

# ***Interactive comment on “Low levels of nitryl chloride: Nocturnal nitrogen oxides in the Lower Fraser Valley of British Columbia” by Hans D. Osthoff et al.***

## **Anonymous Referee #1**

Received and published: 12 February 2018

Osthoff et al present a thorough study of NO<sub>y</sub> composition in the Lower Fraser Valley in British Columbia where air quality episodes can occur, but did not during their study. Notably, despite being a coastal site, low levels of ClNO<sub>2</sub> were observed due to limited nocturnal NO<sub>x</sub> chemistry. A comprehensive description of the results is provided. My main comments below surround the discussion of the aerosol data and the presentation/formatting of the main text. A full list of detailed comments is provided below.

Major Comments: There are numerous places in the manuscript where 1-2 sentence “paragraphs” exist (Section 2.2 and elsewhere throughout); these sentences should be

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integrated in longer paragraphs for improved flow. Currently, this makes the manuscript difficult to read, and it also makes appears sloppy. I disagree with the authors that these revisions should wait until “the type setting stage” (authors’ response to Quick Review), as I believe that it significantly impacts the presentation of the results and discussion. Similarly, please refer to reaction numbers in the text when the reactions are presented (e.g. page 4 and elsewhere).

There are many places in the text that state “(not shown)” with respect to results and ask the reader/reviewer to trust the authors; it would be more helpful for the reader’s evaluation of the results for these data to be presented in the supplementary information.

Section 2.5: More information is needed for the description of the box model. A list of reactions should be provided in the supplementary information. Is chlorine chemistry included? Are aerosols included?

Lines 443-445: This sentence can be strengthened by referring at least to the timing of the ozone maximum for support, and perhaps referring to the next section. Otherwise it sounds like a guess that you cannot support further, which is not true.

Section 3.1.5: This section needs the most revision, particularly with respect to the presentation and discussion of the ACSM data. The authors quantify fractions of “total aerosol mass” (e.g. line 541); however, only non-refractory submicron aerosol was measured. It is expected that refractory sea salt aerosol contributes significantly to this site, so these calculations are expected to be inaccurate. Similarly, the authors discuss the “inorganic mass fraction” and “most abundant inorganic component”, which also are influenced by refractory aerosol, such that the mass fractions are expected to be inaccurate. The discussion of the ACSM data must clearly reflect that only submicron non-refractory mass was measured and that sea salt aerosol (most relevant for CINO<sub>2</sub> production) was not measured.

Lines 509-517: It should be clarified that this only reflects the aerosol <0.5  $\mu\text{m}$  in

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diameter, based on the size range measured by the SMPS. Since aerosol surface area peaks at a higher diameter than aerosol number, it would be expected that this calculation of aerosol surface area may be a significant underestimate. This should be stated, and the implications of this should be discussed where appropriate.

Lines 554-558: The authors should refer to Zhang et al (2007, Environ. Sci. Technol.) for the proper method for examining aerosol acidity using ACSM data. Please show the gas-phase NH<sub>3</sub> data, at least in the supplementary information.

Lines 559-562 and Figure 6 caption: Only non-refractory chloride was monitored by the ACSM, and this should be noted, given the importance for ClNO<sub>2</sub> production. If the signal was below the instrument limit of detection, then the concentration calculated is, by definition, not accurate. The text should be revised to reflect these two important points.

Lines 566-570: The time of year is expected to be quite important for these comparisons. Please provide this information in the discussion.

Lines 616 & 621: Do these dry deposition rates make sense in the context of previously published literature?

Lines 629-630: Why is this data not shown? It is about modeling the “faster Ox loss at the beginning of the night”, which seems central to the section header “Box model simulations of the nocturnal O<sub>3</sub> and Ox loss in the NBL”.

Lines 632-634: Why was the model not simply constrained to measured NO? Did NO under these modeled conditions match what was measured?

Lines 692-694: Not including loss of NO<sub>3</sub> to hydrocarbons is not justified here. Why not assume a generic BVOC as you did in an earlier section, or use the data that you do have? These options seem better than blindly ignoring this NO<sub>3</sub> loss process. Further, on lines 706-707, you state that reaction between NO<sub>3</sub> and isoprene was likely significant, suggesting that that reaction should be included, especially since the

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authors have at least some measurements of isoprene. Also, not including NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> deposition is not justified. It seems that dry deposition could be easily included. Where time periods that fog and rain occurred used? If so, these periods should be removed for these calculations.

Lines 721-723: It is assumed that the production of nitrate on refractory aerosol is minimal, but this is not justified and is a poor assumption. Nitric acid displacement of HCl is one of the most common sea salt aerosol aging pathways (Gard et al. 1998, Science).

Line 757-762: Only non-refractory chloride and nitrate were measured! This should be considered and reflected in this discussion.

Line 827: How does this observation of a lack of non-refractory submicron aerosol chloride compare to other similar inland coastal AMS/ACSM studies?

Lines 913-916: The authors suggest that the lack of particle-phase chloride (should be 'non-refractory' chloride) is in contrast to their previous study, Mielke et al. 2013, in Pasadena, CA. However, in that previous paper, AMS PM<sub>1</sub> showed very little non-refractory chloride, with far higher levels of PM<sub>2.5</sub> chloride (refractory + non-refractory measured by PILS-IC) measured. So, this is not a complete comparison, and in fact, in terms of non-refractory PM<sub>1</sub> chloride, the studies seem fairly similar. This discussion should be reconsidered and revised.

Table 1: Please add the SMPS and ACSM size ranges, as well as note that the ACSM aerosol composition reflects only the "non-refractory" aerosol.

Minor Comments: Line 65: Fix typo – "particle" should be "particulate".

Reaction 6 should include chloride as a reactant.

Please add references to the following lines: 77, 99, 108, 426, 431, 887.

Lines 135-136, 837: Fix reference formatting in sentence.

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Line 337: Fix typo – “day used” should likely be “day were used”.

Section 3.4, Table 2, & anywhere else: “down-dwelling” and “up-dwelling” should be “down-welling” and “up-welling”.

Line 457 & elsewhere: Error should be given as one significant figure, with the average value provided with the same number of decimal places. For example, line 457 should list 64 +/- 1 ppbv, rather than 64.4 +/- 1.2 ppbv.

Lines 459-461: Provide values in parentheses for context.

Line 467: Change “:” to “.”

Line 469: Fix typo – “loss of are” should likely be “loss are”.

Line 482: Fix typo – “at a median value” should be “at median values”.

Lines 483-484: Fix typo – “ratio of this campaign was” should be “ratios of this campaign were”.

Figure 5: Please clarify this figure caption. It was not obvious at first what “lhs” and “rhs” stood for, as these acronyms are not defined.

Lines 601-603, 854-859: Please revise sentences to improve clarity.

Line 658: Fix typo - “are” should be “is”.

Line 664: Delete sentence as this information is already given on line 660.

Lines 730 & 914: Fix typo – “ACMS” should be “ACSM”.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-1027>, 2017.

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