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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 #2

Received and published: 13 June 2013

General Comments:

This paper, using the VOC ratio approach, attempts to evaluate the role of Cl initialised oxidation in an intermediate NO_x environment. Data analysis of the selected hydrocarbon ratios suggests that Cl does not play a role in oxidation, in contrast to previous work reported from the campaign (Young et al., 2012), which used Cl precursor species to assess the impact of this radical. A model, which utilises the master chemical mechanism, has been used to highlight that the formation of secondary radicals, due to the presence of NO, can mask the impact of Cl when using the VOC ratio method. Although the paper is well written and presented, the manuscript fails to assess the impact of Cl chemistry in this environment as the VOC ratio approach used was inappropriate. The model results, as presented and utilised in the manuscript at the moment, cur-

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rently have limited applicability to other studies of this type and although the results fall within the scope of ACP science this paper fails to contribute significantly to scientific progress as is. Therefore, I cannot recommend publication before the comments below are addressed.

Major Comments:

Throughout the paper a sustained OH to Cl ratio of 200 is discussed as a value above which the influence of Cl oxidation on VOC ratios will not be evident. The model used to calculate this value did not contain NOx (condition set 1) but as highlighted in the paper, secondary chemistry occurring in the presence of NO can mask the influence of Cl atoms on oxidation. It is important to know the OH to Cl ratio required to observe the influence of Cl oxidation using the VOC ratio method at typical NOx levels encountered during CalNex (and over the time period Cl was typically enhanced for). I suspect that the ratio required will be a lot lower and, as such, would not have been observed during CalNex? This raises the question as to why this approach has been applied to this dataset? The authors even state in the introduction that VOC tracer ratios may not be a good measure of the indicators of oxidation where secondary radicals dominate.

One could argue that the paper highlights, through the model, that the VOC ratio analysis is inappropriate when assessing the influence of Cl in NOx influenced environments – but from looking at earlier, related work listed in this paper, it is evident that in NOx influenced environments this analysis isn't really used and instead previous analyses have tended to rely on other indirect techniques to assess the extent of Cl oxidation. Previous work by Knipping and Dabdub, (2003) highlights that Cl atom concentrations need to be present within two orders of magnitude of the OH concentrations to play a role in ozone chemistry. Calculations by Young et al. in this paper predict a Cl atom concentration of 2.3×10^3 atoms cm⁻³ (daytime average) and estimate a daytime average for OH of 2×10^6 molecule cm⁻³ which is three orders of magnitude greater. Thus, in agreement with the VOC ratio data in Fig. 2 evidence for Cl oxidation should not be seen using the VOC ratio method.

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Comment

The objectives of the paper are given at the end of the Introduction – I would argue that this paper, using the approach taken, is unable to adequately achieve objective 5: examining the impact of chlorine on tropospheric chemistry in Los Angeles. To achieve this, the authors could perhaps look at VOC oxidation products in the model or even O₃ production with and without Cl oxidation as the model does not seem to be constrained to O₃?

Section 3.3: One problem with this analysis is that the impact of NO_x on secondary radicals will be dependent upon the total VOC concentration and so (because the [VOC] was fixed) the results from the model have limited applicability to other studies. I suggest that further model simulations where the total [VOC] is varied relative to a fixed NO_x concentration could perhaps be more revealing?

Minor Comments:

Pzsenny is spelt wrong throughout the manuscript.

Pg 13668, ln 20: Reference required for stated Cl concentration

Page 13689, Riemer et al., (2008) conclude that Cl chemistry does not compete substantially with oxidation chemistry dominated by OH in Houston which contrasts with the statement in the paper that states that these three indirect methods have shown that Cl may be an important oxidant.

Section 2.1 – the list of measurements is not necessary as these are given in Table 1.

Page 13691, line 14: 'modestly decrease' – by what percentage?

Page 13691: Comment on the impact of underestimating the total VOC concentration in the model on the sensitivity of the VOC tracer ratio.

Page 13691: Comment on the validity of using the average measured VOC concentrations from just before sunrise to initialise the model – how variable is the VOC concentration?

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Page 13694, condition set 3b: why not just switch off the ClNO_2 photolysis – why is it necessary to produce OH from this?

Page 13694, line 21: NO_2 was fixed at 18 ppbv – please justify this value – later you state that the mean NO_x concentration was 15.2 ppbv.

Section 3.3: would be useful for the reader to reiterate which model condition set was used in this section – model condition set 2?

Page 13702, In 19: ‘..incorporation of faster-reacting compounds into VOC tracer ratios provides a more sensitive measure of the influence of Cl .’ What OH: Cl ratio does the model calculate is necessary to observe the influence of Cl oxidation using these faster reacting compounds?

Figure 4B: Why does the black line which represents the model run at 0 ppt NO_2 not overlap with the Cl only reactions?

Figure S1: Comment on the modelled $[\text{O}_3]$ being approximately double the observed concentration.

Figure S1 caption: ‘..calculated using condition set 3..’ – is there no observable difference in O_3 between condition set 3a or 3b?

Table S6: It would be clearer if an absolute $[\text{OH}]$ and $[\text{Cl}]$ is given in column one, so these values can easily be obtained by the reader.

References:

Young et al., Environ. Sci. Technol., 46, 10965-10973, 2012.

Knipping and Dabdub, Environ. Sci. Technol., 37, 275-284, 2003.

Riemer et al., J. Atmos. Chem., 61, 227-242, 2008.

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