

## ***Interactive comment on “Direct N<sub>2</sub>O<sub>5</sub> reactivity measurements at a polluted coastal site” by T. P. Riedel et al.***

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Response to Anonymous Referee #1

We thank Referee #1 for their careful reading of the manuscript and comments; below we provide responses to each comment individually.

General Comment by Referee #1: The technique of using in-field measurement of N<sub>2</sub>O<sub>5</sub> 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 N<sub>2</sub>O<sub>5</sub> with large O<sub>3</sub>. There is no text describing how loss of N<sub>2</sub>O<sub>5</sub> via NO<sub>3</sub> reactions is taken into account. This will be an issue when the reactor

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is at higher temperature than ambient as the relative population of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> will shift towards NO<sub>3</sub> (given that the thermal lifetime of N<sub>2</sub>O<sub>5</sub> is shorter than the residence time within the reactor). Losses of NO<sub>3</sub> with aerosol, the reactor walls, NO or VOC will then lead to a larger loss rate of N<sub>2</sub>O<sub>5</sub> 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.

Author responses follow each comment and are denoted with \*\*.

1. P31913, L1 NO and NO<sub>2</sub> have unpaired electrons, but are rarely referred to as radicals in atmospheric chemistry.

\*\*“radicals” has been removed.

2. P31913, L10 “given the catalytic nature of NO<sub>x</sub>”. I’m not sure what this tries to convey.

\*\*This has been removed.

3. P31913, L25 Mention that ClNO<sub>2</sub> is photo-labile and its formation from N<sub>2</sub>O<sub>5</sub> is thus a route to NO<sub>x</sub> regeneration as well as chlorine release.

\*\*We have added the following statement: “ClNO<sub>2</sub> is a photolabile compound that releases atomic chlorine and NO<sub>x</sub> upon photolysis, its formation and photolysis thereby decreases nocturnal NO<sub>x</sub> losses due to HNO<sub>3</sub> formation while liberating a strong oxidant.”

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

\*\*We have added the appropriate units for the molecular mean speed of N<sub>2</sub>O<sub>5</sub> and the surface area concentration.

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

\*\*This change has been made.

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6. P31916, L24 “means” = “mechanisms”

\*\*We have replaced “means” with “mechanisms”.

7. 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)?

\*\*We estimate how these RH differences could bias the measured uptake probabilities when discussing the surface area measurements made by the SMPS on P31918 L6-12. Additionally, we assume that the particle equilibration time to the flow reactor RH is instantaneous upon entering the flow reactor.

8. 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.

\*\*The Liu et al. (2011) reference provides additional information about the air masses and particle composition specific to this measurement location during the same time period. It was included for this reason. We have added a qualification in this regard.

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

\*\*The reviewed manuscript appears to have dropped punctuation in some places. This is likely an oversight on our part after the typesetting. We will address these issues with the production staff.

10. 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.

\*\*We acknowledge that this estimate is indeed more uncertain than implied by two significant digits. We have changed 61% to “approximately 60%”. Using sampling flows and inlet dimensions and configuration, we are able to calculate an estimate of the particle passing efficiency as a function of size as outlined by Baron and Willeke

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(2001).

11. P31919, L24 Ryder et al is not in the bibliography

\*\* This reference wasn't critical to the conclusions made in the manuscript. We have removed references to the work in preparation.

12. 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).

\*\*We mention this limitation in the Results and Discussion section and have added the following statement: “Non-refractory chloride does not include chloride from sea salt, which is not quantitatively measured by the AMS.”

The ability of the AMS to measure total fine mode chloride remains unresolved, and beyond the scope of this paper unfortunately. We certainly encourage AMS users to reassess the capability to develop a means of measuring both refractory and non-refractory chloride.

13. 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.

\*\*We have added the following statement: “This assumption is appropriate if organics are indeed hydrophobic and do not inhibit water uptake. Over the course of this study, there was significant alkane character to the organic mass which would support the assumption that organic species were hydrophobic (Liu et al., 2011), but we do not have direct knowledge of the particle hygroscopicity.”

14. P31919, L16 different “to”

\*\*This change has been made.

15. P31919, L21 what were the calculated (or assumed) losses resulting from sampling

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aerosol from a 90 degree T-piece?

\*\*We have added the following statement to the text:

“Much of the supermicron surface area is lost when sampling at 2 slpm through the 90 degree tee from the 14 slpm flow which results in a  $d_{50}$  of  $\sim 2.5 \mu\text{m}$ .”

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

\*\*Good point. We have changed these to the inner diameters.

17. P31919, L25 How much O<sub>3</sub> (from the N<sub>2</sub>O<sub>5</sub> source chemistry) was present in the aerosol reactor? Can the authors rule out that this amount of O<sub>3</sub> can impact on the aerosol reactivity to either N<sub>2</sub>O<sub>5</sub> or NO<sub>3</sub>?

