

We thank both referees for their thoughtful comments. We respond to the comments of each in turn.

## Response to Comments by S. Brown (Referee)

### Response to General Comments

We concur with the comments made in this section. Brown points out that in the third section of the paper, the estimates made of the total mass of halogen activated is "*unconstrained by measurements of photolabile halogen species*" and that the authors should "*...provide such note..*". This was our intent with the final paragraph of the paper, "While we have succeeded in showing that there is a correlation between nighttime chemistry in the marine boundary layer and maximum ozone in the valley, we have no definitive proof that photolabile species are causing the effect. Further measurements of photolabile chlorine species in this or similar polluted marine boundary layers and/or other evidence of Cl radicals being involved in the oxidation of VOCs would be needed to confirm this." Clearly, these points should be emphasized earlier in the paper, in the section Brown refers to.

Brown also points out that our observation of a correlation between integrated  $N_2O_5$  and  $O_3$  formation, are consistent with a mechanism related to halogen activation, but it does not provide proof of such a mechanism. You are absolutely correct. We observe a correlation between the overnight integrated  $N_2O_5$  and  $O_3$  formation, which could be consistent with several mechanisms, of which Brown has mentioned a few. It was our intention to communicate this, although it did not come across. We will strengthen this section by discussing all potential mechanisms.

### Response to specific comments:

Page 3, line 63-65: In Spicer et al.,  $Cl_2$  production overnight was not linked to known sources. Known chemistry could not explain the observations of  $Cl_2$ , with the final conclusion being that a non photolytic source of  $Cl_2$  exists at night. In the Finley paper, known mechanisms could not account for the  $Cl_2$  although there appears to be a daytime photolytic source. I will mention some of these other potential sources of  $Cl_2$  including  $ClONO_2 + NaCl$ ;  $NaCl + HOCl$  and OH mediated surface reaction mechanisms although the focus in this paper will be the nighttime mechanisms.

Page 9, line 265: The "wake-induced stagnation effect." is described in the stated reference by Brook et al. It is caused by convergence of flows from ~ 3 directions and a wake effect induced by the high elevation regions of Vancouver island and surrounding Gulf islands. This causes frequent nocturnal "stagnation" in the strait at the convergence zone of the 3 flows (NE, SE and land breeze from the LFV to the east).

Figure 5: The figure caption for Figure 5 will read " ...versus the Saturna CAPMon station (SAT-CAP) and other LFV monitoring stations (refer to Fig. 1)."....

Concerning the artifacts for  $NO_2$  via chemiluminescence instruments with Mo converters; yes this is worth mentioning. The artifact will likely NOT reduce the observed  $NO_2$  levels significantly as one expects in the urban areas of Vancouver that  $NO_x$  accounts for >90% of  $NO_y$ . The SAT-CAP station is run by Environment Canada and had a "true" photolytic convertor instead of a Mo convertor, so it measures true  $NO_2$ ...no artifact should exist. Clarifying statements will be added to the experimental sections.

Page 11, lines 335-337: The  $\pm 10\%$  was assumed.  $1-\sigma$  uncertainties in K quoted in another article [I. Wangberg, T. Etzkorn, I. Barnes, U. Platt, and K. H. Becker, J. Phys. Chem. A 101, 1997, 9694-9698] are also about  $\pm 20\%$ , as you have said for JPL. Instead of quoting 10% error in forward and reverse rate constants and propagating error ( $\pm 14\%$ ), I will quote  $\pm 20\%$  in K value. This gives a final propagated error of 28% in calculated  $N_2O_5$ .

You are also quite correct in your second point here. We have added a statement in the section based on your suggestion... *"An additional uncertainty in the calculated  $N_2O_5$  exists if the  $NO_3$  and  $NO_2$  are not homogeneously distributed along the light path."*

Page 15, line 431: Correct! Substitution is 4 and 5 into 9, rather than 8. This error was corrected before it went to the online version in ACPD.

