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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 #1

Received and published: 12 March 2018

This manuscript summarizes measurements made of organic and inorganic chlorinated species in Manchester, UK. The manuscript focuses on the contribution on ClNO2, Cl2, HOCl and organic chlorides on the daytime Cl radical budget. While the paper is clearly written, there are several shortcomings that need to be addressed prior to publication in ACP. Chiefly among them is an extensive laboratory analysis to validate the identity and calibrate the species presented in this work. As written, most of the paper, with the exception of ClNO2, Cl2, and HOCl observations, could be called speculative and qualitative; however it is presented as quantitative data. The

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topics presented in this manuscript could be a relevant and a beneficial contribution to available literature, however the methods are in need of improvement. My recommendation for this manuscript is to return the work to the authors for major revisions including addition work. This manuscript needs laboratory validation of new species, real calibrations, and true error analysis for all species discussed.

The point of this paper is to evaluate the balance of sources of daytime chlorine radicals as observed in Manchester, UK. As such, it becomes important to both state accurate metrics of accuracy and precision in order to truly determine if the radical contributions from a given source are indeed significant. As such, proper zeroing methodology, calibration, and robust error analysis are required in this analysis, all of which seem lacking.

The zeroing method used in this analysis is to zero with dry nitrogen once every 6 hours. The frequency of zeroing is completely insufficient to capture any real changes in instrument background that may have been occurring that are likely to occur on the time scale of minutes to tens of minutes with changes in atmospheric composition, ambient temperature, humidity, etc. Additionally, the iodide adduct ionization scheme is heavily dependent on the water mixing ratio in the flow tube/IMR. In particular, the sensitivity of formic acid and Cl2 are extremely water dependent, in opposite directions, especially at very low IMR water mixing ratios. Considering a typical operating scheme where the inlet flow is matching the source flow, adding dry air at the inlet will result in a 50% change in the IMR humidity. Therefore, dry N2 zeros used here are not truly reflective of the actual ambient background. How were the zeros applied to the data, linear interpolation? What is the error on consecutive zero values? What is the approximate measurement error induced by both the changes in sensitivity due to dry N2 use and interpolation of infrequent zeros. Not accounting for zeros properly will often induce individual features and a diurnal profile that are impossible to distinguish from true ambient observations. Especially when there are humidity dependent changes in sensitivity that then have a diurnal shape related to ambient RH.

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One of the major issues with the analysis provided here is a lack of true quantification of many species. The authors state that acetic acid was used to provide a sensitivity for the organic chlorine species. Why would the authors expect that the sensitivity of acetic acid is even relatable to a halogenated organic? The addition of a large electronegative group to the molecule could either reduce the sensitivity due to steric reasons or increase the sensitivity due to increased polarizability or dipole moment. The way I read this manuscript is that one third of the results, particularly the newest results are driven by the observations, quantification, and calculation of the impact of these organic chlorine species on the chlorine radical budget. It seems necessary that for validation and calibration purposes, several of these compounds be bought/made and sampled on the CIMS. The results presented in section 4.3 discussing the potential importance of these species uses a seemingly random calibration factor and an assumption of a uniform photolysis rate from CH3OCl for the calculation. Therefore, data presented for the organic chloride species are completely based on assumptions and not hard quantitative information about the particular molecules being discussed. There is no way of determining the actual error on these numbers, therefore no way to determine if these species have a measurable impact on the Cl radical budget.

The calibration of the N2O5 source, upon which the ClNO2 calibration is determined, seems to need additional laboratory work. The synthesis method, based on Kercher 2009 almost always produces a significant portion of HNO3 which would be detected on both the CIMS and the NOx analyzer. Was there HNO3 observed on the CIMS from the N2O5 source?

The comparison of the two methods of ClNO2 calibration showing a difference of 58% does not tell you anything about your measurement uncertainty, only that one of your calibration methods was flawed or incorrect. Again, without a true robust calibration with known errors it is very difficult to determine the relevance of the numbers calculated in this manuscript. Since this calibration was used to establish the ClNO2 concentration, it is necessary to determine the reasons for the differences in the two

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calibration techniques and determine the most accurate calibration method to use, as well as the true instrumental errors.