\*\*As described in Bertram et al. (2009a), O<sub>3</sub> concentrations were on the order of 10 ppbv. These O<sub>3</sub> concentrations are significantly smaller than those typically found in ambient air, so the effects of O<sub>3</sub> from the N<sub>2</sub>O<sub>5</sub> source on the reactivity measurements are likely small, or at least no different than what occurs in the atmosphere.

18. P31919, L26 How much N<sub>2</sub>O<sub>5</sub> 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 N<sub>2</sub>O<sub>5</sub> be the cause of low uptake coefficients compared to ambient aerosol which were less chemically aged?

\*\*As described in Bertram et al. (2009a), N<sub>2</sub>O<sub>5</sub> concentrations at the entrance to the flow reactor were often on the order of 2 ppbv. The possibility for enhanced nitrate effect from synthetic N<sub>2</sub>O<sub>5</sub> was also examined in that publication. This effect would be most pronounced at low surface area and is estimated to bias  $k_{\text{het}}$  low by 20% at most compared to the true value. In this data set, the highest reaction probabilities were measured at lower than average surface area concentrations. Thus we presume that the  $\sim 20\%$  bias is not unreasonable.

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19. P31920, L9 Relative changes in N<sub>2</sub>O<sub>5</sub> signal were used to calculate the uptake coefficient and only MS count rates are plotted. It would however be useful to know (approximately) how much N<sub>2</sub>O<sub>5</sub> is present (for reasons listed above).

\*\*Please refer to comment #18 for approximate N<sub>2</sub>O<sub>5</sub> concentrations.

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

\*\*The air within in the flow reactor is adjusting to the particle laden or particle free conditions. There is an 8 minute mixing time scale (1/e) set by the residence time.

21. P31921, L15 At 750 pptv, the lifetime for NO<sub>3</sub> is only 2s. As N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> will reach equilibrium within the 8 minutes residence time in the reactor, this would result in substantial (indirect) N<sub>2</sub>O<sub>5</sub> loss. 750 pptv thus seems to be a rather high number to use as filter. Also, the presence of other reactive components (towards NO<sub>3</sub>) can impact on the measurements. How do the authors take this into account? Can some variability in the N<sub>2</sub>O<sub>5</sub> lifetime be a result of (highly variable) NO<sub>3</sub> losses?

\*\*As described in Bertram et al. (2009a), the system is somewhat buffered to NO through the reaction of O<sub>3</sub> with NO. 750 pptv was chosen because little evidence of NO effects on the N<sub>2</sub>O<sub>5</sub> signal were seen in field measurements at NO concentrations below this value. Certainly some of the changes in the N<sub>2</sub>O<sub>5</sub> signal could be a result of NO<sub>3</sub> chemistry. In an effort to reduce the potential effects of NO<sub>3</sub> chemistry, N<sub>2</sub>O<sub>5</sub> is generated with excess NO<sub>2</sub> ( $\sim 50$  ppbv) to force the equilibrium toward N<sub>2</sub>O<sub>5</sub>.

22. P31822, L15 The chloride content is not measured by the MS. Why were measurements of ClNO<sub>2</sub> not made along with N<sub>2</sub>O<sub>5</sub> (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.

\*\*Only the non-refractory aerosol chloride content is measured by the AMS, so the large aerosol chloride source from sea spray would not be reported by the AMS. We acknowledge this on P31922 L15-17. Regarding measurements we have added the

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following statement: "Additionally we estimated the CINO<sub>2</sub> branching ratio ( $\phi(\text{CINO}_2)$  - also referred to as the yield) using the reactivity apparatus. Uncalibrated CINO<sub>2</sub> signals were monitored by the CIMS during the N<sub>2</sub>O<sub>5</sub> uptake experiments. Despite the uncertainties resulting from the uncalibrated signals,  $\phi(\text{CINO}_2)$  values obtained are consistent with the low  $\gamma(\text{N}_2\text{O}_5)$  values. The mean  $\phi(\text{CINO}_2)$  was  $\sim 10\%$  with a standard deviation of  $\sim 10\%$ . It should be stated that under atmospheric conditions it is likely that significant CINO<sub>2</sub> formation occurs on supermicron particle surface area, the majority of which is likely lost in transit to the flow reactor as we describe above. Therefore these yield estimates are likely lower limits. With this in mind, the CINO<sub>2</sub> yields show no appreciable trend with AMS measured chloride, H<sub>2</sub>O/NO<sub>3</sub>, or POM/SO<sub>4</sub>. Experiments of this type certainly warrant additional investigations."

23. P31927, L3 suite "of"

\*\*This change has been made.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31911, 2011.

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