

Replies to comments for article “Efficient bulk mass accommodation of N₂O₅ into neutral aqueous aerosol” by G. Gržinić et al.

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Anonymous Referee #1

1. I am a bit confused by the nomenclature. In Figure 2 (and Equation 3) there is a [N₂O₅(p)] term. What is meant by that? It is clearly not the dissolved concentration of N₂O₅ in the particle. Is it instead the concentration of N* in the particle (as stated in line 37)? But this would be orders of magnitude lower than the level of dissolved unlabeled N. So, how do the authors scale N* concentrations to indicate the amount of N₂O₅ that has been taken up to the particle, which is what I believe this term represents? Also please use either C or [] nomenclature for concentration but not both.

Response: Thank you for pointing this out. Since the observables of the present experiment are gas phase labelled N₂O₅ and labelled product, thus labelled nitrate, in the aerosol phase, Equation (3) should more clearly refer to the fate of labelled molecules. We will choose a more clear notation and explain it more explicitly in the text to avoid confusion.

Action in manuscript: notation in equation (3) and Figure 2 changed

2. I must be missing a very important point in the paper, and would like the authors to explain this to make the paper clearer. In particular, I understand that the kinetics experiments with nitrate particles indicate a large uptake coefficient that can be interpreted as a large mass accommodation coefficient. But, I am at a loss to understand why the results with sulfate particles, that show roughly an order of magnitude smaller uptake, cannot also be interpreted as a mass accommodation coefficient measurement. If the reaction proceeds half through the left channel in Figure 3, then the labelled nitrate so formed should stay in solution. If the mass accommodation coefficient is really larger than 0.1 on aqueous droplets then the uptake coefficient in these experiments should have been at least this large. But the observations show much smaller uptake kinetics. Does this not imply that the mass accommodation coefficient on sulfate must not be as large as on nitrate?

Response: This is indeed an important point of the manuscript, and obviously we need to clarify this better. In absence of aerosol phase nitrate, labelled nitronium not undergoing hydrolysis will react with non-labelled nitrate coming into the aqueous phase as well and reform N₂O₅ and equilibrate with the gas phase again. Therefore, in absence of nitrate, uptake of labelled N₂O₅ is exactly following the fate of non-labelled N₂O₅. The fast accommodation and dissociation of labelled and non-labelled N₂O₅ into the aqueous phase is not becoming rate limiting. The amount of aqueous phase N₂O₅, nitronium and nitrate is in effective

Henry's law equilibrium with gas phase N_2O_5 , nitrate from the reaction of nitronium with water is only slowly building up. We will show some box model simulations to show this behavior in the revised version.

Action in manuscript: notation in equation (3) and Figure 2 changed

3. The results are interpreted in terms of bulk processes. With very high concentrations of nitrate, could the chemistry for those particles be happening on the particle surface? In this case the kinetics would be surface-uptake controlled and not bulk-controlled, and then this would not be a measurement of the bulk mass accommodation coefficient. Overall, is it possible that the observations are consistent with (fast) surface uptake for the nitrate experiments and with (slower) bulk uptake for the sulfate experiments?

Response: In principle, we cannot exclude a surface contribution. Since also the suggested bulk accommodation is followed via obviously very fast dissociation into nitronium and nitrate, this process will occur close to the surface anyhow, with a short reacto-diffusive length (in contrast to the much slower hydrolysis reaction of nitronium with H_2O). Therefore, for instance, varying the surface to volume ratio of the aerosol would not allow differentiating bulk from surface accommodation. Though, we would prefer not invoking a surface process if bulk phase processing explains the observation. But we will place a caveat on this in the revised version.

Action in manuscript: short paragraph added towards the end of the results and discussion section.

4. It is stated a few times that nitric acid does not volatilize under the conditions of the experiments (and this was the reason to use neutral particles and not acidic ones). Can the authors confirm that this is the case for their conditions?

Response: it is correct that progressing uptake of non-labelled N_2O_5 during the residence time in the flow tube leads to acidification of the particles. However, with non-labelled N_2O_5 being in the low ppb range, the maximum HNO_3 concentration in the aqueous phase becomes about 10^{-3} M leading to a pH of around 3 so that evaporation should not play a role. As explained in Grzinic et al. (2014), measurable evaporation could be observed in the denuder detection system on the traps following that for N_2O_5 but was not observed in the present study. Though, unambiguous differentiation of that signal between HNO_3 evaporating from the particles and N_2O_5 formed from the back reaction of nitrate with nitronium would not be possible.

Action in manuscript: effects of HNO_3 described at the beginning of the results and discussion section.

5. Table 1: Please list how many experiments were conducted per experimental condition.

Response: Each experiment involved 15-20 activity measurements, each averaged over 60 s, for each injector position. Overall, replicates from several different experiment series

performed on several different operation days of the ^{13}N delivering facilities were averaged to obtain values and standard deviations reported in the table. This is due to the often only limited periods of stable ^{13}N production. This will be added to the experimental section.

Action in manuscript: information added to the end of the experimental section.

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Anonymous Referee #2

1) Most of the discussion centers on the uptake of N₂O₅ to nitrate aerosol. The conclusions drawn suggest large values for alpha and supports N₂O₅ ionization at the particle interface. What is less clear is if this is a general result for all aerosol at the same water activity. In the case of sulfate particles, labelled N₂O₅ likely evaporates from the interfacial region wo/the opportunity for exchange with unlabeled nitrate. The upper limit of 0.03 is achieved that is likely a combination of alpha, KH, and the reaction rates described. If KH and the hydrolysis rates are the same for sulfate and nitrate aerosol, is it correct to generalize the mass accommodation results derived from the nitrate aerosol experiments to all aqueous aerosol of comparable interfacial water activity? It would be helpful for the authors to provide some discussion on these points and the generality of the derived mass accommodation coefficient. I would find it very helpful if there was a second panel to Figure 3, which showed the processes for the sulfate particles.

Response: we agree that the present results are strictly valid only for the compositions used in the present experiments. Since the observed gamma values for the pure sodium sulfate case follow that expected for non-labelled N₂O₅, labelled N₂O₅ seems to follow the fate of non-labelled N₂O₅, since not enough non-labelled nitrate is building up to allow exchange with that pool and larger uptake for labelled N₂O₅. Therefore, in fact, strictly speaking we are unable to prove that alpha and dissociation in aqueous aerosol devoid of nitrate is as fast as in presence of nitrate. Nevertheless, it is reasonable to assume (and all other laboratory studies support this) that water activity drives the reactivity with N₂O₅ apart from the nitrate effect and the particle physical properties. Instead of a second panel to Figure 3, we will provide some results of box model simulations to demonstrate the different behavior of labelled and non-labelled N₂O₅ for the two cases. Unfortunately, the dataset is not large enough in terms of nitrate concentration range to more precisely constrain the individual rate coefficients as a function of water activity.

Action in manuscript: Apart from providing more details by using the box model calculations of both nitrate and non-nitrate containing cases, the discussion is now clearly differentiating between conclusions for nitrate containing aerosol as derived from the present experiments, and possible implications for aqueous aerosol of different composition.

2) Most of the aerosol flow reactor community is familiar with the kinetic equations shown, for unlabeled reactants. Are there any special considerations that need to be accounted for regarding single, vs multiple collisions of the labelled N₂O₅ with aerosol and the walls? Or rather, in Fig. 3, how many times would you expect a labelled N₂O₅ to cycle through a particle or the wall of the flow tube over the time constant of the flow reactor? Is this important to the analysis or derivation of the equations presented?

Response: no it is not important, since we integrate over many labelled molecules arriving in the detection system, and we statistically evaluate in what chemical form they are at the moment of detection. Thus the first order loss rate coefficient is correctly derived from the observed net loss or appearance rates, independent of the number of molecules contributing to these, as long as counting statistics is not limiting the error. In fact, the condensed phase cycling of N₂O₅ is very fast, and so is evaporation back to the gas phase, and the number of times an individual molecule (labelled or non-labelled) is entering the particle phase is limited by the collision rate with the particles, which is on the order of one per second for the aerosol conditions used. Since the number density of labelled molecules in the gas phase is of the same order of magnitude as that of the number density of particles, each particle receives at most one labelled N₂O₅ molecule during the residence time in the flow tube.

Action in manuscript: due to the presentation of a more detailed scheme to showcase the different pathways of labelled and non-labelled N₂O₅ in Figure 3a and e, as well as the aqueous phase turnover rates, this aspect is much more clear now.

3) What is the effect of labelled HNO₃ that is generated in the source region? How would this be interpreted in the experiment. It is not uncommon for N₂O₅ sources to be 10:1 HNO₃ to N₂O₅. What is the expected ratio in this experiment?

Response: The citric acid coating used to trap N₂O₅ would not be able to differentiate from HNO₃, in that sense the detection system is not able to resolve this. Though, the wall loss rate coefficient of labelled HNO₃ is so large that for the present flow tube surface to volume ratio the dominant fraction of it would deposit at the entrance of the flow tube (Guimbaud et al., 2002), which was not observed; the uptake coefficient for labelled N₂O₅ on the reactor walls was in the range of 10⁻⁷, which would also not lead to substantial HNO₃ production.. We will add a note on this in the revised version.

Action in manuscript: more details about the impact of HNO₃ is given at the beginning of the results and discussion section.

4) Like reviewer #1, I am also confused by the notation of [N₂O₅]_p. It would be helpful if equation 3 and Figure 2 were consistent in notation. It would also be helpful to denote between labelled and unlabeled here, as the unlabeled N₂O₅ uptake coefficient to nitrate aerosol could be pretty small even at high labeled N₂O₅ uptake coefficients, correct?

Response: as already mentioned in the response to Referee #1, we will adapt the notation and make clear that the quantities in equation refer to labelled molecules (which were the only direct observables of the experiment). Yes, the net uptake of non-labelled N_2O_5 to nitrate containing aerosol is very low (Table 1, lowest row).

Action in manuscript: notation in equation (3) and Figure 2 changed

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Anonymous Referee #3

1. If I understand correctly, the net uptake is determined by measuring the gas-phase ¹³N and the particle phase ¹³N, where it is assumed particle phase ¹³N was only derived from ¹³N N₂O₅, and that any ¹³N nitrate produced from N₂O₅ stays in the particle phase.

Response: yes, this is correct. Gas phase ¹³N is separated into N₂O₅ /NO₃ and NO₂ respectively, and the contribution of NO₃ to the signal is corrected for as mentioned in the text. After removal of gas phase N₂O₅ at the entrance of the detection system, only nitrate remains in the particle phase. The approach has been tested with ammonium sulfate (Grzinić et al., 2014) and used in a previous study with citric acid aerosol. The potential occurrence of evaporation of ¹³N labelled HNO₃ has been discussed in these previous studies and have been the reason to only work with neutral aerosol in the present study as described in the introduction.

Action in manuscript: This is now more explicitly explained towards the end of the experimental section.

2. Lines 25 on – what are the relative amounts of NO₂ and N₂O₅. NO₂ is known to undergo slow disproportionation to HNO₃. Is this a concern here? What about wall production of ¹³HNO₃ and its incorporation into the particles due to revolatilization?

