

Interactive comment on “Direct N₂O₅ reactivity measurements at a polluted coastal site” by T. P. Riedel et al.

Anonymous Referee #1

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The authors have directly measured N₂O₅ uptake coefficients on ambient aerosol using a flow reactor and compared the results to predictions based on a model constrained by observations of particle surface area and composition. The dataset shows that, whilst the parameterisation captures the nitrate reduction in uptake coefficient, it does not reproduce the low values observed, possibly indicating suppression by organics. This paper represents a valuable step towards understanding what controls N₂O₅ reactivity in the troposphere and should be published. The authors are encouraged to address the comments and questions listed below in revising their manuscript.

General

The technique of using in-field measurement of N₂O₅ uptake coefficient using ambient aerosol is new. Has the apparatus (with the same RH, flow, SA measurement etc) been

C13717

tested in the laboratory using synthetic aerosol samples where lab data for the uptake coefficient exist? The issue here is the mode of generation of N₂O₅ with large O₃.

There is no text describing how loss of N₂O₅ via NO₃ reactions is taken into account. This will be an issue when the reactor is at higher temperature than ambient as the relative population of N₂O₅ and NO₃ will shift towards NO₃ (given that the thermal lifetime of N₂O₅ is shorter than the residence time within the reactor). Losses of NO₃ with aerosol, the reactor walls, NO or VOC will then lead to a larger loss rate of N₂O₅ than due to aerosol uptake alone. Although such effects would lead to an over prediction of the uptake coefficient (i.e. against the trend observed here) they need to be discussed.

Specific

P31913, L1 NO and NO₂ have unpaired electrons, but are rarely referred to as radicals in atmospheric chemistry.

P31913, L10 “given the catalytic nature of NO_x”. I’m not sure what this tries to convey.

P31913, L25 Mention that ClNO₂ is photo-labile and its formation from N₂O₅ is thus a route to NO_x regeneration as well as chlorine release.

P31914, L5 The units of the terms in equation (1) should be listed

P31915, L14 Finlayson-Pitts (also in the bibliography)

P31916, L24 “means” = “mechanisms”

P31917, L10 There were significant changes in RH compared to ambient. Can you quantify the effect on particle surface area, composition and the time scales involved for this (presumably short relative to the reactor residence time)?

P31917, L30 Is the reference to Liu necessary to qualify the statement that marine, urban and continental air masses have different particles types and histories.

P31918, L5-20 several occurrences of missing full-stops (and also elsewhere in the

C13718

manuscript)

P31918, L16 How is the value of 61 % obtained. Whilst listed as an estimate, it appears to be known to 2 decimal places. More details please.

P31919, L24 Ryder et al is not in the bibliography

P31919, L12 The AMS does not measure chloride quantitatively and this needs to be mentioned here. This point comes up again on 31922, L15. It would be useful to hear if the efficiency can be assessed (i.e. approximate correction factors applied).

P31919, L12 Organic species were assumed not to influence the water content of the particles. Please clarify when this assumption is fulfilled and if this is reasonable for this campaign.

P31919, L16 different "to"

P31919, L21 what were the calculated (or assumed) losses resulting from sampling aerosol from a 90 degree T-piece ?

P31919, L22 The outer diameter of the steel piping is less relevant than the inner diameter.

P31919, L25 How much O₃ (from the N₂O₅ source chemistry) was present in the aerosol reactor ? Can the authors rule out that this amount of O₃ can impact on the aerosol reactivity to either N₂O₅ or NO₃ ?

P31919, L26 How much N₂O₅ was present in the aerosol reactor ? I find no indication of this potentially important parameter (for aerosol ageing, in situ-nitrate formation, first order kinetics etc) in the manuscript. Specifically, Could nitrate from synthetic N₂O₅ be the cause of low uptake coefficients compared to ambient aerosol which were less chemically aged ?

P31920, L9 Relative changes in N₂O₅ signal were used to calculate the uptake coefficient and only MS count rates are plotted. It would however be useful to know

C13719

(approximately) how much N₂O₅ is present (for reasons listed above).

P31920, L11 What is/are equilibrating in the equilibration time ?

P31921, L15 At 750 pptv, the lifetime for NO₃ is only 2s. As N₂O₅ and NO₃ will reach equilibrium within the 8 minutes residence time in the reactor, this would result in substantial (indirect) N₂O₅ loss. 750 pptv thus seems to be a rather high number to use as filter. Also, the presence of other reactive components (towards NO₃) can impact on the measurements. How do the authors take this into account ? Can some variability in the N₂O₅ lifetime be a result of (highly variable) NO₃ losses ?

P31822, L15 The chloride content is not measured by the MS. Why were measurements of ClNO₂ not made along with N₂O₅ (it is the same ion chemistry and as been done before by this group) ? This would have given some handle on the contribution of chloride to the uptake coefficient.

P31927, L3 suite "of"

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C13720