Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-9-AC1, 2018

Atmospheric Chemistry and Physics Discussions
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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.

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Received and published: 30 April 2018

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.

Reviewer 1 The authors claim a novel aspect of their findings is the anthropogenic source of reactive chlorine in China (e.g. page 11, line 35). However, this is based on the absence of sodium chloride from an aerosol mass spectrometer (AMS) measure-

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ment. The chloride measured by AMS is only non-refractory (i.e. primarily ammonium chloride) and excludes sodium chloride. According to the AMS method cited in this manuscript (Hu et al., 2016), only non-refractory chloride is measured. Discussions including this must be re-considered.

Response: We firstly agree that there are limitations on the AMS measurements of particulate chloride due to the refractory component which the AMS will not measure, although there have been several further steps in the manuscript to probe the anthropogenic source of chloride observed, such as the correlation with SO2, benzene and CO. Furthermore, the large distance (200k m) of the site from the coast makes it difficult to transport the seasalt to the site. We have now performed a wind rose analysis in more detail to further probe the source of chloride, whose results are shown in figure S1, in which radial and tangential axes represent the wind direction and speed (km h-1) and the colour bar represents the PM2.5 concentration. We see during the campaign, the severe pollution was from the south and southwest, with little contribution from the east part. Therefore, we could deduce that little contribution of the chloride was from the ocean. In addition, we have now done WRF model simulation to observe how a sea salt model results would correlate with ClNO2 profiles. This resulted in a poor correlation (figure S2) whereas total CO, as stated in the manuscript, had a relatively good correlation with ClNO2, further supporting the anthropogenic source of chloride. Furthermore, the modelled seasalt levels are very low, most likely unable to produce the mixing ratios of ClNO2 observed by the CIMS. Figure S3 has been added to the supplementary.

Action: The following text has been added/amended to the model results analysis and acknowledges the AMS limitations and instead highlighting the further support to anthropogenic Cl from low levels of sea salt and correlation within the model analysis. “The high levels of ClNO2 indicate a local significant source of chlorine to support these observations. The dominant source of chlorine atoms for ClNO2 production within models, such as the Master Chemical Mechanism (MCM), is from sea salt. However, the site is situated 200 km from the Yellow Sea and therefore this origin would have a low probability . The mean AMS chloride mass loading was 0.05 μg m-3 for the campaign with a maximum of 1.7 μg m-3. The Cl- from the AMS appears to be correlated strongly with CO and SO2, possibly originating from power plants or combustion sources. It should be noted that the AMS data does not include refractory aerosol and also has a cut off size larger than anticipate size of sea salt particles. Instead, the high Cl- observed appears to originate from mainland areas to the site (Figure 4) rather from the nearest coast, further supporting a strong anthropogenic source. Tham et al., (2016) observed a strong correlation of aerosol chloride with SO2 and potassium from measurements done during the same season in 2014 at Wangdu (semi-rural site 160 km south West of Beijing) and suggested contribution to fine chloride from burning of coal and crop residues. The latter was also supported by satellite fire spot count data (Tham et al., 2016). Riedel et al. (2013) have previously reported high ClNO2 mixing ratios observed from urban and power plant plumes measuring high mixing ratios of gas phase Cl2. The correlation with SO2 indicates coal burning as a potential source of particulate chlorine which is known to be a significant source of PM in the Beijing region (Ma et al., 2017), and the correlation with CO and benzene could be an indicator of biomass burning (Wang et al., 2002). To support this analysis, figure S1 displays a wind rose plot in which radial and tangential axes represent the wind direction and speed (km h-1). The colour bar represents the PM2.5 concentration. We could see that during the campaign, the severe pollution was from the south and southwest, with little contribution from the east part. Therefore, we could deduce that little contribution of the chloride was from the ocean. In order to test the hypothesis of biomass burning as a source of particulate chlorine, biomass burning emissions and transport utilising the EMEP MSC-W chemical transport model driven by meteorology from the WRF-ARW model (Skamarock et al., 2008) were used. Neither of the two biomass burning databases used (FINN and GFAS) contained data on chlorine emissions, so instead the biomass burning emissions of CO (CObb) were tracked and compared to the total mixing ratio of CO (COt) at the Changping site. CO was chosen since the measurements at Changping had shown strong correlation between CO and ClNO2 and because CO could be expected to be co-emitted with chlorine for both biomass burning and industrial combustion. Figure S2 (supplementary) shows time series of the measured ClNO2 mixing ratios at the Changping site, as well as the modelled mixing ratios of COt and CObb. CObb is shown for calculations using either the FINN or the GFAS data base, while for clarity the COt is only shown using the FINN data base. From this figure it is clear that mixing ratios of CObb are very low compared to COt. The two pollution episodes on May 18-May 23 and May 28-June 5, are to some extent visible in all time series, but for the biomass burning CO series, the second episode is much less pronounced. Night-time averages of the mixing ratios shown in figure S2 were calculated for each night for the time period 18:00 to 08:00 local time (UTC+8), roughly corresponding to the period when ClNO2 is not destroyed by photolysis. Nights with significant amount of missing data for the measurements were excluded. Figure S2 shows scatter plots of these averages of ClNO2 against the averages of the other species including their linear fits. The R2 for these fits were 0.48, 0.04, and 0.21 for COt, CObb FINN, and CObb GFAS respectively. The fact that mixing ratios of CObb is so much smaller than COt according to the model, combined with the much better correlation for COt than for CObb strongly suggests that industrial emissions are the dominant source of chlorine, rather than biomass burning. To further investigate the source of chloride, the model was also run to calculate sea salt levels instead of CO. This resulted in a poor correlation between sea salt and the ClNO2 (figure S4). The absolute levels of sea salt calculated by the model were also very low, unlikely to be able to produce the observed mixing ratios of ClNO2 as observed by CIMS."