Response: the ratio of NO₂ to N₂O₅ is about 1 at 50% RH and about 0.45 at 70% RH. In the dry N₂O₅ online production flow tube, NO₂ losses (due to heterogeneous disproportionation) are undetectable (<10⁻⁸). Disproportionation of NO₂ in the aerosol phase is negligible. As mentioned by Referee #2, HNO₃ would rather be of concern as a product of hydrolysis of N₂O₅ on the walls, for which we did not have evidence to impact on the measurements (see our response there). We have been more concerned by evaporation of non-labelled HNO₃ from the walls that might lead to additional acidification and may thus contribute to the evaporation of labelled HNO₃ product from acidic aerosol discussed in our previous studies (Grzinić et al., 2014). But given the *k_w* values reported, and if assuming that all N₂O₅ lost to the walls would lead to HNO₃ in the gas phase and that HNO₃ would be taken up with unit uptake coefficient, particle phase nitrate and acidity remain dominated by that deriving from direct N₂O₅ uptake.

Action in manuscript: The effects of HNO₃ are now discussed in more detail at the beginning of the results and discussion section.

3. I'm not sure that the net reaction probabilities and their interpretation is correct or at least well explained. I can see why the net uptake measured in this ¹³N system on nitrate containing particles would be higher than that for unlabeled N₂O₅ on nitrate containing particles, due to the added channel of "isotope exchange" (for short). But I do not see why there would be an order of magnitude larger net reactive uptake of ¹³N N₂O₅ on nitrate containing particles compared to ¹³N N₂O₅ reacting on sulfate particles. I think a simple box model using the ratio of k₅/k₇ and nitrate and water molalities might help.

Response: as mentioned above we will show some box model simulations in the revised version to show the different behaviors of labelled and non-labelled N₂O₅ in presence and absence of nitrate. Essentially, in absence of nitrate, labelled N₂O₅ behaves as non-labelled N₂O₅, because the amount of non-labelled nitrate in the particle phase is not enough for the 'isotope exchange' to become effective. In turn, it remains difficult to fully constrain rate coefficients for the different elementary reaction based on the limited dataset only.

Action in manuscript: Box model calculations are supplied and explained in the text in detail, along with the comparison between the cases of nitrate containing aerosol and pure sulfate. The isotope exchange becomes much more apparent, also from the more detailed reaction scheme provided in Figure 3, accompanying the box model results.

4. Or the description of the results and their interpretation needs to be clearer. I don't see where the limitation in the sulfate system is to produce that much lower of a net reaction probability, if there is equal probability of ¹³N N₂O₅ becoming ¹³NO₃⁻ and ¹³NO₂⁺. What would be the limitation to ¹³NO₂⁺ in the sulfate particles that doesn't exist in the nitrate particles?

Response: as mentioned just above, ¹³NO₂⁺ simply reacts with non-labelled nitrate back to N₂O₅ if not reacted with H₂O to form labelled nitrate. Therefore, on sulfate, the labelled N has the same fate as non-labelled N.

Action in manuscript: as mentioned above the comparison between the two cases is now explicitly explained in plots of the box model calculation results and the reaction scheme.

5. Lines 10 onward, page 2 – I don't think all previous estimates of bulk accommodation were as low as implied here, only that net reactive uptake was lower. In other papers, a typical assumption was also that the accommodation coefficient was not limiting net uptake, see for e.g. Bertram and Thornton ACP 2009 and others.

Response: ok, we will detail this a bit more to mention the various limiting processes (dissociation, accommodation) and their ranges that have been applied to explain different datasets.

Action in manuscript: An explicit discussion about the different limiting processes is now given.

6. Line 23, page 5 – sentence that starts here as a double negative at the end, making it difficult to interpret the meaning. Suggest: Thus, in this branch, all 13N labels remain in the aqueous phase given that HNO₃ evaporation from neutral aerosol is unlikely.

Response: ok, thank you.

Action in manuscript: text changed accordingly.

7. Line 7, page 6 – this paragraph is interesting. In the Bertram and Thornton parameterization, there is a dependence of the equilibrium between N₂O₅(aq) = NO₃⁻(aq) + NO₂⁺(aq) on the water activity (molar concentration in that paper) that was inferred from the behavior of observed uptake coefficients. This dependence was in addition to that inferred for the fate of the NO₂⁺. Seems this presents a possible physical explanation.

Response: Thank you for this hint; we are going into substantially more detail in the revised version to discuss the different kinetic assumptions in different suggested parameterisations and schemes, along with the box model calculations. This then also includes more details with respect to the dependence on water activity.

Action in manuscript: in addition to the extended discussion, we also reiterate the point of salting effects and the different kinetic regime towards the end of the results and discussion section.

8. Conclusions, last sentence: “The absence of accommodation limitation also helps rationalizing results from field experiments (Phillips et al., 2016; Wagner et al., 2013), where under some conditions uptake coefficients constrained by combined N₂O₅ and aerosol measurements are larger than those suggested by laboratory studies available to date.”

I’m not sure I completely agree with this conclusion. Do the measurements presented herein actually help explain field determinations of the reaction probability being larger than those measured in the laboratory? A few lines above, it was noted that the net reaction probability from this set of measurements was similar to previous values (at least for sulfate particles). The field observations are not deriving accommodation coefficients, but net reaction probabilities. I agree that if some previous laboratory studies concluded mass accommodation coefficients were <0.04, then field observations of net reaction probability greater than 0.04 would not be supported by such a conclusion (or vice versa).

Response: we agree, our point is maybe a bit too far going. We wanted to express the fact that most likely bulk accommodation would not limit uptake; and if strong sinks for NO₂⁺ would be present, accommodation would not limit reaction. We also agree that uptake coefficients inferred from field experiments larger than those in laboratory studies are not that frequent

and often remain uncertain. We will adapt the tonality of our conclusions to reflect this discussion.

Action in manuscript: Throughout the text, we have more clearly differentiated between nitrate containing aerosol to which our experiments relate, and non- (or less) nitrate containing aerosol, for which we can only suggest similar accommodation and dissociation rates. We have dropped the explicit comparison to the two field studies.

However, other laboratory studies and even parameterizations for similar aerosol systems as those used here, have concluded or assumed mass accommodation is not limiting (e.g. Bertram and Thornton, ACP 2009 and references therein), and thus that the limitations are in the chemistry and diffusion.

Response: We will mention the different limitations invoked in the different studies in more detail, and yes, we agree that physical effects (solubility and diffusion) might often be more important than considered so far.

Action in manuscript: as mentioned above, these physical effects are discussed in more detail now.

Thus, I would argue that for the reaction probabilities derived from field measurements that are larger than some laboratory measurements (pretty small fraction) are because of three possible reasons: (1) laboratory measurements have an additional limitation to net uptake not present (or reduced) in the atmosphere (could be salting out as suggested), (2) there are additional faster reaction pathways for N₂O₅ in ambient aerosol particles not yet probed in the laboratory, or (3) because the assumptions required in deriving the reaction probabilities from field observations are flawed.

It is hard to imagine there is something that reacts with NO₂⁺ much faster than Chloride in solution (though it is possible), and in aqueous sea salt particles, the reaction probability is still only measured to be similar to that on aqueous sulfate particles. That to me suggest the limitation that seems to keep reaction probabilities < 0.05 at room temperature is less likely the NO₂⁺ chemistry and instead the solubility, dissociation, and diffusion beforehand. Anyway, that is a long winded way of saying that I don't think there is support for that conclusion as written.

Response: we agree, we will summarize this discussion in the conclusion to reduce the potential impact of knowing that bulk accommodation is fast. The study remains certainly valuable enough because it provides direct evidence for the elementary reactions underlying aqueous phase N₂O₅ chemistry and also allows constraining their rate coefficients at least for an aqueous aerosol with high nitrate content. We will adapt the tonality of our conclusions to reflect this discussion.

Action in manuscript: as mentioned above, we have now avoided a too detailed discussion of field experiments and their implication, but more explicitly constrain the conclusions to the aerosol compositions actually studied.

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Anonymous Referee #4

1. I'd like the authors to include an estimate of the mixing ratio of N₂O₅ in the flow tube, as well as HNO₃, as well as V_a and S_a values (needed in the diffusion correction and to establish the role of possible aerosol size effects in the uptake process).

Response: The aerosol surface area density has already been given in the original table, and the average diameter is mentioned in the text along with the discussion of the diffusion correction.

As mentioned in the reply to question 3 from Referee #2, and question 2 from Referee #3, the design of the experimental setup does not allow to directly assess the levels of HNO₃. As discussed there, for the configuration used in the present setup, we would have lost labelled HNO₃ to the walls efficiently, and based on the measured wall loss rates, the non-labelled HNO₃ levels building up as product would remain low enough to not significantly affect nitrate levels or acidity in the aerosol phase. The gas-phase non-labeled NO₂ and N₂O₅ concentrations were around 10¹¹ molecule cm⁻³. Both aspects will be explicitly mentioned in the revised version.

Action in manuscript: Effects of HNO₃ are discussed in more detail at the beginning of the results and discussion section.

2. The results hang together well but the low uptake onto sodium sulfate aerosol needs to be discussed in more detail. In particular, the question needs to be addressed as to why is it so low - lower than the reported value by Wahner et al. of 0.037 (+ 0.008 - 0.019)?

Response: As mentioned in the response to the question below, crystallization of the Na₂SO₄ aerosol at 50% is the most likely explanation for the low uptake value measured. The value reported in Mentel et al (1999), which was measured at 71% RH, is consistent with our measurement at 70%. However the measurement done at 50% RH is much closer to the values reported in Hallquist et al. (2003) for dry (NH₄)₂SO₄ aerosol. This will be added in the revised version.

Action in manuscript: This has been added to the results and discussion section.

3. The aerosol is dried to 40% RH ('to prevent efflorescence' line 39, page 2). This is quite far below the reported efflorescence RH of Na₂SO₄ of 58%, (e.g. quoted in J. Phys. Chem. A, 2007, 111 (42), pp 10660–10666), so partial or complete efflorescence may explain the low values of uptake observed for the 50% RH case of Na₂SO₄, as uptake onto solid sulfate is known to be slower. Could this be a possible reason?

Response: Indeed, partial or complete crystallization seems like the most likely explanation, as mentioned by the reviewer, and in light of what is reported by Gao et al. 2007 with regards to the efflorescence relative humidity for Na₂SO₄. We will update the paper to reflect this.

Action in manuscript: As mentioned above, this has been added to the results and discussion section.

4. I think the discussion of salting effects requires more detail (do they have any evidence for the salting they propose?) and to be better linked to variation in RH.

Response: within the limited data set of this study, it is difficult to become more conclusive about the salting effects. As mentioned in the discussion, on page 6, from line 7, the fact that the water activity had a stronger effect on the uptake coefficient than different (though still high) nitrate to sulfate molar ratios. As indicated above in response to referee #3, we could only add that Bertram and Thornton (2009) have seen independent evidence for a water activity dependent equilibrium. Also the application of a more detailed kinetic scheme in box model calculations shown in the revised version does not allow constraining the solubility further.

Action in manuscript: This discussion has been added towards the end of the discussion section when reiterating the physical effects on the kinetic regime.

