**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Effect of humidity on nitric acid uptake to mineral dust aerosol particles" *by* A. Vlasenko et al.

Anonymous Referee #1

Received and published: 12 December 2005

This represents the first experimental effort to examine the uptake of HNO3 to mineral dust aerosol, and provides an important extension to past experiments that used bulk samples and which were complicated by issues related to diffusion into the bulk sample. Indeed, largely as a result of different philosophies of data analysis (i.e. which surface area is correct) the literature values of the uptake coefficient vary between about 0.1 and 0.00001. The Vlasenko et al approach partially settles this issue. Whereas I appreciate that this technique is rather difficult when using a non-homogeneous particle sample and a "sticky" trace gas, the data quality is rather low and information necessary to assess the validity of the approach is missing. A major concern is the role of the reactor walls and the fact that the major loss process for HNO3 appears not

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

to be uptake to the mineral dust. The authors should consider the following comments and questions carefully before revising the manuscript.

Abstract, Line 5:

Why does the amount of HNO3 taken up depend linearly on the surface area (SA). The amount of HNO3 taken up should saturate at high SA and there should be an exponential dependence. If it is linear it suggests that only a small fraction of the HNO3 available is taken up and the kinetics of the uptake process (first-order ?) is poorly defined. Why does the HNO3 concentration need to be mentioned in the abstract ? If the uptake coefficient depends on this parameter its dependence should also be mentioned in the abstract.

Page 11826, Line 1

The coarse particles are removed by a cyclone and a virtual impactor. Can the authors give an idea of the efficiency of this process and thereby rule out the presence of particles larger than 1 micron? A few percent of large particles can contribute significantly to the total surface area (and uptake rate of HNO3), yet will not be seen by the DMA.

Page 11826, Experimental

A Teflon tube of small internal diameter (8mm) is used as "flow tube". This is a break from the conventional atmospheric pressure aerosol flow tube, which has a larger diameter to reduce the rate of loss at the wall. The use of PFA will indeed reduce the rate of wall loss compared to e.g. steel of glass, but it still represents a dynamic source / sink of HNO3 in a kinetic experiment. In addition to this, the authors state that the tube must be replaced every 6 hours to avoid uptake to particles attached to the surface. i.e. the critical parameter is not the reactivity of the Teflon, but the reactivity of the aerosol coated wall of the reactor. This effect can be reduced by using larger diameter flow tubes. I do not understand why the wall takes 6 hours to become "reactive" with dust, and would expect a continuous increase in wall reactivity as the experiment pro-

gresses. This is clearly undesirable and indeed, I am surprised that this set-up works ! Did the authors make tests of the capacity of the PFA tube to reversibly adsorb HNO3 and the time response to changes in HNO3 concentrations ? Did they measure wall losses on the partially contaminated flow tube ?

The injector is a second piece of Teflon tubing, with an outer diameter of (presumably) 6 mm. There is therefore a considerable flow restriction between these concentric tubes and very large linear velocities are likely encountered above the outlet of the injector. How will this influence the time for mixing of the injector and main gas flows and the time to reach laminar flow in the main part of the flow tube ? This has repercussions on the calculated reaction time, which, as the authors indicate a few lines lower, is a critical parameter. The next paragraphs do little to reduce these worries as the authors simply state that laminar flow is assumed to be established a few cm downstream of the injector. Unfortunately, there is no information on the total pressure, flow rate the Reynolds number etc to judge this. Such information is important in a flow tube study !

The second "laminar flow tube" used is presented on page 11828. What are the differences between the two reactors (there is no information on even the diameter or material of the slow flowing flow tube). It is also unclear to which flow tube the (incomplete) information in Table 1 pertains.

Page 11830, Line 26

The modulation of the HNO3 signal when dust is added is very small. I see a change from (4.5 +- 1) to (3 +- 1). Also the signal does not immediately fall to the new value, but slowly decreases over time, presumably as the reactor walls become more reactive or as the source of HNO3 from the precoated walls weakens? In a related issue, equation (3) assumes that the wall loss of HNO3 is the same in the absence and presence of dust, which appears not to be the case. Further, the authors derive a residence time for HNO3 on the wall of about 4 minutes (Page 11834, Line 12). Is this reasonable ?