There are important analytical details lacking in the manuscript. Although mixing ratios of HCl, Cl2, ClONO2, HOCl, ClO, and OClO are reported, no information is provided on calibrations for these molecules. These must be included. Calibrations are not reported for any compounds in the particle phase measurements using the FIGAERO inlet. Despite this, and their admission that the observations could be explained by a sampling artifact, a quantification of "particle to gas phase partitioning" for ClNO2 is

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reported (page 9, lines 26-27). The uncertain nature of this observation is consistent with a statement (page 9, lines 23-24) "this suggests the possible presence of ClNO2 in the particle phase", but inconsistent with a later statement (page 9, lines 30-31) "these data indicates a significant amount of the chlorine associated with ClNO2 is not liberated from the particle phase." In order to report this data in the text and figures, filter spike and recovery tests and gas-phase ClNO2 filter sorption tests must be undertaken. Without this analytical rigor, the data is speculative. Similarly, CMBO in the particle phase is reported in Figure 9 (although not explicitly discussed in the text). Considering these particle observations are listed as a major novel finding of this work, they must be clearly justified.

Response: The inorganic halogens, many of which has no stable production method, are attributed the same sensitivity as of ClNO2 which is a commonly used method. For example, Le Breton et al 2017 showed that inorganic halides have a similar sensitivity. Furthermore, the comparable sensitivity for chloroacetic acid and ClNO2 emphasis a similar sensitivity for chloride containing species when applying the iodide ionisation. As specific sensitivity for compounds being evaporated and subsequently ionised in the gas-phase after entering the same IMR would be redundant. However, one may argue that the efficiency of desorption could be quantified. Here the particle phase ClNO2 is attributed to a possible complex within the ambient aerosol. We claim here that we observe higher concentrations in the particle phase compared to the Henrys Law constant which would suggest that the ClNO2 is trapped within a matrix, rather than unable to partition upon heating, i.e. our conclusion would not be effected by a less than unity effectivity of desorption. This would be the same for CMBO, which we quantify using the sensitivity for chloroacetic acid in the gas phase. This kind of calibration procedures has been performed in previous CIMS work.

Action: A clearer explanation of our application on sensitivities has been added to the manuscript and a validation to the approach with relevant citations. It is now stated that the gas phase sensitivities applies to the particle phase data also. The text re-

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garding particle phase ClNO2 has been made more clear to state that we observe higher concentrations in the particle phase due to a matrix effect rather than limitation of liberation from the particle phase during desorption. CMBO is also described to be quantified using the sensitivity for chloracetic acid which applies for both particle and gas phase. “These sensitivities for N2O5 and ClNO2 (9.8 and 1.6 ion counts per ppt Hz-1 for 1x105 iodide ion counts) were applied relatively to that of formic acid. The other inorganic halogens reported in this work were given the same sensitivity as of ClNO2, as Le Breton et al. (2017) reported many inorganic halogens possess a similar, if not the same, sensitivity. This was further supported by our chloroacetic acid calibration. Other acids identified by CIMS which are reported in the literature are given the sensitivity of N2O5 to provide a minimum concentration so no concentrations are over estimated. A post campaign calibration of chloroacetatic acid (99%, Sigma Aldrich) was utilised to apply a sensitivity factor for all Cl-VOCs measured during the campaign. The calibration was performed using the same method as for formic acid and gave a sensitivity of 1.02 ion counts ppt-1 Hz when normalized to 1x105 I- ion counts. Using relative sensitivities will increase the uncertainties, but is a commonly applied method within the CIMS community, although in this specific case it is very likely that the sensitivity is similar for all inorganic/organic halogens, as demonstrated by Le Breton et al. (2017a).”

Throughout the manuscript (see specific examples below), the authors have not properly considered the full literature in their discussion.

Response: The manuscript has been addressed as proposed and the literature discussion has been expanded

Action: The manuscript has been addressed as proposed and the literature discussion has been expanded

The manuscript contains numerous grammatical errors and should be carefully proofread. Response: The manuscript has now been “cleaned” of grammatical and typographical errors to make it more clear and concise

Action: The manuscript has now been "cleaned" of grammatical and typographical errors to make it more clear and concise

Throughout the manuscript, "mixing ratio" and "concentration" are used interchangeably when discussing gas-phase measurements. All instances of "concentration" should be changed to "mixing ratio" (e.g. page 4, line 3 and page 12, line 26).

Response: This has now been corrected

Action: Concentration has been replaced with "mixing ratio" where necessary

Page 2, lines 15-31. The way this is presented, it appears as though the dominant fate of chlorine atoms is reaction with inorganics. In most cases, reactions with organics will be far more important.

Response: This should be rewritten so the reaction pathways are presented correctly

Action: The following text has been written to clearly state that the dominant loss of the chloride atom is via reaction with VOCs "The liberated chlorine will predominantly react with VOCs, with the above pathways representing alternative routes to loss of the chloride atom, and contribute to daytime photochemical oxidation, competing with OH and perturbing standard organic peroxy radical abundance (ROx = OH + HO2 + RO2), O3 production rate, NOx lifetime and partitioning between reactive forms of nitrogen (Riedel et al., 2014)."

Page 4, line 15. IUPAC prefers the term "resolving power" ("resolution" is used to describe another quantity). The m/z must also be defined for the given resolving power. This information should also be reported in Section 2.2.

Response: Resolution has been changed to resolving power and is now reported in section 2.2.

Action: Resolution has been changed to resolving power and is now reported in section

2.2.

Page 5, lines 30-34. The sentence starting with “In this calibration. . .” is repeated

Response: This is correct and should not be repeated

Action: This repetition has now been removed

Page 6, line 20. “Mass” should be “m/z”.

Response: This is correct and will be replaced

Action: “Mass” is now “m/z”

Page 6, line 35. Is there any trend in the measurement discrepancies with RH?

Response: There is no trend observed with RH

Action: This observation has been noted in the text

Page 6, lines 33-36. These two sentences appear to give different numbers to describe the same results. It is confusing.

Response: The gradient of the fit is described in the second sentence whereas the R correlation is described in the first

Action: no changes have been made

Page 9, line 36. Typo in “photolytically”

Response: This typographic error is to be changed

Action: It is now spelt “photolytically”

Page 10, line 1. “Kim et al.” is missing from the references section.

Response: Kim et al must be added to the References

Action: This reference has been added

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Page 10, lines 19-23. Equations 2, 3, 5, and 6 are not balanced.