References

- Gao Y., Yu L.E., and Chen S.B., Efflorescence Relative Humidity of Mixed Sodium Chloride and Sodium Sulfate Particles, J. Phys. Chem. A, 111, 10660–10666, 2007.
- Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1, 5451-5457, 1999.
- Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N₂O₅ on sub-micron sulfate aerosols, Phys. Chem. Chem. Phys., 5, 3453-3463, 2003.

Efficient bulk mass accommodation and dissociation of N₂O₅ into neutral aqueous aerosol

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Abstract. An isotope exchange experiment with the short-lived radioactive tracer ¹³N is used to trace N₂O₅ uptake into nitrate containing aqueous aerosol particles. While uptake of ¹³N labelled N₂O₅ to deliquesced Na₂SO₄ aerosol is consistent with previous studies, in presence of aerosol phase nitrate efficient exchange of labelled nitrate with the non-labelled nitrate pool was observed. The experiments provide direct evidence for efficient bulk mass accommodation of N₂O₅ into aqueous solution with α_b > 0.4 at room temperature, as well as for the fast disproportionation-dissociation into nitronium and nitrate. While for experimental reasons this study is limited to nitrate containing non-acidic aerosol, it is likely that bulk mass accommodation and dissociation is-are not limiting N₂O₅ uptake also under wider ranges of conditions.

1 Introduction

The central role of NO_x in the regulation of the oxidative capacity of the atmosphere is well established. N₂O₅, an important species of the nighttime chemistry of nitrogen oxides, has been identified as one of the major reservoir species and potential sinks of NO_x (Abbatt et al., 2012; Chang et al., 2011). NO₂ reacts with O₃ to form NO₃, which then react together to form N₂O₅ (R1).

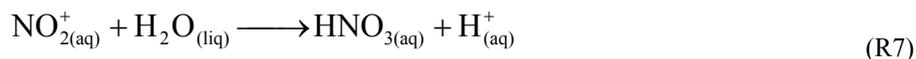


Depending on location N₂O₅ may be removed primarily by heterogeneous hydrolysis to nitric acid or other products on aerosol surfaces, providing thus a nighttime sink for atmospheric NO_x (R2) (Abbatt et al., 2012; Chang et al., 2011).



Removal of N₂O₅ leads to a reduction of atmospheric NO_x and consequent reduction of tropospheric ozone and thus the oxidative capacity of the atmosphere (Dentener and Crutzen, 1993; Evans and Jacob, 2005). The reactivity of N₂O₅ with aerosols has been of ongoing interest for the past two decades. Laboratory investigations have encompassed measurement of uptake kinetics to a wide array of inorganic aerosols, like H₂SO₄/sulphates (Hallquist et al., 2003; Hanson and Lovejoy, 1994), NaCl/marine aerosol (Gaston and Thornton, 2016; George et al., 1994; Thornton and Abbatt, 2005), nitrate containing inorganic aerosols (Hallquist et al., 2003; Mentel et al., 1999; Wahner et al., 1998) and mineral dust (Karagulian et al., 2006; Wagner et al., 2008). Further constraints have also been derived from field observations of N₂O₅ and aerosol abundance and composition (Bertram et al., 2009; Phillips et al., 2016). The uptake coefficient γ (defined as the probability that a gas kinetic collision of a molecule leads to its uptake at the interface) on deliquesced inorganic aerosol is in the 10⁻¹-10⁻² range. Organic aerosol on the other hand presents a wider range of

reactivities, with values approaching those of inorganic aerosols in certain cases such as for malonic acid (Griffiths et al., 2009; Thornton et al., 2003) at around 10^{-2} , while in other cases the uptake coefficients go down to 10^{-3} - 10^{-5} , such as for some polycarboxylic acids like citric acid (Gržinić et al., 2015), succinic acid or humic acid (Badger et al., 2006; Griffiths et al., 2009), long chained fatty acids and polyalcohols (Gross et al., 2009) that indicate varying effects of water content and viscosity on the reactivity and kinetic regime. Additionally, coating aqueous particles with insoluble organic films has shown to have an inhibiting effect on N_2O_5 uptake (Anttila et al., 2006; Folkers et al., 2003) by restricting transport from the gas phase to the aerosol phase, reduced solubility in the organic phase or limited water availability. The hydrolysis of $N_2O_5(g)$ is believed to proceed through a multistep process (Behnke et al., 1997; Mozurkewich and Calvert, 1988): molecular solvation (R3) is followed by dissociation into nitronium (NO_2^+ , or its hydrated form $H_2ONO_2^+$) and nitrate (R4) with a rate coefficient, k_4 , estimated between $10^5 s^{-1}$ and $10^7 s^{-1}$ (Mentel et al., 1999; Bertram and Thornton, 2009; Griffiths et al., 2009). The fate of nitronium is governed by competition between the reaction with nitrate to yield molecular N_2O_5 again (R5) with a nearly collision limited rate coefficient, k_5 , of $2.4 \times 10^{10} M^{-1} s^{-1}$ (Mentel et al., 1999), the reaction with $H_2O(l)$ to yield HNO_3 (R7) (k_7 , between 10^7 and $10^9 M^{-1} s^{-1}$ (Mentel et al., 1999; Behnke et al., 1997)-) or reactions with other nucleophiles (such as chloride ion) not considered further here.



The elementary reactions constituting this mechanism have been suggested based on the kinetic behavior as a function of a range of conditions, but have not been unambiguously been proven by detecting, e.g., NO_2^+ directly. As long as nitrate is a minority species in the aerosol phase, the loss of N_2O_5 is driven by reaction R7. Depending on the water content, either the transfer of N_2O_5 into the aqueous phase, R3, also referred to as mass or bulk accommodation, the dissociation (R4) or R7 are rate limiting according to current understanding (Abbatt et al., 2012).

On the other hand, in presence of significant amounts of nitrate in the aqueous phase, the loss of nitronium ion by reaction with nitrate back to N_2O_5 , R5, becomes significant, and the uptake of N_2O_5 becomes lower with increasing nitrate content in the aerosol phase, typically by an order of magnitude. This effect is referred to as the ‘nitrate effect’ (Abbatt et al., 2012; Bertram and Thornton, 2009; Hallquist et al., 2003; Mentel et al., 1999; Wahner et al., 1998).

Most studies conducted related to N_2O_5 reactivity with aqueous aerosol so far were based on measuring the net gas-phase loss of N_2O_5 due to uptake on an aerosol. The kinetics were described with a simplified lumped mechanism by assigning an effective Henry’s law constant, H , of N_2O_5 of about 2 to 5 $M atm^{-1}$ at room temperature and a net rate coefficient for the overall reaction of N_2O_5 with H_2O to HNO_3 , k_0^{II} , of around $2 \times 10^5 M^{-1} s^{-1}$ (Ammann et al., 2013)(Ammann et al., 2013; Bertram and Thornton, 2009; Griffiths et al., 2009), so that the uptake coefficient can be described via the resistor model as given by equation (1).

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{c}{4HRT\sqrt{D_1 k''[\text{H}_2\text{O}][\coth(r/l) - (l/r)]}} \quad l = \sqrt{\frac{D_1}{k''[\text{H}_2\text{O}]}} \quad (1)$$

Where α_b denotes the bulk mass accommodation coefficient, c the mean thermal velocity of N_2O_5 in the gas phase, D_1 the diffusion coefficient of N_2O_5 in the aqueous phase, usually set to $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for low viscosity aqueous aerosol, $[\text{H}_2\text{O}]$ the concentration of H_2O in M, r the particle radius and l the reacto-diffusive length. ~~The apparent levelling off of γ towards high relative humidity was explained by a limiting α_b was set to about of about 0.03 at room temperature to explain the apparent levelling off of γ towards high relative humidity~~ (Ammann et al., 2013) ~~or by introducing a dependence of the dissociation rate, k_4 , on the water content, leading to an apparent water content dependence of k_0''~~ (Bertram and Thornton, 2009). The effect of nitrate as mentioned above has been taken into account by using equation (2) instead of a fixed rate coefficient k_0'' :

$$k'' = k_0'' \left(1 - \frac{1}{1 + \frac{k_7[\text{H}_2\text{O}]}{k_5[\text{NO}_3^-]}} \right) \quad (2)$$

This expression requires the knowledge of the concentrations of water and nitrate and the ratio of the two rate coefficients k_7/k_5 , for which ~~a-values of between 0.02 and 0.06~~ leads to reasonable consistency with available data (Ammann et al., 2013; Bertram and Thornton, 2009). However, the actual size of the pool of dissolved N_2O_5 (or its dissociated products NO_2^+ and NO_3^-), the true value of the bulk mass accommodation coefficient, α_b , and the rate coefficients for the individual reactions remained ~~obscure/clusived~~. In this study, we make specific use of the short-lived radioactive isotope ^{13}N (Ammann, 2001; Gržinić et al., 2015; Gržinić et al., 2014) to trace the exchange of ^{13}N -labelled nitrate resulting from uptake of labelled N_2O_5 with the non-labelled nitrate pool in the aerosol phase. This allows obtaining a direct estimate of α_b and constraints for the N_2O_5 ~~disproportionation-dissociation~~ (R4) and the recombination reaction (R5). The tracer method is very sensitive in detecting phase transfer of labelled N_2O_5 at very low gas phase concentrations and thus is able to escape any artefact nitrate effect due to build-up of nitrate during the course of a kinetic experiment for experiments with aerosol without any nitrate initially as discussed by Gržinić et al. (~~Gržinić et al., 2015~~). However, this sensitivity comes at the expense of chemical selectivity in the sense that re-evaporating HNO_3 product from an acidic aerosol would interfere with the N_2O_5 measurement as shown in our previous study (Gržinić et al., 2014). We therefore performed the experiments presented here with neutral sodium sulfate and sodium nitrate aerosol to avoid this interference.

2. Experimental section

A detailed description of the experimental method and setup can be found in our previous publications relating to the production of ^{13}N labeled N_2O_5 (Gržinić et al., 2014) and uptake of N_2O_5 on citric acid aerosol (Gržinić et al., 2015). Here we will present a very cursory description of the ^{13}N production method and the changes that have been implemented to the experimental setup for the present uptake measurements.

