

Interactive comment on “Oxidation capacity of the city air of Santiago, Chile” by Y. F. Elshorbany et al.

Anonymous Referee #2

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i) General Comments

The paper by Elshorbany et al. is a detailed description of the atmospheric radical chemistry in Santiago in Chile. The authors have used a large set of measurements to constrain a detailed chemical box model, and then predicted OH concentrations and explored radical budgets using the model. In particular, the authors show that in this specific location and for 2 weeks in March 2005, HONO photolysis is a dominant source of OH radicals. My main concern with the paper is that given there are only 2 weeks of measurements, the authors are perhaps reading a little too much into the significance of their results. The structure of the paper could also be improved; some of the sentences and paragraphs are currently very long.

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ii) Specific comments.

1. Abstract. 2 weeks does not constitute an extensive campaign.
2. Abstract, line 11-13 has poor wording. What does the 'same OH radical budget' mean?
3. page 19125. I am a bit confused by the definition of oxidation capacity here. Is this not just a total OH (HO₂, O₃) reaction rate?
4. Page 19126. It is true that the BERLIOZ measurements were in excellent agreement with the model results but for only one day unlike the other references cited that were for longer periods. It is therefore hard to draw too much from comparisons to such a small data set.
5. Page 19127. I found the whole of this page quite hard to follow. The authors need to tidy up this paragraph. Some parts are repetitive and some poorly worded and it gets very confusing to try and unpick which studies included measured (or not) HONO, which included heterogeneous sources etc. Also, there is an inaccuracy in the reporting of the results of Emmerson et al. (2007). Having gone back to the original paper, I do not understand where the authors have got the figure of 3% for net formation of HONO from? The paper shows that HONO photolysis produces 21×10^5 molecule cm⁻³ s⁻¹ of OH, but reaction with NO consumes 22×10^5 molecule cm⁻³ s⁻¹. There is net loss of OH in other words.
6. Page 19131. Do you actually use the <new HO₂> term anywhere? The term you define is very much a lower limit as it does not include photolysis of higher aldehydes, dicarbonyls and contribution from O₃-alkene reactions. According to Emmerson et al. (2007), the source you include here only represents about 20% of new HO₂.
7. Page 19132. You need to say more about the Holland et al. (2003) parameterisation. Presumably it is methodology you have adopted rather than being location specific (latitude, time of year etc.)

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8. Page 19134. This point links back to point 3 above, the terminology regarding the oxidation capacity is confusing here. In the sentence starting at the end of line 22, you state that - the OH radical...reaching a maximum of 3.2×10^8 molecule (NOT molecules by the way) $\text{cm}^{-3} \text{s}^{-1}$. So you are expecting a concentration but are given a flux.

9. Page 19135-19136 and figure 5. Found these very confusing. Cannot see where some of these reaction rates have come from. Also, some of the reaction rates mentioned in the text seem to have been presented in figure 5, but others have not and there seems to be no rationale? I think there is also an issue here between what constitutes radical production versus initiation? One might argue that the formation of OH from $\text{HO}_2 + \text{NO}$ is propagation rather than production, which is why it is important that you define the terminology being adopted here. Figure 5 should also be explained more clearly. Why are the selected reaction rates shown, or else made more complete (or omitted altogether).

10. In the same section, the authors state that $L(\text{OH} + \text{VOCs})$ is much more important than $L(\text{OH} + \text{NO}_2)$. This simply does not make sense when you consider figure 4 which appears to show that they are more or less equal. The rationale for deriving equation 2 is therefore very shaky which explains why using it gives such an under-estimate of the true story. Not sure what the authors are trying to show here?

11. On line 25 of page 19136, how is this equation derived and what does it mean? It does not seem to be used anywhere else anyway? This whole section (pages 19135-19136) is poorly worded and needs major improvements.

12. Page 19138, end of section 3.4 OH uptake is irrelevant here. What is far more important is HO_2 uptake and the authors should go back to the relevant literature and update their discussion accordingly.

13. Page 19143, line 10. Unlikely that HCHO contributes this much given you have excluded photolysis from higher aldehyde species as stated earlier in point 6.

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14. Page 19144. What are - unpredicted high background concentrations of HCHO? How can you have high background concentrations? The terminology is confusing. Also, this whole sentence needs rewording as it is rather vague.

15. Page 19145. Again terminology confusing here. Have you considered the primary production of HO₂ and RO₂ by ozone-alkene reactions? Particularly important for RO₂. If not, your figures are an under-estimate. Also, confusing between OH production, PR and alkene-OH production.

16. I cannot follow the argument at the top of page 19148 at all. There appears to be some reasoning missing here. The authors need to justify how the j plots confirm their former assumptions?

17. Conclusions - For reasons stated above, disagree that OH loss was dominated by reaction with hydrocarbons. Also not sure authors have proved that nitric acid channel not important. Finally, OH production terminology needs clarification as stated above.

18. Figure 5. Incomplete as per comments above.

iii) Technical points.

1. Page 19126, line 12. Do not need generally and reasonably in this sentence.

2. Page 19132, where you list MCM references you should also include the Jenkin et al. (2003) paper for completeness.

3. Page 19135, lines 22-24. This sentence does not make sense and contains errors - what is new OH₂???. The term OH₂ is also used on page 19144.

4. Page 19145, line 9. Remove <by> at beginning of sentence

5. Title of 3.8.2 should be Alkene ozonolysis contribution

6. Page 19148, line 23, two typos surface not surfaces and reaction not reactions.

7. Figure 2. Caption not consistent with labels on figures. Ratio or % for (b)?

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19123, 2008.

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