Response: This is correct and should be amended

Action: The reactions are now balanced

Page 11, lines 9-12. Budgets of chlorine atoms are also available for Los Angeles (Riedel et al., 2012; Young et al., 2014).

Response: These two manuscripts will be discussed in the text Action: These manuscripts have been cited and referenced and it is acknowledged that measurements in urban Los Angeles yield similar production rates of the chloride radical to Beijing, although it is noted that higher concentrations of HCl observed in these measurements contribute significantly to the radical production where as in this paper we see little HCl contribution

Page 11, lines 23-24. The authors say "a number of studies have deemed chlorine atom chemistry to be insignificant with respect to O3 production and competing VOC oxidation to OH" and cite a single study to justify that a "significantly different approach is needed to assessing oxidation chemistry and photochemical smog in Asia". In fact, many studies examining this issue globally have shown a demonstrable impact of chlorine atoms on oxidation chemistry (e.g. (Osthoff et al., 2008; Riedel et al., 2014; Sarwar et al., 2014)). This suggests similar techniques can be applied to understand Asian air quality. It is also not clear what the nature of the "significantly different approach" suggested by the authors might be.

Response: We agree with the reviewer that this section is to be rephrased and the conclusion is not fully supported by the text

Action: The text now reads "Although several studies have demonstrated a non-negligible impact of chlorine oxidation chemistry (e.g. Oshoff et al., 2008, Riedel et al., 2014 and Sarwar et al., 2014), the impact of Cl chemistry varies significantly between various areas and atmospheric conditions, e.g. Bannan et al., 2015, 2017 deemed the impact from chlorine atom chemistry to be relatively low with respect to O3 production and competing with OH radicals for VOC oxidation”

Page 11, line 29. The authors mention that steady-state OH was calculated. More details are needed here. What measurements were included in this calculation? How were those measurements made? Page 11, lines 29-33. Calculated chlorine atom to measured OH concentrations are available for Los Angeles (Young et al., 2014).

Response: Reviewer 2 also had some comments about the steady state calculations, to which will also be addressed here to provide a complete picture to the reviewer of how this section has been amended and improved. The reviewers are correct that the reaction of OH+ HCl was accidentally omitted from the text in the original manuscript. The section has now been corrected for that omission. The reviewers are also correct that only using the small subset of hydrocarbons measured by the PTRMS would result in significant errors in estimated steady state Cl atom concentrations. However, we did not just use PTRMS measurements. In previous work (Bannan et al., 2015) we have shown that it is possible to calculate Cl atom concentrations, using a simple steady-state expression with the Cl atom production rate estimated from the observed loss rate of ClNO2 and removal of Cl atoms via reaction with the VOC concentrations supplemented with data from the Boston tailpipe study (AQIRP, 1995) and LA VOC study (Fraser et al., 1997), i.e. missing VOC concentrations are estimated simply by using the ratio of measured VOCs and missing VOCs from these urban studies and measured VOC data in this study. The removal of Cl atoms via reaction with VOCs can then be determined using Eq. 1-3, and NIST kinetic data (Manion et al., 2014) (Eq 1) (Eq 2) (Eq 3) Here the simple steady state approach agreed well with the MCM, despite a much more simplistic approach. We used an identical approach in this work utilizing the tailpipe VOC concentrations (AQIRP, 1995). However, we further simplify the approach by using one term CH4 equivalent which accounts for relative concentration and reactivity towards Cl, i.e. if a VOC reacts 1000 times faster it is the equivalent of 1000 CH4 or more formally for each VOC its CH4 equivalent is kCl + VOC [VOC]/ kCl +

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CH4. Whilst the approach is a simplification it has been shown that using these emissions it is possible to estimate the Cl atom production in a Megacity environment and produces results that are comparable with much more thorough modelling approach using e.g. the MCM. It also generates a metric, CH4 equivalent, which can be used as a comparative measurement from city to city. Photolysis rates were measured by a spectradiometer for O3, NO2, HCHO, HONO and H2O2. The photolysis rate of any given species was calculated by normalizing to the cross section and quantum yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015). The reviewer is correct that Cl atoms will produce peroxy radicals which can perturb HOx/NOx cycles, and we were only considering the initial oxidation of VOCs. The text has been corrected to reflect that.

Action: the following text has been added to the manuscript and text has been added to the supplementary " "Here, a simple steady state calculation will be used to determine the Cl atom mixing ratio summarised below, but detailed within the supplementary: Cl2 + hv → Cl + Cl (1) ClNO2 + hv → Cl + NO2 (2) ClONO2 + hv → ClO + NO2 (3) HOCl + hv → OH + Cl (4) OClO + hv → O + ClO (5) OH + HCl → Cl + H2O (6) Cl + O3 → ClO + O2 (7) Cl + CH4 equivalent → HCl + products (8)

[Cl]SS = {2J1[Cl2] + J2[ClNO2] + J3[ClONO2] + J4[HOCl] +J5[OClO] +k7 [OH][HCl]} / {k7[O3] + k8[CH4] equivalent} (9) Where [CH4] equivalent represents the reactive VOC present as if it were reacting as CH4 Bannan et al., (2005), were able to use this steady state approach to compare the relative loss via reaction with OH compared with Cl atoms. Although this approach is an estimation, it was shown to produce comparable to results with that of the more rigorous MCM approach."

Page 14, lines 17-20. In the final paragraph of the paper, the authors claim that "chlorine atom chemistry may be under represented within models due to the lack of quantification and identification of particulate Cl-VOC products. This work provides instrumental capability to probe the competition between OH and Cl oxidation chemistry and quantify the SOA yields as a result of both pathways." This paper does not demon-

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strate quantitative measurement of particulate Cl-VOCs, as no calibrations or desorption efficiencies have been presented or discussed. Furthermore, the authors have not sufficiently shown that particulate Cl-VOCs are necessary to understand the relative impacts of chlorine atoms and OH on air quality.