The ^{13}N short lived radioactive tracer ($T_{1/2} \approx 10 \text{ min.}$) is produced via the $^{16}\text{O}(\text{p},\alpha)^{13}\text{N}$ reaction in a gas target by irradiating a 20% O_2 in He flow with 11 MeV protons produced by the Injector II cyclotron at the Paul Scherrer Institute, Switzerland. The highly oxidized ^{13}N labeled species are reduced to ^{13}NO for transport via a 580 m long PVDF capillary tube to the laboratory. Figure 1 shows a schematic of the experimental setup used in this study. ^{13}NO containing gas from the accelerator facility (50 ml/min) is mixed with $\sim 3 \text{ ml/min}$ of 10 ppmv non-labeled NO in N_2 from a certified gas cylinder and nitrogen carrier gas (only a very small fraction of NO is labeled with ^{13}N , about 10^{-6} and lower). This gas flow is mixed in the N_2O_5 synthesis reactor with a 50 ml/min

flow containing ~8 ppmv O₃ produced by irradiating a 10% O₂ in N₂ gas mixture with 185nm UV light. The reactor is a glass tube of 34 cm length and 4 cm inner diameter, lined with PTFE foil and operated under dry conditions to minimize hydrolysis of N₂O₅ on the walls. The gas phase chemistry of NO with O₃ results in the formation of NO₂, NO₃ and finally N₂O₅ (R1). The resulting gas flow is mixed with a secondary gas flow containing aerosol (720 ml/min) in an aerosol flow tube. This flow tube differs from the one that we used in our previous studies in that it is optimized for measurement of uptake coefficients in the 10⁻¹-10⁻² range. It consists of a glass tube 39.3 cm in length and 1.4 cm in inner diameter. The inside of the glass tube is coated with halocarbon wax to minimize N₂O₅ losses to the wall by heterogeneous hydrolysis. A PTFE tube (6 mm diameter) is inserted coaxially into the flow tube to act as injector for the N₂O₅ flow. The injector contains holes at the end which allow the N₂O₅ flow to be injected perpendicularly to the aerosol flow. Mixing is assumed to be rapid, and a laminar flow profile is assumed to have been established in the first few cm. A black shroud is used to cover the N₂O₅ synthesis reactor and the aerosol flow tube in order to prevent NO₃ photolysis and thus N₂O₅ loss. Aerosol is produced by nebulizing 0.1% wt. NaNO₃, Na₂SO₄ and 1:1 NaNO₃/Na₂SO₄ solutions in MilliQ water. The resulting aerosol flow is dried over a Nafion membrane diffusion drier (RH of the drying gas outside is adjusted to 40% RH to prevent efflorescence), passed through an ⁸⁵Kr bipolar ion source and an electrostatic precipitator to equilibrate the charge distribution and subsequently remove the charged particles, respectively. A humidifier is placed after the ion source to adjust the humidity of the gas flow to the required experimental levels. The overall gas flow exiting from the aerosol fast-flow reactor is split into two flows via a T-connector, one to an SMPS (Scanning Mobility Particle Sizer) system used to characterize the aerosol, consisting of a ⁸⁵Kr bipolar ion source to re-establish charge equilibrium, a differential mobility analyzer (DMA, TSI 3071) and a condensation particle counter (CPC, TSI 3022). The other part of the gas flow is directed into a parallel plate diffusion denuder system, where the various ¹³N containing gaseous species (N₂O₅, NO₃ and NO₂) are trapped by lateral diffusion and chemical reaction on a series of parallel, selectively coated aluminum plates: citric acid for trapping N₂O₅ and NO₃, a 1:1 mixture of NDA (N-(1-naphthyl) ethylene diamine dihydrochloride) and KOH for trapping NO₂. The aerosol particles, which have small diffusivity, pass without loss through the denuder system and are trapped on a glass fiber filter placed at the exit. The radioactive decay of ¹³N is measured by placing a CsI scintillator crystal with PIN diode detectors (Carroll and Ramsey, USA) on each of the denuder traps and the particle filter. ¹³N decays by β⁺ decay and the resulting positron annihilates with an electron with emission of two coincident γ-rays in opposite directions. The resulting signal can be related to the concentration of the species in the gas and particle phase by comparing the NO₂ concentration measured with a NO_x analyzer to the ¹³NO₂ and ¹³N₂O₅ signals on the denuder plates and particle filter, respectively. The gas-phase non-labeled NO₂ and N₂O₅ concentrations were around 10¹¹ molecule cm⁻³. The signal on the particle filter is related to aerosol phase nitrate after removal of dissolved N₂O₅ by stripping the gas phase N₂O₅ in the denuder system. The equilibrium established by R4 and R5 is fast enough to ensure that. In turn, the amount of dissolved N₂O₅ remains orders of magnitude smaller than the amount of nitrate built up in the particle phase along the flow tube, so that the net loss of N₂O₅ in the gas phase corresponds to the net gain of nitrate in the particle phase. Unfortunately, due to experimental limitations, only a limited number of measurements could be performed. The ¹³N tracer technique is dependent on smooth operation of the accelerator facilities and constant online ¹³N production to be successful, which is not always the case. Individual experiments involved the acquisition of datapoints consisting of 15-20 activity measurements, each integrated over 60 s, for a given injector position. Overall, replicates from several different experiment series performed on several different operation days of the ¹³N delivering facility were averaged to obtain values and standard deviations reported in Table 1.

3. Results and Discussion

The measurements were performed at 50% and 70% RH for all three of the solutions in question. The operating procedure is similar to the one reported by Gržinić et al. (Gržinić et al., 2015; Gržinić et al., 2014), although in this case the experiment was performed by measuring the change in signals under variation of the position of the injector (reaction time) and not aerosol surface to volume ratio. Appropriate corrections have been applied to the N_2O_5 signal to account for NO_2 interference on the denuder coating used for N_2O_5 (citric acid) as well as for the small amounts of NO_3 present in the gas phase, as described in our previous studies. Before each experimental run a wall loss measurement was performed without aerosol by moving the injector in 5-10 cm steps along the length of the aerosol flow tube and measuring the gas phase N_2O_5 signal, in order to obtain the pseudo-first order wall loss rate constants (k_w) for each experiment. These values varied between $\sim 3 \times 10^{-2}$ and $\sim 7 \times 10^{-2} \text{ s}^{-1}$, depending on humidity. ~~Because of the short residence time in the aerosol flow tube and its reduced surface to volume ratio, losses to the wall were less pronounced than in our previous studies. The citric acid coating used to trap N_2O_5 in the denuder system is not able to differentiate N_2O_5 from HNO_3 . Though, any significant presence of HNO_3 formed along the walls upstream of the aerosol flow tube would have been noticed due to its very large wall loss rate coefficient (Guimbaud et al., 2002), which was not observed; the uptake coefficient for labelled N_2O_5 on the reactor walls calculated from k_w was in the range of 10^{-7} , which would not lead to substantial HNO_3 production.~~ NO_2 concentrations in the system were measured by switching a NO_x analyzer in place of the SMPS system at the beginning of the experiment. By comparing this result to the $^{13}N_2O_5$ and $^{13}NO_2$ signals from ^{13}N labelled N_2O_5 and NO_2 , the concentration of non-labelled N_2O_5 in the system was also calculated, as described in our previous studies (Gržinić et al., 2015; Gržinić et al., 2014). The uptake measurements were performed in a similar fashion to the wall loss measurements, although in this case aerosol was introduced at each step. By using Eq. 3, which describes gas-aerosol phase interaction kinetics, we can estimate the uptake coefficient.

$$\frac{C_p^*(t)}{C_g^*(t=0)} = \frac{1 - e^{-(k_w + k_p)t}}{1 + \frac{k_w}{k_p}} \quad (3)$$

$$k_p = \frac{S_p \omega \gamma_{eff}^*}{4} \quad (4)$$

where $C_g^{*(t=0)}$ is the gas-phase labelled N_2O_5 concentration in molecules cm^{-3} at time zero, $C_p^{*(t)}$ is the N_2O_5 -labelled particle phase nitrate concentration in the particle phase expressed as number of particle phase labelled nitrate ions per volume of gas phase in ions cm^{-3} , k_w is the wall loss constant, measured as described above, and k_p denotes the apparent first order rate constant for gas-phase loss of labelled N_2O_5 to the aerosol phase, which can be related to the effective uptake coefficient (γ_{eff}^*) of labelled N_2O_5 by Equation 4, where S_p is the total aerosol surface area to gas volume ratio of the aerosol and ω is the mean thermal velocity of N_2O_5 . Figure 2 shows the appearance of ^{13}N in the aerosol phase as a function of time performed together with least-squares fits using Eq. (3) with γ_{eff}^* as the only variable. The true uptake coefficients were then obtained by correction for gas phase diffusion of N_2O_5 , as described by Pöschl et al. (2007), which leads to considerable corrections for uptake coefficients above 0.1 and particle diameters around 400 nm. The diffusion coefficient was taken as $0.085 \text{ cm}^2 \text{ s}^{-1}$ at room-ambient temperature and ambient pressure (Tang et al., 2014). Table 1 shows the results obtained for the various aerosols, with corresponding experimental parameters, including γ_{eff}^* as returned from the fits to the data and γ^* after the diffusion correction. In absence of aerosol phase nitrate, the obtained γ^* results for Na_2SO_4 at 70% RH are is comparable to those that reported by Mentel et al. (Mentel et al., 1999). At 50% RH, it is likely that the Na_2SO_4 particles remained effloresced (Gao et al., 2007) (the lowest RH in the aerosol conditioning system was 40%), explaining the low γ of 0.0053, which is comparable to that previously reported for dry ammonium sulfate

(Hallquist et al., 2003). In presence of aerosol phase nitrate, uptake of ^{13}N -labelled N_2O_5 is drastically higher than the net uptake of non-labelled N_2O_5 observed in earlier studies by (Bertram and Thornton, 2009; Griffiths et al., 2009; Hallquist et al., 2003; Mentel et al., 1999; Wahner et al., 1998) or that predicted by the IUPAC recommended expression also included in the table. A strong dependence of γ^* -on humidity is observed, with an increase by a factor about three from 50% to 70% relative humidity. On mixed $\text{Na}_2\text{SO}_4 / \text{NaNO}_3$ aerosol, the uptake is very close to that of pure NaNO_3 aerosol, at both humidities. Since the measured uptake coefficient for ^{13}N labelled $^{13}\text{N-N}_2\text{O}_5$ into the nitrate containing aerosol is about an order of magnitude larger than any uptake coefficient measured into not strongly acidic aqueous aerosol in previous studies, room temperature estimates of the bulk mass accommodation coefficient, α_b , our results provide a direct indication demonstrate that gas – aqueous phase exchange of N_2O_5 at room temperature and its dissociation is are considerably more very efficient than previously thought under comparable conditions, as also suggested by Mentel et al. (Mentel et al., 1999), based on experiments with NaNO_3 , Na_2SO_4 and NaHSO_4 aerosol.

More insight into the interpretation of the present experiments with ^{13}N labeled N_2O_5 can be obtained by deconvoluting the chemical mechanism of N_2O_5 hydrolysis (R3-7) to take into account the fate of the labelled and non-labelled species separately. Assuming that the labeled N_2O_5 molecules contain only one ^{13}N atom (due to the very low labeled to non-labeled NO ratio of around 10^{-6}) and under the assumption that no isotopic effects are in play, the chemical mechanism can be assumed to proceed as shown in Figure 3a. We first assume that upon dissociation of $^{13}\text{NNO}_5$, there is an equal possibility that the ^{13}N label will end up either in the nitronium ion (NO_2^+) or in the nitrate ion (NO_3^-), with rate coefficients $k_4/2$. In the first scenario (left-right branch of the pathway for ' $^{13}\text{N}^*\text{NO}_5$ ' in Fig. 3a mechanism) the ^{13}N label ends up on the nitrate ion (R4''²²). The corresponding non-labelled nitronium ion, if not reacting with H_2O , R7²², may-reacts with the excess non-labelled nitrate to reform non-labelled N_2O_5 (R5), while only This N_2O_5 is predominantly non-labeled, since a negligible fraction reacts with the labeled $^{13}\text{NO}_3^-$ ion (R5'') and thus most of the labeled $^{13}\text{NO}_3^-$ is lost in the excess nitrate pool present in the aerosol and the likelihood of recombination of the non-labelled nitronium with the labeled nitrate is very small. N_2O_5 re-evaporating to the gas phase is therefore non-labeled. Thus, in this branch, all ^{13}N labels remain in the aqueous phase given that if evaporation as HNO_3 does not occur, which is unlikely for our neutral aerosol. As evident from the experiments, the net rate of transfer of labelled N_2O_5 into the aerosol nitrate pool, and thus the combination of bulk accommodation and dissociation, is very highfast.