Page 14-16, Equations 6-13. I note the confusion, however I think I would have to disagree with the statement ... *"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"*

As I understand it, the formal general definition of lifetime is actually the amount of a substance divided by the LOSS rate (not the source rate) [see for example D.J. Jacob, Introduction to Atmospheric Chemistry, Princeton University Press, 1999, page 25-26] . Thus, equation 8 is necessary since it is the most basic definition of the lifetime of  $NO_3$ , including all possible losses including reaction with  $NO_2$  to form  $N_2O_5$ . Equation 9 is then necessary since it formally defines the lifetime of  $NO_3$  in the  $NO_3/N_2O_5$  reservoir including direct and indirect losses but IGNORING losses due to exchange of  $NO_3$  and  $N_2O_5$  . Although this was the intent of most previous literature on the subject, I do not believe it has been communicated effectively in all previous papers. I believe it is necessary to distinguish  $\tau$  and  $\tau^*$  since they are in fact different.  $\tau_{NO_3}$  is the true lifetime of  $NO_3$  and  $\tau^*_{NO_3}$  is the lifetime of  $NO_3$  in the  $NO_3/N_2O_5$  system ignoring fast interchange between these species (ie  $\tau_{NO_3} < \tau^*_{NO_3}$  ).

It is true that equations 11 are not necessary and we may eliminate them in the final version. They were added for completeness. It may be that under polluted conditions, people may choose to use  $\tau^*_{N_2O_5}$  instead of  $\tau^*_{NO_3}$  since  $N_2O_5$  accounts for most of the amount of the reservoir. Note that what we have done here is similar to defining a lifetime for "odd oxygen"  $\{[O] + [O_3]\}$  in the stratospheric system in which most of the amount of  $O_x$  is actually  $O_3$ .

As you have suggested we will add a note that  $d[NO_3]/dt$  and  $d[N_2O_5]/dt$  in the equations are those due to chemistry alone; and do not transport fluxes. As mentioned to reviewer 1, who made the same comment, this is not a new imposition to the lifetime because we have added a derivative to the expression. This limitation also applies to all previous literature where the steady state lifetimes of  $NO_3$  have been calculated.

Page 16, lines 472-475: Good Point. We will add the following statement...

"It is also true that the shorter lifetimes encountered in this study compared to that in Brown (ie-greater reactivity of  $NO_3$  and  $N_2O_5$ ) lead to better agreement between the steady state and non steady state assumption.

Page 17-18, lines 508-532: I think your point is partially covered by the existing sentence... *"Depletions of monoterpenes and isoprene by NO<sub>3</sub> after sunset are also known to occur in continental areas (Geyer et al., 2001; Brown et al., 2009), as are certain reactive anthropogenic hydrocarbons (Dimitroulopoulou and Marsh, 1997)."*

To strengthen the argument, but not to attribute it solely to biogenics the following sentence will be added.

*"This apparent decay of  $k_x$  would be consistent with oxidation and significant depletion of species that have significant reactivity with NO<sub>3</sub>, many of which may have significant daytime fluxes."* (ie - biogenics AND anthropogenics AND DMS)

Page 20, lines 576-577: Clearly there is still some uncertainty here and my statement unintentionally oversteps the limitations of our current analysis. ie- We CANNOT determine from our analysis if the N<sub>2</sub>O<sub>5</sub> loss we see early in the evening is due to reaction with water vapor or due to heterogeneous losses on aerosols. We found it intriguing that the loss rate early in the evening agreed with the calculated loss rate using the current, but uncertain, recommendation for reaction of N<sub>2</sub>O<sub>5</sub> with water vapor. We will change several statements as follows, taking into account your comments...to get across the current uncertainty...

*"Losses of N<sub>2</sub>O<sub>5</sub> are thought to occur through homogeneous reactions with H<sub>2</sub>O (R10), with the current but tempered recommendation [Atkinson, 2004] of both a first order and second order dependence on H<sub>2</sub>O based upon recent work (Wahner et al., 1998), and...."*

*I will add a statement to the effect you have suggested :*

Some field studies have found good agreement between observed NO<sub>3</sub> 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).

"An intriguing result is that the magnitude of the observed value of  $k_y$  is consistent with the homogeneous gas phase hydrolysis rate of N<sub>2</sub>O<sub>5</sub>,  $k_{\text{homo}}$ , during the first few hours after sunset. Despite this, our result cannot be used as proof that the homogeneous reaction is indeed occurring since we cannot definitively differentiate between a homogeneous and heterogeneous reaction with the current analysis."

We have removed the following statement

~~However, we also observe that the losses of N<sub>2</sub>O<sub>5</sub> via the homogeneous hydrolysis mechanism are not insignificant, ranging in this study from up to 100% early in the night to a minimum of 23% later in the night, although this should be tempered by the uncertain nature of the current recommendation for the homogeneous rate constant of N<sub>2</sub>O<sub>5</sub> with H<sub>2</sub>O.~~

The conclusion section will also be modified accordingly.

