**Atmospheric
Chemistry
and Physics
Discussions**

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

Y. F. Elshorbany et al.

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Answers to Anonymous Referee #2

We would like to thank the referee #2 for his/her valuable comments and corrections.

General Comments:

The referee's main concern is the short duration of the campaign and the risk of over-interpretation of the results. However, for this type of studies, we think that the experimental conditions and meteorological parameters are of higher importance than the time duration of the study. In this study a large suite of simultaneous measurements have been used to constrain a detailed chemical box model including the fast, highly sensitive measurements of HONO using the LOPAP instrument. The results of the study have been discussed in details in terms of their significance and with ade-

quate comparisons with other similar studies. The current study represents also the first detailed chemical analysis of the radical budget in Santiago. In addition, the main scientific findings of this work (i.e.: that HONO is a major direct source of OH radicals, contribution 52%, 24 h average) were confirmed in another 2 week winter campaign in Santiago from the same year (manuscript in preparation), for which the relative contribution of HONO was even stronger (ca. 66 %, 24-h average). In addition, the high contribution of HONO is also in agreement with other studies for which HONO was sensitively measured (for example, see Ren et al., 2003; Acker et al., 2006b). In conclusion, we are quite confident about the significance of the results presented.

1. Abstract.

The term "extensive" was deleted.

2. Abstract.

The lines 11-13 have been revised again by one of the native English co-authors. The "same OH radical budget" will be corrected to "similar OH concentration".

3. Page 19125.

The term "oxidation capacity" defines the total capacity of an air mass to oxidize and therefore remove pollutants from the atmosphere. The oxidation capacity is thus the total loss rate of the trace gases due to reactions with the corresponding oxidizing species (OH, O_3 and NO_3) as mentioned also by referee #2. However, HO_2 is an important intermediate that is being formed and/or consumed through the oxidation process and is an important source of OH, which is already considered. The definition, excluding HO_2, is thus correct in its current form. For further details to the definition of the oxidation capacity, please also refer to answer to referee #1.

4. Page 19126.

First of all, the conclusions given by Mihelcic et al. (2003) are based not only on one day, but on two days of the BERLIOZ campaign for which the modelled OH concentra-

tion was in good agreement with that measured under high NOx conditions (see sec. 4.2, Mihelcic et al. (2003)). In addition, we think that for the analysis of the radical budget, the measurement conditions and meteorology are of higher importance than the duration of the measurements. And finally, as mentioned by the referee, other cited references also show the good agreement between measured and modelled (MCM) radical budgets. Thus, the current statement is correct and the conclusion is well supported.

5. Page 19127.

The mentioned paragraph has been revised and corrected again by one of the native English co-authors. For the average of the total TORCH campaign the statement by the referee is correct. However, as already clarified in the response to the referee during the pre-review process, HONO does contribute to 3% during the Heatwave period of the TORCH campaign (for which the conditions are more similar to Santiago). This was stated in Emmerson et al. (2007) in the third line of page 172 from the bottom ("...only 3% of initiation via OH occurred through HONO photolysis at this time"). Thus, the statement is correct.

6. Page 19131.

The term "new HO2" has been used often in section 3.3 (e. g. to define the POH(HO2=>OH)recycled) and sec. 3.8.1. The term "new HO2" in our study stands only for HCHO photolysis because the other OVOCs were not measured. However, the secondary formed OVOCs have been shown not to have any considerable contribution to the net radical budgets (see section 3.5, and see also answer to point 15). Thus, the statement is correct, "new HO2" is defined and used accordingly and the conclusion is well supported.

7. Page 19132.

An appropriate comment has been added to account for the use of the parameterization

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of Holland et al. (2003). For more details, see also reply to referee #1.

8. Page 19134.

The terminology has been discussed already in point 3. The mentioned statement has been corrected to "the OH radical was the dominant oxidant during daytime contributing by a maximum of 3.2x10ˆ8 molecule cm-3 s-1 (94 %) to the total oxidation capacity at about 15:00 h."

9. Page 19135-19136 and figure 5.

Referee: Cannot see where some of these reaction rates have come from?

Answer: Line 8 page 19135 states that "the total production and destruction rates of OH and HO2 are calculated by MCM model...". For the specific reaction rates, the reaction used to generate it has been written following the text (e.g. P19135 lines 16-20).

