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 #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 ^{13}N is separated into N_2O_5 /NO_3 and NO_2 respectively, and the contribution of NO_3 to the signal is corrected for as mentioned in the text. After removal of gas phase N_2O_5 at the entrance of the detection system, only nitrate remains in the particle phase. The approach has been tested with ammonium sulfate (Grzinic et al., 2014) and used in a previous study with citric acid aerosol. The potential occurrence of evaporation of ^{13}N labelled HNO_3 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.

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 NO_2 to N_2O_5 is about 1 at 50% RH and about 0.45 at 70% RH. In the dry N_2O_5 online production flow tube, NO_2 losses (due to heterogeneous disproportionation) are undetectable ($<10^{-8}$). Disproportionation of NO_2 in the aerosol phase is negligible. As mentioned by Referee #2, HNO_3 would rather be of concern as a product of hydrolysis of N_2O_5 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 HNO_3 product from acidic aerosol discussed in our previous studies (Grzinic et al., 2014). But given the k_w values reported, and if assuming that all N_2O_5 lost to the walls would lead to HNO_3 in the gas phase and that HNO_3 would be taken up with unit uptake coefficient, particle phase nitrate and acidity remain dominated by that deriving from direct N_2O_5 uptake.

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 N_2O_5 in presence and absence of nitrate. Essentially, in absence of nitrate, labelled N_2O_5 behaves as non-labelled N_2O_5, 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.

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, $^{13}NO_2^+$ simply reacts with non-labelled nitrate back to N_2O_5 if not reacted with H_2O to form labelled nitrate. Therefore, on sulfate, the labelled N has the same fate as non-labelled N.

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.

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.

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.

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 NO_2^+ 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.

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.

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 N_2O_5 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.