Atmos. Chem. Phys. Discuss., 5, S5455–S5466, 2005
www.atmos-chem-phys.org/acpd/5/S5455/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

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

A. Vlasenko et al.

Received and published: 10 February 2006

General response

We appreciate the positive evaluation of our experimental efforts for this difficult system. We also appreciate the many constructive comments, which help to improve the manuscript. We are however concerned about some of the statements regarding proper data analysis and evaluation. Even though we admit that there are some obvious errors in some of the uncertainties listed and as a result also in the reported uptake coefficients, we were trying our best to make cautious statements about all our results and their implications, and we can try to improve the text with respect to these uncertainties even more. We are fully aware that the data quality is not as good as one may have wanted, but still seems comparable to other aerosol flow tube studies. The general point we would like to make here is that while the method allows us to investigate this reaction under nearly atmospheric conditions in an elegant way, it brings with it a number of other complications, which range from the complexity associated with the use of a large accelerator facility and security issues to the inherent constraints imposed by the specific detection method. We note that this type of experiments still has a campaign-like character due to limited access to the irradiation facility necessary for the production of the radioactive isotope. This referee is also criticizing the overall design of the experiment and expresses doubts, whether it ‘works’ at all. As will be pointed out in more detail below, our design is not just a bad choice, which is not working in the end, but is the result of a number of constraints such as the kinetics of the reaction, accessible flow rates, denuder design and detection geometry on the denuders. The design follows closely those already used and published earlier (Guimbaud et al., 2002, and references cited therein). As will also be pointed out below is the fact that the loss of radioactively labeled HNO3 along the flow tube is entirely driven by retention due to physical adsorption on the wall and the associated radioactive decay of the short-lived nitrogen isotope, and not by chemical reaction on the walls, which has been carefully checked in every experiment leading to an individual data point reported here. This aspect has obviously not been recognized by this referee and much of the criticism derives from this point. Nevertheless, we will make sure that this aspect receives more emphasis in the revised version.

Specific comments: We will retrace our response along the specific comments made by this referee:

Comment: 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.

Response: The linear dependence of the amount of HNO3 taken up on the aerosol surface area is explained in detail on p.11834, line 27. We actually designed our experiments so that only a small fraction of HNO3 is taken up (10% of HNO3 available in the gas phase). This leads to much less distortion of the HNO3 concentration profile along the reactor while the aerosol is present (and much less effect of HNO3 evaporating from the walls in the areas where HNO3 would be strongly depleted in the gas phase). Especially for this case of a sticky gas, the check whether the observable particulate signal is due to the aerosol surface present in the reactor, this provides a useful quality check and a proof that kp is indeed proportional to the aerosol surface area and is not convoluting any further wall effects. Deviations from first-order behaviour can be extracted from measurements performed at different concentrations.

Comment: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.

Response: In a substantial part of the atmospheric chemistry literature, the uptake coefficient is treated as a quantity, which should be independent of concentration and time, and it is often considered as characteristic constant of a reaction, similar to a rate constant of a gas phase reaction. However, as pointed out e.g. by Ammann et al. (2003), Pöschl, Rudich and Ammann (2005) and in many other studies of uptake to solid and liquid surfaces, the uptake coefficients do indeed depend on concentration and time. Therefore, the uptake coefficient should really be considered an observed reaction rate under the given experimental conditions. Reporting an uptake coefficient without specifying concentration and time is not useful. Reporting an uptake coefficient should be considered equivalent to reporting an ozone formation rate in a chamber experiment. In principle one would wish to be able to retrieve the underlying physical parameters, which drive the uptake coefficient. This has also implications to some other referee comments regarding the value of our results in comparison to a more detailed kinetic study. In our case, it seems not more than correct to report the concentration at which the reported uptake coefficient has been measured. We will amend the abstract to mention the concentration dependence and make sure that this aspect is emphasized in the text.

Comment: 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.

Response: A detailed description of this point is published in the study also cited in the text, which was devoted to carefully characterize our dust aerosol source (Vlasenko et al. 2005). The SMPS measurement was backed up with an optical particle counter (OPC) measurement, to cover the particle size range above 1 micron. Those measurements were clearly showing that the particle counts were dropping as expected for the virtual impactor separation characteristics, and the overall size spectrum was log-normal. It was found that the sole use of the SMPS system resulted in a systematic 25% underestimation of Sp. This is taken into account by correcting the aerosol surface as reported by the SMPS when calculating the uptake coefficients. Note that while the SMPS system was always attached to our flow system, the OPC measurements were only done occasionally and offline as described in Vlasenko et al. (2005). Unfortunately, apart from citing the reference, we have not added this explicitly in this manuscript, we thank the reviewer for pointing this out. This point will be emphasized more in the revised version with details how the correction was made.

Comment on flow reactor design, surface to volume ratio, laminar flow profile and particle losses

Response: The residence time of the particles in the reactor is adjusted to allow a small depletion of gas phase HNO3 until the end of the flow tube as already pointed out above. The flow rates used are constrained by the overall dilution of the source of radioactively labeled molecules, as well as by the separation of gas and particulate phases in the denuder. This laminar parallel plate denuder can not be operated at flow rates higher than 1lpm (see Ammann (2001) and Guimbaud et al. (2002) for more about the performance of this device) in conjunction with the size of the scintillation crystals used for the detection of the gamma-rays. Extracting only a fraction of the flow for detection would reduce the signal to noise ratio especially in the particulate filter detection, which would be undesirable also. Given the flow rate of 1 lpm with a Reynolds number of around 130, the laminar flow profile establishes within about 5 cm, also behind the injection point, where still nearly half of the cross sectional area is available. Our measurements mentioned in the text to assess the degree of mixing did not show any deviation from laminar flow dynamics. Under the constraints given above, making the tube wider but shorter would result in more difficulties to establish laminar flow on the same time scale. We have a detailed Monte Carlo model combining wall interactions and diffusional transport available (Bartels-Rausch et al., 2005), which tells us that for this geometry transport of a trace gas along the tube in absence of aerosol is almost entirely driven by the adsorption equilibrium with the wall. The residence times of HNO3 derived here based on the loss of the radioactive tracer have also been checked in the form of response curves with non-radioactive HNO3 detected by a chemiluminescence detector in our earlier experiments and is also consistent with the literature (Neuman et al., 1999). We agree that reducing the surface to volume ratio does indeed reduce the total amount of HNO3 adsorbed to the wall as compared to that present in the gas phase in the reactor. However, this does not necessarily lead to a corresponding reduction of the residence time of the individual HNO3 molecules, which determines kw in our experiments. Note again also in this context that the slight depletion of gas phase HNO3 in presence of aerosol does not lead to a massive evaporation from the surface. We feel that in section 3.3 and Figure 4, we have clearly enough described the fact that kw is entirely due to adsorption and chromatographic transport, which finally leads to decay of the radioactive tracer. The capacity of the PFA tube to reversibly adsorb HNO3 can be estimated from the retention time of H13NO3 and the HNO3 flux into the reactor and is about 2Œ10ˆ13 molecules per cm-2 reactor surface. This number is per se not very interesting in the context of the present paper, but is surprisingly similar to HNO3 saturated coverages on other surfaces. All relevant literature as mentioned above with more information is cited in the text. We also clearly describe how we routinely measure kw before and after every aerosol admission into the reactor, being fully aware of the problems caused by particles depositing on the walls. Note that in contrast to all other aerosol flow tube studies in the literature, we are admitting only electrically neutral particles into the reactor. This massively reduces wall losses especially on insulating surfaces. We will give a little more details in the revised text that we had observed kw increasing after extended aerosol exposure, which finally led to the strict tube replacement schedule as already mentioned in the original version.

Comment: 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 !

Response: Thank you for pointing this out. All the measurements were done at total pressure of 1 atm in the reactor. The Reynolds number is ˜ 130 for the flow used in the kinetic experiment. This in formation will be added to the text.

Coment: 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.

Response: Thank you for identifying this omission. The corresponding information on the second flow tube used for the processing and hygroscopicity experiments will be added to the text, and Table 1 will be amended to clarify this.

Comment: 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.

Response: Note that the response time of the detector signal is given by the half-life of the isotope detected, which is 10 min. We are recording count rates with 3 min intervals. The inverted count rates (i.e. fluxes) therefore need at least two to three intervals to become statistically relevant. Furthermore, the residence time of HNO3 in the flow tube is 4 min. Taking this into account, the response of HNO3(g) as observed is consistent with these response times. Note that when the aerosol is switched off then the gas phase signal always recovered to its initial value. So we do not have indications to assume that kw changes while the aerosol is present in the reactor. We will make a comment on the response time issue in the text.

Comment on residence time, uncertainty of kw and resulting uncertainty of the uptake coefficients reported.

Response: As mentioned above, this residence time is reasonable. Note that this is the overall retention time in the flow tube, not the microscopic residence time at one individual encounter with the wall. As we have clearly described in the text, and we will repeat it at appropriate places in the revised text, kw was determined for each HNO3 concentration and also for each individual tube separately, as shown in Figure 4 for two examples. The data points shown in Figure 6 contain an individual kw measurement, which was performed before the first aerosol admission and rechecked at full reactor length after the last aerosol admission. Therefore, we insist that our data are not affected by an increasing influence of dust on the wall. As explained in the text on page 11838 line 22, the humidity dependence measurements leading to Figure 8 were only done by measuring uptake to the particles at the longest reaction time of 2s, where also kw was only based on the change in signals between 0 and 40cm in absence of aerosol. This was to achieve a humidity series in one individual tube in spite of the long equilibration times in the flow system after humidity changes. We will emphasize this more in the revised version. The uncertainty of kw listed in Tab.2 had been erroneously taken from these measurements. Because the loss measurement at 40cm is much more accurate than at shorter lengths, this led to lower errors. We will add changes to Tab.2, which also for the other quantities cites precision estimates only, and not including further issues brought up in the discussion later on in the manuscript. While these systematic errors affect the overall uncertainty of the uptake coefficients, they do not change the uncertainty of the relative humidity dependence. Nevertheless, we will make sure that we will come up with more consistent error values in the revised text.

Comment: The data are corrected for diffusion effects using D(HNO3) = 0.118 cm2 /s. The collision partner (N2 or air ?) should be quoted.

Response: Text will be amended to include this information.

Comment on variability of H13NO3 source and aerosol source, uncertainty of aerosol surface area associated with shape issues.

Response: We fully agree with the referee that the stability of the HNO3 source and the dust generator are very important parameters for the evaluation of the kinetic data. Note that the H13NO3 source is continuously monitored by extracting and measuring a small fraction of the flow of HNO3 entering the injector, as described in the text and shown in figure 3. Regarding the stability of the dust source, we are citing our separate study, where we characterized the stability of the dust source especially with regard to the surface area (Vlasenko 2005). The degree of the stability can also be estimated from the uncertainty for the Sp given in Tab.2. We make quite some emphasis in the text (p.11840, line 25) about the problem of relating the measured mobility diameter to the surface are of non-spherical particles. The more elaborated methods cited in the text to include a fully microscopic model of interaction would need much more detailed knowledge or assumptions about internal structure and fractal dimension, which goes far beyond the aims of this study. We feel that we add a fair and safe uncertainty to the aerosol surface area with respect to this issue. But as noted above, this additional uncertainty, which goes on top of the precision uncertainty of the smps measurement, has not entered Table 2 as systematic error adding to the uncertainty of the uptake coefficient. This will be changed in the revised text.

