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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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Point 1: Referee #3 comments on the comparison of the uptake coefficients obtained in this study at ambient relative humidities (12%-74%) with those reported in earlier studies under dry conditions. Such a literature comparison has to involve an extrapolation of our data set to dry conditions and as well it bears the difficulties to compare the reactive surface measured in our aerosol experiments with the surfaces of the powder samples used in the previous studies, which are quantified either as geometrical surfaces of the sample or as BET-surfaces of the sample.

Answer: First we would like to explain that we could not obtain measurements under dry conditions with our experimental set up which would have allowed a direct comparison with the previous studies. The reason for this is that we used the photolysis of water vapour (at 40 % relative humidity) to in situ generate HNO3 and H13NO3, respectively. This limits the possibility to lower the humidity in flow reactor. Nevertheless, we judged it to be important to compare our results with the previous measurements on powder samples under dry conditions as the combined data covers the large humidity range from dry conditions to high relative humidities as they are typically found in the troposphere. And of course such a relation is of paramount interest for the interpretation of experiments under dry conditions.

As described in the manuscript, when we perform an extrapolation of our data to low humidity (0.1%) along the water absorption isotherm we would cautiously favour a low uptake coefficient of 10-3 and this number would still be based on the mobility diameter measured with SMPS. We think that the SMPS based surface area is relatively close to the BET area, especially as our earlier SEM investigations cited in the text revealed mostly compact (though not spherical) particles. It makes therefore sense to compare our uptake coefficients with those obtained from the Knudsen cell by normalizing to the BET surface area - after of course taking into account that the humidity was entirely different and in full knowledge of the debate which of the normalization methods is appropriate for the rates of uptake of HNO3. In absence of aerosol flow tube measurement under dry conditions we are not able to further underline this comparison, and it remains speculative. Of course, in absence of a humidity dependence below 10%, we could also compare our results to those reported from the Knudsen cell with normalization to the geometric surface area. We will emphasise this in the revised text to make the current link between the humidity issue and the problem of the surface area to which the data are normalised more easy to understand.

To further clarify this topic we will add a column in Table 3 specifying the type of surface area quantification used in the individual studies.

Point 2: 2) Furthermore, the aerosol flow tube provides the unique possibility to test which surface area better describes the real surface area. The BET surface area increases with the mass of the particles whereas the geometric surface area with their

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size. Experiments where the size of the aerosols is varied but the total aerosol mass is held constant (or vice versa) can therefore give an idea if the BET surface area or the geometric surface is more close to the reactive surface.

Answer: We actually show an experiment (Fig. 5) in the manuscript were we held the aerosol size constant but increased the total aerosol particle number concentration. The other proposed experiment (increasing the aerosol size and keeping the total aerosol mass constant) would be quite difficult to perform with the given setup. And it would be the latter experiment which could give us the information if the rate of the reaction increases with the total aerosol mass or the total aerosol surface. Therefore, we can not clarify the point. Note further that the smps derived surface area is not precisely the geometric surface area. It is related to the drift velocity of a particle in the gas, which is in turn the result of momentum exchange with the particles. This process explores a rough surface similar to chemically interacting gas molecules.

Point 3: The authors observed a concentration dependence of the uptake coefficient in agreement with previous studies. However, they used only two different concentrations. Could it be, that even at the lower concentration the uptake coefficients are underestimated due to an onset of saturation?

Answer: The data for the experiment at the lower HNO3 concentration is shown in Figure 6. From the comparison of the model fit with the data points we conclude that the measured uptake coefficient is not affected by a saturation effect, as there is no decrease of the reaction rate with increasing reaction time within the uncertainty of the experiment. This referee is right, the uptake coefficient could be even lower at lower gas phase concentrations. This is the reason, why we mention the gas phase concentration wherever the uptake coefficient is mentioned.

Point 4: As referee 1 pointed out, the adsorption isotherm of water given in Figure 8 fits not necessarily the uptake coefficients. The data can be represented by a linear dependence or even be independent of RH up to RH of 40 % followed by an increase in the uptake at higher RH. Such an interpretation would also be in agreement with the hygroscopic growth experiments shown in Figure 9 where an increase in the hygroscopic growth is only observed after reaction at 85% RH.

Answer: We agree with the referees, the adsorption isotherm of water was used to provide a reasonable explanation for the increase in reactivity, which is based on known adsorption behaviour of water on minerals. But also a linear fit or more complicated fits, as suggested, would represent the data quite well and might be chosen to describe the observed dependence. Our take home message of this is that the reactivity probably increases with the amount of water adsorbed on the surface.

Point 5: Finally, Seisel et al. [2004] showed that HNO3 is reacting on dry mineral dust with the surface-OH groups and formed coordinated nitrate. If water is present on the surface the mechanism must not necessarily be the same. It may well be that some kind of solvated nitrate (as observed by Goodman et al. [2001]) is formed which results in different uptake kinetics.

Answer: The observed increased uptake kinetics at higher humidities may be a sign that additional reactions than the substitution of surface-OH groups by nitrate as demonstrated by Seisel et al. [2004] may gain importance. Such processes may involve the partial dissolution of mineral constituents as discussed on page 11838. However, in absence of insitu information about the chemical mechanism of the reaction, we prefer to not go further in mechanistic speculations than those listed in form of the hydrolysis reactions and discussed thereafter.

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

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