

Interactive comment on “NO₃ radical measurements in a polluted marine environment: links to ozone formation” by R. McLaren et al.

Anonymous Referee #1

Received and published: 17 December 2009

General comments.

This is a well-written and interesting paper showing new data and a new analysis method. Measurements of the NO₃ radical in the Georgia Strait near Vancouver Island and links between nighttime nitrogen oxide chemistry and photochemical ozone production on subsequent days are presented. Overall, the manuscript scores well in the 15 different evaluation points highlighted by the ACPD instructions to reviewers. I recommend publication after the following concerns have been addressed.

(1) The analysis as presented in equations (4-7) neglects the potential effects of transport of NO₃ and NO₂ into and out of the DOAS light path but fails to mention this clearly. The air mass between the DOAS light source and retro-reflector will have changed during this interval even when winds are fairly calm; any concentration changes during this

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time interval observed are thus due to both chemistry and transport. In other words, the derivatives, $d[\text{NO}_3]/dt$ and $d[\text{N}_2\text{O}_5]/dt$, as defined via equations (4-7), cannot, in my opinion, be accurately determined simply by measuring $[\text{NO}_3]$ and $[\text{NO}_2]$ at the same location 10 to 15 minutes apart, without making a crucial assumption about the effects of transport. I suggest that the authors add a few sentences discussing the impacts of transport on their analysis method following the words “observational data” on page 24549, line 10. Transport effects may be minimal if the observed air masses are fairly homogeneously mixed and not impacted by nearby emissions; if that was the case, the authors should present supporting data (e.g., measurements of inert pollution tracers such CO, CO₂ and/or SO₂) if they exist.

(2) It is interesting to note that the observed NO₃ and N₂O₅ lifetimes in this study were short, consistent with observations made near the surface in New England and other coastal locations (e.g., Ambrose, J. L., et al. (2007), Nighttime nitrate radical chemistry at Appledore island, Maine during the 2004 international consortium for atmospheric research on transport and transformation, *Journal of Geophysical Research-Atmospheres*, 112(D21), D21302, Brown, S. S., et al. (2007), Vertical profiles in NO₃ and N₂O₅ measured from an aircraft: Results from the NOAA P-3 and surface platforms during the New England Air Quality Study 2004, *Journal of Geophysical Research-Atmospheres*, 112(D22), D22304, doi:22310.21029/22007JD008883). In the analysis presented here, homogeneous hydrolysis appears to be a major nocturnal NO_x loss process, which I believe to be incorrect. The 1st and 2nd order rate constants for homogeneous hydrolysis of N₂O₅ reported by Wahner and coworkers (1998) were, in fact, upper limits and have recently been shown to be inconsistent with field measurements of NO₃ and N₂O₅ (Brown, S. S., et al. (2006), Variability in nocturnal nitrogen oxide processing and its role in regional air quality, *Science*, 311(5757), 67-70 – this paper should be added to the citations) and are also inconsistent with the high yields of ClNO₂ reported by Osthoff et al. (2008). I would argue that the observed short lifetimes are at least in part due to some process or processes other than homogeneous hydrolysis. The dependence on relative humidity would also be

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consistent with a heterogeneous loss process via growth of the aerosol surface area density. Since there is convincing evidence in the literature that the homogeneous hydrolysis rate constants reported by Wahner et al. are too large, I recommend changing the relevant sections of the manuscript.

(3) I was wondering if the authors could comment on biases in the analysis that arise from the fact that only relatively large NO₂ (2 ppbv) and NO₃ (4 pptv) mixing ratios could be observed. This biases the entire data set towards relatively long lifetimes of N₂O₅ and NO₃ and may have affected the conclusions.

(4) Re: Comparison of steady state with the non-steady state method. Figure 7 is rather unfortunate since the results are roughly the same with either method – so what, then, are the advantages of the new method? Consider adding a plot such as Figure 7 for N₂O₅. Perhaps it will show a difference between steady state and non-steady state?