The data in Figure 4 show that the HNO3 loss in the absence of aerosol is associated

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

with large scatter. It is unclear how such scattered data can give rise to values of kw listed in Table with errors of just 2-4 percent. The errors associated with kw are important when one realises that kw is actually much larger than kp. i.e. the process of interest (uptake to particles) is a factor 2-3 smaller than the overall loss rate in the absence of particles. At this point, the accuracy of the uptake coefficients measured has to be questioned, and suspicions that the experiments were not well designed and did not work particularly well are confirmed. The variability of kw (e.g. from during an uptake experiment due to increasingly contaminated walls, from experiment to experiment, and also due to different amounts of water vapour) will be critical in determining the uptake coefficient.

Page 11835, Line 6

The data are corrected for diffusion effects using $D(HNO_3) = 0.118$ cm2 /s. The collision partner (N_2 or air ?) should be quoted.

Page 11835, section 3.5

The data from the uptake of HNO_3 to Arizona Test Dust (ATD) are displayed in Figure 6. As mentioned above, the modulation in the HNO_3 signal is too low to define the order of the kinetics. For this rason the authors evaluate only the increase in the nitrate associated with the dust to derive the uptake coefficient. The precision of uptake coefficient extracted from the data will depend on the stability of the HNO_3 source and the stability of the aerosol source as the injector is moved. The accuracy will depend on the correction for kw and on the surface area of the dust. The authors should mention how stable the dust supply is and how well the SA is characterised, and describe how the measured mobility diameter is related to the surface area of a non-spherical particle !

Page 11836, Line 2-

The authors find that the uptake coefficient depends on the concentration of HNO_3 (once again suggesting non-first order kinetics). This is most likely related to deple-

tion of reactant (i.e. depletion of reactive dust SA) on the time scale of the uptake (a few seconds). The authors recognise at this point that a more substantial data set is required to derive the elementary processes of the uptake, and suggest that this will be forthcoming in a future publication. One must then ask whether this "advance" publication of poorer quality data is necessary.

Page 11838, section 3.7

The authors see an effect of humidity on the uptake coefficient, which they suggest is a result of the presence of H_2O on the dust surface. Have they ruled out that this is just the result of an enhanced value of kw. i.e. did they do experiments in which the influence of humidity on kw was investigated ? The wall loss rate of HNO_3 will certainly depend on RH.

Figure 8 shows a dependence of the uptake coefficient on H_2O, and the eye is guided by an adsorption isotherm. The data is however not of sufficient quality to prove that the H_2O effect is described by the isotherm given. Indeed, a linear dependence would fit just as well. Note also that previous experiments (cited later) have shown that the uptake coefficient at zero RH (i.e. Knudsen studies) is not zero as this plot wrongly indicates!

Can the ACE-Asia field campaign data really be used to support the contention that the uptake of HNO_3 to dust is influenced by humidity. What values of the accommodation coefficient did the field campaign return, and what assumptions were implicit in the analysis ?

Page 11840, section 3.8, Table 3.

I suggest that the authors re-read the literature publications in which data on HNO_3 + dust were obtained. In some instances, they have confused the flux of molecules into the reactor (molecules /s) with the concentration, which was actually orders of magnitude lower than listed, and thus significantly lower than in the present study.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

In this context, Table 3 needs to be extended to at least mention how the uptake coefficient was derived in the Knudsen reactor experiments (geometric surface area versus BET surface area versus pore diffusion model). The use of different areas has results in uptake coefficients for HNO3 on e.g. CaCO3 that have varied from about 0.1 -0.2 (Fenter 1995 and Hanisch 2001, using the geometric surface area) to 0.002 (2005) or 0.00025 (2000) or 0.000014 (2000) from Grassian and co-workers, who considered the internal surface). Note that the data of Underwood et al, 2000 (uptake coefficient to CaCO3 of 1.4e-5) is missing from the list.

Minor corrections:

Page 11829, Line 11 replace "during" with "over a period of "

Page 11834, Line 22 Ě..taken up on the aerosol surface areaĚĚ

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11821, 2005.

EGU