It is very likely a bad assumption that ClONO2 has the same sensitivity as ClNO2. ClONO2 is likely to have more fragmentation pathways in the IMR than ClNO2.

How do the authors know that the correlation of I2NO2- and NO2 is not indicating that the I2NO2 product is simply some ion formed from various components of NOx. Did the authors add NO2 to the instrument to validate the presence of the I2NO2 cluster ion? If so that should give you a calibration factor, do the concentrations match up? What if the sensitivity is nonlinear, can't that explain the difference and not necessarily a NOy fragmentation product? Why is this section even in this manuscript? What does this have to do with the observations and impact of chlorinated species? In my opinion, all of section 2.3 should be removed from this manuscript and is only a distraction.

The iodide system is based on detection via clustering, so I would assume that this particular instrument would be tuned to promote the formation and stability of ion clusters. As such, the authors need to reconsider the identification of both IClONO2 and IC2H4O5. If the authors truly are observing ClONO2 that would be one of the first if not the first boundary layer tropospheric observations of that species and would be of significance. I would offer this alternative that IClNO2 is known to fragment to ICl under varying IH2O conditions. That ICl can the cluster with NO3 in the ion flow tube to produce IClNO3. Given the correlation between ClNO2 and ClONO2 in figure 2, there is a significant possibility this is what is occurring. Deviations in the correlation could be driven by changing NO3- levels. I can also contribute that from my experience, heating and cooling of Teflon lines used in source nitrogen will change the amount of Cl- in the ion flow tube. In the case of C2H4O5 the simple explanation without evoking a rare molecule is this is formed during the daytime from the cluster of acetic acid and ozone. This peak is always identified and used in the high res mass list in my own analysis and should be universally included in Iodide adduct mass lists. I encourage the authors to return to the lab and investigate these alternative possibilities prior to publishing this

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work.

On the topic of the N2O5 interference, C2H4O5, why is it that the authors indicate that they cannot measure N2O5 during the day, but do not reciprocate the interference. The unknown C2H4O5, which I believe is acetic acid and O3, could be present in the evening as well rendering the N2O5 nighttime measurement suspect. The high-resolution fitting routine should be able to provide some degree of separation between these two species, at the very least in a qualitative sense or to bound the potential magnitude of any interference when the routine is run both including and excluding the C2H4O5 peak. In any case, presentation of this N2O5 discussion is also seemingly unnecessary to this manuscript as the measurements are not discussed or presented anywhere in the manuscript. Therefore I would suggest removal of this discussion.

It does not contribute to the manuscript to include the two discussion about DCM and chloroform for seemingly no other reason than to show first detection. If you do not see them, why is this information relevant? You have calibration factors for these and not the organic chloride compounds of interest. You can use the calibration factors and the detection limit calculated here to at least make a statement of the maximum potential concentration in the atmosphere during your study, if you really need to make a statement about these.

What does the sentence "Methyl chloride and chlorovaleric acid were also detected in the laboratory but not quantified" mean? Did you see them in the ambient data? Were they accidentally detected when sampling lab air? Again, why is this information in the manuscript? Why did you look for these if they are not in the atmosphere.

Because of the potential to have a changing Cl- (m/z 35) in the system and ICl- from ClNO2, I have concerns about the validity of the chlorinate organic observations. It is difficult to interpret these signals as ambient observations especially since the zeros are performed so infrequently and no information can be provided indicating the humidity dependence of the sensitivity of those molecules. It is possible that these features

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are driven by instrumental conditions and not reflective of the ambient atmosphere. Do the authors have any data showing instrument zeros occurring during the peak of a high concentration incidence, where the zero doesn't also reduce the instrumental Cl-? Basically, do these species zero? It is difficult to tell from figure 2 and 4, but the peak in organic chloride species and minimum in daytime humidity seem to be coincident on a daily basis. That could be indicative of an ion chemistry sensitivity change. The only way to truly tell if these signals are real is to first establish that you can detect the individual molecules, show a lack of humidity dependence or remove any humidity dependence, and properly account for instrument zeros. Otherwise this data is purely speculative and qualitative, and in the worst-case scenario not real ambient observations.

On page 8, line 276 the authors mention a persistent interference on HOCl, what is that interference? How can the authors conclude that the rest of the data is free of said interference? Why can the two peaks not be resolved via high resolution fitting?

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