In the other scenario (right-left branch of ' $^{13}\text{N}^*\text{NO}_5$ ' pathway in Fig. 3a) of the mechanism, ^{13}N ends up on the nitronium ion (R4²¹), and there are two possibilities for its further fate. The $^{13}\text{NO}_2^+$ can react with water (R7²¹), bringing the label into the particulate nitrate pool. Alternatively $^{13}\text{NO}_2^+$ can react with NO_3^- from the nitrate pool (R5') to reform $^{13}\text{NNO}_5$ which can eventually re-evaporate. Obviously which of these two sub-channels are prevalent depends on water and nitrate concentrations as well as the rate coefficients of the two competing reactions. The water and nitrate concentrations for the conditions of the present experiments were derived from the AIM model (Clegg et al., 1998) and are also listed in Table 1. In presence of nitrate, (R5') is the dominant pathway, as shown by Mentel et al. (Mentel et al., 1999) and Wahner et al. (Wahner et al., 1998), where values for the ratio k_5/k_7 of 35 around 900 and 40260, respectively, have had been used as fitting parameters to explain the entirety of the nitrate effect. This is consistent with the fact that the net uptake of ^{13}N labelled N_2O_5 is more than an order of magnitude larger than that of non-labelled N_2O_5 , indicating that the R5' sub-channel is dominant.

In Figure 3b, we report the results of box model calculations (described in the supporting information) for the scheme shown in Figure 3a to substantiate these effects for NaNO_3 aerosol at 70% RH. We have used the rate coefficients for $k_4 = 5 \times 10^6 \text{ s}^{-1}$, $k_5 = 2.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_7 = 2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ as suggested by Mentel et al. (1999) for NaNO_3 aerosol at various humidities; the bulk accommodation coefficient α_b was set to one. Figure 3b (left y-axis) directly demonstrates the rapid removal of labelled nitrogen from aqueous phase N_2O_5 and its appearance as labelled nitrate. Parallel to that, labelled N_2O_5 disappears much more quickly from the gas phase and appears as aerosol phase nitrate than non labelled N_2O_5 , as shown in Figure 3d. It is also instructive to look at the

rates of individual reactions contributing to the aqueous phase budget of labelled species plotted in Figure 3b and those of the non-labelled species in Figure 3c: Even though R5' brings back half of the labelled N_2O_5 (rate of R5' is half of the dissociation rate, Figure 3b), the fraction of labelled N_2O_5 drops below half of its initial value, since the exchange reactions R4 and R5 are fast, so that it may cycle through the aqueous phase part of the scheme many times. The rate of R5" (labelled nitrate with non-labelled nitronium) is not getting competitive, so that labelled nitrate remains in the nitrate pool. The γ^* values calculated from the net N_2O_5 loss rates are about 0.26 for labelled N_2O_5 , in good agreement with the value observed in the experiment, 0.29, and 0.0033 for non-labelled N_2O_5 . The latter is consistent with the observation by Mentel et al. but lower than that suggested by the parameterization given in equation (1) based on the IUPAC recommendation and listed in Table 1 or that suggested by Bertram and Thornton (2009) or Griffiths et al. (2009) developed based on a wider data set with other aerosol compositions. Box model simulation of the mixed salt case (not shown), also at 70% RH, returns essentially the same results, 0.25 and 0.009, for the uptake coefficient of labelled and non-labelled N_2O_5 , respectively, also in line with our measured γ^* of 0.26 for labelled N_2O_5 . The right column of Figure 3, plots e,f,g,h, present the box model results for Na_2SO_4 aerosol at 70% RH. The main difference is that in this case, R5 represents only a negligible pathway for non-labelled nitronium resulting from R4", so that the majority of labelled nitrate recycles back to labelled N_2O_5 via R5". As a result, both labelled and non-labelled species behave exactly parallel, both in terms of rates and concentration. When solubility and rate coefficient are taken the same as those for the nitrate aerosol, the magnitude of the calculated uptake coefficient is an order of magnitude too high. The difference between the kinetics described by Mentel et al. (1999) and Bertram and Thornton (2009) is that overall uptake is limited by the dissociation, k_4 , in the latter, while Mentel et al. suggest faster dissociation and limitation by the interplay of the reactions of NO_2^+ with H_2O and NO_3^- . Replacing k_4 by the parameterization suggested by Bertram and Thornton, keeping k_5 as before, but replacing k_7 such that $k_7/k_5=0.06$ as suggested by Bertram and Thornton, yields $\gamma = 0.06$, in reasonable agreement with the uptake coefficient measured here (0.027). However, this can as well be achieved by the Mentel et al. kinetics scheme via lowering k_7 by one order of magnitude to achieve lower net uptake, which is what has been used in the calculations shown in Figure 3f,g,h. In view of the limited dataset it has been beyond the scope of this study to ~~Since the uptake coefficient of ^{13}N labelled N_2O_5 was similar for the aerosol composed of a 1:1 nitrate to sulfate molar ratio mixture and for the pure nitrate aerosol at both humidities, the present results do not allow retrieving more precise rate coefficients for R4, R5 and R7.~~ The present results clearly indicate that accommodation and dissociation of N_2O_5 are not limiting net uptake for aerosol containing substantial amounts of nitrate, but indicate that R4 and R5 are fast enough to not become rate limiting, and that R7 is at least an order of magnitude slower than R5, consistent with k_5/k_7 ratios reported earlier. Furthermore, these experiments provide direct evidence that these elementary steps actually exist, because otherwise exchange with the non-labelled nitrate pool would not occur.

The measured uptake coefficient increases with RH (water content) as the increase in water concentration promotes the reaction of $^{13}NO_2^+$ with water (R7²) while at the same time a decrease in nitrate concentration suppresses the $^{13}NNO_3$ reformation sub-channel (R5²). However, as argued above, in presence of nitrate at several M, the dominant fate of the label in the ~~right-left~~ branch of the mechanism in Fig. 3a is the reformation of labeled N_2O_5 . ~~If bulk accommodation would limit uptake, In such a situation the measured uptake coefficient would be only slightly larger than $\alpha_b/2$, with $\alpha_b/2$ contributed by the left-right branch of the mechanism shown in Fig. 3, and a minor contribution from the right-left branch.~~ Our results therefore strongly indicate that α_b must be at least about twice as high as the uptake coefficient of ^{13}N -labelled N_2O_5 measured for $NaNO_3$ and $NaNO_3/Na_2SO_4$ aerosols and thus $\alpha_b > 0.4$ when including the uncertainties related to aerosol surface to volume ratio and correction for gas phase diffusion. In the box model simulations discussed above, α_b has been set to one. The only systematic uncertainty not considered in this is the assumption that isotope effects do not influence the symmetry of the disproportionation reaction (R4).

Interestingly, the measured uptake coefficient is more sensitive to the water activity, irrespective of whether it is pure nitrate or mixed nitrate / sulfate particles, than to the fractional nitrate content. In spite of the fact that the expected ratio $k_7[\text{H}_2\text{O}] / k_5[\text{NO}_3^-]$ (see Table 1) increases substantially from pure nitrate to mixed nitrate / sulfate, still bulk accommodation and dissociation are not limiting, and the efficient exchange of the label with the non-labelled nitrate pool dominates the behavior. Thus, indicating that an increase of α_b , solubility in terms of salting effects, or of the dissociation could explain the ~~might~~ increase of the uptake coefficient of labelled N_2O_5 by a factor of ~~three-four~~ from 50 to 70 % RH. ~~In combination with the insensitivity to composition (water molarity increases much less), this suggests that salting effects should be considered for N_2O_5 to effectively reduce its solubility (and maybe also α_b) for high ionic strength. As discussed first by Mentel et al. (1999), and later by Griffiths et al. (2009) and Bertram and Thornton (2009), the kinetic regime may shift between limitation by R7, R4 or R3 between low and high water activity, and it remains difficult to unambiguously assign the kinetic regime. Also from the present study, the evidence for the fast dissociation is very strong for the high nitrate mole fractions used, and we can only suggest that the dissociation is similarly fast for the salt aerosol in absence of nitrate.~~

On a side note, in principle, we cannot exclude a surface contribution. Since also the suggested bulk accommodation is followed via obviously very fast dissociation into nitronium and nitrate, this process will occur close to the surface anyhow, with a short reacto-diffusive length (in contrast to the much slower hydrolysis reaction of nitronium with H_2O). Therefore, for instance, varying the surface to volume ratio of the aerosol would not allow differentiating bulk from surface accommodation. Though, we would prefer not invoking a surface process if bulk phase processing explains the observations.

Obviously, for this technique the fast isotope exchange that allows tracking the dissociation of dissolved N_2O_5 to work depends on the presence of a nitrate pool ~~has to be available and, which it~~ has to be substantial enough to ‘trap’ the ^{13}N tracer and prevent its release. In other words, this method traces uptake of N_2O_5 into the non-limiting pool of aqueous nitrate. In absence of nitrate, R7^{21} and R7^{22} dominate in both branches (Fig. 3e), and the measured uptake coefficient for the ^{13}N labelled N_2O_5 is comparable to that reported with other techniques for the same aerosol, in the range of a few 10^{-2} for Na_2SO_4 at 70% RH in this study or for $(\text{NH}_4)_2\text{SO}_4$ reported by Gržinić et al. (Gržinić et al., 2014), both consistent with available literature. For comparison, calculated uptake coefficients based on the parameterization and values from the IUPAC evaluation (Ammann et al., 2013), implemented in equation (1) and (2), are also listed in Table 1.

Conclusion and atmospheric implications

Highly efficient uptake of ^{13}N -labelled N_2O_5 into nitrate containing aqueous aerosol was observed and attributed to the exchange of ^{13}N labeled nitrate as disproportionation-dissociation product of N_2O_5 with the nitrate pool in the aqueous phase. This allows deriving-suggesting a very large value for the bulk mass accommodation coefficient for N_2O_5 into an aqueous aerosol at room temperature of $\alpha_b > 0.4$ at high relative humidity and fast dissociation at $> 10^6 \text{ s}^{-1}$. This also provides direct evidence that the fast disproportionation-dissociation into nitrate and nitronium at $> 10^6 \text{ s}^{-1}$ actually occurs, and thus also supports the arguments behind the nitrate effect. The observed behavior of ^{13}N -labelled N_2O_5 is similar to that observed by Wachsmuth et al. (Wachsmuth et al., 2002), where $^{83-86}\text{Br}$ isotopes have been used to determine the bulk accommodation coefficient of HOBr on aqueous bromide containing aerosol. The large value of α_b obtained for N_2O_5 at room temperature implies that other limiting processes must be at work to explain the insensitivity of the uptake coefficient to water content at high relative humidity (Abbatt et al., 2012; Griffiths et al., 2009; Thornton et al., 2003), which was partly interpreted as accommodation limitation. Possible other aspects may be the temperature dependence of the solubility of N_2O_5 or salting effects as discussed in these previous studies, for which also strong indications come from this study to explain the strong water activity dependence of the observed uptake coefficient of ^{13}N labelled

N₂O₅. At least this study would exclude any accommodation limitation and supports previous indications that reaction and diffusion limit uptake of N₂O₅ to low viscosity aqueous aerosol (Gaston and Thornton, 2016). ~~The absence of accommodation limitation also helps rationalizing results from field experiments (Phillips et al., 2016; Wagner et al., 2013), where under some conditions uptake coefficients constrained by combined N₂O₅ and aerosol measurements are larger than those suggested by laboratory studies available to date.~~

Acknowledgements

The authors would like to thank the staff of the PSI accelerator facilities and of the isotope production facility IP-2 for their invaluable help during experimental work. Technical support by M. Birrer is much appreciated. This study was supported by the Swiss National Science Foundation (grants no. 130175 and 149492).

