Atmos. Chem. Phys. Discuss., 5, S540–S544, 2005
www.atmos-chem-phys.org/acpd/5/S540/
European Geosciences Union


Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Supersaturation, dehydration, and denitrification in Arctic cirrus" *by* B. Kärcher

**B. Kärcher**

Received and published: 21 April 2005

1. Equilibrium calculation for nitric acid uptake

I agree with the reviewer that the novel concept of trapping deserves a more detailed discussion. In the revised manuscript, I will present both, a critical discussion and results from a more conventional calculation of uptake closer to previous estimates of nitric acid uptake.

The results to be shown will be taken from an hypothetical simulation in which I calculate gas dissolution into STS particles as before, but do not allow $HNO_3$ to be trapped. Rather, using the ice surface area density $A$, temperature $T$, and the remaining partial pressure of $HNO_3$ $p_n$, I compute the amount that would be adsorbed in equilibrium ac-



Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper
EGU

cording to the frequently employed dissociative Langmuir isotherm $\theta$ (e.g., Popp et al., 2004). The amount of $HNO_3$ locally adsorbed per $cm^3$ of air on ice crystals is given by

$$c = A\sigma\theta(T, p_n)\,,$$

where $\sigma$ is the maximum number of available surface sites and $\theta$ is calculated using the heat of adsorption $Q = 10.5$ kcal/mol (as in the baseline simulation) to ensure consistency with the parameters used in the trapping model. This amount is calculated each time step and summed over all individual crystals in each altitude bin.

I stress that $c$ is calculated assuming surface equilibrium uptake, but it is not buried in ice, i.e., the burial step is entirely neglected as if the ice crystals stayed at saturation. As $HNO_3$ does not stay in the ice phase, there is no need to evaporate $HNO_3$ once the ice particles sublimate.

This approach without any burial effect mimicks the way most measurements of $HNO_3$ uptake have been interpreted in the past. It predicts an $HNO_3$ partitioning factor $\phi = c/c_{\mathrm{total}}$ which is smaller by up to a factor of 50 compared to the red solid curve shown in Figure 7. This suggests that burial leads to enhanced uptake, at least in this type of long-lived cirrus.

Although I will carefully spell out the uncertainties of the trapping model, I do note that there is experimental (laboratory) evidence for the fact that growing ice surfaces lead to enhanced uptake of HCl (Abbatt et al., 1992; Huthwelker, 1999) and $HNO_3$ (Jon Abbatt and Maria Ullerstam, personal communication, 2005).

2. Updraft velocity

The reviewer states that the updraft velocity of 5 cm/s applied in the cloud simulations for 7 hours is "a very extreme case". More specifically, he/she argues that the ECMWF model would not support the existence of such continuous forcing by looking at 100 hPa geopotential height charts and comparing the variations on March 28.

While I admit that the model assumption of constant vertical uplift is an idealization, I do



ACPD
5, S540–S544, 2005

not agree with the reviewer on this point. First, the lidar measurements (Reichardt et al., 2002, their Figure 1b) clearly show that while the cloud drifted across the measurement site, its top was lifted from 8.5 km to more than 10 km within 7 hours with an almost constant rate. Admittedly, some variation is present in the top heights, likely caused by turbulence or mesocale variability in the wind fields. For instance, the cloud top seems to stagnate or slightly sink after 6 hours. Regardless, it is very hard to understand what else should have caused this overall uplift other than an almost continuously acting, synoptic-scale forcing. Actually, values 4–6 cm/s can be derived from the observed cloud top heights.

Second, looking at hemispheric geopotential height maps at the stratospheric 100 hPa level is misleading. The cloud formed in the upper troposphere; thus 200–300 hPa levels up to the tropopause (the approximate cloud top altitude) are more appropriate to compare with. I have checked that tropopause variations from ECMWF T511/L60 Operational Analyses on March 28 were comparable to (e.g., $\sim$ 2.5 km height change within 12 hours over Northern Scandinavia) the imposed 1.5 km uplift in 7 hours.

Third, the ECMWF model is able to resolve vertical wind amplitudes of the order 5 cm/s with the T511/L60 resolution, although it is clear that one might expect dynamical variability which is unresolved by this model.

