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Atmospheric
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Discussions

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

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Answers to Anonymous Referee #1

We would like to thank referee #1 for his/her valuable comments and corrections. The raised concerns - including the main concern about the correlation of the net HONO formation rate against different j-values - are addressed below.

P19125 line 7:

To our opinion, the definition of the "oxidation capacity" by Geyer et al. (2001) reflects the capacity of an air mass to oxidize trace gases, since it represents the total loss rate of trace gases due to oxidation with the corresponding oxidizing species. This number is equal to the loss rate of oxidizing species in the atmosphere, i.e. also describes how many OH and NO3 radicals and O3 (number) are consumed per volume

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and time. Integrating over the day leads to total number of radicals consumed per volume (see top of page 19135). Thus, the "oxidation capacity", defined by Geyer et al., already includes the number of oxidizing species, as proposed by referee #1. However, we may have misunderstood this concern and referee #1 intended to suggest the use of concentrations of oxidizing species. However, this would not describe the "oxidation capacity", since the flux of radicals and the rate of loss of oxidized species is not directly linked to the concentration of oxidizing species. The concentration of oxidizing species can be quite high in remote regions (for example OH: see Brauers et al., 2001 for Atlantic Ocean or Berresheim et al., 2003 for Mediterranean coast; [OH] up to 2x10ˆ7 cm-3) although the loss rate of trace gases will be quite low owing to low trace concentrations. This will lead to low fluxes of radicals (low oxidation capacity) although their concentrations are high.

P19130 line 19:

The reduction of 29.4% of cis-2-pentene was observed when ozone was passed over the adsorption tubes for a time period of 3 h under a constant ozone mixing ratio of 135 ppbv. However, the campaign averaged ozone concentration used here to calculate the radical budget by alkene ozonolysis did not exceeded 65 ppbv (Fig. 2a). In addition, the average and median O3 values (averaged over the same time intervals of VOC samples) were only 26 and 21 ppbv, respectively. Assuming linear ozone interference we have estimated that the maximum reduction of individual alkenes and the averaged reduction for all alkenes due to the ozone interference was $<$15% and ca. 4%, respectively. These errors are in between the range of the total accuracy of the VOC measurements (ca. 20 %) and are expected to be smaller than the uncertainty for non-quantified alkenes, which would also contribute to the oxidation capacity (see text, page 19136 lines 27 and top of next page).

P19132 line 11:

corrected.

P19132 line 12:

The photolysis frequency of HONO and HCHO were calculated using the parameterization of Holland et al. (2003) for the following reasons:

1. We had unfortunately no axcess to a spectro-radiometer, but only to two filter radiometers (j(NO2) and j(O1D)).

2. The parameterization by Holland et al., 2003 cover a variety of meteorological conditions (zenith angle = 31°-90°, 300-400 DU total ozone, 0-8 octa cloud cover, 6°-28°C ambient temperature). In Santiago, the average campaign maximum zenith angle of 32°, annual mean (1979-2004) total ozone column of 281 +/- 8 DU (Diaz et al., Photochemistry and Photobiology 82, 834-843, 2006), clear sky and ambient temperature range of 12°-32°C, lies within the range of meteorological parameters used to generate the j-parameterization by Holland et al., 2003 justifying its use. In addition, any difference in ozone column, particle scattering etc. between the Holland et al. and this study, would only effect the quadratic term in the Holland et al. parameterization, since the range of the action spectra of HONO and HCHO are in between the experimentally considered wavelength intervals of O3 (j(O1D): short wavelength range) and NO2 (j(NO2): longer wavelength range).

3. Since the Holland et al. parameterization is based on our measured photolysis frequencies (j(NO2) and j(O1D), which also deviate from their corresponding MCM modelled values), we think that these values have higher accuracy than the MCM modelled values.

4. Nevertheless, using the photolysis frequencies (j(HCHO rad) and j(HONO)) calculated by MCMv3.1 or Holland et al. (2003) will not significantly change the relative importance of the primary radical sources. That is, using the MCM parameterization in the evaluation, the contributions of the net radical sources to radical initiation will be: HONO, 60%; alkenes ozonolysis, 22%; HCHO, 14% and O3, 4% while the currently used values calculated using Holland et al. (2003) are HONO, 52%; alkenes ozonoly-

sis, 29%; HCHO, 15% and O3, 4%. Thus, the given high contribution of HONO (52 %) even reflects only a lower limit.

In conclusion, we think that the parameterization of Holland et al. (2003), which is based on our measured photolysis frequencies is more appropriate for this study compared to the use of modelled values. Reasons 2. and 3. will be added to the text accordingly to account for the use of the Holland et al. (2003) parameterization.

