Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-236-RC2, 2018

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Observations of organic and inorganic chlorinated compounds and their contribution to chlorine radical concentrations in an urban environment in Northern Europe during the wintertime" *by* Michael Priestley et al.

Anonymous Referee #2

Received and published: 30 March 2018

This manuscripts reports measurements of inorganic chlorine species (ClNO2, Cl2 and HOCl) and chlorinated, oxygenated volatile organic compounds (ClOVOC) taken in Manchester, UK using time of flight chemical ionization mass spectrometry. The authors quantify average concentrations of these species, their diurnal profile as well as their contribution to the total chlorine radical budget.

The manuscript is well written and these measurements and data are of interest to the ACP community. However, I have major concerns regarding the quantification of measured species, as detailed in my comments below, which should be addressed before publication.

General comments

- The sensitivity of the iodide CIMS is known to depend on relative humidity. This needs to be accounted for in quantification of the analyzed species. This means that the authors will need to redo calibrations at different relative humidity and apply adjusted calibration factors accordingly. This is likely to affect the observed diurnal trends as RH generally varies over the course of the day (with temperature)

- The authors measured backgrounds every 6 hours for 20 minutes and state that they calibrated for formic acid throughout the campaign and during the campaign. I request that the authors provide results from these background measurements and calibrations, e.g. as supplemental information, and interpretation thereof. Some of the questions I would like to see addressed are: how much did background concentrations vary? Which background was subtracted when concentrations varied significantly between two background measurements (i.e. was linear interpolation used)? Overall, how large was the effect of background subtraction on the reported species concentrations? How much did the instrument sensitivity (measured as sensitivity to formic acid) change over time? Were any patterns observed in this change over time?

- Instrument background and inlet effects are expected to vary with relative humidity. This should be addressed in the manuscript. At least authors should take some background measurements in the lab at different relative humidity and report observed differences. (They may also be able to do this in the field considering these measurements were taken from their university campus; albeit in a different season.)

- I have major concerns about the quantification of ClOVOC – see additional specific comments below. If quantification (as a first order estimate) is retained in the revised manuscript, the large uncertainty (from assumptions including using the sensitivity of acetic acid) should be stated again in the results and/or discussion section, not just the methods section

Specific comments:

- Line 129: the authors describe how they minimized losses to the sample line. Did they then characterize the losses? What were they?

- Line 142-144: the authors state that they used the sensitivity of acetic acid for the detected (oxygenated) organic chlorine species (ClOVOC). No justification is provided why this may be appropriate, and I am not convinced that it is. They did calibrate for some non-oxygenated organochlorides. What were the sensitivity of those and how much did it differ from that of acetic acid? I recognize that it might be difficult to obtain standards of the oxygenated organochlorides, but could the authors calibrate for one ClOVOC? Again, how does that sensitivity compare to the sensitivity of the other organochlorides and other oxygenated organics? How does it depend on RH (see comment above)? Overall, with the work that has been done so far, I am unconvinced that it is appropriate to quantify ClOVOC. Also, qualitative trends (which are interesting in the absence of calibration) need to be adjusted for RH effects.

- Lines 159-161: the authors state that they “feel” this calibration method works well, but that is not very convincing, also considering that the results differ by 58% compared to the other calibration method applied. They authors then state that they consider this 58% their measurement uncertainty. A few points regarding this are that: 1) the measurement uncertainty is not mentioned anywhere else in the paper but should be - quantitative results should be stated with a measurement uncertainty 2) other variables are expected to increase total uncertainty, including inlet and background effects and changes in instrument sensitivity. These other factors should be included in the total measurement uncertainty.

- Line 164-166: do these previous studies ensure a 100% conversion efficiency (as currently stated) or do they assume it? If they ensure it, how so? If they assume it, what is the justification?

- Line 175: what justifies the assumption that ClONO2 would have the same sensitivity as ClNO2?

- Line 188-190: the authors state that HCl was not measured; however, discussion later in the manuscript seems to suggest HCl was not detected, which is different. Please clarify.

- Line 190 (loss processes of Cl): Why do the authors not include the VOC + Cl loss mechanism? (Presumably, this is how the observed ClOVOC are formed.)

- Equation 7 – why does this equation not include photolysis of the organochlorides (ClOVOC)?

- Line 203-206: Have the authors checked whether photolysis of other ClOVOC are available in other models/databases, e.g. the JPL kinetics database https://jpldataeval.jpl.nasa.gov/? How do the photolysis rates compare?

- Line 236-238: please justify not accounting for LOD when calculating statistics on the observed concentrations

- Line 267: the authors find that the behaviors of ClONO2 and ClNO2 are very similar. Is this consistent with what we would expect? Could the observed ions be fragments of each other (i.e. only be one species)?

- Line 330-332: what is the LOD for these species?

- Section 4.2: Could you compare these predicted Cl concentrations with predicted OH concentrations (to be able to assess the importance of Cl chemistry compared to OH chemistry)?

- Line 417: what makes the assignment of the molecule tentative?

- Line 435-436. The authors state that ClOVOC can be a source of Cl. Aren't VOCs also a Cl sink? See comment above.

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