

Response to reviewers on "Chlorine oxidation of VOCs at a semi-rural site in Beijing: Significant chlorine liberation from ClNO₂ and subsequent gas and particle phase Cl-VOC production" by Michael Le Breton et al.

Report 1

I thank the authors for having taken many of my suggestions in consideration and having made many appropriate changes. This manuscript will require further edits before it can be considered for publication as the present version seemed to have been submitted in a bit of a rush. It would have been nice to see a marked-up version of the paper that indicated what precise changes were made (there was a marked-up version but of another paper attached to the author-response-version2.pdf file).

Major comments

1 - Many of the "measurements" (HCl, Cl₂, ClONO₂, HOCl, ClO, OClO, CMBO, IOPEX, ...) continue to be presented with units of mixing ratios, even though the instruments making these measurements have not been properly calibrated for these compounds.

For example, the authors stated in their response letter that "Le Breton et al 2017 showed that inorganic halides have a similar sensitivity. Furthermore, the comparable sensitivity for chloroacetic acid and ClNO₂ emphasize a similar sensitivity for chloride containing species when applying the iodide ionisation". It is unclear if this paragraph refers to the 2017a or 2017b paper and what is meant by the terms "similar" and "comparable", since these are qualitative, not quantitative descriptors.

It'd be OK if the data were presented as raw data with units of Hz or counts and the subsequent discussion of the data (including that of Cl VOCs) adjusted accordingly. The use of concentration or mixing ratio units, however, is not justified.

The manuscript has now been amended to present uncalibrated species with units of counts.

2 - The calculations of Cl and OH concentrations using simplistic steady state equations remain questionable. For starters, some of the input parameters are highly uncertain (see point #1 above). There are also some pretty coarse assumptions being made about the Cl and OH hydrocarbon reactivity at this site.

Yes, one can calculate concentrations using rough approximations and steady state assumptions ("In previous work (Bannan et al., 2015) we have shown that it is possible to calculate Cl atom concentrations using simple state expressions"). However, simply having these type of calculations before does not mean that this approach gives accurate results (as the text in the supplemental suggests, see specific comment below).

Furthermore, just because a past steady state calculation "agreed well with the MCM" does not mean it will agree for other data sets (not sure what "agreeing well" even means in this context). Besides, chlorine chemistry is a recent addition to the MCM and is likely still incomplete, such that it hardly constitutes a gold standard.

We agree with the referee and we hope that we have clarified the uncertainty in the steady state calculations through the modified text that follows in the main text and the SI section

Main text:

Although this approach is an estimation, it was shown to produce results comparable with that of the more rigorous MCM approach although we do acknowledge large errors will be present in the radical species calculations, which is detailed in the supporting information.

SI section:

There is a large uncertainty in the radical concentrations estimated in this work using the steady state method and this is fully acknowledged. The production rates for Cl are calculated directly from measurements of species, e.g. ClNO₂ concentrations and their photolysis rates, estimated by a photochemical model and so that aspect of the calculation has a relatively small uncertainty. There will be missing sources of Cl production that are not measured but the main known precursors are represented in these calculations. However, the loss rate carries the bulk of the uncertainty in these calculations; first it is known that not all VOCs are measured and even after estimation of missing VOCs there will be some missing loss. Second, calibration of some VOCs in this campaign will be uncertain, hence the reporting of counts per second rather than absolute numbers. Third, the rate coefficients associated with the loss processes will carry some uncertainty too. Finally, the distribution of missing VOCs is based on USA and European emission profiles and these may be different from those from Asia. Therefore, the uncertainty in radical concentration using this method will be at least 50%, where 20% is from rate coefficient uncertainty, taking into consideration temperature

dependences, and an estimated 30% from uncertainty in concentration measurements. However, OH reactivity measurements (e.g. Yang et al., 2016) provide a direct measurement of total loss rates and although not a direct comparison with Cl loss rates they can serve as a guide. Using 20s^{-1} as an estimate for the total loss rate for OH the steady state calculations are predicting loss rates in the range $10\text{-}15\text{ s}^{-1}$. Therefore, a 50% uncertainty and recognising that the concentrations generated are almost certainly an upper limit provides some further context to these calculations.

3 - some "action" items identified by the authors themselves have not been completed - for example, reactions are still not numbered consecutively (see specific comments below), entire paragraphs appear without sub- and superscripts, the references continue to have doi's missing, plus there are still numerous grammatical errors that need be corrected.

The reactions are now numbered consecutively and all sub and superscripts are now applied appropriately

Specific comments

pg 1 / lines 29 and 30. Use of pptV and ppt is inconsistent. The acronym ppt should be defined as it could be misunderstood as part per thousand.

ppt and ppb is now consistently used throughout the text

pg 2 / line 29. "The liberated chlorine will predominantly react with VOCs"

This should be one of the reactions listed above. Cl will more quickly abstract a hydrogen from a hydrocarbon (or add to a double bond) than react with O₃.