Page 20, line 597-598:

The reference to ClNO had been removed before the paper was posted to ACPD, for exactly the reasons you have mentioned.

Page 21, equation (17): Perhaps what you are suggesting is something similar to what we have done with equation 19 to estimate  $\text{ClNO}_2$  production. Still, the 50/50%  $\text{NO}_3/\text{N}_2\text{O}_5$  reactivity split likely changes from night to night, and one still needs an estimate of the fraction of the  $\text{N}_2\text{O}_5$  heterogeneous reaction that produces photolabile species versus  $\text{HNO}_3$ .

Section 5, Conclusions: We will look for some efficiencies to shorten the conclusions

## **Response to Comments by Anonymous Referee #1**

### Response to General Comments

1. The referees comments are expressed well. The first reviewer made the same comment. Yes, the derivatives,  $d[\text{NO}_3]/dt$  and  $d[\text{N}_2\text{O}_5]/dt$  are due to chemistry alone and do not include the effects of transport of inhomogeneous air masses. Ultimately, to use this approach, one depends on a large fetch of homogeneous air close to the site. Note that this limitation not only applies to the non-steady state approximation outlined here but also applies to lifetimes calculated using steady state lifetimes in all previous publications on this subject. The addition of the derivatives to the lifetime expression do not suddenly impose a new limitation. We will add some cautionary notes concerning this. Unfortunately, we have no auxiliary tracer data to support the study.

2. Yes. Again, the first referee, Brown, made the same comment. It was never our intention to suggest that our analysis can be used as proof that the homogeneous hydrolysis of  $\text{N}_2\text{O}_5$  is occurring, although our text in existing form seems to suggest this. ie- We CANNOT determine from our analysis if the  $\text{N}_2\text{O}_5$  loss we see early in the evening is due to reaction with water vapor or due to heterogeneous losses on aerosols. We found it intriguing that the loss rate early in the evening agreed with the calculated loss rate using the current, but uncertain, recommendation for reaction of  $\text{N}_2\text{O}_5$  with water vapor. To see our planned changes, see the response to Brown under: Page 20, lines 576-577:

3. A valid point. As the  $\text{NO}_3$  and  $\text{NO}_2$  distributions suggest in Table 1,  $\text{NO}_3 > 4\text{ppt} \sim 75\%$  of the time and  $\text{NO}_2 > 2\text{ppb} \sim 90\%$  of the time. Due to the detection limit limitation of our set-up, we have excluded analysis on 25% of the low  $\text{NO}_3$  concentration data. More than half of this eliminated data appears in the light periods of dusk and dawn when photolysis losses would complicate the lifetime analysis. Thus we have only eliminated  $\sim 10\%$  of the true dark nighttime data. We do not consider this to be a significant bias.

4. It is unfortunate that we did not present this non-steady state analysis in a situation where differences might be more obvious. But science is science whether there is a positive or negative result and we still feel it very important to communicate this result. Since these measurements represent the most polluted marine environment in which  $\text{NO}_3$  lifetime analysis has been attempted in the literature (to the best of our knowledge) we felt it important to eliminate in advance the potential criticism that steady state analysis is uncertain especially under high  $\text{NO}_2$  conditions, as shown by Brown in the 2003 paper. That potential uncertainty has been eliminated. Added to this, after reading all the literature on  $\text{NO}_3$  lifetime analysis, we felt it was important to illustrate that it IS possible to calculate lifetimes under those conditions when the steady state assumption may not apply. The map and method has been laid out for future analysis, perhaps in slightly cooler marine environments.

Minor, specific comments and technical corrections

Abstract Line 8. : Thanks for the suggestion. we have done so.

page 24533, line 10. okay

page 24535 line 4. It has been reworded. *"The primary purpose of the study was to measure nighttime NO<sub>3</sub> and NO<sub>2</sub> and to determine the levels of N<sub>2</sub>O<sub>5</sub> in the MBL at a suitable..."*

lines 13 – 21 and page 24536 lines 1 – 9. We prefer the non tabular format for reactions. It is also not necessary to give detailed kinetic expressions for reactions that we do not use in our analysis. All rate values that are used in our analysis have been referenced. ie - we use rate coefficients for k<sub>2f</sub> and k<sub>2r</sub> from Atkinson 2004, to calculate N<sub>2</sub>O<sub>5</sub>, as already indicated in the text.