Response: The final paragraph has been clarified to state that these results highlight the deficiency in chlorine atom chemistry within models which could be a result of lack of quantification and identification of Cl VOCs in the gas and particle phase. The work here provides instrument capability to both identify and quantify the Cl VOCs in both the particle and gas phase which were shown in the steady state calculations to be important contributors to daytime oxidation. We believe the calibration of chloroacetic acid can be used for indirect quantification of Cl-VOCs and where the ability to measure the precursors to chloride radical production does demonstrate the ability to quantify the chloride radical budget and particulate Cl-VOCs. Action: The text has been amended and reads as follows "The results highlight deficiency in chlorine atom chemistry descriptions within models; possibly due to a lack in quantification and identification of Cl-VOC products in gas and particle phase. This work provides instrumental capability to probe the competition between OH and Cl oxidation chemistry and quantify their effect on ozone and SOA formation."

Figures would be more clear if panels were labelled with (A), (B), etc. Axis labels are often missing or unclear. For example, in Figure 1, presumably all the x-axes should be "m/z" and in Figure 5, the right-hand y-axis of the top left graph is unlabelled.

Response: These plots will be made clearer

Action: Axis have been labelled and the panels are now marked A, B, C etc

Page 23, lines 2-6. In the Figure 7 caption, it would be helpful to be explicit that terms are calculated and not measured.

Response: This is true and will be amended to state they are not measured values

Action: The caption now states these are steady state values

Reviewer 2

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

Response: These are to be addressed

Action: Sections are now sequential and reaction numbers are ordered appropriately

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.

Response: The inorganic halogens have been given the same sensitivity to that of ClNO2. It has been shown by Le Breton et al 2017 that the inorganic halogens have a high and similar, if not the same, sensitivity to iodide ionisation. The acids presented are given the highest sensitivity (that of N2O5) to provide a minimum mixing ratio. As stated in the text, due to reduced availability of Cl-VOCs for laboratory calibration, CMBO and other Cl VOCs are given the same sensitivity as of chloroacetic acid, which is similar to that for ClNO2 which supports literature findings that inorganic halogens/functional groups possess a similar sensitivity. Detailed information about the PTR MS measurements can be found in Yuan et al 2012 and 2013. In brief, 28 masses are measured for the campaign at 1 Hz. Zero air, which was produced by ambient air passing through a platinum catalytic converter at 350 ïĆřC (Shimadzu Inc., Japan), was measured for 15 min every 2.5 hours to determine the background. used to measure background Aromatics 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). Photolysis rates were measured by a spectradiometer for O3, NO2, HCHO, HONO and H2O2. The photolysis rate of any given species was a given species was calculated by normalizing to the cross section and quantum yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015).

Action: The text regarding inorganic halogen quantification now states “The other inorganic halogens reported in this work are assumed to have the same sensitivity as ClNO2. This is in line with that Le Breton et al. (2017) reported many inorganic halogens possess a similar, if not the same, sensitivity, which is also supported by our chloroacetic acid calibration.” The text states for other acids “Other acids identified by CIMS which are reported in the literature are given the sensitivity of N2O5 to provide a minimum concentration so no concentrations are over estimated.” The text states for photolysis rates “Photolysis rates were measured by a spectradiometer for O3, NO2, HCHO, HONO and H2O2. The photolysis rate of any given species was calculated by normalizing to the cross section and quantum yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015). The text details the PTR calibration in the calibration section “Detailed information about the PTR MS measurements can be found in Yuan et al 2012 and 2013. In brief, 28 masses are measured for 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. used to measure background Aromatics 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).

- 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

Response: Reviewers 1 and 2 comments regarding the steady state calculations have been collected and answered below. The reviewers are correct that the reaction of OH+ HCl was accidentally omitted from the text in the original manuscript. The section has now been corrected for that omission. The reviewers are also correct that only using the small subset of hydrocarbons measured by the PTRMS would result in significant errors in estimated steady state Cl atom concentrations. However, we did not just use PTRMS measurements. In previous work (Bannan et al., 2015) we have shown that it is possible to calculate Cl atom concentrations, using a simple steady-state expression with the Cl atom production rate estimated from the observed loss rate of ClNO2 and removal of Cl atoms via reaction with the VOC concentrations supplemented with data from the Boston tailpipe study (AQIRP, 1995) and LA VOC study (Fraser et al., 1997), i.e. missing VOC concentrations are estimated simply by using the ratio of measured VOCs and missing VOCs from these urban studies and measured VOC data in this study. The removal of Cl atoms via reaction with VOCs can then be determined using Eq. 1-3, and NIST kinetic data (Manion et al., 2014) (Eq 1) (Eq 2) (Eq 3) We were able to show that the simple state approach agreed well with the MCM, despite a much more simplistic approach. We used an identical approach in this work utilizing the tailpipe VOC concentrations (AQIRP, 1995). However, we further simplify the approach by using one term CH4 equivalent which accounts for relative concentration and reactivity towards Cl, i.e. if a VOC reacts 1000 times faster it is the equivalent of 1000 CH4 or more formally for each VOC its CH4 equivalent is kCl + VOC [VOC]/ kCl + CH4. 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 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. Photolysis rates were measured by a spectradiometer for O3, NO2, HCHO, HONO and H2O2. The photolysis rate of any given species was calculated by normalizing to the cross section and quantum yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015). The reviewer is correct that Cl atoms will produce peroxy radicals which can perturb HOx/NOx cycles, and we were only considering the initial oxidation of VOCs. The text has been corrected to reflect that.

Action: the following text has been added to the manuscript and text has been added to the supplementary “Here, a simple steady state calculation will be used to determine the Cl atom mixing ratio summarised below, but detailed within the supplementary: Cl2 + hv → Cl + Cl (1) ClNO2 + hv → Cl + NO2 (2) ClONO2 + hv → ClO + NO2 (3) HOCl + hv → OH + Cl (4) OClO + hv → O + ClO (5) OH + HCl → Cl + H2O (6) Cl + O3 → ClO + O2 (7) Cl + CH4 equivalent → HCl + products (8)

[Cl]SS = {2J1[Cl2] + J2[ClNO2] + J3[ClONO2] + J4[HOCl] +J5[OClO] +k7 [OH][HCl]} / {k7[O3] + k8[CH4] equivalent} (9) Where [CH4] equivalent represents the reactive VOC present as if it were equivalent CH4 Bannan et al., (2105), were able to use this steady state approach to compare the relative loss via reaction with OH compared with Cl atoms. Although this approach is an estimation, it was shown to produce comparable to results with that of the more rigorous MCM approach.”