3. Reference to early denitrification work

The reviewer proposes to cite Hübler et al. (1990), an early study of observed denitrification due to sedimenting particles in the lower stratosphere. Several other papers could be cited that document PSC-induced denitrification. I did not cite these references because I am dealing with cirrus processes operating at lower altitudes.

Actually, there are no publications I am aware of that would unambiguously demonstrate that cirrus clouds lead to a vertical redistribution of $HNO_3$. The available concomitant $HNO_3$ and cirrus measurements can at most be used to point to the potential for denitrification.



ACPD
5, S540–S544, 2005

This does not mean that cirrus-induced denitrification does not occur in the atmosphere. Rather, the lack of clear observations points to the difficulty to measure denitrification (wind fields and cirrus properties are much more variable compared to the lower stratosphere), and of course, one is not able to say how much $HNO_3$ should be present in the absence of uptake and sedimentation (because an equivalent to robust stratospheric correlations between $NO_y$ and $O_3$ does not exist in the troposphere).

4. Supersaturation relaxation time

I agree that a plot of the $e$-folding time $\tau$ for the reduction of the water vapor content above ice saturation will support the discussion of elevated in-cloud supersaturations ($s$).

A approximate solution of the kinetic equation governing $s$ (as noted e.g., in Kärcher and Lohmann (2002)) leads to the following expression:

$$\tau = \frac{1}{4\pi n r D \beta - a_1 w} ,$$

with $a_1 \simeq 10^{-5}$ cm$^{-1}$, the updraft velocity $w$, the diffusion coefficient $D$ for water vapor in air, the kinetic correction term $\beta$, and the total crystal number density $n$ and mean crystal radius $r$. The values of $\tau$ become large when the updraft-induced cooling $\propto w$ approximately balances the diffusional water vapor sink $\propto nr$. It can be shown, however, that the latter term is typically much larger than the former in a developed non-evaporating cloud, i.e., $\tau \propto 1/(nr)$.

I will add a scatter plot of $\tau$ as a separate figure. The supersaturation relaxation times are extracted from the model every 6 min at each vertical level within and below the fall streak (visible, e.g., in $n_i(z,t)$ from Figure 2) whenever $s > 0$,

$$\tau = \left( \frac{1}{s} \left| \frac{ds}{dt} \right| \right)^{-1} .$$

This definition naturally includes both, the deposition and the cooling term.



**ACPD**

5, S540–S544, 2005

Selected $\tau$-values will be plotted versus $nr$ and color-coded by $s$. Here $n$ and $r$ are the total crystal number density and mean crystal radius at each altitude bin. Points with $|ds/dt| < 5 \times 10^{-5}$ are excluded to eliminate cases with excessively high $\tau$.

The new figure shows that $\tau$ generally decreases inversely proportional to $nr$ in the relaxation phase and ranges between 4–150 min. These rather long time scales render the appearence of rather persistent in-cloud supersaturations of 0.2 or so (as shown in Figure 3) plausible. The highest supersaturations (0.4–0.5) only occur prior to nucleation and are comparatively rare events.

References

Abbatt, J.P.D., et al., Interaction of HCl vapor with water ice: Implications for the stratosphere. J. Geophys. Res. 97, 15 819–15 826, 1992.

Hübler, G., et al., Redistribution of reactive odd nitrogen in the lower arctic stratosphere. Geophys. Res. Lett. 17, 453, 1990.

Huthwelker, T., Experimente und Modellierung der Spurengasaufnahme in Eis. Dissertation, Universität Bonn, Bonn, Germany, 1999.

Kärcher, B., and U. Lohmann, A Parameterization of cirrus cloud formation: Homogeneous freezing including effects of aerosol size. J. Geophys. Res. 107, 4698, doi:10.1029/2001JD001429, 2002.

Popp, P., et al., Nitric acid uptake on subtropical cirrus cloud particles. J. Geophys. Res. 109, D06302, doi:10.1029/2003JD004255, 2004.

Reichardt, J., et al., Correlations among the optical properties of cirrus cloud particles: Implications for spaceborne remote sensing. Geophys. Res. Lett. 29, doi:10.1029/2002GL014836, 2002.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1829, 2005.