The comment about surface deposition of N<sub>2</sub>O<sub>5</sub> is an interesting comment. We will consider adding a relevant comment in the final version.

page 24536, line 5. completed.

line 6. completed.

line 13. Will do, although many references to daytime NO<sub>3</sub> < detection limit of 1ppt exist from literature in the 80's and 90's.

line 19: but "N<sub>2</sub>O<sub>5</sub> or ClONO<sub>2</sub>" might imply that one of them is responsible and it is not known which one. I will reword to read...

"...time ago that both N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub> can react individually with NaCl(s)..."

page 24539, line 6. The NO<sub>3</sub> data were not corrected for the temperature-dependence of the NO<sub>3</sub> absorption spectrum, which would be a very small correction at 18°C, much less than the uncertainty of the measurements. It is much more important to do this at lower temperatures.

page 24541, line 13. completed.

line 18. completed.

page 24542, lines 3-7.

The most significant factor for low levels of ozone in urban areas are almost certainly due to titrations of ozone by NO, as we have mentioned first. Deposition of ozone in a **shallow** layer over land is a second factor we mentioned and NOT insignificant. Note that the nighttime inversions over land are stronger and frequently more shallow than over water....in addition to the fact that the deposition velocity of O<sub>3</sub> over land is higher than over water by about a factor of 6 (~ 0.4 cm s<sup>-1</sup> vs 0.075 cm s<sup>-1</sup>). Using these numbers and inversion heights, h, of 100m over land and 200m over water, the lifetimes of ozone with respect to deposition ( $\tau = 1/k_d = h/v_d$ ) are ~ 6.9 hrs over land and 79 hrs over water. Obviously these are highly dependent on conditions, but using these

reasonable numbers we see that the lifetime of  $O_3$  is an order of a magnitude smaller over land than over water which can remove over up to 75% of  $O_3$  over land in the absence of NO during the course of a 10 hr night. But titration in the urban area via NO typically removes 100% in a matter of hours.

In the reaction sequence R1-R14, we have included only chemical reactions. Our intention is not to include equations for physical processes, which can be mentioned in the text when relevant.

The point about the potential deposition of  $N_2O_5$  is well taken. We will look into this.

line 21. The magnitude of a projection is likely not reliable but the trend of the projection likely is. Emission inventories are developed using bottom up engineering approaches. The GVRD (now Metro Vancouver), from which these estimates come from, has a history of developing the most detailed spatial emission inventories in Canada. I believe the projection is relevant information since it makes a statement about the potential for the relative importance of Cl/OH chemistry in this region in the future. The NO<sub>x</sub> (and potentially Cl contribution) over the Strait of Georgia is not projected to go away.

Page 24543, line 24-25. Vancouver falls within NNW to NNE sector from Saturna. Station T1 on Robson Street (i.e.-the heart of the action in Vancouver Winter Olympics 2010) is directly north. Land breezes at night carry Vancouver emissions west from the city where they enter the Strait, and then encounter the NW winds. This is well documented in literature. I will add a reference [Brook, 2004, and others]

Page 24544, line 10-11. My understanding is that gases mix rapidly vertically in an unstable air mass (aka - daytime convective boundary layer) but vertical mixing is much slower in a night time stable boundary layer (non-convective) as would exist at night. Stratification occurs in nighttime inversions due to the positive temperature gradient ( $dt/dZ > 0$ ), much as occurs in the stratosphere. This slows the vertical mixing significantly...it is not necessarily rapid, and certainly slower than daytime.

Line 21 The authors know the region was polluted with NO<sub>2</sub> due to our measurements. We know that marine vessels played a role because we could see the vessels (and their plumes at a distance) as was mentioned. We also know the flux of regional pollutants ( $kg/m^2$ ) is quite high from the emission inventories (modeling estimates).

page 24545, line 9. Okay.

lines 16 – page 24546, line 8. This section could be shortened somewhat. We will consider this...although comparison of results to other literature is somewhat standard protocol.

line 20 – equation (2). yes, ClNO<sub>2</sub> would be a nocturnal reservoir species. But since we do not have measurements of ClNO<sub>2</sub>, it doesn't make sense to define a new quantity  $F^*(NO_x)$  in this paper that we cannot calculate. Thus, we would prefer to retain  $F(NO_x) = [NO_3] + 2[N_2O_5] / ([NO_2] + [NO_3] + 2[N_2O_5])$ , which has been published recently in other literature that we can compare to. We can only be as inclusive as our measurements here....ideally we would use NO<sub>y</sub> and have a measure of NO<sub>y</sub> (presumably ClNO<sub>2</sub> would be measured by a NO<sub>y</sub> instrument).