Referee: Some of the reaction rates mentioned in the text seem to have been presented in Fig. 5, but others have not and there seems to be no rational? Figure 5 should also be explained more clearly. Why are the selected reaction rates shown, or else made more completely (or omitted altogether).

Answer: Figure 5 has been designed and used to show the balance between LOH(OH+VOC) and POH (sec.) representing the formation and loss of OH through the propagation process. In addition, the net radical sources and sinks (total rate of radical initiation and the termination rates) are also shown. Due to the balance between LOH(OH+VOC) and POH (sec.), the production and destruction rates incorporating the other secondary reactions (e.g. RO2=>RO=>HO2; or RO2=>RONO2) are not included in Figure 5. In addition, these secondary processes have been shown not to contribute to the net radical sources (see section 3.5, radical propagation).

Referee: What constitute radical production versus initiation? One might argue that the formation of OH from HO2+NO is propagation rather than production, which is why it

is important that you define the terminology being adopted here.

Answer: We do not see any confusion between "radical production and destruction" and "initiation, propagation and termination", this is a well defined and established terminology through the literature (e.g. Emmerson et al., 2007; Volkamer et al., 2007) and have been used in the current study accordingly. The initiation process includes radical production from new sources (OH new) (e.g. photolysis of HONO, HCHO, O_3,...) while the propagation process include destruction and production of OH as a result of the initiation process and may result in new OH. The termination process includes only the permanent loss of radicals. In line 23 Page 19136 it is stated that "OH production is dominated by the recycling reaction of HO_2 with NO, $POH(HO_2 => OH)recycled....$". Thus, as mentioned above, the recycling process incorporate OH production as well as OH loss (P19136 line 4). Accordingly, the terminology used in the study is as aforementioned well established and used accordingly.

10. In the same section.

In Figure 4, two Y-axes with two different scales are shown. Thus, the two rates are completely different as correctly mentioned in the manuscript.

11. On line 25 of page 19136:

The derivation of the mentioned equation is well defined in page 19136, line 23 to page 19137 line 2. The parameters used to generate the equation are either defined previously in P19131 line 11 for "new HO_2" or directly following the equation "P19137 line 2". For correctness, "HO_2 new" in the equation has been corrected to "new HO_2". The defined parameters of the mentioned equation have been used many times following the equation (P19137 line 3-7, line 14) and frequently through the text (e.g. P19138 line 20, P19139 line 11). Thus, the whole mentioned section "P19135-19136" is correct and this section as well as the other sections have been thoroughly reviewed linguistically by one of the English co-authors.

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12. Page 19138 end of section 3.4.

In agreement with the referee's comment, we refer to Yoshino et al. (2006) who found that OH uptake on aerosol surfaces could not account for the missing OH reactivity as stated in (Yoshino et al., 2006, page 7876, section 3.3). But why should heterogeneous loss of HO_2 affect the OH reactivity at all? HO_2 is not in the OH reactivity definition (see sec. 3.4), for which only the second order rate constant and the concentration of the oxidized species are included. Heterogeneous loss of HO_2 on aerosol surfaces may only affect the HO_2 steady state concentration (Emmerson et al., 2007). However, since no aerosol measurements were done during our measurements campaign in Santiago, this issue can not be tested in the current study. In addition, under such high NO_x conditions in Santiago, HO_2 uptake on aerosol surfaces is not expected to have any considerable effect. Ren et al., 2006 (page 258, last paragraph) have also shown that because of the very high NO_x conditions, OH-HO_2 cycling is extremely fast, making it difficult for the heterogeneous loss of HO_2 on aerosol surfaces to have a noticeable effect on the HO_2 steady state concentrations. For self-correctness, the reference "Ren et al., 2006" has been deleted from the mentioned sentence. The sentence is thus correct and consistent with the previous discussion.

13. Page 19143, line 10.

As aforementioned (Point 6), the term "new HO_2" in our study stands only for HCHO photolysis because the other OVOCs were not measured and the secondary formed OVOCs have been shown in section 3.5 not to have a considerable contribution to the net radical budgets. The contribution of HCHO has been determined accordingly as discussed in section 3.6. The statement is thus correct and conclusion is well supported.

14. Page 19144.

The background HCHO (BKG) in the text stands for the fraction of the HCHO that is not accounted as photochemical or emitted HCHO. The background HCHO (BKG) is

defined according to the equation in line 17 page 19143. Explanations of the high HCHO background (residual HCHO) are given on page 19144, line 23 to P19145, line 5. The background HCHO in line 18, page 19143 is now defined more clearly by adding "...which stands here for the residual HCHO that can not be accounted as photochemical or primary".