Minor, specific comments and technical corrections

Abstract Line 8. The \leftrightarrow symbol indicates resonance structures. Please replace with a proper double-headed arrow. A proper double-headed arrow can be found here: <http://www.rsc.org/education/teachers/learnnet/RSCfont.htm>

page 24533, line 10. Consider also citing Noxon, J. F., et al. (1980), NO₃ in the Troposphere, *Geophys. Res. Lett.*, 7(2), 125-128.

page 24535 line 4. In the phrase “measurements of NO₃ and NO₂ (and calculated N₂O₅) by DOAS” strike “and calculated N₂O₅” as one cannot measure “calculated N₂O₅”.

lines 13 – 21 and page 24536 lines 1 – 9. The reaction scheme is better put in a table. It would also be helpful to give values or equations/expressions for rate coefficients (if known; please give references) as they are used to calculate, amongst other things, concentrations of N₂O₅.

I am also curious why surface deposition was ignored here (it was, after all, considered

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for ozone, see further below).

page 24536, line 5. Missing superscript (H⁺)

line 6. The \leftrightarrow symbol indicates resonance structures. Please replace with a proper double-headed arrow.

line 13. Following “typically less than 1 ppt”, please give a citation. Suggestions: Geyer, A., et al. (2003), Direct observations of daytime NO₃: Implications for urban boundary layer chemistry, *Journal of Geophysical Research-Atmospheres*, 108(D12), 4368, doi:10.1029/2002JD002967, Brown, S. S., et al. (2005), Aircraft observations of daytime NO₃ and N₂O₅ and their implications for tropospheric chemistry, *J. Photochem. Photobiol. A-Chem.*, 176(1-3), 270-278, and/or Osthoff, H. D., et al. (2006), Observation of daytime N₂O₅ in the marine boundary layer during New England Air Quality Study - Intercontinental Transport and Chemical Transformation 2004, *Journal Of Geophysical Research-Atmospheres*, 111(D23), D23S14, doi:10.1029/2006JD007593.

line 19: replace “N₂O₅ and ClONO₂” with “N₂O₅ or ClONO₂”. The “and” implies that both N₂O₅ and ClONO₂ have to be present for the reaction to occur.

page 24539, line 6. Were the NO₃ data corrected for the temperature-dependence of the NO₃ absorption spectrum?

page 24541, line 13. Missing comma between “ppt” and “respectively”.

line 18. Change “The profile shows NO₃ increasing after” to “The profile shows mixing ratios of NO₃ increasing after”

page 24542, lines 3-7. I don't fully buy the explanation made for low levels of ozone in the surface layer. To my knowledge, deposition of ozone is not sufficient to titrate ozone to zero at night; more likely explanations are: 1) titration of ozone by NO and unsaturated hydrocarbons emitted from the ground and anthropogenic sources, and 2) conversion of ozone to other forms of nocturnal odd oxygen such as NO₃ and N₂O₅ (see Brown, S. S., et al. (2006), Nocturnal odd-oxygen budget and its impli-

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cations for ozone loss in the lower troposphere, *Geophys. Res. Lett.*, 33(8), L08801, doi:08810.01029/02006GL025900.).

If the authors insist that surface deposition of ozone is sufficiently fast to compete with the other processes, then surface deposition processes of NO₃ and N₂O₅, whose deposition velocities are likely greater than that of ozone, should be included in the chemical mechanism (R1-R14).

line 21. "... and are projected ... by 2030". Is this relevant and/or reliable information? I personally don't have much faith in people with crystal balls, nor do I see the relevance of this prediction to this paper. Consider striking this sentence.

Page 24543, line 24-25. "The NW sector likely contains outflow emissions from Vancouver as well as marine vessel emissions". When I look at the map, Vancouver is located NNE relative the sample site, so at first glance it's unlikely that the NW sector contains outflow emissions from Vancouver. Can the authors substantiate this statement (e.g., are there measurements of tracers, or have previous studies identified this flow pattern in this region?)

Page 24544, line 10-11. "Vertical mixing over water in the MBL will be slow." How slow, and what is "slow"? Did you authors perhaps mean "entrainment to a height of 200 m will likely be slow"? My understanding is that gases mix rather rapidly (vertically and horizontally) within a boundary layer...