page 24547, line 25. The lifetimes are not necessarily lower limits. They can be biased high or biased low depending on if the nighttime reservoir is growing or shrinking

pages 24548 and 24549 – see comments above? Not sure what is meant here.

page 24551. As we explained earlier in these responses, we believe that the issue of bias is minor (i.e.-we are losing only 10% of our data during true nighttime conditions). Put another way, we do not analyze data when NO<sub>3</sub> and/or NO<sub>2</sub> are below detection limits, and thus we are biasing our results slightly towards more polluted conditions, by excluding some data with clean conditions. Thus, the analysis is applicable to all but the cleanest conditions. The bias may be the opposite of what you think.

page 24552 – line 9 “Eq (9)”. Yes, we meant equation 13. Thanks.

line 12: We will add “presumed slow heterogeneous losses of NO<sub>3</sub>” but I will look for supporting reference(s). The new measurements with alkene monolayers sound like very unique surfaces and are likely not applicable to MBL aerosols.

line 14, equation (14), and line 15. Okay, we will change to refer to Reactions 4 & 7.

page 24553, line 7. Okay reference will be added for these stated rate constants.

page 24554, lines 14 and 18. References will be added. Thanks for the reference.

page 24555, line 4. As seen in the response to Brown, we have now struck this whole sentence, which should be acceptable to the referee.

page 24556, equation (16). Yes. This was a typesetting error by ACPD. Concerning P<sub>i</sub>, sorry for the confusion....I will change instantaneous concentration of product to p<sub>i</sub> and total accumulated amount stays as P<sub>i</sub>

lines 9/10. Done. No losses of products. Better to strike it.

*"For photolabile species such as ClNO<sub>2</sub>, and Cl<sub>2</sub> that have few losses at night, accumulation will occur overnight such that the total accumulated concentration by morning, P<sub>i</sub>(t), assuming constant conditions ~~and no losses~~, is given by:*

page 24560. Done

page 24564 line 15. d[N<sub>2</sub>O<sub>5</sub>]/dt ? YES. Typo has been corrected.

page 24565 lines 7-9. I may shorten the conclusions. If not the statement here will be qualified with a statement that the apparent agreement between the observed loss rate of N<sub>2</sub>O<sub>5</sub> and the calculated homogeneous loss rate of N<sub>2</sub>O<sub>5</sub> could be coincidental and may not be used as proof one way or another of homogeneous loss of N<sub>2</sub>O<sub>5</sub>.

line 12. Done.

line 14. Changed to ... "are in the range, k<sub>het</sub> = (1.2±0.4) ×10<sup>-3</sup> s<sup>-1</sup> - (1.6±0.4) ×10<sup>-3</sup> s<sup>-1</sup>, (excluding or including homogeneous loss component, respectively) consistent with other recent reports for heterogeneous loss of N<sub>2</sub>O<sub>5</sub> in the marine boundary layer.

line 29. Done.

page 24750, lines 4-7. Pages 324-328 now added.

page 24573, Table 2. Both  $r$  and  $r^2$  are acceptable in literature, although, generally I have seen more criticisms for scientists including  $r$  instead of the more conservative  $r^2$ . Statistically the percentage of variance attributable to the correlation is predicted by  $r^2$ , a valid reason for using it and not  $r$ . Including  $r^2$  is not misleading since the sign on the slope tells us if it is positive or negative correlation. The stations with negative slopes are not statistically significant....I would interpret them as being zero within error.

page 24578 We will remove one or stations. They are there just to give an indication of the range of  $\text{NO}_2$  seen in the valley.

page 24580, suggested changes can be made.

page 24582, Will change sec to s. Arrows are meant to guide the reader's eye to the correct y-axis range. Typo is fixed.

page 24583, Figure 10. I am wondering if a tighter correlation could have been obtained with max 1-hr next-day ozone and nocturnal  $\text{NO}_x$ .

Perhaps, although mechanistically, there is no rational for expecting a correlation with  $[\text{NO}_2] + [\text{NO}_3] + [\text{N}_2\text{O}_5]$ ? Perhaps we could explore a separate correlation with  $\text{NO}_2$  or  $[\text{NO}_2]^2$  in order to explore recent suggestions of ClNO production from  $\text{NO}_2$  surface reactions.

page 24585. Okay. We will consider improving the clarity of the figure.

Thanks for all your thoughtful comments.