

Interactive comment on “Nitric acid partitioning in cirrus clouds: a synopsis based on field, laboratory and model studies” by M. Krämer et al.

Anonymous Referee #1

Received and published: 21 February 2003

This manuscript describes new measurements taken during Polstar (1998) that target the amount of NO_y that is adsorbed to cirrus cloud particles. There is also an assessment of similar measurements performed in other field campaigns and in the lab, and nitric acid-to-ice uptake models are evaluated. This is an important issue in atmospheric chemistry because if there is substantial adsorption of nitric acid to cirrus and the ice particles gravitationally settle, there will be significant redistribution of NO_y throughout the free troposphere. Experiments to assess this phenomenon in both the lab and the field are exceedingly difficult to perform because of a number of reasons: 1. The partial pressures of nitric acid in the upper troposphere are low and hard to detect, 2. The surface area of ice is not easily measured in both the lab and field, 3. The time history of the cirrus cloud particles will affect the amount of nitric acid that may be present on them.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Although the paper presents interesting data, the current version of this paper is not ready for publication in ACP. In particular, the paper is at times not clearly written and some conclusions are made without addressing the uncertainties in the measurements. However, if the following points are addressed in detail, a revised version could be publishable and would be a valuable paper.

Point 1. An analysis of the data shows that when cirrus clouds are cold (Polstar measurements) there is little NO_y adsorbed whereas more is adsorbed on warmer clouds (Success measurements). My feeling is that the reason for this is largely due to cloud surface areas and the temperature correlation is just an indication of the amount of surface area that might be available in a cirrus cloud. To illustrate, note that the Success measurements were made at temperatures only 7 degrees warmer than those for Polstar II (1998) and yet the surface areas in those clouds were close to a factor of seven times higher. For this reason, there was observed to be much more adsorbed NO_y. Although I think the authors arrive at this same conclusion (although this is not entirely clear, see Point 6 below), the argument is buried in the paper and will be lost to most readers.

Point 2. The paper does not do a good job of relating the laboratory measurements to the field observations. First, there is no discussion of specific surface areas of the ice samples used in either the lab or field studies. Are the cirrus particles assumed to be spherical and smooth? To what degree were the "integrated ice surface AREAS underestimated when compared to the ice amount measured with the FISH instrument" (page 420)?). Why is a surface coverage of 10^{15} molecules/cm² used for a full monolayer when the evidence from the studies of Hynes et al. (2002), Abbatt (1997) and Arora et al. (1999) suggest that 10^{14} molecules/cm² is closer to a saturated surface coverage? The use of the Arora et al. (1999) data seems misguided because in that experiment the nitric acid partial pressure with which the nitric-acid coated particles were at equilibrium was not known, i.e. it is not known where the data from that experiment should be placed on the adsorption isotherm. In this sense, I don't see how

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

these data can be used in this analysis.

Point 3. Although there are uncertainties quoted for most field measurements, there is no uncertainty stated for the most important quantity, the amount of NO_y adsorbed on the particles. The conclusions made must explicitly take into consideration, in a quantitative manner, this uncertainty along with that (i.e. 80%) in the gas-phase nitric acid. On that topic, what does an 80% uncertainty mean, that the value can range from 20% to 180% of the quoted value? Similarly, an uncertainty of " a factor of plus or minus 2" has no meaning (page 420).

Point 4. To what degree does nitric acid evaporate from the cirrus particles as they are sampled by the forward-facing NO_y detector? For example, is there ram heating of the flow as it is sampled?

Point 5. An important part of the data analysis relates to the amount of nitric acid that is dissolved in the aerosol component. To determine this, there is an assumption made that the aerosols are liquid and composed of sulfuric acid, nitric acid, water and (in one scenario) ammonia. What if the particles are solids? If they are ammoniated, this is not unlikely at these low temperatures. There is now evidence that there is a substantial organic component to the aerosols even in the upper troposphere. Again, how would this affect the conclusions?

Point 6. Section 4.2.3 was hard to follow. However, I gather that the authors have fitted a dissociative Langmuir adsorption model to the data and so infer that the heat of adsorption is a temperature-dependent quantity. Is there a physical rationale as to why this quantity would be so highly temperature dependent over such a small temperature range? Quantitatively, how robust is this conclusion given the experimental observations? My understanding of the decreased uptake at low temperatures (see Point 1 above) is that the surface areas are low in cold cirrus. It is not clear to me this factors into the analysis in this section. In a nutshell, are surface areas driving low uptake at low temperatures or is the thermodynamics (i.e. small heat of adsorption)? It is not

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

clear from the paper what the authors believe to be the case.

Point 7. The authors do not address in detail the time history of the air masses that they are sampling. Might nitric acid have been scavenged from them by previous exposure to cirrus, so limiting the amount that is observed on the ice particles? Is it safe to make the assumption that the gas-phase is in equilibrium with the cirrus, especially given the very small uptake coefficient measurements recently made by Hudson et al. (2002)?

Figure 1: There is no vertical label in the upper frame.

Figure 2: It is not clear where the different lines in Figure 2 come from. There is no label on the vertical axis.

Figure 3: The reader should not be referenced to a later figure to see the legend.

Figure 4: There are no vertical labels in a number of plots. The plots are too small.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 413, 2003.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)