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

A. Vlasenko et al.

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General response: We appreciate the positive comments and evaluation of our approach to address some aspects of this difficult reaction system.

Response to specific comments:

1. Is it correct to say that the aerosol surface area is “controlled” by the SMPS system (page 11826)?

Ok, we will change this.

2. I have a general question of how the overall reaction time (of 1.9 seconds) is determined.Is this just from the bulk velocity/flow tube length? Was the mixing length considered, where the nitric acid and dust first diffuse together (page 11826 and other

locations)?

The overall reaction rate is calculated from the volumetric flow in the reactor. The degree of mixing was tested in experiment and discussed line 25 p.11826. We will specify more precisely that we observed complete mixing of the flows after 0.2 s, hence the mixing time in the reactor has to be shorter than 0.2 s. In view of some of the systematic uncertainties discussed, it seems not appropriate to include a detailed residence time distribution for the particles in the analysis.

3. What other chemicals arise from the nitric acid production scheme, such as ozone, HO2 or H2O2 (page 11827)?

We are happy to provide more details about the nitric acid production scheme, and we will include additional information. The photolysis of the H2O/O2/N2 mixture leads to OH and HO2 radicals as well as O3, the concentration of each of which depends on humidity, O2 content and light intensity [Aschmutat et al. 1994]. As shown in this reference, the concentrations of the radicals can be constrained by measurement of O3. As mentioned in the text, the system was optimized with respect to O2 content to keep O3 below 30ppb under all conditions. This also ensured that the levels of HO2 were presumably low. We are aware that we cannot assess contamination by H2O2 from radical recombination at the walls.

4. “was measured” to “were measured” and “is illustrated” to “are illustrated” on page 11829.

Thank you. These errors will be corrected.

5. Why were some experiments not conducted without the addition of extra, nonlabeled NO2 (HNO3)? With much lower partial pressures of nitric acid, these experiments would have given more information about the nature of the initial uptake coefficient of nitric acid onto a surface that is not in the process of getting saturated (page11830).

We agree with the Referee that information at much lower pressures of HNO3(g) would

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be very valuable. However, note that the production of the 13N isotope brings with it some production of non-labelled NOx from radiation chemistry in the target with N2 impurities in the carrier gas (He). Working at low concentration is therefore a trade-off between diluting the tracer containing gas to reach low concentrations of non-labelled HNO3 and getting low fluxes of the radioactive tracer. Adding the retention losses along the flow tube, this limits the range of concentrations at the lower end for aerosol experiments. While the chemical reaction itself does not lead to lead to deactivation of all reactive sites at 1011 cm-3, the adsorbed precursor may very well reach saturation. This is also the reason why we report these uptake coefficients with caution and with mention of the gas phase HNO3 concentration to which they apply.

6. Was there any indication that the wall loss rate constant increased after a kinetics experiment had been conducted involving dust? I.e. how did exposure to dust affect the wall loss rate constant (page 11834)?

The dust aerosol is generated in the submicron range with a mode at 200nm. These particles are transported without significant losses (diffusion, gravitational settling or impaction) through the flow reactor. Furthermore, note that we are working with neutral particles, which reduces losses to insulating surfaces massively. As mentioned in the text, we recheck the signal level of H13NO3(g) before and after each aerosol admission. We also always kept the aerosol admission periods as short as possible to allow a reasonable life-time of our flow tube, which was strictly set to 6h. We will make sure that this is emphasized also at other locations in the manuscript to avoid misunderstandings.

7. There appears to be an error in the aerosol surface area quoted on page 11837, perhaps in the units?

What we mean by these units is aerosol surface area (cm2) per volume of gas (cm3). In principle, this can be reduced to cm-1, but this notation (units cm2∙cm-3) is widely used in literature for aerosol surface area concentration.

8. Perhaps change the word “row” to “suite” on page 11839.

Thank you, we will change this

9. I am not convinced that the uptake coefficients would necessarily scale to 10Ĺ-3 for dry conditions, and so compare well to the data of Goodman et al. (p11840). Instead, could some of the difference arise from the fact that the Goodman et al. uptake coefficient is corrected for the BET surface area whereas it is not in this paper? Also, it might be worth pointing out in the paper why drier conditions were not studied (presumably, the water was needed to make OH).

