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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.

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We thank Reviewer 2 for their thoughtful comments. However, we are concerned that a misunderstanding has occurred over the goals of this manuscript. We address here the general and major comments of this Reviewer. Minor comments will be addressed after the receipt of all reviews and comments. Our responses to these comments are below.

General Comments: This paper, using the VOC ratio approach, attempts to evaluate the role of Cl initialised oxidation in an intermediate NOx 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

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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, currently 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.

Response: We believe there has been a mis-communication in or misunderstanding of the ultimate objective of this paper. Our goal was to rigorously evaluate the most commonly used method to assess the importance of Cl oxidation (the VOC tracer ratio method) in an urban environment. As noted by the Reviewer and demonstrated by this paper, the method can be easily misinterpreted when applied to a high-NOx environment. However, we disagree with the Reviewer's assertion that this method has not been used to describe NOx-influenced environments. The peer-reviewed literature contains examples of the use of VOC tracer ratios in NOx-affected environments (e.g. (Rudolph et al., 1997;Gorham et al., 2010)) that have not considered the potential influence of NOx. Furthermore, this technique is often used as a first-pass filter to determine whether Cl chemistry influences a given environment, including those influenced by NOx. Thus, we feel that an examination of the limitations of this tracer method is useful to the atmospheric chemistry community.

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

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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?

Response: The given ratio of 200 is the value required to observe the influence of Cl. The point of this discussion is that the presence of NOx changes the initial OH to Cl ratio. Hence the simulations over a range of NOx levels, including zero NOx. Indeed, the approach was applied to this data set precisely to demonstrate that it does not work well at high NOx.

Reviewer comments continued: 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

Response: Indeed, this is the point of our paper.

Reviewer comments continued: – 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.

Response: On this point, we disagree with the Reviewer. Please see comments above regarding the prior use of the VOC tracer ratio method in NOx impacted environments.

Reviewer comments continued: 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 x 10ËĘ3 atoms cm-3 (daytime

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average) and estimate a daytime average for OH of 2 x 10ËĘ6 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.

Response: Yes, this is the purpose of our analysis.

Reviewer comments continued: 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.

Response: The paper and its predecessor (Young et al., ES&T, 2012) quantify the role of ClNO2 photolysis as a primary radical source. The point of this paper is that secondary OH generated from reactions of Cl obscures the traditional method used to understand the impact of Cl, even though the Cl plays an important role (9% in this case) in generation of primary radicals.

Reviewer comments continued: 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?

Response: We agree with the Reviewer concerning O3 modeling, which would be very useful in helping to assess the influence of Cl. We have initiated such an effort, but have judged it to be beyond the scope of this manuscript.

Reviewer comments continued: Section 3.3: One problem with this analysis is that the impact of NOx 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 NOx concentration could perhaps be more revealing?

Response: We further agree with the Reviewer that the results of this study are limited by the VOC mixture chosen. However, this was limited by the available Cl kinetic and

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mechanistic data available in the literature. The concentrations chosen do represent those observed in Los Angeles during CalNex. However, even with varied concentrations, the trends observed in this proof-of-concept will be maintained. We have run additional model simulations with varied VOC concentrations. With increased VOC concentrations, secondary OH also increases. This would affect the quantitative impact of NOx, but the qualitative effect remains unchanged. We have added a figure to the SI demonstrating this effect and text in the paper: "These model results describe a single VOC concentration. Results are qualitatively similar when concentrations of VOCs are changed (Figure S2)."

Minor Comments: Response: To be addressed after Discussion is closed. 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? Page 13694, condition set 3b: why not just switch off the ClNO2 photolysis – why is it necessary to produce OH from this? Page 13694, line 21: NO2 was fixed at 18 ppbv – please justify this value – later you state that the mean NOx 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, ln 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 [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 [OH] and [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.

Response Sources Cited

Gorham, K. A., Blake, N. J., VanCuren, R. A., Fuelberg, H. E., Meinardi, S., and Blake, D. R.: Seasonal and diurnal measurements of carbon monoxide and nonmethane hydrocarbons at Mt. Wilson, California: Indirect evidence of atomic Cl in the Los Angeles basin, Atmos. Environ., 44, 2271-2279, 2010.

Rudolph, J., Ramacher, B., Plass-Dulmer, C., Muller, K.-P., and Koppmann, R.: The indirect determination of chlorine atom concentration in the troposphere from changes in the patterns of non-methane hydrocarbons, Tellus, 49B, 592-601, 1997.

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

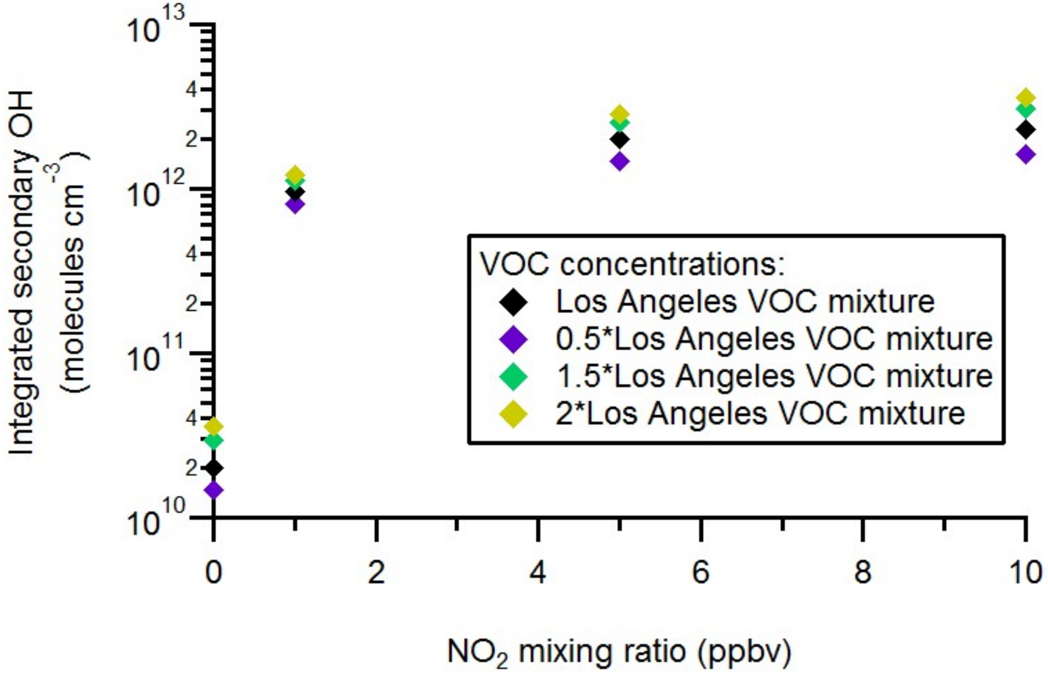

Fig. 1. Figure S2. Relationship between integrated secondary OH and NO2 mixing ratio as a function of VOC concentration.