Response to Reviewers

Again we thank the reviewers for their further comments which are addressed below. The response to each point immediately follows each comment and is coloured red. Updated quotations from the manuscript are in blue. Quotes from the original text are in green.

Reviewer 2.

Review of “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 M. Priestley et al. ACP-2018-236

Anonymous Referee Comments

The improvements to the manuscript provide a sufficient change relative to previous versions to warrant publication of this manuscript to ACP. I have only minor comments which should be addressed prior to publications.

Detailed Comments:

I still remain apprehensive about the robustness of the zero determinations. The authors cite stability in instrumental mass calibration parameters and lack of IH2O changes as evidence of a stable background. The background however is a function of what has been previous sampled as well as instrumental parameters. As to figure 3 in the response, the authors should color the data by date/time and the correlations with ambient humidity will stand out. The jumps observed and scatter are most likely due to changes in tuning or sensitivity throughout the project, e.g. single ion current adjustments. I am happy to concede as the authors clearly state how backgrounds were performed in the manuscript for the readers.

As described in the response we recognise the limitations of the background method. We feel the 20 minute background time is a good compromise between reducing data capture losses and being sufficiently long enough to remove the effects of any species that are still present in the instrument.

I would like to see more information of the actual sensitivities included in the body of the manuscript, perhaps in the individual molecule sections in 3.1…

The calibration factors of the Cl species have been added to the text.

“The Cl_2 calibration factor is 4.6 Hz ppt^{-1}.”

“As all chlorinated VOCs we observe are oxygenated we assume the same sensitivity found for 3-chloropropionic acid (10.32 Hz ppt^{-1})“

“$ClNO_2$ was calibrated by the method described by Kercher et al. (2009) with N_2O_5 synthesised following the methodology described by Le Breton et al. (2014) giving a calibration factor of 4.6 Hz ppt^{-1}.“

“We calibrate HOCl using the methodology described by Foster et al. (1999) giving a calibration factor of 9.22 Hz ppt^{-1}."

If the detection limit for CH2Cl2 is 143 ppb and CHCl3 is 11ppb you could at most be missing 150ppb of Cl from those sources. How would that effect your budget?

We have not considered these species as sources of Cl as their photolysis rates are negligible at ground level as provided by the TUV model (described in section 2.2).

In the conclusion you should be explicit in saying those levels were below detection limit and removing the phrase "were not detected".

This distinction has been made more explicit by replacing the text in green with the text in blue

No aliphatic or polychlorinated species were detected, although the ToF-CIMS with I^- is sensitive towards them e.g. methyl chloride (CH_3Cl) dimethyl chloride (CH_2Cl_2) and chloroform ($CHCl_3$).

Although the ToF-CIMS with I^- is sensitive towards chlorinated and polychlorinated aliphatic compounds e.g. methyl chloride (CH_3Cl) dimethyl chloride (CH_2Cl_2) and chloroform ($CHCl_3$), their concentrations were below the detection limit.

On page 9, section 3.1 you are comparing CL2 observations to C2H4O5 and C10H14O4 to imply photochemical formation or lack thereof. How can you interpret the source of a compound that you have not identified and only have a molecular formula for?

OVOCs have a variety of primary and secondary sources, so differences in their diurnal profiles are expected. Whilst we do not know the identities unequivocally, the behaviour of $C_2H_4O_5$ is similar to Cl_2, O_3 production and the incidence of direct solar radiation, suggesting photochemistry whereas $C_{10}H_{14}O_4$ did not exhibit any of these behaviours. We make the assumption that a highly oxidised molecule such as $C_2H_4O_5$ with a high O:C ratio is more likely to be the product of photo-oxidative processes than the result of direct emission.

I do not see why the section on the newer ClNO2 calibration method is included here if the conclusion is that the approximations are incorrect and the sensitivity determined is wrong. Why not just drop that portion, use the Kercher 2009 method here and work on the method for a future publication?

We accept that the Kercher method is well established and reliable and so use it as our calibration method. We feel the TF-CIMS method is of interest to the community who, as well as ourselves, may also want to develop it further.

In your response, page 2. Where does the idea that formic acid has one of the strongest humidity dependences known for iodide adduct CIMS come from?

We make this observation based on our experience of calibrating many organic and inorganic compounds.

Abstract line 30, add space after contributing
Page 3, line 87, There seems to be a word missing in the last sentence.

Page 5 and 6, remove the quotes from this paragraph.

These typos have been corrected