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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Evaluating evidence for Cl sources and oxidation chemistry in a coastal, urban environment" *by* C. J. Young et al.

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We thank the Reviewers for their thoughtful comments. Our responses to the comments are below and changes to the manuscript are indicated.

Anonymous Referee #1 This is an interesting paper. While the VOC ratios show no evidence of Cl oxidation, the authors argue that a large fraction of OH is in fact initiated by Cl. The authors also find that the lifetime of Cl atoms are shorter than OH by an order of magnitude based on reactivity calculations. The idea is new and can be of interest to the community. However, I find that this paper is lack of quantitative results and in-depth discussions. Therefore I hope the authors to clarify the following issues before I can recommend the paper for publication:

1. The major conclusion of this paper is that Cl leads to significant production of secondary radical (mainly OH discussed in this paper). But it is not clear to me how this secondary OH is formed. In my understanding the main mechanism is that Cl produces RO2, which leads to the production of HO2 and then produces OH via HO2+NO. Is there other pathway to produce secondary OH? This deserves some clarification.

The Reviewer is correct in saying the main propagation mechanism is through reaction of RO2 and HO2 radicals with NO. Further secondary radicals can be produced through the formation of photolabile products, such as formaldehyde (HCHO). When photolyzed, these species form additional radicals that can be considered secondary. In order to clarify this point, text has been added: "…R'CO formed from reaction (R5) is typically an aldehyde or ketone, which can photolyze or react with OH or Cl, substantially increasing the efficiency of propagation depending on the time scale for photolysis. Initiation of radical propagation through reaction (R4) requires the presence of NOx."

2. If secondary OH is mainly produced from Cl-initiated RO2, given the lifetime of RO2 is on the order of minutes, I would expect the impact of Cl chemistry on OH/O3 is limited in the early morning, rather than the whole day. This can also be seen from Fig 4a, which shows that the integrated secondary OH production levels off around noon time, reflecting a much smaller production of OH after the morning.

It is true that Cl produced from the photolysis of ClNO2 will initiate most chemistry in the morning. Through the process of production of stable intermediate species (e.g. HCHO, O3), the impact of morning radical initiation to oxidation later in the day can be substantial. This was not fully evident in the model chemistry that produced Figure 4a, as production of OH from O3 was disabled. A similar lasting effect of secondary radicals was described by Alicke et al. [2002] as a result of morning photolysis of HONO and production of OH. However, this fact does not affect the impact of secondary radicals on VOC tracer ratios, which are only sensitive when Cl concentration is highest (i.e. in the early morning).

3. Chain termination. The secondary OH produced from Cl-initiated RO2, will also react with NO2, leading to chain termination via OH + NO2. In terms of the production of RO2 and secondary OH, I don't see much difference between OH-initiated and Cl initiated chemistry. The major difference is that Cl-initiated RO2 is largely from Cl + alkanes/alcohols, while OH-initiated RO2 is from OH + Biogenics/aldehydes etc., as shown in Fig 7. But these RO2 are all terminated by OH + NO2.

The Reviewer makes a valid point. If a given number of Cl atoms are formed, they will initially produce more secondary OH than the same number of OH radicals. Through radical propagation, this will lead to more secondary radicals overall.

4. The impact of NOx on ClNO2-initiated chemistry. It seems to me that the higher OH production at higher NOx conditions, as shown in Fig 4., is mainly due to the faster OH production through RO2/HO2 + NO. This needs some discussion, so that the reader can understand how exactly the influence of NOx obscures the importance of Cl as a primary oxidant.

Additional text has been added to clarify this point: "As the fixed NO2 mixing ratio increases from 0 to 25 ppbv, production of secondary OH increases, as initiation of radical propagation through reaction (R4) is enhanced."

5. I am wondering if authors could compare the secondary OH production from ClNO2-initiated chemistry to the secondary OH production from OH-initiated chemistry. This can be easily done in the model. While the authors claim Cl leads to significant production of secondary OH, it is not clear if how significant this is compared to the standard chemistry. It would be a lot more helpful if the authors can show the impact of Cl chemistry on OH/O3/HO2/RO2 by turning off Cl chemistry in the model. I think such information would be of great interest to the reader, and also helps to address the importance of Cl chemistry in a coastal, urban environment.

We agree with the Reviewer that this is an interesting problem. In the model, we observe that more secondary radicals are formed when Cl is the radical initiator. The

reasons for this are not currently fully understood. Although we have initiated a study of these processes, we felt a full exploration was beyond the scope of this paper. The question is being pursued as part of a separate study.

Sources Cited Alicke, B., U. Platt, and J. Stutz (2002), Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, Journal of Geophysical Research-Atmospheres, 107(D22), 8196, doi: 8110.1029/2000JD000075.

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