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

Response: Many CIMS papers refer to relative calibrations. Here we apply this method to non-calibrated compounds but do apply a maximum sensitivity to limit their impact on model calculations. Their semi quantitative nature will be noted within the text.

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Action: The compounds which are not directly are noted in the calibration section to ensure the reader is aware that the values are semi quantitative.

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

Response: This has been altered

Action: the comma has been replaced with “and”

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

Response: This will be changed (we have changed concentrations to mixing ratios)

Action: The units now used are pptV and referred to as mixing ratios and referred to as mixing ratios

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.

Response: We agree that the OH + HCl reaction must be included within the reactions presented and noted in the text. The hydrogen abstraction to form HCl is within the text and reaction list, although we have no further iterated to the reader that this is the major reaction pathway for chloride-VOC reactions.

Action: The reactions listed (now R1-R11) contain the OH + HCl reaction. We have amended the text to state hydrogen abstraction is the dominant pathway for chloride oxidation “The oxidation mechanism of saturated hydrocarbon (R12-R13) is initiated by reaction with OH or chlorine atom to form an organic peroxy radical (RO2), and H2O or HCl depending on the oxidant, which is the dominant pathway for chloride-VOC reactions.”

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 ..."?

Response: This reviewer is correct. Text has been added to clarify this point and that we only consider the initial oxidation of VOCs

Action: The following text has been added "The oxidation of VOCs by chlorine atoms is thought to be significant in the early hours of the day while OH mixing ratio are low and chlorine atom production is high through the photolysis of ClNO2, as well as feeding into the standard HOx/NOx cycles via production of peroxy radicals from reactions with alkanes."

lines 11/12 – there are two reactions labelled R11

Response: This is correct and should be changed

Action: Reactions here are now R11 to R14

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

Response: The Liu et al 2016 has been cited which calculates a yield of 15% for comparison. Action: The Liu et al 2016 has been cited which calculates a yield of 15% for comparison, although this is known to be a factor of 2 higher than used in standard climate models.

pg 4 line 24 – how were photolysis rates determined?

Photolysis rates were measured by a spectradiometer for O3, NO2, HCHO, HONO and H2O2. The photolysis rate of any given species was a given species was calculated by normalizing to the cross section and quantum yields taken from the recommendations of the Jet Propulsion Laboratory (JPL) kinetic evaluation report (Burkholder et al., 2015).

Action: The text now states “Photolysis rates were measured by a spectradiometer for O3, NO2, HCHO, HONO and H2O2. Inorganic halogen photolysis rates were extracted relatively from these J rates.”

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

Response: These references have been noted as 2017a and 2017b in the text and reference list

Action: These references have been noted as 2017a and 2017b in the text and reference list

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

Response: Detailed information about the PTR MS measurements can be found in Yuan et al 2012 and 2013. In brief, 28 masses are measured for the campaign at 1 Hz. Zero air, which was produced by ambient air passing through a platinum catalytic converter at 350 ïĆřC (Shimadzu Inc., Japan), was measured for 15 min every 2.5 hours to determine the background. used to measure background Aromatics 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).

Action: The text now states in section 2.1 “Detailed information about the PTR MS

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measurements can be found in Yuan et al 2012 and 2013. In brief, 28 masses are measured for 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. used to measure background Aromatics 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)."

line 17 - section 2.3 is absent.

Response: This is correct and will be amended

Action: Calibration is now section 2.3

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

Response: As described above, these were given the highest sensitivity to limit their impact on the modelling results

Action: This has now been described in the text more clearly

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.

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Response: The technique has been described by Faxon et al 2017 in full detail and the CEAS measurements confirm the accuracy of the calibration technique

Action: The technique has been described by Faxon et al 2017 in full detail and the CEAS measurements confirm the accuracy of the calibration technique

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

Response: The sources stability over time has not been thoroughly tested for longer than a week, upon stable cooling I believe it can be used as a reproducible source. The CEAS utilised a different calibration technique as the N2O5 CIMS calibration was performed post campaign. The CEAS was separately calibrated as detailed in Wang et al 2017a "Development of a portable cavity-enhanced absorption spectrometer for the measurement of ambient NO3 and N2O5: experimental setup, lab characterizations, and field applications in a polluted urban environment" A brief description of the CEAS calibration has been added, stating that the mirror was calibrated for daily and the filter replaced hourly "The CEAS utilised a dynamic source by mixing NO2 and O3 to generate stable N2O5 for calibration (Wang et al., 2017). The source was used to calibrate the ambient sampling loss of N2O5 in the sampling line, filter, the preheater cavity and optical cavity. This was performed pre and post campaign. During the campaign the reflectivity of the high reflectivity mirror was calibrated daily and filter changed hourly."

Action: The following text was added "The CEAS utilised a dynamic source by mixing NO2 and O3 to generate stable N2O5 for calibration (Wang et al., 2017). The source was used to calibrate the ambient sampling loss of N2O5 in the sampling line, filter, the preheater cavity and optical cavity. This was performed pre and post campaign. During the campaign the reflectivity of the high reflectivity mirror was calibrated daily and filter changed hourly."

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

Response: It has not been verified with the CEAS, but has with the CIMS in previous literature (Faxon et al., 2017) and the good agreement here between the CEAS and CIMS illustrate its ability.

Action: As stated above, the instruments were not calibrated using the same source, but independently calibrated. The above text was also added.

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

Response: The sensitivities have been added

Action: The following text has been amended “These sensitivities for N2O5 and ClNO2 (9.8 and 1.6 ion counts per ppt Hz-1 for 1x105 iodide ion counts) were applied relatively to that of formic acid.”

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.

