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Interactive comment on “Reactive uptake coefficients for heterogeneous reaction of N2O5 with submicron aerosols of NaCl and natural sea salt” *by* D. J. Stewart and R. A. Cox

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Referee’s comment:“Stewart and Cox have presented a concise description of their measurements of the reaction of N_2O_5 on NaCl aerosol particles. However, it seems that a few details in their methodology need to be addressed. These details may lead to a significant change in their results for the reaction rate coefficient k_r.”

We have reanalysed the data for the observed uptake rates on NaCl and sea salt aerosol. As predicted there are some changes in the derived uptake coefficients, but they don’t change the overall conclusions of the work. We will produce a revised version of the paper describing the new analysis. We offer the following detailed responses to the points raised.

Specific comments. “The authors posit that γ is a function of particle size. In principle, they should be able to show this by showing a dependence of measured γ on particle size distribution. Unfortunately, this was not shown. In this respect it is worth pointing out that the weak size effect observed by Thornton et al. was not for the same type of aerosols. Nonetheless, it would help the reader if it is stated that it is assumed that γ is a function of particle size, preferably at the beginning of the analysis section. Mentioning this early on is important because if the uptake coefficient is $\gamma(r)$, then it should be included in the kinetic expression E1. Then E1 would be integrated over the size distribution where $k^I = \Sigma dk^I$ where $dk^I = 0.25\gamma(r)cdSA(r)$."

We have amended our manuscript to treat the size dependence of the uptake coefficient more explicitly, in line with the referees suggestions. We have expanded the experimental section (on page 575) regarding the data analysis to include a discussion of the polydisperse nature of the aerosol and the uncertainties arising from this complication.

"If the width of the distribution is not too large, (ln $\sigma <= 0.3$) E1 can be used but then γ is for a radius of $r_p * \exp(2.5 * (ln\sigma)^2)$ where r_p is the peak of the number distribution (e.g., JGR, v100, 18775, 1995, Appendix.) However, it is not clear that this shortcut is valid here as the standard deviation, which really appears to be $\log_{10}\sigma$, is quoted at 0.27. The change in procedure detailed here may lead to a larger reacto-diffusive length and thus to significant changes in the extracted rate coefficients. Yet their discussion of size dependent effects alludes to some sort of correction in this respect but it is hard to tell exactly what was done. If the authors do as is recommended above and start out with the assumption that γ is a function of r, this may help the paper's clarity."

We are unable to make the approximation used in JGR, 1995 because of the large width of the aerosol size distributions (about ln $\sigma = 0.65$) used in this work. This means that the uptake coefficients are not representative of any one particular particle size. As a starting point we have assumed that uptake coefficients derived using equation E1 are for the surface-area weighted mean radius. We have amended the document to state this explicitly. In light of the width of our distribution, we have extended the analysis to examine the effect of the main approximations used in the earlier analysis

Firstly, the uptake is assumed to be volume limited, and equation E3 is used to derive a pseudo first-order rate coefficient, k$_r$. These values are the same as reported in table 2. We agree with the referee that this leads to an underestimate of reacto-diffusive length, and have examined this point further in the discussion.

To this end, equation (E2) is now used to examine the effect of the assumption of volume-limited uptake, making use of the size distributions obtained from the DMA. Using the k_r values reported in table 2, uptake coefficients are calculated as a function of radius using equation E2 and these are used as input to calculate a rate coefficent for each size bin. These are then summed, taking into account the measured size distributions, to give an overall rate coefficient which is compared with the observed rate coefficient, k$^{\mathrm{I}}$. In general, we find that the pseudo first-order liquid phase rate coefficient, k$_r$, calculated using equation (E3) overestimates the overall rate of uptake, and that best fits are obtained with values of k$_r$ in the range 900 to 1500 s^{-1}. These are significantly lower than the values of k$_r$ calculated using equation E3, leading to an increase in the reacto-diffusive length.

These fitted values of k$_r$ are then used in equation E4 to calculate the thick film uptake coefficients. These are only slightly higher than those reported in table 2.

“The middle paragraph on p.10 is notably confusing as they are quoting a different value for l than that in Table 2.”

This will be amended in the new text; there were a number of errors in the text and in Table 2 which we will correct in the new document

“Furthermore, one should not use the volume approximation E3 when l is comparable to, or less than, the peak radii for the volume distribution.”

Nevertheless, our re-analysis, taking into account the size-dependence of the uptake, shows that the errors introduced can be corrected by an iterative procedure. E3 pro-

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vides a good starting point for this process.

“Finally, it is not clear what $< r >$ is: they quote values near 100 nm whereas the peak of the volume distribution is 250 -300 nm.”

The text now makes a clear distinction between surface-area weighted and volume-weighted mean radii. Please note that Figure 1 shows the size distributions in terms of particle diameter.

“Finally, it is not clear that HNO_3 concentrations can be neglected in the droplets. In addition to the nitrate effect, this will affect the pH of the droplets. As the authors indicate, a few hundred ppbv [N_2O_5] converted to HNO_3 and fully taken up and distributed throughout the volume of the droplets will result in 1-2 M [NO_3^-].”

The reaction of N_2O_5 in NaCl produces $NaNO_3$, not HNO_3. However, the possibility that nitric acid is formed elsewhere in the aerosol flow tube and deposited into the aerosol does exist, but we believe that once formed on the surface of the flow tube, nitric acid will remain adsorbed. The possible role of NO_3^- inhibition is discussed in the article but we do not think there will be a pH effect.

“One may need to consider that [nitrate] is larger near the surface of the droplets as N_2O_5 (and HNO_3) uptake is ongoing: the time constant for equilibration of [NO_3^-] within the droplets is on the order 10^{-4} s (compare to the hydrolysis rate of 1-to-10x10^4 s^{-1} for N_2O_5.)”

This is a good point but we dont have any way of quantifying the inhibition in a non-homogeneous reaction medium. It is certainly possible that formation of NO_3^- at the droplet surface in the initial stages of the reaction could be responsible for reduced measured uptake coefficients. The initial uptake kinetics are not accessible due to mixing constraints We see no deviation from first order kinetic behaviour which would reflect a time dependence of the uptake rate in the accessible region.

The new values of k_r are much lower, and the discussion on the relative rates for nitate

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inhibition will be revised accordingly

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