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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chlorine oxidation of VOCs at a semi-rural site in Beijing: Significant chlorine liberation from $ClNO_2$ and subsequent gas and particle phase Cl-VOC production" *by* Michael Le Breton et al.

Anonymous Referee #2

Received and published: 2 March 2018

Le Breton and coworkers present data acquired using a commercial instrument, an iodide FIGAERO-ToF-CIMS, collected 40 km NW of Beijing in the summer of 2016. Mixing ratios of N2O5 and ClNO2 were quantified and a large number of halogenated molecules, some of which oxidation products of VOCs, were identified for the first time. The authors claim to have quantified particle phase ClNO2. Overall, the manuscript contains results that will be of interest to the broader atmospheric chemistry community and can probably be published after my comments below have been addressed.

Major comments

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Discussion paper

- The manuscript suffers from organizational issues. Reactions are not consecutively numbered, sections were skipped, etc.

- Mixing ratios of a variety of trace gases, including HCl, Cl2, ClONO2, HOCl, OClO and ClO as well as CMBO, isoprene, IOPEX, and benzene as well photolysis frequencies are presented but it is unclear in many cases how these data were acquired or how instrumental response factors were determined.

- Furthermore, concentrations of Cl and OH were calculated on the basis of steady state assumptions. These calculations are questionable since the only VOC measurements were by PTR-MS, an instrument that quantifies many but not all VOCs. Crucially, a PTR-MS usually does not quantify alkanes, whose abundances are important sinks for Cl atoms.

- Some data (e.g., OClO, CMBO, ClO, ClONO2, IOPEX) are only semiquantitative and should be presented as such.

Specific comments

pg 1 line 27 –replace the comma with "and"

line 29 – ppt is not a concentration unit – please rephrase

pg 2 lines 17 – (O3, HOx, and NOx levels via ... (R1-R9)). Most of the Cl will likely abstract hydrogens from hydrocarbons (R11), in particular at this site. Another important reaction omitted here is OH+HCl->H2O+Cl. Consider reorganizing the introduction to reflect this.

pg 3 lines 2-4. –"This perturbation is currently thought to only be significant in the early hours of the day while OH concentrations are low and chlorine atom production is high through the photolysis of ClNO2."

I don't think this is correct. Reaction of Cl with alkanes produces peroxy radicals, which feed into the "regular" HOx/NOx cycles. Thus, the early morning injection of radicals

impacts (perturbs) radical chemistry for the remainder of the day. Perhaps the authors meant to say "Oxidation of VOCs by Cl is currently thought to be ..."?

lines 11/12 – there are two reactions labeled R11

line 31 – "36%" - please add the value for SOA yield from OH initiated oxidation of isoprene for comparison.

pg 4 line 24 – how were photolysis rates determined?

line 31 – there are two Le Breton et al. 2017 references. Please label them 2017a and 2017b.

pg 5 lines 1-2 Please provide more detail as to how the PTR-MS was calibrated, what molecules were quantified, etc.

line 17 - section 2.3 is absent.

Please describe how the response factors for HCl, Cl2, ClONO2, HOCl, OClO and ClO (Figure 3) were determined

lines 24-25 – "The N2O5 diffusion source was held at a constant temperature (-23 C), and the mass loss rate was characterized gravimetrically for a flow rate of 100 sccm."

N2O5 is quite hygroscopic, such that the diffusion source could "gain weight" simply by absorbing residual moisture. Another potential error with this method is "loss" of NO3 (e.g., through reaction with impurities on the wall) followed by loss of NO2 (toward which the CIMS is probably blind). All this probably doesn't matter since there was a CEAS on site.

How stable/accurate/reproducible is this source? Could it be used as standalone N2O5 calibration method?

Please state if the diffusion source method has been verified using CEAS (which I assume it has).

Line 36 – "these sensitivities" – please state the instrumental response factors here.

pg 6 line 20/21 –"A quadrupole CIMS may not be able to resolve the peak adjacent to ClO at mass 178 and the second dominant peak for the ClNO2 fit would result in a 10% over estimation."

Please clearly state what ions are present at mass 178.