Line 21 "impacted by emissions from marine vessels and from regional anthropogenic emissions". How do the authors know this? Were there measurements of SO₂, CO₂, NO_y, or particulate matter?

page 24545, line 9. Following the sentence beginning with "This is generally true" please cite Osthoff, H. D., et al. (2007), Temperature dependence of the NO₃ absorption cross-section above 298 K and determination of the equilibrium constant for NO₃+NO₂ <-> N₂O₅ at atmospherically relevant conditions, *Phys. Chem. Chem.*

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Phys., 9(43), 5785-5793.

lines 16 – page 24546, line 8. This section could be shortened somewhat. A comparison of observations of N₂O₅:NO₃ ratios (and calculated N₂O₅:NO₃ ratios) in different regions is not very informative as these ratios are mainly functions of temperature and [NO₂].

line 20 – equation (2). For marine boundary layer data, I would also consider CINO₂ a nocturnal NO_x reservoir species, especially at the high NO_x levels and N₂O₅:NO₃ ratios described in this study. Thus, the equation should be changed to $F(\text{NO}_x) = \frac{[\text{NO}_3] + 2[\text{N}_2\text{O}_5] + [\text{CINO}_2]}{([\text{NO}_2] + [\text{NO}_3] + 2[\text{N}_2\text{O}_5] + [\text{CINO}_2])}$. Also, at the colder temperatures described here, PAN should be considered a nocturnal NO_x reservoir.

page 24547, line 25. "are cast in doubt". True, but how about: "are lower limits"? pages 24548 and 24549 – see comments above

page 24551. As I said earlier, I am concerned that the data set is biased towards long lifetimes.

page 24552 – line 9 "Eq (9)". This equation does not contain k_x or k_y. Did you mean eq (13), perhaps?

line 12: "The slow heterogeneous loss of NO₃". There have been some recent lab investigations describing fast het. uptake of NO₃ (e.g., Gross, S., and A. K. Bertram (2009), Products and kinetics of the reactions of an alkane monolayer and a terminal alkene monolayer with NO₃ radicals, *J. Geophys. Res.-Atmos.*, 114, D02307, doi:02310.01029/02008JD010987 and Gross, S., and A. K. Bertram (2008), Reactive uptake of NO₃, N₂O₅, NO₂, HNO₃, and O₃ on three types of polycyclic aromatic hydrocarbon surfaces, *J. Phys. Chem. A*, 112(14), 3104-3113). Perhaps better to say "presumed slow heterogeneous losses of NO₃"?

line 14, equation (14), and line 15. k_{NONO3} and k_{i,NO3} were already defined as k₄ and k₇ earlier.

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page 24553, line 7. References are needed for the values of KOH,DMS and KNO₃,DMS.

page 24554, lines 14 and 18. Citations are needed for both deliquescence and efflorescence points of sea salt, e.g., Tang, I. N., et al. (1997), Thermodynamic and optical properties of sea salt aerosols, Journal of Geophysical Research-Atmospheres, 102(D19), 23269-23275.

page 24555, line 4. "losses of N₂O₅ via the homogeneous hydrolysis mechanism are not insignificant". I disagree with this statement. Consider replacing the "are not" with a "may not be".

page 24556, equation (16). [N₂O₅] should not be subscript. equation (17). I was at first confused by the symbols Pi and Pi(t) as they are not referring to the same thing. Please choose more dissimilar symbols.

lines 9/10. remove space from "Pi (t)". Also, "no losses" of what? Products? Reactants?

page 24560, line 14. Subscripts needed for N₂O₅.

page 24564 line 15. d[N₂O₅]/dt ?

page 24565 lines 7-9. "The loss coefficient ... night." See my earlier concern.

line 12. Replace "moist" with deliquesced.

line 14. Please give a range estimate.

line 29. Square brackets are missing in d[O₃]/dt

page 24750, lines 4-7. Page numbers are missing from the citation.

page 24573, Table 2. Giving r₂ is misleading. State r instead. If there are negative r values, please provide an explanation.

page 24578, Figure 5 is too crowded. Consider removing some traces and showing C8655

them in a supplemental material section. The vertical axis title should have a subscript.

page 24580, Figure 7. Please abbreviate seconds with "s" in axis title. Also, use notation that is consistent with the main text (e.g., tau* and tauss), not SS and non-SS.

page 24582, Figure 9. Please abbreviate seconds with s in axis titles. What do the arrows mean in the figure? Caption: typo: psuedo.

page 24583, Figure 10. I am wondering if a tighter correlation could have been obtained with max 1-hr next-day ozone and nocturnal NO_x (e.g., NO₂+NO₃+2N₂O₅)?

page 24585. Figure 12. The clarity of this figure could be improved by moving the captions "Day +0.5" and "Day +1.5" off the maps (they are hard to spot on the maps) and offsetting the top and bottom panels from each other.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24531, 2009.