The Supplement related to this article is available online

References

- Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, *Chem. Soc. Rev.*, 41, 6555-6581, doi: 10.1039/C2CS35052A, 2012.
- Ammann, M.: Using ¹³N as tracer in heterogeneous atmospheric chemistry experiments, *Radiochim. Acta*, 89, 831-838, 2001.
- Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, *Atmos. Chem. Phys.*, 13, 8045-8228, doi: 10.5194/acp-13-8045-2013, 2013.
- Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N₂O₅, *J. Phys. Chem. A*, 110, 10435-10443, 2006.
- Badger, C. L., Griffiths, P. T., George, I., Abbatt, J. P. D., and Cox, R. A.: Reactive uptake of N₂O₅ by aerosol particles containing mixtures of humic acid and ammonium sulfate, *J. Phys. Chem. A*, 110, 6986-6994, 2006.
- Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO₂, from the reaction of gaseous N₂O₅ with NaCl solution: Bulk and aerosol experiments, *J. Geophys. Res.*, 102, 3795-3804, doi: 10.1029/96jd03057, 1997.
- Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N₂O₅ reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, *Atmos. Chem. Phys.*, 9, 8351-8363, 2009.
- Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K., and Coffman, D. J.: Direct observations of N₂O₅ reactivity on ambient aerosol particles, *Geophys. Res. Lett.*, 36, 2009.
- Chang, W. L., Bhawe, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N₂O₅: A Review, *Aerosol Sci. Technol.*, 45, 665-695, doi: 10.1080/02786826.2010.551672, 2011.

- Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system $\text{H}^+\text{-NH}_4^+\text{-Na}^+\text{-SO}_4^{2-}\text{-NO}_3^- \text{-Cl}^- \text{-H}_2\text{O}$ at 298.15 K, *J. Phys. Chem. A*, 102, 2155-2171, 1998.
- Dentener, F. J. and Crutzen, P. J.: Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NO_x , O_3 , and OH , *J. Geophys. Res.*, 98, 7149-7163, doi: 10.1029/92JD02979, 1993.
- Evans, M. J. and Jacob, D. J.: Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH , *Geophys. Res. Lett.*, 32, 2005.
- Folkers, M., Mentel, T. F., and Wahner, A.: Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N_2O_5 , *Geophys. Res. Lett.*, 30, 2003.
- Gaston, C. J. and Thornton, J. A.: Reacto-Diffusive Length of N_2O_5 in Aqueous Sulfate- and Chloride-Containing Aerosol Particles, *J. Phys. Chem. A*, 120, 1039-1045, doi: 10.1021/acs.jpca.5b11914, 2016.
- [Gao Y., Yu L.E., and Chen S.B.: Efflorescence Relative Humidity of Mixed Sodium Chloride and Sodium Sulfate Particles, *J. Phys. Chem. A*, 111, 10660–10666, 2007.](#)
- George, C., Ponche, J. L., Mirabel, P., Behnke, W., Scheer, V., and Zetzsch, C.: Study of the Uptake of N_2O_5 by Water and NaCl Solutions, *J. Phys. Chem.*, 98, 8780-8784, 1994.
- Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive Uptake of N_2O_5 by Aerosols Containing Dicarboxylic Acids. Effect of Particle Phase, Composition, and Nitrate Content, *J. Phys. Chem. A*, 113, 5082-5090, 2009.
- Gross, S., Iannone, R., Xiao, S., and Bertram, A. K.: Reactive uptake studies of NO_3 and N_2O_5 on alkenoic acid, alkanolate, and polyalcohol substrates to probe nighttime aerosol chemistry, *Phys. Chem. Chem. Phys.*, 11, 7792-7803, 2009.
- Gržinić, G., Bartels-Rausch, T., Berkemeier, T., Türler, A., and Ammann, M.: Viscosity controls humidity dependence of N_2O_5 uptake to citric acid aerosol, *Atmos. Chem. Phys.*, 15, 13615-13625, doi: 10.5194/acp-15-13615-2015, 2015.
- Gržinić, G., Bartels-Rausch, T., Birrer, M., Türler, A., and Ammann, M.: Production and use of ^{13}N labeled N_2O_5 to determine gas-aerosol interaction kinetics, *Radiochimica Acta*, 102, 1025–1034, doi: 10.1515/ract-2014-2244, 2014.
- [Guimbaud, C., Arens, E., Gutzwiller, L., Gäggeler, H. W., and Ammann, M.: Uptake of \$\text{HNO}_3\$ to deliquescent sea-salt particles: a study using the short-lived radioactive isotope tracer \$\text{N-13}\$, *Atmos. Chem. Phys.*, 2, 249-257, 2002.](#)
- Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N_2O_5 on sub-micron sulfate aerosols, *Phys. Chem. Chem. Phys.*, 5, 3453-3463, 2003.
- Hanson, D. R. and Lovejoy, E. R.: The Uptake of N_2O_5 onto Small Sulfuric-Acid Particles, *Geophys. Res. Lett.*, 21, 2401-2404, 1994.
- Karagulian, F., Santschi, C., and Rossi, M. J.: The heterogeneous chemical kinetics of N_2O_5 on CaCO_3 and other atmospheric mineral dust surrogates, *Atmos. Chem. Phys.*, 6, 1373-1388, 2006.
- Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, 1, 5451-5457, 1999.
- Mozurkewich, M. and Calvert, J. G.: Reaction probability of N_2O_5 on aqueous aerosols, *J. Geophys. Res.*, 93, 15889-15896, doi: 10.1029/JD093iD12p15889, 1988.
- Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F., Borrmann, S., Bingemer, H., Lelieveld, J., and Crowley, J. N.: Estimating N_2O_5 uptake coefficients using ambient measurements of NO_3 , N_2O_5 , ClNO_2 and particle-phase nitrate, *Atmos. Chem. Phys.*, 16, 13231-13249, doi: 10.5194/acp-16-13231-2016, 2016.
- [Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, *Atmos. Chem. Phys.*, 7, 5989-6023, 2007.](#)

Tang, M. J., Cox, R. A., and Kalberer, M.: Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: volume 1. Inorganic compounds, *Atmos. Chem. Phys.*, 14, 9233-9247, 2014.

Thornton, J. A. and Abbatt, J. P. D.: N₂O₅ reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, *J. Phys. Chem. A*, 109, 10004-10012, 2005.

Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N₂O₅ hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size, *Phys. Chem. Chem. Phys.*, 5, 4593-4603, 2003.

Wachsmuth, M., Gäggeler, H. W., von Glasow, R., and Ammann, M.: Accommodation coefficient of HOBr on deliquescent sodium bromide aerosol particles, *Atmos. Chem. Phys.*, 2, 121-131, doi: 10.5194/acp-2-121-2002, 2002.

Wagner, C., Hanisch, F., Holmes, N., de Coninck, H., Schuster, G., and Crowley, J. N.: The interaction of N₂O₅ with mineral dust: aerosol flow tube and Knudsen reactor studies, *Atmos. Chem. Phys.*, 8, 91-109, 2008.

Wagner, N. L., Riedel, T. P., Young, C. J., Bahreini, R., Brock, C. A., Dubé, W. P., Kim, S., Middlebrook, A. M., Öztürk, F., Roberts, J. M., Russo, R., Sive, B., Swarthout, R., Thornton, J. A., VandenBoer, T. C., Zhou, Y., and Brown, S. S.: N₂O₅ uptake coefficients and nocturnal NO₂ removal rates determined from ambient wintertime measurements, *J. Geophys. Res.*, 118, 9331-9350, doi: 10.1002/jgrd.50653, 2013.

Wahner, A., Mentel, T. F., Sohn, M., and Stier, J.: Heterogeneous reaction of N₂O₅ on sodium nitrate aerosol, *J. Geophys. Res.*, 103, 31103-31112, 1998.

Table 1. Experimental parameters and results

Aerosol	NaNO ₃	NaNO ₃	NaNO ₃ / Na ₂ SO ₄	NaNO ₃ / Na ₂ SO ₄	Na ₂ SO ₄	Na ₂ SO ₄
Molar mixing ratio	-	-	1:1	1:1	-	-
Temperature (K)	295±1	295±1	295±1	295±1	295±1	295±1
RH (%)	50±1	70±1	51±1	70±1	51±1	70±1
Average S/V ratio (m ² /m ³)	5.66×10 ⁻³	5.00×10 ⁻³	3.36×10 ⁻³	4.76×10 ⁻³	3.42×10 ⁻³	3.00×10 ⁻³
γ^* (eff (13NNO ₅))	0.057	0.18	0.054	0.17	0.0052	0.025
Error ^a	±0.004	±0.02	±0.008	±0.02	±0.002	±0.003
γ^* (13NNO ₅) ^b	0.067	0.29	0.063	0.26	0.0053	0.027
Total error ^c	±0.02	±0.1	±0.02	±0.2	±0.002	±0.008
[H ₂ O] (M) ^d	28.5	38.2	34.4	41.6	38.6	43.8
[NO ₃ ⁻] (M) ^d	13.1	8.78	4.60	3.29	0	0
k_7 [H ₂ O] / k_5 [NO ₃ ⁻] ^e	0.044	0.087	0.15	0.25	-	-
γ (non-labelled N ₂ O ₅) ^f	0.0050	0.010	0.013	0.019	0.044	0.047

^a 95% confidence level of the fit of eq. (3) to the data as shown in Fig. 2

^b corrected for diffusion in the gas phase

^c including 30% uncertainty related to the aerosol surface to volume ratio

^d from AIM model (Clegg et al., 1998)

^e $k_7/k_5 = 0.02$

^f calculated using equations (1) and (2), with $k_0^{\text{II}} = 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $H = 2 \text{ M atm}^{-1}$

