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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Direct $N_2O_5$ reactivity measurements at a polluted coastal site" *by* T. P. Riedel et al.

**T. P. Riedel et al.**

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Response to Anonymous Referee #2

We thank Referee #2 for reading the manuscript and providing helpful comments; below we provide responses to each comment individually.

General Comment by Referee #2: This paper presents new measurements of N2O5 reactivity and uptake coefficients at a coastal site in southern California. These are the first measurements using this apparatus, previously described by the same research group, that incorporate an explicit comparison to a recently derived parameterization of the dependence of N2O5 reaction probability on nitrate and chloride content of aerosol. Thus, the study serves as an important first-test for this parameterization, especially



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since it was done at a coastal, presumably chloride-rich, site. The writing is clear and the methodology is sound. The conclusions are well-reasoned and will add to the growing understanding of this important nighttime reaction. I recommend publication subject to consideration of the following, minor comments. In particular, the authors may want to clarify the degree to which the nitrate and organic aerosol content correlate, since their study shows clear evidence for a nitrate effect, but since it also requires additional suppression of the reaction probability to bring model and measurement into agreement.

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

Page 31913, line 9: A 1999 reference may not be completely appropriate for projections of future NOx trends from 2012

**We have also added a more current reference (Ohara et al., 2007).

Page 31915, equation (2): Equation not clear. What quantities are in the ratio? This should be expressed as rate coefficients rather than references to the reactions themselves, I believe.

**We agree that the quantities should be the rates of the respective reactions. We have added "Rate" before each quantity in the ratio in an effort to keep the expression as simple and succinct as possible.

Page 31916, line 13: Suggest replacing "elusive" with "not clear from the available data."

**This change has been made.

Page 31918, line 10-12: Up to 50% error in the gamma values based on the hygroscopic growth factors of the particles. What was the method used to calculate the hygroscopic growth? The AIM model referred to later?

**We used the hygroscopic growth factor of pure ammonium sulfate to serve as an



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upper limit to the water uptake. The AIM model was not used for these error estimates.

Page 31919, top: Was there any primary organic (POA) observed? Too small to be included? Also, there is no real use made of the organic categories later in the paper. Would it be appropriate to sum, rather than differentiate them?

**The factor analysis used to differentiate the organic species into OOA, MOA, and BBOA, did not include a POA factor, so it was not included. While we don't use the different factors explicitly in analysis, we chose to include the factors to potentially help illustrate the different kinds of air masses sampled. We have added a clarifying statement about our intent.

Page 31919, bottom: Is there any observable loss of particulate, and surface area, during transit through the halocarbon wax coated (i.e., non-metallic) flow reactor?

**As described in Bertram et al. (2009a), there are slight loses in particle number (on the order of 5% loss) and total surface areas losses of $\sim$25% for laboratory generated malonic acid particles. We did not assess the passing efficiency for this particular study, but in other studies ambient particle surface area losses within the flow reactor are stated to be $\sim$10%.

Page 31921, line 11: Wind rose in Figure 1 – the strongest winds were from the SSE and NNW, so transport from San Diego and L.A. is event driven, but the overall wind pattern shows no particular preferred direction - i.e., it appears that there is plenty of light wind data with no particular direction. Fairly typical for nighttime, surface-level winds. Also, the legend is difficult to read – suggest increasing font size.

**Indeed there were many occasions when the nighttime winds were light and local aerosols were sampled. In total, a large variety of different aerosol particles were likely sampled that originated from a variety of locations including very local sources as well as Los Angeles and San Diego.

We have increased the size of the legend.



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Page 31923 – 31924: Discussion of parameterized vs. observed reaction probabilities. Two comments. First, the parameterization does not include organics, which could explain the lower observed reaction probabilities. This point is treated in the discussion that follows, but could be referenced here as well for clarity. Second, the comparison is for averaged quantities – 24 hour averages of data taken at approximately 1 hour resolution (but then filtered, so fewer than 24 points per daily averaged point). Is there any possibility that the separate averaging of quantities used to derive the parameterization differs from the averaged reaction probabilities due to non-linear dependencies? The authors could add a comment on any such effect.

**As you have stated we discuss the lack of organic effects in the parameterization later in the text. As suggested we add a reference to this section alerting readers to our detailed discussion of this point in the following sections.

In an effort investigate artificial relationships that may result from differences in averaging between the AMS and the reaction probability measurements, we also chose AMS data only from time periods simultaneous with each reaction probability measurement so that the averaging was the same for all observed quantities. However, this selection did not substantially change the results from simply doing 24 hour bins.

Page 31924, line 23-25: What is the correlation between nitrate and organic? Could a co-variance explain the part of the variability not captured by the variation in nitrate alone? A simple correlation plot might be useful to clarify this point, which the authors do raise in the following paragraphs. Inclusion of the additional plot is at the author's discretion. The authors may also wish to discuss the reliability of the calculated water content from the AIM model. Presumably, a reduction in the calculated water content could bring the observations and the parameterization into agreement. Could the dependencies in figure 5 be used to fit the aerosol water content, for example?

**Indeed, as we acknowledge at the end of the "Results and discussion" section, there is a correlation between nitrate and organic ($\sim$0.7). Our current understanding of the



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nitrate effect, as illustrated by the “organic-free” parameterization, captures the behavior of the observations reasonably well. We don’t intend to imply that we therefore understand also the role of organics only that the observations appear to be consistent with an assumption that the nitrate/water ratio drives a significant fraction of the reaction probability variability. We clarify that the effect of organics remains unclear with the added statement:

“The explicit role of organics species on gamma(N2O5) remains to be determined and should be a topic of future investigations. ”

The AIM model represents our best estimate at particle water content, though the reviewer is correct in that it may likely have errors, and we were unable to verify its accuracy for the measurements described here. However, the AIM model predictions of particle water do compare reasonably well to measurements as shown in Engelhart et al., 2011 when using only the inorganic species to calculate particulate water. We have added a reference to the Engelhart et al., 2011 study in the text with the statement:

“The AIM model has been shown in other publications to reasonably estimate the particulate water content based on the inorganic particle composition (Engelhart et al., 2011).”

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