P19135 line 12:

Basically, the OH production can not be zero at any time because the alkene ozonolysis as a primary OH source is also active during night in addition to OH formation due to oxidation of VOC by the nitrate radical (although very small absolute contributions). We agree however with referee #1 that the difference is a very small number (<10ˆ7 molecule/cm3/s) and that this ratio is not comparable to that in the cited references as they have reported a high measured ratio at a time of the day when the production and loss rates was more than one order of magnitude higher than ours in the early morning. The statement has been corrected accordingly.

P19135 line 17:

While the reaction of OH with VOC is the main source of RO2, there are other RO2-sources e.g. alkene ozonolysis and the photolysis of aldehydes, ketones and dicarbonyls (see e.g. Emmerson et al., 2007). Thus, the RO2 is a result of all of these production rates. Therefore, the loss rate of RO2 through its reaction with NO (34.6 ppbv h-1) should be greater than the production rate of RO2 from only the reaction of VOC+OH (24.9 ppbv h-1). Similarly, Emmerson et al. (2007) reported an RO2 production rate from OH+VOC of 226x10ˆ5 molecule cm-3 s-1 much lower than RO2 loss rate due to RO2+NO of 348x10ˆ5 molecule cm-3 s-1. Therefore, the statement is correct in its current form.

P19135 line 23:

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Although an average of 28% of the measured HCHO has been determined as photochemical, total measured HCHO was considered as a net source of HO2 for the following reasons:

1. In other urban studies, the photolysis of total measured HCHO has been used as a net source of HO2 (see e.g. Volkamer et al., 2007, Emmerson et al., 2007) and thus the comparison with other studies is more feasible for the reader than when using only a fraction of this parameter. In addition, it is already mentioned in the text that on average only 28% of the measured HCHO is accounted as photochemical and thus, the reader should be able to calculate the contribution of the primary fraction of HCHO to the HO2 (if desired).

2. Calculating the contributions of the different net radical sources based on only 72% of the measured HCHO will not change the relative importance of their contributions to the radical budgets. That is, based on 72% of the measured HCHO, contributions of the different net radical sources (on a 24-h basis) will be: HONO, 57%; alkenes+O3, 29%, HCHO, 9%, O3, 5% in comparison of the currently used values (total HCHO) of 52%, 29%, 15% and 4%, respectively. Thus, we think that reporting the different net radical contributions based on total measured HCHO is more appropriate for this study.

P19136 line 15:

Using Equation 2 will lead to an overestimation of HO2 as a net source of OH for the following reason: If only the loss of OH due to reactions with only measured VOC are considered, then the production of HO2 that results from secondary VOC oxidations will be neglected. This will result in the loss rate of HO2 from the reaction of (HO2 + NO) being much higher than the HO2 production rate from (RO2 (measured VOCs) + NO = HO2), resulting in too high OH production from HO2. For clarification we have changed to "...HO2 as a net source of OH..."

P19138 line 26:

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Firstly, NOx is considered as a pollutant as well. Secondly, the previous statement (line 22) shows that the comparison is based not only on the high NOx conditions (which was not essentially the highest during the Heatwave period in Emmerson et al.) but also on the stagnant condition which is assumed to be the common factor between Santiago air basin and the Heatwave stagnant period of the TORCH campaign. Therefore, the statement is justified.

P19142 line 15:

Typo: corrected .

P19142 line 17:

The MCM model was not run unconstrained to either alkenes ozonolysis or alkenes ozonolysis + HONO, thus their contributions were not directly determined from the MCM runs. However, the excellent agreement between the diurnal OH concentration profiles obtained by both PSS and MCM models shows that the major net radical sources incorporated inside the PSS assumption are predominant. If in the PSS model the alkene+O3 source (Rubio) or the HONO and alkene+O3 sources (Rappenglück) are not considered, the max OH concentration would be reduced from 1.38x10ˆ7 to 1.28x10ˆ7 and 4.1x10ˆ6, respectively. For comparison, Rubio et al. estimated 8.8x10ˆ6 and Rappenglück et al. 2.6x10ˆ6. Thus, the trend observed for different calculated OH levels could be explained by the different considered OH sources. However, absolute values of calculated OH concentrations are expected to be different, caused by different trace gas levels during the different campaigns. For example, the lower value for the Rubio et al. study (8.8x10ˆ6 vs. 1.28x10ˆ7 for same assumptions used here) can, at least in part, be explained by the lower HONO values in Rubio et al. compared to this study. Nevertheless, "Possible" is inserted before "Reasons" in P19142 line 15.

