

Interactive comment 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.

Anonymous Referee #1

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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 manuscript is missing key measurement details that preclude an effective assessment of the quality of the data interpretation. Significant revisions are required before this manuscript can be considered for publication in ACP.

General comments

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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) measurement. 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.

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 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.

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

The manuscript contains numerous grammatical errors and should be carefully proof-read.

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Specific comments

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).

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.

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.

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

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

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

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

Page 9, line 36. Typo in “photolytically”

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

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

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

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,

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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.

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).

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 demonstrate 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.

Figures would be more clear if panels were labeled 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 unlabeled.

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

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