We state below the equations that OH "will predominantly react with VOCs with the pathways listed (R2-R11) representing alternative routes to loss of the chloride radical. The description of VOC oxidation then follows in the next paragraph.

pg 2 / line 31 HO₂, RO₂ etc. should have subscripts

These formulas have now been subscripted

pg 3 / line 7 - "The oxidation mechanism of saturated hydrocarbon (R12-R13) is"

Please rephrase.

This has been rephrased to read

"Saturated hydrocarbons are usually oxidised by reaction with OH or chlorine atom to form an organic peroxy radical (RO₂), and H₂O or HCl depending on the oxidant (R12 and R13), which is the dominant pathway for chloride-VOC reactions."

pg 4 / lines 7-12 A major factor (which should be acknowledged here) is the availability of aerosol chloride, which varies considerably between measurement locations.

The following sentence has been added

"A major factor in the variation of ClNO₂ mixing ratios is the availability and abundance of aerosol chloride which can vary significantly, although is predominantly present as sodium chloride from sea salt."

pg 5 / lines 6-9. Thanks for adding more detail on the photolysis rate measurements. Please state whether this a commercial instrument, how and when last it was calibrated, and clarify the statement "The photolysis rate of any given species was calculated by normalizing to the cross section and quantum yields" as this doesn't sound right.

The instrument is a commercial Metcon UF CCD, which was calibrated by high power halogen lamp after the field campaign. The statement is rewritten as: "Photolysis rates were measured by a commercial spectroradiometer for O₃, NO₂, HCHO, HONO and H₂O₂ (Metcon UF CCD), the instrument was calibrated by high power halogen lamp after the field campaign. The photolysis rate of other related species were scaled by the recommendation of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015). Before the campaign the was instrument calibrated through comparison with a chemical actinometer in 2014 (Zou et al., 2016)."

pg 5 / lines 10-20 Numerous grammatical errors in this paragraph. Please correct.

The grammatical errors in this paragraph have been addressed

It now reads

“An Ionicon Analytik high sensitivity PTR-MS (Proton TRansfer Mass Spectrometer) as described by de Gouw and Warneke et al, (2007) provided supporting precursor VOC measurements. Detailed information about the PTR MS measurements can be found in Yuan et al 2012 and 2013. In brief, 28 masses are measured throughout the campaign at 1 Hz. Zero air, which was produced by ambient air passing through a platinum catalytic converter at 350 °C (Shimadzu Inc., Japan), was measured for 15 min every 2.5 hours to determine the background. Aromatic masses (m/z 79 for benzene, m/z 93 for toluene, m/z 105 for styrene, m/z 107 for C8 aromatics and m/z 121 for C9 aromatics), oxygenated masses (m/z 33 for methanol, m/z 45 for acetaldehyde, m/z 59 for acetone, m/z 71 for MVK+MACR and m/z 73 for MEK), isoprene (m/z 69) and acetonitrile (m/z 42) were calibrated by using EPA TO15 standard from Apel-Riemer Environmental Inc., USA. Formic acid (m/z 47), acetic acid (m/z 61), formaldehyde (m/z 31), and monoterpenes (m/z 81 and m/z 137) were calibrated by permeation tubes (VICI, USA).“

Please state the uncertainty of the PTR-MS data.

The uncertainties of most species are below 10%, which is detailed in the previous work (Liu, Y. 2015, ACP). This is now stated in the text.

line 38. N2 should have a subscript (twice).

N2 now is subscripted

pg 6 / lines 3-21 Numerous sub- and superscripts missing in this paragraph

Sub and superscripts are now properly utilised in the entire manuscript

line 25-26 " but is a commonly applied method within the CIMS community "

This is bad practice and done only by certain groups - most in the community strive to calibrate their instruments properly. Please remove this phrase.

This sentence has been removed as the data shown for uncalibrated species is now displayed in counts

pg 8 / line 5 "The high level of agreement". Be quantitative and state the level of agreement

The following sentence has been added

“The high level of agreement (R^2 of 0.76) from low mixing ratio measurements and a species with a short lifetime from different inlets confirms the accuracy and reliability of the CIMS measurements for this campaign.”

pg 8 / lines 8-15. A comparison of N_2O_5 mixing ratios would be more meaningful if the production rate of NO_3 (i.e., NO_2 & O_3 concentration) and the steady state lifetime of N_2O_5 were provided for context.