P19142 line 24:

Although Rohrer et al., 2006 study was mainly focused on the analysis of their long

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term measurements at Hohenpeissenberg, Rohrer et al., 2006 have shown that the linear correlation between OH and j(O1D) can also be retrieved from other recent field measurements campaigns of quite diverse environments (including urban conditions), different instrumentations and of shorter time durations (last paragraph, page, 184, Nature, vol. 442 and see Supplementary Figure 3). Therefore, the current statement is correct and an additional reference has been added (Kanaya et al., 2007).

Section 3.7:

The word "measured" will be inserted before "OH" in P19142 line 27 and the word "also" will be deleted from P19142 line 28. In addition, since the model is constrained with measured parameters, the OH is controlled by both, the chemistry of the model and the diurnal variation of the trace gases and j-values etc.. Thus, modelled OH does not simply reflect the chemistry of the model. For example, if HONO would be much lower (equal to the PSS) and ozone much higher, a better correlation to j(O1D) would be expected using the same chemistry of the model.

P19144 line 20:

In P19144 line 20, it is stated that "The average background baseline ... of HCHO represents about 20%" and NOT the total average background of HCHO. The baseline of the background determines the average HCHO background values during the early morning and afternoon and cuts off the high unpredicted HCHO background during daytime (P19144 line 22). On a 24-h average basis, the background of HCHO does indeed accounts for ca. 38% of the total measured HCHO (P19143 line 25). The statement is thus correct in its current form. For clarification, the following sentence defining the baseline has been inserted before "which" in P19144 line 20 and the statement rearranged accordingly: "The baseline of the background determines the average HCHO background values during the early morning and afternoon.". In addition, a baseline for the background is drawn in Fig. 11.

P19144 line 24:

Typo: corrected.

P19144 line 27:

An appropriate reference "Carslaw and Beevers, Atmos Environ, 2005" has been added.

Section 3.8.3:

The sentence in P19147, line 10 shows that OH is typically overpredicted by the MCM, but we would need higher OH in the atmosphere to explain the very high HONO levels by gas phase chemistry only (PSS). Thus, the mentioned statement shows that even uncertainties in OH modelled can not explain the measured HONO levels. This argument therefore suggests the existence of the proposed daytime source of HONO. In addition, the suggested sentence by the referee will be a repeat of the sentence in P19146 line 23. Thus, the sentence is correct and follows the previous discussions.

Section 3.8.3 and Conclusion:

The mentioned correlation considers the net production rate of OH radical due to HONO photolysis given by (jHONOx[HONO] - k(OH+NO)x[OH]x[NO]) and NOT the total production rate of OH by HONO photolysis simply given by (jHONOx[HONO]). Since the net production reflects only 34% of the total production caused by large values for k(OH+NO)x[OH]x[NO] and since it is also controlled by the trace concentrations (HONO, NO OH) it is therefore not necessary that the net OH production by HONO correlates with any j-value. For example, it could also be possible, that HONO is formed by any unknown NO2 reactions (i.e. not photochemically). Therefore, owing to the diurnal variation of the NO2 concentration (high in the morning/evening, low during noon), the net OH production by HONO would not correlate directly with photolysis (at any j-value) (even though OH is still formed by the HONO photolysis...). In addition, assuming steady state (as is done in all other studies on this topic, e.g. Acker et al., 2006a), the net OH production by HONO photolysis given by (jHONOx[HONO]

- k(OH+NO)x[OH]x[NO]) is equal to the net HONO production, (d[HONO]/dt)net, as well. If the steady state assumption is not valid (for example in the case of strong gradients), at least 1-D modelling including experimental flux measurement data would be required. But this is out of the scope of the current study. Thus, we consider that the statement is correct in its current form. Besides this, any correlation of the concentration (HONO-HONOPSS), as considered by the referee, will not describe a HONO source, since absolute HONO levels are also influenced by its photolytic lifetime, i.e. a certain value for (HONO-HONOPSS) will translate into a small net HONO source in the morning (low j(HONO)) and a large net HONO source during noon (high j(HONO)). However, since we intended to investigate the net HONO source, absolute concentrations cannot be used here.

P19159 line 8 should be P 19150 line 8:

Since the major contribution of HONO was also observed in rural studies (for example, see the study of Acker et al. (2006a) from Hohenpeissenberg) this general statement is correct.

Fig. 3b:

The colours of the figure are now clearly defined.

Fig. 4:

The log scale can not be used for negative values (loss rates). Using all positive values (alternatively) will reduce the clarity of the figure. Therefore Figure 4 has not been changed.

Fig. 11a:

Figure corrected accordingly.

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