this value to their model based on laboratory data available at the time. It is not really clear that their model “requires” such a large gamma value.

The reviewer’s comment is correct - that Dentener and Crutzen used the laboratory values in their models. However, if they turned off the heterogeneous hydrolysis, they got disagreement with deposition patterns. Therefore, it is clear that the heterogeneous hydrolysis is needed at high latitudes, although the actual threshold value of gamma was not determined by the modeling study. We will reword this section to be more accurate in the revised version.

---

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper