Referee 1

The presented work deals with experimental aspects of an important interfacial reaction of a NO*y* species for which considerable experimental backlog and remaining necessity exists regarding its role in numerical modeling of the troposphere. Definitive experimental results regarding the fundamental reactivity of “mineral dust” under tropospheric conditions are still outstanding and impatiently expected. The authors have investigated the reactions of N_2O_5 on the mineral dust proxies Illite and Arizona Test Dust (ATD) as a function of relative humidity at ambient temperature in order to discover a potential systematic trend of the uptake coefficient γ with the goal to extract fundamental chemical kinetic laws applicable to mineral dust of a given provenience. The authors have developed a superb, extremely sensitive and simple optical monitor of N_2O_5 and/or NO_3•free radical, namely cavity ring-down spectroscopy at 662 nm, that they have successfully applied to this laboratory study. I generally concur with the results and discussion by the authors but have a few remarks that I would like to see answered to the benefit of the readership of Atmospheric Chemistry and Physics.	We thank the referee for the detailed review and positive assessment of the topical nature of the work and quality of the experimental tools.
Pg. 24864, lines 9 to 16, and pg. 24865, lines 21 and following: authors claim an exponential rate law for the sum of k_d+ k_w as a consequence of the correlation between $[N_2O_5]$ and N_d displayed in Figure 4, both for Illite and ATD. However, at a closer look, $[N_2O_5]$ visibly droops below the straight line that is heavily weighted towards the high values of $[N_2O_5]$ at the beginning (origin) of the plot (Figure 4). This is unusual, because in general the opposite is true owing to the increasing importance of the background as the signal decreases in amplitude. The measurement precision being what it is, and surmising that the authors do the best job they can, a slightly different interpretation may be proposed.	We write that the variation of the N_2O_5 signal with the number of dust particles is “consistent with” the expressions involving the terms kd and kw we have used to derive the uptake coefficient, which suggest an exponential dependence of N_2O_5 concentration on the dust numbers for a given interaction time. We use the word “consistent” as we indeed recognise that the data no not extend over an extended variation in N_2O_5 signal (factor of 10) as would be the ideal case. Within experimental scatter there is an exponential dependence between the N_2O_5 signal and the number of dust particles. The

One may claim that at these fairly large values of [N_2O_5] partial saturation of uptake may occur at steady-state which would make the uptake rate constant k_d faster at lower values of [N_2O_5] under conditions of reversible and partial saturation of reactive surface sites. This “fall-off” effect of the apparently increasing value of k_d with decreasing [N_2O_5] may also be observed for N_2O_5/Saharan Dust in Figure 4 of the cited paper Tang et al. 2012 (PCCP, 2012, 14, 8551-85561). The authors gloss over the single-exponential rate law a bit fast for my taste in order to arrive at the probable, but perhaps debatable conclusion of “first-order” rate law for uptake.	“droop” identified by the reviewer is present in only two of the six decays presented. In one case (Illite) it is not observed in the dataset taken at the longest interaction time (injector position), where a change in the uptake rate due to surface saturation should be most apparent. In a revised version, we write: “While the N_2O_5 decay does not span a sufficient range to prove that these equations are appropriate, the experimental dataset displayed in Figure 4, plotting the measured N_2O_5 concentrations versus the dust aerosol number concentration for both illite and ATD particles at three different injector positions, is consistent with this.”
Knudsen flow reactor studies have shown over and over again that the rate constants generally do not follow first-order behavior, but the authors are a bit quick to dismiss these studies as not “atmospherically relevant”. I in part agree – surprisingly - with this statement because the evidence is subtle. However, these studies teach one a lot about rate laws and reaction products that are not (yet) accessible using AFT’s owing to experimental complexities. I am not so sure about the statement on top of pg. 24864 that γ is “in any case not dependent on the initial N_2O_5 concentration”. This rate law check is rarely performed, if at all, by flow tubers, more frequently by proponents of Knudsen flow reactor studies.	We are not entirely sure what the referee means when he says that, in Knudsen studies “rate constants generally do not follow first-order behavior”. We assume he refers to the fact that the loss rates are not independent of the initial trace-gas concentration and that the uptake coefficient derived from these loss rates are not independent of the surface area (or mass) of the bulk substrate. There is no reason why an aerosol flow tube (which overcomes the problems with diffusion limited uptake experienced by coated wall flow tubes) cannot deliver the same information regarding rate laws as a Knudsen reactor. Likewise, detection of products (both gas and aerosol phase) is possible as described in Tang et al. 2012. The uptake coefficients we derive here and elsewhere for N_2O_5 (Tang et al. 2012) are, within experimental uncertainty, independent of the initial concentration of N_2O_5. And show no systematic dependence on the surface area. There is nothing ambiguous about this statement.

