**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "NO$_3$ radical measurements in a polluted marine environment: links to ozone formation" *by* R. McLaren et al.

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General comments:

This is an interesting paper presenting new measurements of NO3 and a few related trace gases in a polluted marine environment on an island off the coast of British Columbia. The measurements and associated analysis are novel in several respects. First, although there have been previous studies that considered nighttime chemistry in the Lower Fraser Valley (LFV), this is the first such study in the marine boundary layer in that region. Second, the study presents a new analysis methods for understanding the relationship between lifetimes and reactivity of NO3 and N2O5. This analysis is applied to understand the trends in reactivity of the two compounds through an average night, and comparisons are made to similar analysis at other marine sites around the

world. Finally, there is an analysis of potential overnight halogen activation at this site and its relationship to air quality across the LFV region. These three aspects of the paper represent a new contribution and merit publication in ACP.

Of the three topics considered, the first two are relatively straightforward (though interesting). I have provided some minor comments below to which the authors should respond prior to publication. The third topic regarding halogen activation and O3 formation is very interesting and new, but clearly less certain than the rest of the paper. The first part of this analysis considers only the potential for the total mass of halogen activated, which is likely to be correct, although the authors should provide some note that the estimates are unconstrained by measurements of photolabile halogen species. The second part, correlating estimated overnight N2O5 (and by extension, halogen) production with inland O3 concentrations during sea breeze events on the following day, shows that such correlations are weak but statistically significant. Here the authors should consider other possible explanations for such a correlation, since presumably there are many: boundary layer depths and concentrations of local emission during sea breeze events, recirculation of pollutants during such events, and simple transport of NOx from the marine boundary layer, where it was observed to be abundant at night, inland during the following day. Although it is intriguing to consider the chemical mechanism related to halogen activation as an O3 source, the authors should note in this context that the observations are consistent with such a mechanism (i.e., observed enhancements are similar to those predicted from a limited set of modeling studies currently available), but do not provide proof of such a mechanism.

As a final comment, the paper is somewhat long – an effort to shorten it somewhat would be helpful to future readers.

Specific comments:

Page 3, line 63-65: Although there is a potential link between N2O5 reactions on acidic aerosol and Cl2 production, the particular Cl2 observations described here have been

linked to HOCl, rather than N2O5, as an intermediate. This should be noted alongside the potential N2O5 mechanism.

Page 9, line 265: Please define "wake induced stagnation effect."

Figure 5: "SAT-CAP" that appears in the legend should be more clearly defined in the figure caption in addition to its definition in the text. Earlier in the manuscript, NO2 measurements are listed as being carried out by "standard methodologies." Presumably, this means chemiluminescence instruments with Mo converters. These are known to have artifacts for NO2 and may report oxidized NOy species as NO2. If the data in figure 5 are from such instruments, it would be helpful to add a note to this effect since the reported NO2 levels are rather large. Such measurement artifacts might also play a role in the comparison between nearby sites, though they would not explain why the DOAS NO2 was higher.

Page 11, lines 335-337: Uncertainties in calculated N2O5. Is there a reference for the 10% uncertainty in forward and reverse rate coefficients, or is this assumed? The NASA/JPL recommendation gives the overall uncertainty in the equilibrium coefficient as 20% at 298, similar to the presumed uncertainty here. Also, should note the possibility for additional uncertainty in average N2O5 along the light path if the NO3 and NO2 are not homogeneously distributed.

Page 15, line 431: substitution is 4 and 5 into 9, rather than 8, correct?

Page 14-16, Equations 6-13. Equations 10,12 and 13 appear to be correct, and provide a an elegant, interesting and useful approach to understanding the reactivity of NO3 and N2O5 without reference to the (sometimes problematic) steady state approximation. However, I find the definitions of τ^* in equations (8), (9) and (11) to be confusing, especially since the quantity is re-defined (correctly, I believe) in equation (13). The confusion is simply that lifetimes are normally taken as concentration divided by source (rather than loss), and in this case, there is explicitly no assumption of equality between source and loss. These three equations (8,9,11) do not seem needed for the

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derivation, since one can get from (7) to (12) by simply dividing through by [NO3].

Also, it will be worth noting in this section that the d[NO3]/dt and d[N2O5]/dt in the equations are those due to chemistry alone; the observations will include concentration changes due to transport effects. The added uncertainty, or the conditions under which the transport effects would be minimal (i.e., well mixed air masses with constant values of tracers across a three-point derivative) should be noted at the end of this section. The analysis should work for measurements in reasonably well-mixed air masses from fixed locations, but would not work well, for example, from a mobile platform (ship or aircraft).

Page 16, lines 472-475: Another key difference with the 2003 Brown et al. study was in the inferred lifetimes, which were much longer. Shorter lifetimes (i.e., greater reactivity of NO3 and N2O5) should lead to much better agreement with steady state, as seen here.

Page 17-18, lines 508-532: Also worth noting that the apparent decay of kx would be consistent with (or evidence for) oxidation of biogenic VOC that had been emitted during daytime but not at night.

Page 20, lines 576-577: Notable here that some field studies have found good agreement between observed NO3 and loss due to homogenous hydrolysis (Ambrose, JGR 2007), while others have found the recommended homogeneous hydrolysis rate coefficient to likely be too large (Brown, JGR 2009).

Page 20, line 597-598: ClNO is not a product of N2O5 uptake, but rather NO2 uptake (i.e., derived from N2O4). Characterizing its contribution would be more difficult as it will not necessarily scale with the integrated N2O5 production. Also, some studies have suggested that ClNO hydrolyzes rapidly on liquid water surfaces (Finlayson Pitts, Nature, 1983) to provide a HONO, rather than a halogen, source.

Page 21, equation (17): Would the analysis be similar if one simply integrated the

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N2O5 production rate (k1[NO2][O3]), multiplied by the fraction of this production that reacts as N2O5 vs NO3 (determined here as roughly 50%)?

Section 5, Conclusions: Suggest shortening this section as it provides a rather long summary of the main text of the paper itself.