Response: The peaks have been stated and are now included in figure 1

Action: The peaks have been stated and are now included in figure 1

It is unclear what is meant by "second dominant peak for the ClNO2 fit" – is this at m/z 208? Response: There is a second peak fitted (as shown in figure 1) which is identified as a cluster of nitric acid with water forming an adduct with iodide that will contribute to up to 10% of the counts at this unit mass

Action: This identification has been stated in the text and provided in figure 1

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

Response: The Wang et al 2018 paper focuses on analysis of N2O5 from the CEAS

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utilising the CIMS ClNO2 data. We therefore believe that reporting the typical concentrations and diurnal trends suffice here as the focus is more on the inter-comparison rather than production rates of N2O5 and ClNO2. This information can be added if requested by the editor, although we believe it does not contribute to the manuscript.

Action: NA

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

Response: They were not on the same inlet and faced different directions

Action: This is now stated in the text

line 36 – The offset should have units of ppt

Response: this has been amended

Action: this has bene amended

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

Response: The average error has been reported now in the text, 11%.

Action: The text now reads “The largest error between the two measurements occurs at night during the higher levels of N2O5, although averaging at 4 ppt (representing 11% error on the average campaign concentration)."

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

Response: The details of the heated IMR have been added to section 2.2, although this section still refers to this setup to clarify the possible physical differences resulting in variation of the measured mixing ratio.

Action: Section 2.2 now reads “The ionized gas was then carried out of the ion source and into the Ion-Molecule Reaction (IMR) chamber, which was heated to 40 degrees

Celsius to reduce wall loss, through an orifice (Ø = 1 μm).”

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.

Response: We agree with the reviewer and have now renamed this section and added two sub sections

Action: This section is now named “3.3 Inorganic chlorine: Abundance, profiles and source” We have added section 3.3.1 called “Abundance and profiles” and section 3.3.2 called “Source of chloride”

line 24 – mixing ratio, not concentration

Response: This is to be changed

Action: mixing ratio is now used instead of concentration

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

Response: yes

Action: the text now states “510 ppt (standard deviation (σ) 270 ppt)”

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

Response: text has been added to hypothesise this as a possibility to the reader

Action: The following text has been added “IMR chemistry is also not a possible source as these reactions would occur throughout the day, therefore skewing all of the data and not just the night-time levels, although there is a possibility that ClONO2 can be formed in the IMR by reactions between ClO and NO2.”

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.

Response: The response here is similar to the first comment by reviewer 1. We acknowledge the limitations of the AMS data and will provide that information to the reader. We ran the WRF model simulation to observe how the sea salt model results correlate with ClNO2 profiles. This resulted in a poor correlation (figure S4) whereas total CO, as stated in the manuscript, had a relatively good correlation with ClNO2, further supporting the anthropogenic source of chloride. Furthermore, the modelled sea salt levels are very low, most likely unable to produce the mixing ratios of ClNO2 observed by the CIMS. Figure S4 has been added to the supplementary.

Action: Section 3.3.2 has been amended as displayed below to acknowledge the AMS limitations and further show model runs indicating no correlation between sea salt and ClNO2 "The high levels of ClNO2 indicate a local significant source of chlorine to support such high yields. The dominant source of chlorine atoms for ClNO2 production within models, such as the Master Chemical Mechanism (MCM), is from sea salt, although the site is situated 200 km from the Yellow Sea and therefore has low probability that the Cl- has this origin. The mean AMS chloride mass loading was 0.05 μg m-3 for the campaign with a maximum of 1.7 μg m-3. The Cl- from the AMS appears to be correlated strongly with CO and SO2, possibly originating from power plants or combustion sources. This could be a result of Cl- originating from anthropogenic sources, although the AMS data does not include refractory aerosol and also has a cut off size larger than most sea salt particles. The high Cl- observed appears to flow into the site from the

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mainland (Figure 4) and not from the nearest coast, further supporting a strong anthropogenic source. Tham et al., (2016) observed a strong correlation of aerosol chloride with SO2 and potassium in the same season in 2014 at Wangdu (semi-rural site 160 km south West of Beijing) and suggested contribution to fine chloride from burning of coal and crop residues. The latter was also supported by satellite fire spot count data (Tham et al., 2016). Riedel et al. (2013) have previously reported high ClNO2 mixing ratios observed from urban and power plant plumes measuring high mixing ratios of gas phase Cl2. The correlation with SO2 indicates coal burning as a potential source of particulate chlorine which is known to be a significant source of PM in the Beijing region (Ma et al., 2017), and correlation with CO and benzene is an indicator of biomass burning (Wang et al., 2002). In order to test the hypothesis of biomass burning as a source of particulate chlorine, biomass burning emissions and transport utilising the EMEP MSC-W chemical transport driven by meteorology from the WRF-ARW model (Skamarock et al., 2008) were ran. Neither of these two biomass burning databases available contain data on chlorine emissions, so instead the biomass burning emissions of CO (CObb) were tracked and compared to the total mixing ratio of CO (COt) at the Changping site. CO was chosen since the measurements at Changping had shown strong correlation between CO and ClNO2 and because CO could be expected to be co-emitted with chlorine for both biomass burning and industrial combustion. Figure S2 (supplementary) shows time series of the measured ClNO2 mixing ratios at the Changping site, as well as the modelled mixing ratios of COt and CObb. CObb is shown for both the FINN and GFAS model runs, while COt is only shown for the FINN run since it looks almost completely the same for the GFAS run. From this figure it is clear that mixing ratios of CObb are very low compared to COt. The two episodes of increased mixing ratio, May 18-May 23 and May 28-June 5, are to some extent visible in all time series, but for the biomass burning CO series, the second episode is much less pronounced. Night-time averages of the mixing ratios shown in figure S3 were calculated for each night for the time period 18:00 to 08:00 local time (UTC+8), roughly corresponding to the period when ClNO2 is not destroyed by photolysis. Nights with significant amount of missing data for the measurements were excluded. Figure S3 shows scatter plots of these averages of ClNO2 against the averages of the other species. Figure S3 also shows a straight line fitted for each of these scatter plots. The R2 for these lines were 0.48, 0.04, and 0.21 for COt, CObb FINN, and CObb GFAS respectively. The fact that mixing ratios of CObb is so much smaller than COt according to the model, combined with the much better correlation for COt than for CObb strongly suggests that industrial emissions are the dominant source of chlorine, rather than biomass burning. To further support probe the source of chloride, the model was run to calculate sea salt levels instead of CO and resulted in a poor correlation with the ClNO2 time series (figure S3). The absolute levels of sea salt in the model were also very low, unlikely able to produce the observed mixing ratios of ClNO2 observed by CIMS." line 28 - Please describe the WRF model in the methods section, not in the results section. Response: The model description has bene moved to section 2.3 "model setup" Action: A new section (2.3) has been populated with the model description.

