Atmospheric Chemistry and Physics Discussions

Interactive Comment

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

Anonymous Referee #1

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This thorough study of the OH radical budget in Santiago de Chile is based on measurements of a set of trace gases which included HONO but did not include OH, using a box model based on the MCM. The accuracy of the MCM for the simulation of the OH budget is supported by previous studies in other urban environments, adequately cited in the manuscript, where OH was measured and compared with simulations using the MCM. The relevance of HONO photolysis and also of ozonolysis of alkenes is demonstrated for the HOx chemistry in the urban air mixture of Santiago. Also evidence for a significant daytime HONO source is presented.

My one bigger concern is a statement about the daytime HONO source correlating with j(NO2) in the Conclusions that is not adequately supported in the manuscript and may be wrong.

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Detailed comments:

P 19125 line 7: The "oxidation capacity", as defined by Geyer et al. (2001), is actually a concentration turnover rate, with the unity molec./cm3/s. In my view, this is an unfortunate definition, since "oxidation capacity" should denote the capacity of an air mass to oxidize trace gases, depending only on the number of oxidizing radicals X, not on the concentration of oxidizable trace gases contained in the air mass. A more appropriate name for this could be "oxidation turnover".

P 19130 line 19: For cis-2-pentene a reduction of 29.4% was observed with 135 ppbv O3. If up to 126 ppbv were observed in Santiago, it seems significant negative interferences from ozone cannot always be excluded.

P 19132 line 11: typo: "were" instead of "where"

P 19132 line 12: The parameters derived by Holland et al. were derived for the BERLIOZ campaign and may only be valid there. The authors should comment why they think the same parameters can be applied for Santiago in March.

P 19135 line 12: Production and loss of OH should be about equal at all times, as the lifetime of OH is extremely short and both terms are usually very large. An exception may be given very early in the morning, when production is very low and OH actually increases. I agree with the authors that the 1.7 times higher production than loss in the model is probably due to HONO photolysis, but it is only possible because the production is essentially 0 otherwise, so the difference is a small number. This is not comparable to what Shirley et al. and Sheehy et al. discuss, as they compare loss and production rates directly derived from measurements, not from a model. They found a difference of 108 molec./cm3/s, which would lead to a spectacular increase of OH in the model.

P 19135 line 17: According to Fig. 5, production of RO2 from reaction of VOC+OH is 24.9 ppbv/h. How can the loss rate of RO2 through its reaction with NO be greater

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(34.6 ppbv/h) ?

P 19135 line 23: If 28% of HCHO is formed photochemically, HCHO should be considered a net source of HO2 only to 72%.

P 19136 line 15: Eq. 2 would lead to an underestimation of the OH loss rate. But why would this lead to an overestimation of HO2 as an OH source ?

P 19138 line 26: It is high levels of NOx, not just high levels of pollutants, that push the conversion of OH into RO2 and of HO2 into OH into balance.

P 19142 line 15: typo: theses

P 19142 line 17: Does MCM produce similar values as the previous studies if HONO photolysis or alkenes ozonolysis are taken out ?

P 19142 line 24: Rohrer et al. have shown a that OH has a linear correlation at Hohenpeissenberg over a time period of several years, but it is only one site, and a rural one. Even though sometimes urban air is advected to this site, it has undergone some photochemical processing on the way and is not comparable to air found in an urban environment like Santiago.

Section 3.7: While it is interesting to note that OH modelled for Santiago correlates well also with j(NO2), it should be clearly stated that Kanaya et al. used measured OH. Any correlation found for modelled OH simply reflects the chemistry included in the model.

P19144 line 20: The background HCHO seems to be more than 20% in average according to Figure 11a.

P19144 line 24: typo, should be "photochemically produced"

P19144 line 27: missing a reference for NO2 from direct emissions

Section 3.8.3: I agree with the authors that their results point to a strong daytime source of HONO. However, I find their argumentation somewhat confusing, since it involves a

circular argument. The OH simulated with the MCM has been shown to compare well with measured OH in urban environments, where HONO is a mayor source of OH. In Santiago, according to the manuscript, HONO is the main source for OH. I think it would be clearer to say that only 65% can be explained from the photostationary state of OH and NO according to MCM, while the rest must have other sources, than to argue that MCM would have to produce 55% more OH to explain the measured HONO.

Section 3.8.3 and Conclusions: I do not agree with the idea that plotting P_R or the net OH production from HONO photolysis vs. j(O1D) or j(NO2) is a good test for evaluating the nature of the HONO source. A good test would be to plot the net HONO production vs. the photolysis frequencies. With lifetimes of several minutes, HONO is usually not in steady state, and production and sink are not equal. Therefore the net OH production from HONO is equal to the net HONO sink, but not to the net HONO production.

The net HONO sink is directly proportional to j(HONO), which has been calculated from j(O1D) and j(NO2). The found correlation is likely to be partly due to the correlation of j(HONO) with j(O1D) and j(NO2). HONO production is unknown, but how does HONO correlate with the measured photolysis frequencies ? Especially the part of HONO that exceeds the photostationary state concentration (HONO-HONO$_{PSS}$)?

P 19159 line 8: add "in urban environments". In cleaner air HONO has been found to play no or only a minor role.

Fig. 3b: Most figures are discernible also in greyscale, this one isn't. Better choose a dark and a light color.

Fig. 4: Better one log scale for all than different scales for some curves.

Fig. 11a: Set tick marks at full hours.

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

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