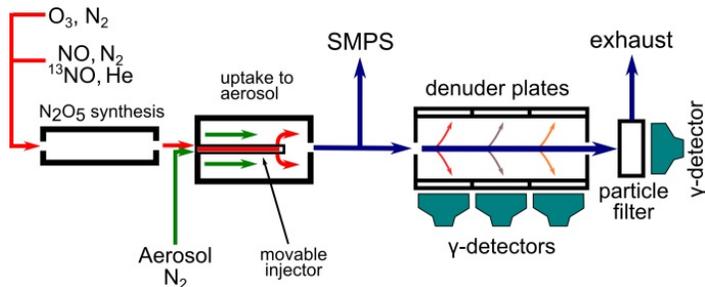


Fig. 1. Schematic of the modified experimental setup used in this study

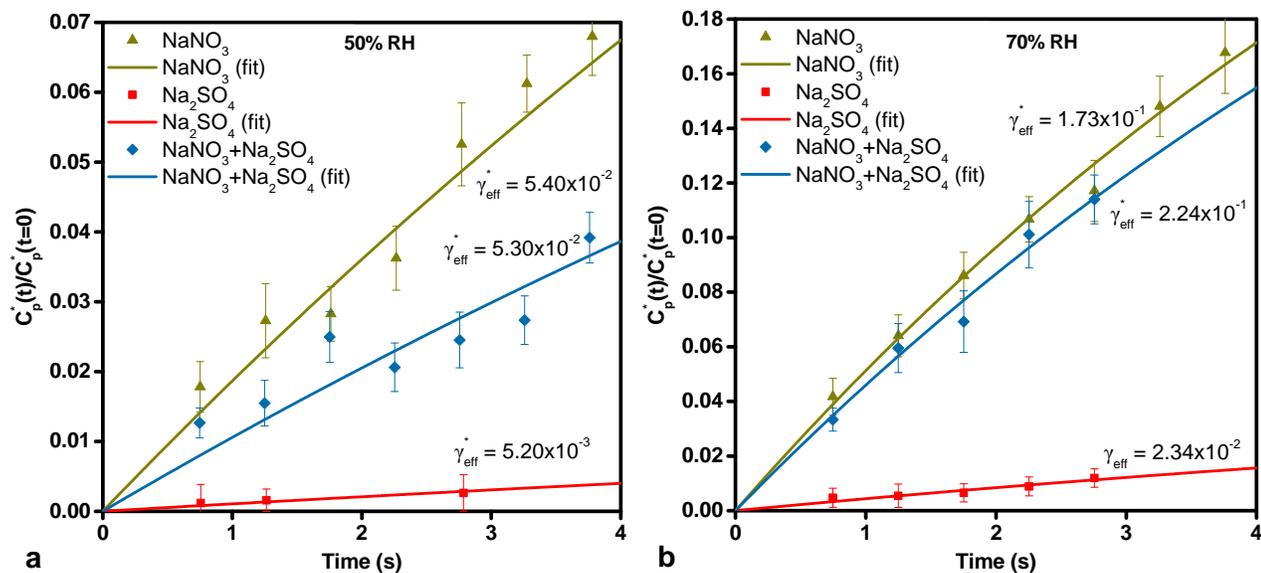


Fig. 2. Normalized particle-phase N₂O₅-labelled nitrate concentration vs. time graph for ~~the~~ experiments performed at 50% RH (a) and 70% RH (b). The data points represent the measurement data, the error bars represent the standard deviation of the measurements, the curves are a least-squares fit of Eq. 1 to the measured data.

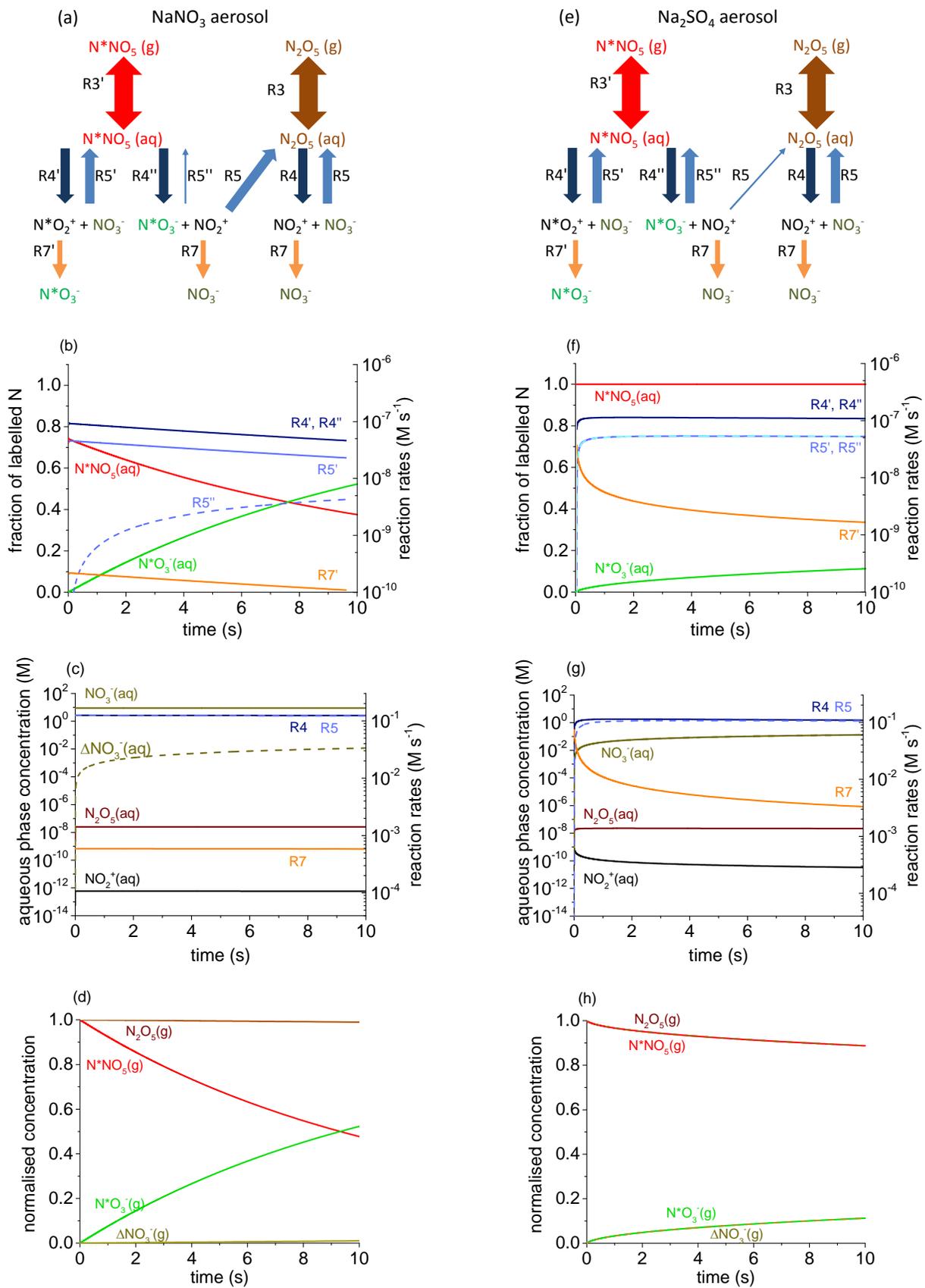


Fig. 3. (a) The chemical mechanism of ~~¹³N-labeled~~ N_2O_5 hydrolysis and chemical isotope exchange in nitrate containing solutions. N^* refers to ^{13}N . (b, c, d) Results of box model calculations for NaNO_3 aerosol at 70% RH: evolution as a function of time of: (b) the fraction of labelled N_2O_5 in the aqueous phase (red, left axis) and ratio of labelled nitrate to the total number of labelled N_2O_5 initially available (green, left axis); rates of reactions relevant for the budget of aqueous phase ^{13}N (light to dark blue, right axis); (c) rates of reactions relevant for the budget of non-labelled species in the aqueous phase; (d) ~~e~~Evolution of normalized gas phase N_2O_5 (labelled, red; non-labelled, brown) and aqueous phase nitrate (labelled, green; non-labelled, olive) as a function of time. (e, f, g, h) scheme and plots of the same quantities, but for Na_2SO_4 aerosol at 70% RH in absence of pre-existing nitrate.

Supplement material to:

Efficient bulk mass accommodation and dissociation of N₂O₅ in neutral aqueous aerosol

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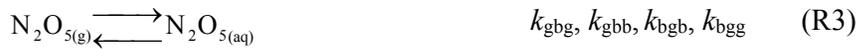
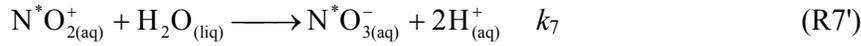
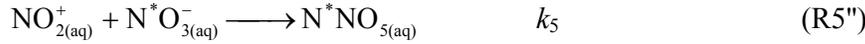
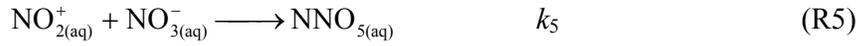
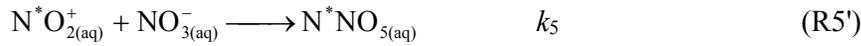
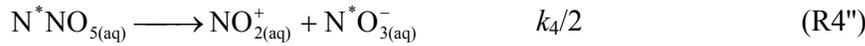
Description of box model calculations

The box model calculations are explicitly treating N₂O₅ chemistry in the aqueous phase for both labelled and non-labelled N₂O₅ molecules, as well as exchange of both with the gas phase. Diffusion is neglected in both phases. Labelling of reactions is done as in main text and as indicated in Figure 3a of the main text.

The following chemical reactions have been used to describe the aqueous phase chemistry of non-labelled N₂O₅:



The chemical scheme for labelled N₂O₅ is analogous and assumes that the position of the labelled N* atom within the N₂O₅ is not relevant, such that upon dissociation, labelled nitronium and labelled nitrate are formed at equal rates, but that otherwise the rate coefficients are the same as for the non-labelled species:



Due to the small fraction of labelled N, reactions among labelled species are not included in the scheme. The set of differential equations listed in Table S1 were used to solve for the evolution of all gas and aqueous phase species with time using Matlab.