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

Response: We have now utilised the WRF simulations further to support the hypothesis that the ClNO2 measured cannot be a product of only seasalt particle heterogeneous reactions and anthropogenic chloride must play a significant role

Action: NA

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.

Response: We agree this is too strong a claim and have rephrased the sentence

Action: The sentence now reads "The fact that mixing ratios of CObb is so much smaller than COt according to the model, combined with the much better correlation for COt than for CObb strongly suggests that industrial emissions are a more significant source of chlorine, rather than biomass burning.”

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

Response: This has been placed into its own section

Action: Section 3.4 is now “particle phase ClNO2” and the other sections following have been renumbered

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

Response: Yes we did but again dominating in the particle phase

Action: The m/z axis has been expanded to 210.5

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.

Response: This is a assumption to be stated

Action: This assumption is now stated

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

Response: This is merely a ratio of the red and blue (gas and particle) time series in panel A of figure 5.

Action: We feel this does not need to be added as it is just utilisation of the data already displayed in the figure

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

Response: The term significant has been replaced with “non-negligible”

Action: The term significant has been replaced with “non-negligible”

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

Response: The reactions have been renumbered and balanced

Action: The reactions have been renumbered and balanced

line 25 - Please number the steady state expression.

Response: This has been done

Action: The steady state expression is number (8)

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)).

Response – the above 2 comments have been answered in the first question regarding the ss as mentioned within the response.

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?

Response: We agree with the reviewer that other studies need to be considered in this section. We still believe that comparing urban and rural sites, or indeed urban and marine sites is an important factor as this paper postulates the impact of anthropogenic chloride and challenges the significance of sea salt as the major source for ClNO2 production. Therefore we would like to keep this comparison within the manuscript.

Action: The following text has bene added to consider previous calculations of chloride radical production. “Studies of chloride atom production in Los Angeles by Riedel et al. (2012) and Young et al. (2014) indicate that the high production rate in Beijing is somewhat typical of urban sites, although HCl and ClNO2 contribution to radical production is the same, whereas here we see very little chloride atom production from HCl in comparison to ClNO2.”

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

Response: We have now added to this section to present the steady state in a more detailed manor and supported its utilisation referencing the Bannan et al paper which was compared against the MCM for OH radical concentrations. We therefore feel its role within the manuscript has been validated and adds to reliable scientific analysis of the dataset Action: NA

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

Response: The lifetime of isoprene is 1-2 hours according to Atkinson et al. (2000) , but we do not know the lifetime of CMBO

Action: Although this assumption is made based on the diurnal profiles, we agree we cannot assume the lifetime of CMBO is longer than that of isoprene and therefore have removed this phrase from the manuscript.

line 34 – "The concentrations of Cl and isoprene were relatively low" How low is relatively low? Please be quantitative.

Response: Quantitative values will be added t the text

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Action: The exact mean values have been added “1.6x105 molecules cm-3 s-1 Cl and 0.5 ppb isoprene”

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

Response: In response to the below comment, we now acknowledge in the manuscript that CMBO may not be unique to isoprene-chlorine reactions and therefore could have alternative sources

Action: We have added the following text to support the qualitative analysis of the CMBO time series “CMBO may also not be unique to only isoprene-chloride reactions and therefore have alternative sources not represented in this data set.”

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

Response: We agree with the reviewer that it may be a unique marker of chlorine chemistry, but not proven to be unique to isoprene reactions

Action: The sentence has been rephrased to state “unique marker of chlorine chemistry”

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.

Response: The text states the observation and examines the possible causes which we do not categorically prove is only an instrument artefact therefore we state in the conclusion that it is indeed identified but at unusually high concentrations. We do not state it is quantified as the quantification in the gas phase is sufficient and the same sensitivity as for the particle phase.

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Action: The text now reads “ClNO2 was identified in the particle phase at higher ratios with respect to its gas phase component than expected, which may only prove to be significant at such elevated mixing ratios as observed in East Asia.”

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

Response: The reference has been checked and any inaccuracies or missing doi’s have been added

Action: The reference has been checked and any inaccuracies or missing doi’s have been added

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.

Response: These peaks have bene identified and labelled din the MS plot

Action: The peaks for ions C8H5NO4, C6F3HO3, C9H8NO3, IHNO3H2O and C9H5SO4 are now colour labelled in the MS plot

