Interactive comment on “Direct $\text{N}_2\text{O}_5$ 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 $\text{N}_2\text{O}_5$ 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 $\text{N}_2\text{O}_5$ with large $\text{O}_3$. There is no text describing how loss of $\text{N}_2\text{O}_5$ via $\text{NO}_3$ reactions is taken into account. This will be an issue when the reactor is at higher temperature than ambient as the relative population of $\text{N}_2\text{O}_5$ and $\text{NO}_3$ will shift towards $\text{NO}_3$ (given that the thermal lifetime of $\text{N}_2\text{O}_5$ is shorter than the residence time within the reactor). Losses of $\text{NO}_3$ with aerosol, the reactor walls, $\text{NO}$ or VOC will then lead to a larger loss rate of $\text{N}_2\text{O}_5$ 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 NO2 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 NOx”. I’m not sure what this tries to convey.
   **This has been removed.

3. P31913, L25 Mention that ClNO2 is photo-labile and its formation from $\text{N}_2\text{O}_5$ is thus a route to NOx regeneration as well as chlorine release.
   **We have added the following statement: “ClNO2 is a photolabile compound that releases atomic chlorine and NOx upon photolysis, its formation and photolysis thereby decreases nocturnal NOx losses due to HNO3 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 $\text{N}_2\text{O}_5$ and the surface area concentration.

5. P31915, L14 Finlayson-Pitts (also in the bibliography)
   **This change has been made.
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 (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
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 d50 of \(\sim 2.5 \mu m\).”

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 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?

**As described in Bertram et al. (2009a), O3 concentrations were on the order of 10
ppbv. These O3 concentrations are significantly smaller than those typically found in
ambient air, so the effects of O3 from the N2O5 source on the reactivity measurements
are likely small, or at least no different than what occurs in the atmosphere.

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

**As described in Bertram et al. (2009a), N2O5 concentrations at the entrance to the
flow reactor were often on the order of 2 ppbv. The possibility for enhanced nitrate
effect from synthetic N2O5 was also examined in that publication. This effect would be
most pronounced at low surface area and is estimated to bias khet 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.

19. 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).

**Please refer to comment #18 for approximate N2O5 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 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?

**As described in Bertram et al. (2009a), the system is somewhat buffered to NO
through the reaction of O3 with NO. 750 pptv was chosen because little evidence of
NO effects on the N2O5 signal were seen in field measurements at NO concentrations
below this value. Certainly some of the changes in the N2O5 signal could be a result
of NO3 chemistry. In an effort to reduce the potential effects of NO3 chemistry, N2O5
is generated with excess NO2 (\(\sim 50\) ppbv) to force the equilibrium toward N2O5.

22. P31822, L15 The chloride content is not measured by the MS. Why were measure-
ments 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.

**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
following statement: "Additionally we estimated the ClNO2 branching ratio (phi(ClNO2)
- also referred to as the yield) using the reactivity apparatus. Uncalibrated ClNO2
signals were monitored by the CIMS during the N2O5 uptake experiments. Despite
the uncertainties resulting from the uncalibrated signals, phi(ClNO2) values obtained
are consistent with the low gamma(N2O5) values. The mean phi(ClNO2) was ∼10%
with a standard deviation of ∼10%. It should be stated that under atmospheric condi-
tions it is likely that significant ClNO2 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
ClNO2 yields show no appreciable trend with AMS measured chloride, H2O/NO3, or
POM/SO4. Experiments of this type certainly warrant additional investigations."