A case in point related to the subject is made by Karagulian et al. (2006) cited by the authors where k_d (or γ_{ss}) decreases by a factor of three upon increasing [N_2O_5] by a factor of ten at N_2O_5 concentrations equal to or lower than used by the present authors. The same behavior of partial saturation of reactive surface sites has been observed for NO_3 interacting with mineral dust (Karagulian et al.,PCCP 2005, 7, 3150). Over the years I have not come across a single uptake process that was independent of the concentration of the gas phase species, with the exception of unitary systems, such as H_2O vapor on H_2O ice.	We refer the referee to our previous study (Tang et al. 2012) in which uptake coefficients of N_2O_5 showed (within experimental scatter) no dependence on N_2O_5 when the latter was varied by a factor of 60.
The gas-kinetic parameter Z_{11} (gas-wall collision rate) of a gaseous ensemble of molecules is proportional to the total surface area of the particles present. Figure 2 displays the distribution of the number concentration as a function of the aerodynamic diameter. A more appropriate display would be to plot the surface distribution as a function of Stokes (= geometrical) diameter in order to obtain an appropriately surface-weighted average value for A_d rather than the number concentration-weighted value. I assume that the authors have taken Figure 2 in order to deduce the "average surface area of dust particles" (pg. 24864, line 7). It would be instructive to compare the absolute values of the so-derived γ with the procedure presented by the authors. I am sure that the surface-weighting of the distribution of Figure 2 leads to the inverse shown: large particles are more important than the smaller ones, which leads to the suppression of the mode at 1.8 mm and the emphasis of the mode at 8 mm for ATD. For illite there will be a shift of the mode towards higher values. As a result γ_{exp} may become smaller if A_d shifts to higher values owing to surface-weighting.	The surface areas used were, of course, calculated from the surface weighted distribution. We already state this on page 24861. We did not derive an average surface area from the peak of the number distribution. The relation between stokes and aerodynamic diameters is given on page 24861. We prefer to plot the distribution as measured rather than subsequent to the conversion factors and assumptions listed in the text. We agree that the larger ATD particles will dominate the uptake. This will however not lead to a change in our calculated uptake coefficient as we have already used the correct surface area (see above). On page 24861 the average surface areas for ATD and Illite are listed. Due to the large diameter mode, the ATD particles have average surface areas a factor 6 larger than Illite even though the small modes are both at about 1.8 microns. To clarify, we now write: "The average surface area were calculated by dividing the total surface area (per volume) of all the particles with the number (per volume) of the particles"

It is not quite clear how absolute concentrations of N_2O_5 have been obtained by the authors. Although this knowledge is not necessary in the present context if first-order behavior of the rate law is postulated, this question triggered my curiosity as the authors reveal the N_2O_5 concentration, on the order of (8-24) 10^{12} molecule cm^{-3} (Table 1).	The flow tube concentration of N_2O_5 is derived from the CRD measurement (which is absolute) and the dilution factor between flow tube and CRD. This is described on page 24862.
A first-order rate constant for disappearance of NO_3, k_I= 0.6 ±0.27 s^{-1}, was measured at ambient temperature by Karagulian et al. (2005, see above) for a FEP-coated Knudsen flow reactor. The authors measure k_w that is approximately a factor of six lower than this value (Schuster et al., 2009) at ambient temperature.	It is unclear what comparing wall loss rates in a FEP coated Knudsen reactor (mTorr pressure) or a FEP coated glass tube tells us. The former is limited by surface reactivity, the latter by diffusion.
However, caution needs to be exercized because N_2O_5 is undergoing dissociation at roughly 100°C such that the NO_3 disappearance may be faster. We routinely “sacrificed” about 50% of NO_3 in favor of NO_2 in our studies when we generate $NO_3$from thermal dissociation of N_2O_5.	Knowledge of the first order loss of NO_3 in the cavity at 100 °C is important only for absolute determination of concentrations. As we measure relative changes in concentration of N_2O_5 here, cavity losses of N_2O_5 or NO_3 are not relevant.
What is the HNO_3 level in your experiment? This is another pegpoint for the quality of the used N_2O_5.	The N_2O_5 crystals were carefully prepared using dried gases, and as N_2O_5 will strip H_2O from glass and Teflon walls of H_2O after a while. Also, eluting the N_2O_5 from a crystalline sample at -50 °C will favour transfer of N_2O_5 rather than HNO_3 to the gas-phase. We have not measured the HNO_3 impurity in this study but do not expect it to be larger than the < 5 % reported previously from this lab (Wagner et al, Atmos. Chem. Phys. 8, 91, 2008) We mention this in the revised manuscript.

Pg. 24860, lines 13 to 18: Figure 2 conveys a fairly moderate aerosol number concentration for small diameters, and a reasonable one for larger particles. Nevertheless, the surface area of suspended particles is much smaller than the surface area of the vessel walls.	It is not the sensitive detection of N_2O_5 that enables the "separation" of kw and kd, but the stability of kw. As the referee correctly indicates, kw is stable ("independent of fluctuations") as it is diffusion limited.
I do not get a feeling for the importance of $k_w$vs. K_d while reading the paper, which would be useful in view of the highly reactive nature of the dust-laden walls of the flow tube. It is a clever idea by the authors to make the wall-loss rate independent of fluctuations, but I am left with the question of the absolute values of both contributions to the total rate of N_2O_5 disappearance. Is it the extremely sensitive detection of NO_3 that enables the successful separation of k_w and k_d? This point should be belabored a bit more by the authors	As we state on page 24864, we do not need to know kw as long as relative changes in N_2O_5 concentrations induced by dust pulses are larger than fluctuations in kw on the same time scale. However, we recognise that this information is useful and now write: "The wall loss constant, k_w was about ~0.04 s^{-1} which can be compared to a first-order loss rate constant due to uptake to illite of k_d ~0.1 when N_d = 5000 cm^{-3}. Note that it is the stability (rather than size) of k_w during an experiment that limits the experimental accuracy."
Pg. 24866, lines 24 and following regarding surface OH-groups and pg. 24868, line 26 and following: What are the alternatives between reaction of N_2O_5 with surface OH-groups and heterogeneous hydrolysis? It would be instructive to clearly formulate the different reaction paths.	As we monitor only the gas-phase loss of N_2O_5, we cannot (and do not attempt to) derive detailed mechanistic information, but have simply shown that our RH dependences can be considered consistent with conclusions made in previous studies in which surface spectroscopy (Seisel et al., 2005) and theory (Messaoudi et al 2013) revealed an important role of OH groups for uptake of N_2O_5 to mineral substrates.
First remark: N_2O_5 hydrolysis like any other organic or inorganic hydrolysis is either general acid- or base-catalyzed because both H_2O and N_2O_5 are closed shell compounds and react only slowly in the absence of a catalyst. A second remark concerns the surface OH-groups which either behave as acids or bases. In the presence of adsorbed H_2O (which is seldom absent) it is probably immaterial (and impossible) to distinguish between hydrolysis and acid/base-catalyzed (hydrolysis) reaction. For instance, TiO_2(rutile, boehmite or anatase) have surface OH-groups ranging from very acidic to very basic all at once! I can think of the following in this regard: acidic OH group: $M^+OH^- + NO_2^+NO_3^- \rightarrow MO^- + HNO3$(or	The two reaction mechanisms, e.g. reaction with OH groups and hydrolysis by surface adsorbed water, have been proposed, formulate, and detailed by Seisel et al (2005). Therefore, we have referred to original work of Seisel. We do not see any gain in adding more speculative discussion of a mechanism on which we have no real handle in these experiments.

nitrate after neutralization) + NO_2^+ basic OH group: $M^+OH^- + NO_2^+NO_3^- \rightarrow M^+ + HNO_3 + NO_3^-$ In my view the basic pathway is favored because it generates the stable nitrate anion compared to the unstable nitronium ion. But surprises do happen: remember the heterogeneous reaction of N_2O_5on deliquescent sea salt particles...There the nitronium ion was surprisingly stable.	
Pg. 24867, line 14 and following: This is the first time I hear that quartz does not have (intrinsic? What is that?) surface OH-groups.Fused and crystalline quartz and Pyrex (75% fused SiO_2) are slightly acidic just because of surface OH-groups. You may even titrate them as a function of rh. All inorganic oxide surfaces have surface OH-groups capping (terminating) the surface. But perhaps the authors address a distinctly different point that I did not get	This is true. We have revised the text as below. As we are blind to the surface, this discussion is not intended to be more than speculative / qualitative in nature. The results for ATD reveal a rather different picture, with lower uptake coefficients (factor ~10 lower than illite at 0 % RH) and (at most) a weak dependence on RH. The lower uptake coefficients may be related to the mineral composition of ATD which consists mainly of feldspar and quartz (Broadley et al., 2012), which may have less (and/or less reactive) surface OH groups. The weak dependence on RH is probably related to the fact that the hygroscopic growth of ATD particles is very small (Gustafsson et al., 2005;Vlasenko et al., 2005) and therefore even at high RH, the amount of adsorbed water on the surface does not contribute significantly to N_2O_5 solvation/ionisation but may still result in deactivation of surface OH groups as shown by Goodman et al. (2001). Surface sensitive methods would be required to confirm this postulate.
The equilibrium between N_2O_5, NO_3 and NO_2 should perhaps make reference to the additional and irreversible pathway $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ which is responsible for the slow N_2O_5 degradation to NO_2 in static or long-residence time (= slow flow) laboratory experiments, especially at elevated temperatures where the forward reaction of N_2O_5 decomposition is fast.	This reaction has never been firmly established as the source of N_2O_5 loss (see Sander, S. P.,et al.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov., 2011. It might not be a gas-phase process and is usually ignored.
Pg. 24857, line 15 and following: laboratory experiments established the existence and properties of $ClNO_2$long before they were detected in the field!	We have added a reference to the pioneering laboratory study (Finlayson-Pitts, 1989).
Pg. 24861, line 24: “bin” instead of “pin”	correction will be made

(probably)	
Pg. 24867, line 3: “...uptake coefficient (0.04) on illite is similar to....”	correction will be made
Pg. 24867, line 26: “Bulk samples”.	correction will be made
Pg. 24868, line 12: “studying”; line 26: “...that under these....”	corrections will be made
Pg. 24869, line 24: “deserts”	correction will be made
Amendment from Referee 1	
I would like to post an amendment to the third "bullet" in my referee comment: (a) the length scale of the average size of the mineral dust particles (illite, ATD) are micrometers, not millimeters; (b) I stand by my point on surface-weighting of the size distribution function in terms of number concentration: at constant mass the total surface area decreases as does the gas-wall collision frequency "omega" on all particles considered in the volume. This should make "gamma" larger, not smaller, at a given (measured) value of the rate constant k according to: k = gamma x omega.	This comment has been answered as described above.