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

Response: They will be defined

Action: C and M are now defined in the caption

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

Response: The labels are correctly labelled

Action: The labels are correctly labelled

References AQIRP, 1995, Effects of gasoline T50, T90 and sulfur on exhaust emissions of current and future technology vehicles. Auto/Oil Air Quality Improvement Research Program, Technical Bulletin No. 18. Bannan T. et al., (2015). The first UK measurements of nitryl chloride using a chemical ionisation mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation. J. Geophys. Res., 120(11), 5638-5657. Burkholder, J.B. et al. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 18. Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 2015. Fraser, M. P., G. R. Cass, B. R. Simoneit, & R. A. Rasmussen (1997). Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons. Environmental science & technology, 31(8), 2356-2367 DOI: 10.1021/es960980g Gao, J., Tian, H., Cheng, K., Lu, L., Zheng, M., Wang, S., Hao, J., Wang, K., Hua, S., Zhu, C., and Wang, Y.: The variation of chemical characteristics of PM2.5 and PM10 and formation causes during two haze pollution events in urban Beijing, China, Atmospheric Environment, 107, 1-8, https://doi.org/10.1016/j.atmosenv.2015.02.022, 2015. Hofzumahaus, Andreas, Franz Rohrer, Keding Lu, Birger Bohn, Theo Brauers, Chih-Chung Chang, Hendrik Fuchs, et al. "Amplified Trace Gas Removal in the Troposphere." Science 324, no. 5935 (2009): 1702. Manion, J. A., R. E. Huie, R. D. Levin, D. R. Burgess Jr, V. L Orkin, W. Tsang, W. S. McGivern, J. W. Hudgens, V. D. Knyazev, D. B Atkinson, E. Chai, A. M. Tereza, C.-Y. Lin, T. C. Allison, W. G. Mallard, F. Westley, J. T. Herron, R. F. Hampson, and D. H Frizzell (2014) NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2013.03, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320. Web address: http://kinetics.nist.gov/ Tang, R., Wu, Z., Li, X., Wang, Y., Shang, D., Xiao, Y., Li, M., Zeng, L., Wu, Z., and Hallquist, M.: Primary and secondary organic aerosols in summer 2016 in Beijing, Atmospheric Chemistry and Physics, 18, 4055-4068, 2018. Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., and Zhao, Y.: Chemical characterization and source apportionment of PM 2.5 in Beijing: seasonal perspective, Atmospheric Chemistry and Physics, 13, 7053-7074, 2013. Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S. H., Wang, M., Zeng, L. M., Zhang, Q., Song, Y., Zhang, J. B., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, Artn

D24302, 10.1029/2012jd018236, 2012. Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.: VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China, Atmos. Chem. Phys., 13, 8815-8832, 10.5194/acp-13-8815-2013, 2013.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-9/acp-2018-9-AC1-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-9, 2018.

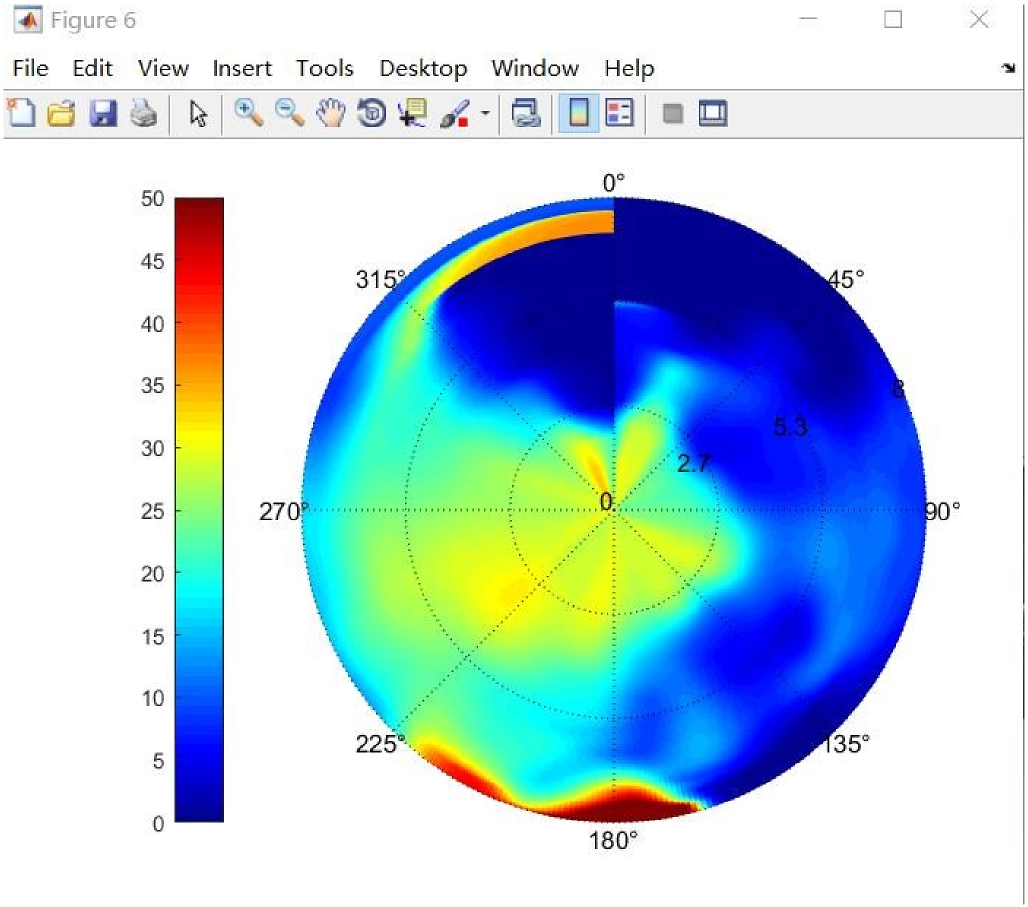

Fig. 1.

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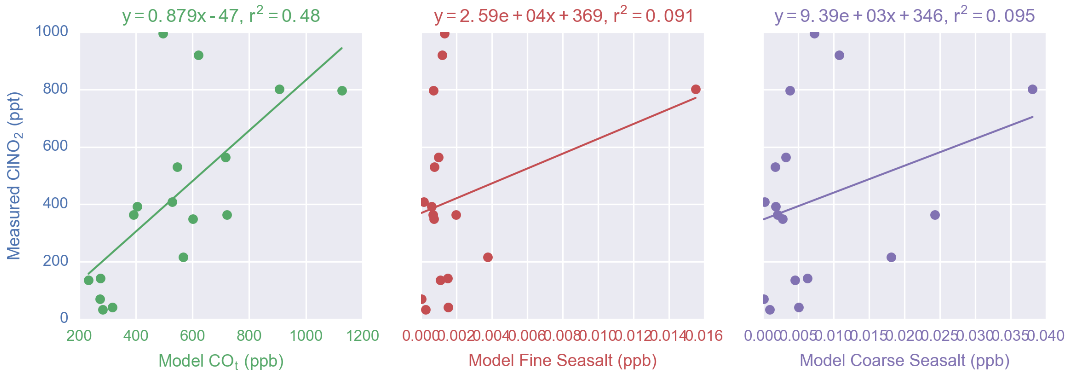

Fig. 2.

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