The following text was added to the end of the paragraph directing the reader to a manuscript (Wang et al 2018) which evaluated the production rates and fate of N_2O_5 from the same campaign and data set

“Further analysis of N_2O_5 nighttime chemistry was performed by Wang et al (2018) who calculated an average steady state lifetime of 310 ± 240 s and mean uptake coefficient of 0.034 ± 0.018 .”

pg 8 / lines 19-. Seems like the authors gave up on sub- and superscripts entirely at this point.

Sub and superscripts are now properly utilised in the entire manuscript

pg 11/ line 28-35. There are 15 reactions (numbered R1-R15) listed in the introduction on page 2 and 3. Some of the same reactions stated again but numbered differently here.

The equations for the steady state calculation are now labelled “ss” to reduce confusion to the reader on reaction numbers and imply that these reactions are relevant to the steady state calculation

pg 12 / line 7 " Steady state calculations reveal a sharp rise of chlorine atoms produced at sunrise peaking at 1.6×10^5 molecules cm^{-3} around 7 am which then gradually decreases, contributing to Cl atom production until 2 pm (Figure 7a). "

The text gives a chlorine atom concentration, whereas Fig. 7a only gives the production rate. Consider showing the magnitude of the assumed sink (chlorine reactivity in $1/\text{s}$, next to OH reactivity in $1/\text{s}$) in the supplemental and adding a disclaimer, such as "If a Cl sink as shown in Fig. X and a steady state w.r.t. production and loss are assumed, ..."

The referee is correct that we assume a steady state approximation, as shown in equation 9. We have added more text to clarify the uncertainty in the steady state assumption concentration, see answer to previous question. However, we feel that the figure is more informative if production rate is shown rather than steady state, as this reflects the measurements that were taken during the campaign.

pg 15 / line 21 "enabling an average daytime peak mixing ratio of chlorine atoms of 1.6×10^5 molecules cm^{-3} ." Stating a number for actual Cl atom concentration is not justified here given the large uncertainty with the magnitude of the hydrocarbon sink for Cl.

The concentration stated of chlorine atoms has been removed

Supplemental / pg 1 / line 20 " it has been shown that using these emissions it is possible to estimate the Cl atom production" The statement, as written, suggests that such calculations give accurate results. This has not been shown. Please rephrase.

This has been rephrased to read

“ . Whilst the approach is a simplification of course, it has been shown that using these emissions it is possible to estimate the Cl atom production, albeit it with some significant error due to significant number of estimations made, in a Megacity environment and produces results that are comparable with the much more thorough modelling approach of the MCM. It also generates a metric, CH₄ equivalent, which can be used as a comparative measurement from city to city. “

Reviewer 2

The manuscript by Le Breton et al. describes measurements of reactive chlorine species in the gas and particle phase in Beijing. They use this data to understand the sources of chlorine atoms and constrain the chlorine budget. The revised paper is greatly improved and, subject to addressing the comments below, can be considered for publication in ACP.

The authors have improved details regarding experiments, calibrations, and models, including much more information about relevant caveats and assumptions. This greatly improves the paper. Given the uncertainties the authors have described, their word choice throughout should reflect these uncertainties. There are two cases where word change is required. Firstly, the source of aerosol chloride does have some uncertainty, because no measurement of sea salt was made. Thus, the end of the first paragraph in Section 3.3.2 should reflect this. Instead of “we could deduce that”, use “it is

likely that” or equivalent. Secondly, the second paragraph of Section 3.4 begins with an assumption about the accuracy of methods/assumptions, and is followed (page 11, lines 1-2) with “this data indicates”. Again, terminology that incorporates the stated uncertainty (e.g. suggests) should be used.

We have considered the phrasing and terminology of the data throughout the manuscript and also specifically changed the two examples as follows

The phrase “it is likely that” has been used to replace “we deduce that” and “this data suggests that” has replaced “this data indicates” as suggested.

The manuscript still contains several grammatical errors and should be carefully proofread (e.g. page 5, lines 13-16).

The grammatical errors within the manuscript have been addressed

In several places throughout the manuscript the incorrect terms “chloride atom” or “chloride radical” are used (e.g. page 2, line 30).

The term chloride radical is now used consistently within the text

Mixing ratios are still given as ppt, ppb, etc. In the response file, the authors indicate they have changed all to pptv, ppbv, etc. This still needs to be completed (including in figures).

All units are now in ppt and ppb

Figure 2: there is overlap between panels B, C, and D.

This overlap of panels has been altered

Figure 5: the axes could still be more clear here (e.g. the difference between the right and left axes of panel B are unclear; some of the axes also appear to be floating and it isn’t clear to which panel they belong). The axes should not use [ClNO₂] because this indicates a concentration and the graphs depict a mixing ratio.

Figure 5 has been amended as recommended

Figures 9-11: the axes use [ppt], which incorrectly implies concentration instead of mixing ratio.

The axis have now been changed to ion counts