It is unclear what is meant by "second dominant peak for the ClNO2 fit" – is this at m/z 208?

line 32 – please put the N2O5 mixing ratios in context – (temperature, O3 and NO2 levels, NO3 production rate etc.)

line 33 – Were the instruments operated on the same inlet? If not, there may be scatter simply from sampling air at slightly different locations.

line 36 – The offset should have units of ppt

pg 7 line 2 – "although averaging at 4 ppt" perhaps better to give a relative error here

line 3 – please move details on how instruments were operated (heated IMR) to section 2.2

line 21- "Inorganic chlorine abundance and profiles". There is a lot presented in this section, BB, WRF etc, that goes well beyond inorganic chlorine abundances and profiles. This section should be broken up into smaller, more coherent pieces.

line 24 – mixing ratio, not concentration

line 25 – "σ 270 ppt" is this standard deviation?

lines 33 – pg 8 line 9. Please comment on the possibility of chlorine nitrate forming on the inner walls of the inlet.

pg 8 line19. –" This suggests the chlorine has an anthropogenic source and not marine" I disagree.

One has to be careful with the interpretation of AMS data. The "standard" AMS chloride product only includes non-refractory aerosol, i.e., does not include sea salt chloride – for one, it does a poor job volatilizing NaCl, and most AMS have a size cut off of 1 micron that filters out most of the larger sea salt aerosol particles. The correlation of AMS chloride with anthropogenic tracers may arise from acid displacement of sea salt chloride in polluted air (that is high in SO2). I'd suggest rewording the entire paragraph (lines 14-27). I don't doubt that anthropogenic Cl sources contribute, but there aren't enough data (shown in this paper) to proof a negligible marine influence.

line 28 - Please describe the WRF model in the methods section, not in the results section.

I'd remove the WRF simulations as they may not account for local BB – chemical tracers would be more robust.

pg 9 line 13. All that is shown is that WRF modeling suggests BB to be a small source of chlorine – it doesn't show industrial emissions. Please rephrase.

line 14 The particle desorption profiles should be discussed in their own section.

lines 14-20. Did you observe the peak at 210? Please expand the AMU axis in Figure 5 to show it.

line 30 " these data indicates a significant amount of the chlorine associated with ClNO2 is not liberated from the particle phase" it should be "these data indicate"

More to the point, you observe that you can drive off ClNO2 if you heat aerosol. Have you considered that additional ClNO2 could be formed by thermally driven reactions? If not, please state that this is a major assumption made here.

line 31-33 "The slope" please show this plot (perhaps as an insert in Figure 5).

Personally, I wouldn't call 5% "significant" considering this is much less than the measurement (calibration) error.

pg 10 line 18 The numbering of the reactions is inconsistent with those on pg 2. Some reactions are unnecessarily duplicated.

line 25 - Please number the steady state expression.

A major source of Cl atom is the reaction OH + HCl -> H2O + Cl, which should not be omitted here. line 26 - And how was "equivalent CH4" determined for this site? It must be massive.

It is very likely that the PTR-MS misses most of it, for example all of the alkanes (Table 2 of de Gouw's Mass Spectrometry Reviews 26, 223 (2007)).

line 32 – How can HCl become a dominant source of Cl atom if it's not part of the steady state expression?

pg 11 line 9 – "The results show that both at the UK marine and urban site max chlorine atom concentrations are more than an order of magnitude lower than the mean of Beijing." Considering the uncertainty of the Cl atom sinks, the authors should only compare Cl atom production rates. Comparing rural and urban sites (Weybourne with Beijing) is like comparing apples and oranges. Many other groups have calculated Cl atom production rates from ClNO2 photolysis, including many polluted urban sites. How do the numbers of this study stack up to these?

line 29 – " Steady state calculations of OH (as described by Whalley et al., 2010)"

Such calculations require comprehensive knowledge of the VOCs, CO, NOx, etc. present., more than is provided by a PTR-MS (whose list of VOCs monitored is not comprehensive).

Imo, the entire section comparing OH and Cl abundances is questionable.

pg 12 line 30 – "longer atmospheric lifetime" how long are the lifetimes of CMBO and of isoprene?

line 34 – "The concentrations of Cl and isoprene were relatively low" How low is rela-

tively low? Please be quantitative.

If CMBO abundances did not follow those of its precursors, does that imply that CMBO can be primary (or originates from other precursors)?

How certain are we that CMBO is a unique marker of chlorine-isoprene chemistry (line 25)?

pg 13 line 36 " ClNO2 was potentially identified in the particle phase "

I agree, but in the preceding text, ClNO2 was not only identified but also quantified, or was it? Either way, the earlier section is inconsistent with the much more conservative conclusion in the end.

pg 14 – many references are incomplete (e.g., Pszenny et al.) and most are missing their doi.

pg 19 – Figure 1. Please identify the green, gold/yellow, and magenta lines. For the second panel, it would be useful to show a blank (zero) measurement also.

pg 20 – please define the "C" and "M" terms

pg 23 – Figure 7A or 7B – one of the "y" axes is mislabeled.

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