Comment: The authors find that the uptake coefficient depends on the concentration of HNO3 (once again suggesting non-first order kinetics). This is most likely related to depletion of reactant (i.e. depletion of reactive dust SA) on the time scale of the uptake (a few seconds). The authors recognize 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.

Response: Within the uncertainty of our experiments at the two concentrations reported, we have no indications of a time dependence. We are clearly stating on (p11835) that we are making a steady state approximation while doing this first order analysis (using kp). In absence of a clear sign of time dependence, the concentration dependence is reminiscent of saturation by an adsorbed precursor to reaction, the details of which cannot be resolved based on the present data, as mentioned in the text. The main aim of this study is to demonstrate uptake of HNO3 to aerosol particles for the first time at all and to identify that uptake depends on humidity. The concentration dependence is surprising. If it motivates further research, we do not see a reason for not reporting it. Also note again that uptake coefficients are only normalized rates and are not universally applicable rate constants. They only apply to the specific conditions of the experiments. More universally applicable rate parameters underlying the observed uptake coefficients should be and will be the aim of another study mentioned in the text. We do not see the point of showing poorer quality data here.

Comment: The authors see an effect of humidity on the uptake coefficient, which they suggest is a result of the presence of H2O 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 HNO3 will certainly depend on RH.

Response: As mentioned clearly in the text and also in response to other comments above, the effect of RH on Kw is taken into account. Each individual measurement of uptake as shown in Figure 3 is accompanied by a measurement of the H13NO3 loss in absence of aerosol at full reactor length before and after every aerosol admission at each humidity. The effect of humidity is also discussed in the text on p11834.

Comment: Figure 8 shows a dependence of the uptake coefficient on H2O, and the eye is guided by an adsorption isotherm. The data is however not of sufficient quality to prove that the H2O 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!

Response: We are nowhere stating that we are proving that the isotherm describes the humidity dependence. We are talking about possible explanation etc. and we are scaling the isotherm to the data, not more, and as recognized by this referee, as a guide to the eye. We are not discussing the magnitude of the BET parameters, it is a simple plot. It is simple scientifically reasonable arguing that the amount of water increases along such an isotherm rather than along a straight line, which would of course also fit through the data. Even though the Knudsen studies cited are indeed working at zero humidity, more strongly bound water was present in those samples as discussed in those papers. The BET isotherm is only a model of reversibly adsorbed water. In addition, in our plot, the solid line clearly stops at about 1% relative humidity. We are discussing the relative humidity issue as compared to the Knudsen studies in the text. We will carefully recheck our wording in this paragraph to make sure that the isotherm is put in this context when comparing to our data.

Comment: Can the ACE-Asia field campaign data really be used to support the contention that the uptake of HNO3 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 ?

Response: The study of Maxwell-Meier et al. (2004) does not report the exact values of the uptake coefficient. The authors wrote that 'The observations suggest that mass accommodation coefficients for HNO3 uptake by the mineral dust are a few orders of magnitude below 1 ... The results suggest that there may be some evidence for an increasing loss of carbonate (e.g., reaction of acidic compounds with mineral dust), with increasing relative humidity.' This is perhaps not a very strong support since the Maxwell-Meier at al. made assumptions about reaction time (from back trajectories) and degree of reaction (from the change of aerosol carbonate content). In addition, Referee 4 brought to our attention a recent study by Umann et al. (2005). The study of Umann et al. (2005) is perhaps the first field report on the uptake coefficient of mineral dust reaction with nitric acid. Although, the authors reported no RH-dependence of the uptake coefficient, the absolute values of the uptake coefficient are in surprising agreement with the values of our study for the respective humidity range. The text will be changed to include this newer reference as well.

Comment regarding Table 2 comparing to literature data

Response: We agree, we have indeed copied the wrong number from the Hanish et al. data. The table will be amended, taking also into account the other issues, especially also to mention the method to assess the surface area.

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