15. Page 19145.

As mentioned before (Point 6), our study is focusing on the balance between LOH (OH+VOC) and POH (sec.) (section 3.5) as a result of the high recycling efficiency, mainly due to high NOx conditions in Santiago. These conditions have resulted in the net radical sources used in the PSS approach to be the dominant sources of (new OH). The total rate of radical initiations includes only sources that produce OH primarily (net radical sources) except HCHO as the only measured OVOCs. Basically, RO2 formation from the reaction of (alkenes+O3) can not be included in the total rate of radical initiation as the formed RO2 undergoes loss reactions (e.g. RONO2, PAN,..) which can not be neglected. However, the primary production of HO2 and RO2 from the reaction of (alkenes+O3) as well as from the photolysis of sec. OVOCs is already considered in the recycling process (see sec. 3.5). That is, the POH(HO2=>OH) is based on the modelled HO2 by MCM (which is a result of all RO2 and HO2 sources including alkenes+O3). Thus, the balance between LOH (OH+VOC) and POH (sec.) incorporate all RO2 and HO2 (except HCHO) inside the recycling process. From the very good agreement between the OH concentration calculated by both PSS and MCM, we concluded that the primary sources included in the PSS assumption are predominant and thus there is no need for further detailed flux analysis. Similarly Emmerson et al., 2007 considered this reaction (alkenes+O3=>RO2, HO2) only as RO2 and HO2 flux but not as a net OH source. Using a similar approach based on measured parameters to calculate the total OH production, Shirley et al. (2006) did not consider the reaction of (alkenes+O3=>RO2, HO2) as net OH radical source, but included it in the measured HO2 budget. Thus, in our study, HO2

and RO2 formation from the reaction of (alkenes+O3) are considered in the recycling process but not as a net OH radical source. The total alkene OH radical production rate is the production rate of only the alkenes ozonolysis and is defined as (sum(kO3+alkene)x[alkene]x[O3]xOH-yield). For clarification, the following statement has been added "given by sum(kO3+alkene)x[alkene]x[O3]xOH-yield (see sec. 2.3.1)", after "production" in line 24, P19145.

16. Page 19148

As mentioned in the introduction and on the previous page (19147, lines 24-28), several photochemical mechanisms have been postulated to explain high daytime concentrations of HONO in the atmosphere. The postulated reactions, i.e. nitrate photolysis, photosensitized reduction of NO2 on humic substances and nitrophenol photolysis, should correlate to the solar flux. This is demonstrated by the good correlation of the net HONO production (calculated from the difference between the PSS and the experimental HONO, which is the "daytime source of HONO") with j(NO2) and j(O1D), thus "confirming former assumptions". However, caused by the different wavelength dependency of the different sources postulated (19147, lines 24-28) and the different diurnal behaviour of j(NO2) and j(O1D) (no UV-light for high SZA, stronger scattering of blue light...), the better correlation of the daytime source of HONO with j(NO2) shows that a photochemical process in the long wavelength range is of importance here. Thus, the nitrate photolysis, which would correlate to j(O1D), can be excluded. To clarify, we have added on page 19147, line 24 "photochemical" behind "Three..." and on page 19148, line 2: "...of a photochemical production of HONO." behind "former assumptions".

17. Conclusion

For OH loss please refer to answers on points 10 and 15 above.

For Nitric acid channel, please refer to answer on point 16.

For the used OH production terminology, please refer to answers on points 9 and 15.

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17. Figure 5.

Please refer to answers 9 and 15.

III) Technical points

1. Page 19126, line 12.

The sentence corrected accordingly.

2. Page 19132.

The mentioned reference has been added.

3. Page 19135, lines 22-24 and Page 19144.

OH2 (typo error) corrected to HO2.

4. Page 19145, line 9.

"by" removed from the beginning of the sentence.

5. Title of 3.8.2.

Title corrected accordingly.

6. Page 19148, line 23.

Typos corrected accordingly.

7. Figure 2.

This is the value of the HONO/NOx ratio in percent units; i.e. ratio of 0.08 is shown as 8%. The "%" unit is shown on the figure between "[ ]" like all other figures and thus we think needs no more clarification.

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

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