We agree with this reviewer that exptrapolation of our data along the isotherm to low humidity is speculative. In addition, the BET isotherm describes reversible adsorption of water, and does not address the type of chemisorbed water possibly present in the Knudsen cell experiments, which were performed in complete absence of water vapor. We are assuming that when going along the isotherm, the amount of water at e.g. 0.1% humidity would present an upper limit to the amount of water in the other studies. We will add a sentence explaining this difference. Note that the surface area issue has been discussed separately in the text. Regarding this issue, we think that the aerosol particle surface area provided by the smps is close (not precisely because of the particle shape issues mentioned in the text) to the BET surface area. Therefore, this comparison is an attempt to bridge the results of the different experimental approaches, i.e. aerosol flow tube and Knudsen cell. But as noted by other referees as well, there is no clear reason for preferring BET surface area normalized data over the geometric area normalized data from Knudsen cell studies.

10. On page 11841 it is stated that there may be no more than a 20% correction to the dust surface area based on the agglomeration effect. Where does this estimate come from? Could an estimate come from analysis of specific surface areas that have been measured by BET methods of dust samples of this type?

This estimate comes from an earlier investigation of resuspended ATD particles by

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scanning electron microscopy (SEM) [Vlasenko et al. 2005]. We observed that some of the larger particles (>200 nm) are agglomerates of a few (not many) individual grains, which deviate from the spherical shape assumed by the SMPS surface determination. Based on this finding we estimated that we possibly underestimate the particle surface concentration by up to 20% (keeping in mind that still the majority of the particles were close to spherical). We have not performed BET measurements of collected aerosol samples. As mentioned in the text, in theory one could correct for shape issues and fractal properties, but we believe that we would need microscopic information about the structure, which goes beyond what is reasonably available presently.

11. Concerning the relationship of the measured uptake coefficient to the atmosphere it might be worth pointing out that all atmospheric measurements either use a total dust mass or surface area assuming spherical geometry, i.e. the measurements made in this paper (also assuming spherical geometry) are well suited to comparison to those that may prevail in the atmosphere.

This is indeed the case. This point will be added to text in the context of the atmospheric implications.

12. Could comparison to the uptake kinetics of nitric acid on other mineral dust surfaces, such as those studies by Frinak et al. also be presented?

According to the chemical analysis Fe is a minor constituent (2% of the elemental composition) of the ATD. We feel that such a comparison would be rather confusing and we would like to avoid another complicated comparison on different materials measured by a different technique. But the reference by Frinak et al. will be added in the introduction.

13. Table 2. I am surprised by the very low uncertainties in the aerosol surface area. Are these precision uncertainties only?

The Sp uncertainties in Tab.2 are calculated as standard deviations of Sp for the time of the experiments. The dust aerosol generation is stable with respect to particle number and size distribution. Perhaps the major uncertainty of measured surface area is associated with the assumption of spherical shape. Upon revision, we will add the systematic errors and integrate them into the uncertainties of the uptake coefficients. Note however, that for an individual measurement as that shown e.g. in Figure 6, the relatively low uncertainties as shown in Table 2 apply.

14. Following on with point 13, what is the estimated uncertainty from the unmeasured surface area at particle diameters larger than 1 micron for the ATD and SiO2 (see Figure 2)? What transmission losses in the SMPS prevail for particles between about 0.5 and 1 micron, where a lot of the aerosol surface area is present? How do these factor into uncertainties in the reported uptake coefficient?

We agree with the reviewer that this is an important detail. The uncertainty associated with particles outside the range of the smps system has been investigated in detail earlier for our dust aerosol source [Vlasenko et al., 2005, Fig.3, p456]. The SMPS measurement was backed up with an optical particle counter (OPC) measurement to obtain a full log-normal size distribution, also showing the strong drop at larger sizes given by the characteristics of the virtual impactor. It was found that the sole use of the SMPS system resulted in a systematic 25% underestimation of Sp. Because for the present work, the OPC measurements were performed off-line, we scaled the smps data obtained on-line to combined spectra from the OPC and smps obtained off-line to get the true aerosol surface area (without increasing the uncertainty). Unfortunately, we have not explicitly mentioned this procedure apart from citing the other work. We will add this important information. As mentioned above, we will revise the way the systematic errors discussed in the text and propagated into the uptake coefficient are reported.

15. I note that the data in Figure 5 are very nice, for a difficult experiment.

Thank you! Obviously, referee 1 was not impressed as much.

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16. Figure 6. What is the (g) term referring to in the y-axis caption?

This term refers to “gas phase concentration”, as opposed to the particulate counterpart. The explanation is given in the figure caption.

17. There is a missing left bracket in the caption for Figure 8.

The figure caption will be corrected.

References

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