Interactive comment on “Direct N$_2$O$_5$ 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
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 NOx”. 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 NOx 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
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 calculated the uptake coefficient and only MS count rates are plotted. It would however be useful to know
(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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