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

Anonymous Referee #1

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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 RO_2, which leads to the production of HO_2 and then produces OH via HO_2+NO.

Is there other pathway to produce secondary OH? This deserves some clarification.

2. If secondary OH is mainly produced from Cl-initiated RO_2, given the lifetime of RO_2 is on the order of minutes, I would expect the impact of Cl chemistry on OH/O_3 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.

3. Chain termination. The secondary OH produced from Cl-initiated RO_2, will also react with NO_2, leading to chain termination via OH + NO_2. In terms of the production of RO_2 and secondary OH, I don't see much difference between OH-initiated and Cl-initiated chemistry. The major difference is that Cl-initiated RO_2 is largely from Cl + alkanes/alcohols, while OH-initiated RO_2 is from OH + Biogenics/aldehydes etc., as shown in Fig 7. But these RO_2 are all terminated by OH + NO_2.

4. The impact of NO_x on $ClNO_2$-initiated chemistry. It seems to me that the higher OH production at higher NO_x conditions, as shown in Fig 4., is mainly due to the faster OH production through RO_2/HO_2 + NO. This needs some discussion, so that the reader can understand how exactly the influence of NO_x obscures the importance of Cl as a primary oxidant.

5. I am wondering if authors could compare the secondary OH production from $ClNO_2$-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 $OH/O_3/HO_2/RO_2$ 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 13685, 2013.