The exchange rate coefficients to describe gas-aqueous and aqueous-gas transfer of N_2O_5 were obtained from the steady state condition given by Henry's law equilibrium, thus gas – aerosol equilibrium in absence of chemical reaction (assuming that the gas phase chemical reactions of N_2O_5 are in steady state on the time scale of gas – aerosol equilibration). The steady state of the gas phase N_2O_5 concentration in equilibrium with aqueous phase N_2O_5 is described by:

$$\frac{d[\text{N}_2\text{O}_5]_{\text{g}}}{dt} = k_{\text{bg}} [\text{N}_2\text{O}_5]_{\text{aq}} V_p N_{\text{av}} - \frac{\alpha_b \omega}{4} S_p [\text{N}_2\text{O}_5]_{\text{g}} = 0 \Rightarrow k_{\text{bg}} = \frac{\alpha_b \omega S_p}{4 V_p N_{\text{av}} H'}$$

$$H' = \frac{[\text{N}_2\text{O}_5]_{\text{aq}}}{[\text{N}_2\text{O}_5]_{\text{g}}} = \frac{[\text{N}_2\text{O}_5]_{\text{aq}}}{N_{\text{av}} p_{\text{N}_2\text{O}_5} / RT} = H \frac{RT}{N_{\text{av}}}$$

k_{bg} is the first order rate coefficient for the release to the gas phase in units of s^{-1} , V_p is the total aqueous phase aerosol volume per volume of gas phase in liter cm^{-3} , S_p the total aerosol surface area per volume of gas phase in $\text{cm}^2 \text{cm}^{-3}$, $p_{\text{N}_2\text{O}_5}$ is the partial pressure of N_2O_5 in atm,

R is the gas constant ($8.314 \text{ J mole}^{-1} \text{ K}^{-1}$), T is the temperature, H is the Henry's law constant in M atm^{-1} , H' is the ratio of the aqueous phase molarity of N_2O_5 to the gas phase concentration in molecule cm^{-3} and N_{av} is Avogadro's number (note that $[\text{N}_2\text{O}_5]_{aq}$ is in units of M, while $[\text{N}_2\text{O}_5]_g$ is in units of molecule cm^{-3}). The same result can also be obtained from considering steady state for the aqueous phase N_2O_5 concentration in an individual aerosol particle:

$$\frac{d[\text{N}_2\text{O}_5]_{aq}}{dt} = -k_{bg}[\text{N}_2\text{O}_5]_{aq} + \frac{\alpha_b \omega S_p}{4v_p N_{av}} [\text{N}_2\text{O}_5]_g = 0 \Rightarrow k_{bg} = \frac{\alpha_b \omega S_p}{4v_p N_{av} H'} \quad \frac{s_p}{v_p} = \frac{S_p}{V_p}$$

Where v_p is the volume of an individual aerosol particle in liter, and s_p its surface area in cm^2 . Thus, the rate coefficients describing the gas – aqueous phase exchange are:

$$k_{gbb} = \frac{\alpha_b \omega S_p}{4v_p N_{av}} \quad \left[\frac{\text{mole cm}^3}{\text{s liter molecule}} \right]$$

$$k_{gbg} = \frac{\alpha_b \omega S_p}{4} \quad [\text{s}^{-1}]$$

$$k_{bgg} = \frac{\alpha_b \omega S_p}{4v_p N_{av} H'} \quad [\text{s}^{-1}]$$

$$k_{bgb} = \frac{\alpha_b \omega S_p}{4H'} \quad \left[\frac{\text{molecule liter}}{\text{s cm}^3 \text{ mole}} \right]$$

The apparent net uptake coefficient, γ and γ^* , can be derived from the effective loss rates of the gas phase N_2O_5 and N^*NO_5 , respectively, obtained from the solutions to the differential equations, via:

$$\gamma = \left[-\frac{d[\text{N}_2\text{O}_5]_g}{dt} \right] / \left[\frac{\omega}{4} S_p [\text{N}_2\text{O}_5]_g \right] = \left[k_{bgb} [\text{N}_2\text{O}_5]_{aq} - k_{gbg} [\text{N}_2\text{O}_5]_g \right] / \left[\frac{\omega}{4} S_p [\text{N}_2\text{O}_5]_g \right]$$

$$\gamma^* = \left[-\frac{d[\text{N}^*\text{NO}_5]_g}{dt} \right] / \left[\frac{\omega}{4} S_p [\text{N}^*\text{NO}_5]_g \right] = \left[k_{bgb} [\text{N}^*\text{NO}_5]_{aq} - k_{gbg} [\text{N}^*\text{NO}_5]_g \right] / \left[\frac{\omega}{4} S_p [\text{N}^*\text{NO}_5]_g \right]$$

We note that due the fact that we neglect aqueous phase diffusion in the kinetics, these uptake coefficients are only representing estimates and should be compared with caution to the measured data. In principle they represent the uptake coefficients expected for small enough particles (smaller than those in the experiments) such that liquid phase diffusion would not play a role. While the apparent reacto-diffusive length based on the net hydrolysis kinetics is rather large, the true dissociation as suggested here is rather fast. Inclusion of diffusion would require an explicit depth resolving model, which was beyond the scope of this analysis. The

purpose of the simulations here was to simulate the behavior of labelled and non-labelled N_2O_5 in the aqueous phase and especially the exchange of labelled nitrate with the non-labelled nitrate pool for the case of NaNO_3 .

For the simulations of the NaNO_3 and mixed $\text{Na}_2\text{SO}_4 / \text{NaNO}_3$ cases, we used the parameters for the kinetics as compiled by Mentel et al. (1999). The aerosol composition was derived from the E-AIM model as described in the main text and listed there in Table 1. Mentel et al. (1999) assumed the solubility of N_2O_5 to be 5 M atm^{-1} (2 M atm^{-1} in the IUPAC recommended parameterization). As mentioned in the main text and in the other recent studies (Bertram and Thornton, 2009), in view of the fact that the concentration of nitronium has never been measured, the solubility and also the other rate coefficients determining its concentration are not well constrained. Mentel et al. set the dissociation rate coefficient, k_1 , to $5 \times 10^6 \text{ s}^{-1}$, the rate coefficient for the recombination, k_2 , to $2.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and the first rate coefficient for the reaction of nitronium with water, $k_3 \times [\text{H}_2\text{O}]_{\text{aq}}$, to $\times 10^9 \text{ s}^{-1}$ (note that the values given in Mentel et al.'s Table 2 are on a molality unit basis). This set of parameters that led to agreement with their own data and also nicely explain the data with labelled N_2O_5 presented in this study in the main text without further adjustments.

For the simulations of the Na_2SO_4 case, the dissociation and recombination rate coefficients were kept constant, but the rate of reaction of nitronium with water, $k_3 \times [\text{H}_2\text{O}]_{\text{aq}}$, was reduced by one order of magnitude to $\times 10^9 \text{ s}^{-1}$, to obtain net uptake coefficients in agreement with the measurement. As mentioned and discussed in the main text, reducing the dissociation rate would have a similar effect. However, the parallel behavior of labelled and non-labelled N_2O_5 for the Na_2SO_4 aerosol is not affected by that.

References

- Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, *Atmos. Chem. Phys.*, 9, 8351-8363, 2009.
- Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, 1, 5451-5457, 1999.

Table S1: Differential equations. $[\text{N}_2\text{O}_5]_{\text{aq}}$ is in units of M, while $[\text{N}_2\text{O}_5]_{\text{g}}$ is in units of molecule cm^{-3} . The rate coefficients are explained in more detail below.

$\frac{d[\text{N}_2\text{O}_5]_{\text{aq}}}{dt} = -k_1[\text{N}_2\text{O}_5]_{\text{aq}} + k_2[\text{NO}_2^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} - k_{\text{bgb}}[\text{N}_2\text{O}_5]_{\text{aq}} + k_{\text{gbb}}[\text{N}_2\text{O}_5]_{\text{g}}$	D1
$\frac{d[\text{N}^*\text{NO}_5]_{\text{aq}}}{dt} = -k_1[\text{N}^*\text{NO}_5]_{\text{aq}} + k_2[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} + k_2[\text{NO}_2^+]_{\text{aq}}[\text{N}^*\text{O}_3^-]_{\text{aq}} - k_{\text{bgb}}[\text{N}^*\text{NO}_5]_{\text{aq}} + k_{\text{gbb}}[\text{N}^*\text{NO}_5]_{\text{g}}$	D2
$\frac{d[\text{NO}_2^+]_{\text{aq}}}{dt} = k_1[\text{N}_2\text{O}_5]_{\text{aq}} + \frac{k_1}{2}[\text{N}^*\text{NO}_5]_{\text{aq}} - k_2[\text{NO}_2^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} - k_2[\text{NO}_2^+]_{\text{aq}}[\text{N}^*\text{O}_3^-]_{\text{aq}} - k_3[\text{NO}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}}$	D3
$\frac{d[\text{N}^*\text{O}_2^+]_{\text{aq}}}{dt} = \frac{k_1}{2}[\text{N}^*\text{NO}_5]_{\text{aq}} - k_2[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} - k_3[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}}$	D4
$\frac{d[\text{NO}_3^-]_{\text{aq}}}{dt} = k_1[\text{N}_2\text{O}_5]_{\text{aq}} + \frac{k_1}{2}[\text{N}^*\text{NO}_5]_{\text{aq}} - k_2[\text{NO}_2^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} - k_2[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} + k_3[\text{NO}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}}$	D5
$\frac{d[\text{N}^*\text{O}_3^-]_{\text{aq}}}{dt} = \frac{k_1}{2}[\text{N}^*\text{NO}_5]_{\text{aq}} - k_2[\text{NO}_2^+]_{\text{aq}}[\text{N}^*\text{O}_3^-]_{\text{aq}} + k_3[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}}$	D6
$\frac{d[\text{H}_2\text{O}]_{\text{aq}}}{dt} = -k_3[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}} - k_3[\text{NO}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}}$	D7
$\frac{d[\text{H}^+]_{\text{aq}}}{dt} = 2k_3[\text{N}^*\text{O}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}} + 2k_3[\text{NO}_2^+]_{\text{aq}}[\text{H}_2\text{O}]_{\text{aq}}$	D8
$\frac{d[\text{N}_2\text{O}_5]_{\text{g}}}{dt} = k_{\text{bgg}}[\text{N}_2\text{O}_5]_{\text{aq}} - k_{\text{gbg}}[\text{N}_2\text{O}_5]_{\text{g}}$	D9
$\frac{d[\text{N}^*\text{NO}_5]_{\text{g}}}{dt} = k_{\text{bgg}}[\text{N}^*\text{NO}_5]_{\text{aq}} - k_{\text{gbg}}[\text{N}^*\text{NO}_5]_{\text{g}}$	D10

Table S2. Data for NaNO₃, Na₂SO₄ and 1:1 NaNO₃/Na₂SO₄ aerosol experiments shown in Figure 2 of the main text.

NaNO ₃					
50% RH			70% RH		
Time (s)	$C_p^*(t) / C_p^*(t=0)$	std.dev.	Time (s)	$C_p^*(t) / C_p^*(t=0)$	std.dev.
0.75	1.78E-02	3.63E-03	0.75	4.17E-02	6.74E-03
1.26	2.73E-02	5.30E-03	1.25	6.40E-02	7.70E-03
1.76	2.83E-02	3.91E-03	1.75	8.61E-02	8.49E-03
2.27	3.62E-02	4.58E-03	2.25	1.07E-01	8.33E-03
2.77	5.25E-02	5.94E-03	2.76	1.17E-01	1.12E-02
3.28	6.12E-02	4.09E-03	3.26	1.48E-01	1.10E-02
3.78	6.80E-02	5.59E-03	3.76	1.68E-01	1.49E-02
Na ₂ SO ₄					
51% RH			70% RH		
Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.	Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.
0.76	1.18E-03	2.65E-03	0.75	4.70E-03	3.48E-03
1.26	1.57E-03	1.61E-03	1.25	5.44E-03	4.31E-03
2.79	2.63E-03	2.61E-03	1.75	6.52E-03	3.32E-03
			2.25	8.86E-03	3.45E-03
			2.76	1.19E-02	3.36E-03
NaNO ₃ +Na ₂ SO ₄					
51% RH			70% RH		
Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.	Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.
0.75	1.27E-02	2.14E-03	0.75	3.33E-02	4.19E-03
1.25	1.55E-02	3.26E-03	1.25	5.95E-02	8.93E-03
1.75	2.50E-02	3.65E-03	1.75	6.92E-02	1.13E-02
2.25	2.06E-02	3.47E-03	2.25	1.01E-01	1.21E-02
2.76	2.45E-02	3.99E-03	2.76	1.14E-01	8.94E-03
3.26	2.74E-02	3.47E-03			
3.76	3.92E-02	3.61E-03			