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Interactive comment on “Radical budget analysis in a suburban European site during the MEGAPOLI summer field campaign” by V. Michoud et al.

Anonymous Referee #2

Received and published: 22 August 2012

Review Michoud et al. (2012), ACPD, 12, 15883-15943

This manuscript reports atmospheric measurements of trace gases made at a suburban area near Paris during the MEGAPOLI field campaign. This dataset was used to test our understanding of the ROx chemistry through an intercomparison of calculated (PSS, 0-D box modeling) and measured (CIMS) concentrations of OH and HO₂+RO₂ radicals. In addition, a detailed analysis of the radical budget was also performed to provide insights into processes driving the radical chemistry in this environment. Overall, this study indicates that our understanding of the daytime ROx chemistry is well understood at this site.

Substantial conclusions have been reached and this manuscript will be of interest for the atmospheric community. I therefore recommend publication in ACP after the au-

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thors address the following comments:

Major comments:

I agree with anonymous referee #1 that the approach used to calculate steady state concentrations of OH is not usual. However, I think that Eqs. 4 and 5 are valid as long as the following assumptions are fulfilled: (1) total initiation and termination rates of ROx radicals balance each other, (2) radical losses other than OH+NO₂ and OH+NO are negligible, and (3) the gross formation rate of OH from HONO photolysis is included in the ROx initiation rate.

I have however some concerns about these calculations:

P15895: Eq. 2: “ $J(\text{O1D}) \times [\text{O3}] \times \Phi_{\text{OH}}$ ” should read “ $2 \times J(\text{O1D}) \times [\text{O3}] \times \Phi_{\text{OH}}$ ” since each O1D atom react with water to form 2 OH radicals. Was the right equation used in the calculations?

P15895: Eq. 2: “ $J(\text{HCHO})[\text{HCHO}]$ ” suggests that both photolytic pathways of HCHO, one leading to H+HCO and one leading to H₂+CO, were used in the PSS calculations. Only the pathway leading to the formation of H+HCO should be used since it is the only one to contribute to the formation of HO₂. What did you use in the PSS calculations? I recommend to use the notation “ $J(\text{HCHO_Rad})$ ” in Eq. 2.

Minor comments:

P15890 L3: “a box model containing the Master Chemical Mechanism (MCM) and constrained with all the species and the parameters measured during MEGAPOLI Åž. Please indicate what types of constraints were used. How many VOCs, J-values. . . ?

P 15891 L10: “radical quencher” should read “radical scavenger”

P15891 L23: Were the instrumental sensitivities for OH and HO₂+RO₂ measured periodically during MEGAPOLI? If so, how variable were they?

P15892 L25: The uncertainty of 20% stated for $J(\text{O1D})$ is similar to that stated on L8

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for J(NO₂). I would have expected a larger uncertainty for J(O₁D) values compared to J(NO₂) since the J(O₁D) filterradiometer response factor was derived from an inter-comparison to the TUV model while the J(NO₂) filterradiometer was calibrated. Could the authors comment on this point?

P15896 Eq. 4: “kNO+NO₂” should read “kOH+NO₂”

P15896 Eq. 5: “kOH+NO₂” should read “kOH+NO₂ [NO₂]”

P15898 L6-7: “loss cycles” should read “termination rates”

P15899 L10-11: How did you choose dilution losses of 1 and 2 hours for the unmeasured oxidation products?

P15900 L9-10: “For the multifunctional species, the highest deposition velocity by function was adopted”. What is “the deposition velocity by function”? Please clarify.

P15902 L23-25: “The PSS approach appears to be sufficient to explain OH concentrations in polluted environments, as it has been already shown in the highly polluted urban area of Santiago, Chile (Elshorbany et al., 2009).” It should be clearly stated that Elshorbany et al. did not compare calculated OH concentrations to field measurements since OH was not measured in Santiago. These authors compared the PSS calculations to the outputs of a box model.

P15903 L16-17: “The model is in pretty good agreement with the observations for several days of the campaign (07/09; 07/11; 07/13; 07/15; 07/19; 07/20; 07/21), the difference being within the measurements uncertainties” and “On some other days, the model largely overestimates OH measurements. . .” Please state quantitatively how the measured and modeled concentrations agree.

P15904 L3-5: “Thus, the model including a detailed description of radical sources and sinks enables to represent the processes involved in OH budget under intermediate and low NO_x levels better than the PSS calculations.” It would be interesting to briefly discuss the main sinks that were not included in the PSS calculations and their contri-

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butions to the total loss rate of radicals.

P 15904 L9-11: “both versions of the model overestimate measured RO₂ concentrations on 7/20 and 7/24 and underestimate the measurements on 7/16.” And “The NO_x levels were quite low on 7/20 and 7/24 and quite high on 7/26.” Please be quantitative.

P15905 L16: “These simulations lead to a rise of radical concentrations in the model, with a larger impact of alkene ozonolysis on radical concentrations (OH, HO₂ and RO₂) during the night than during daytime, as expected.” Please indicate why it is expected.

P15906 L6 and Line 9: Was the HCHO concentration changed by +-25 or +- 10%

P15908 L12-13: “These reactions act as propagation reactions, leading mainly to RO₂ formation but also directly to HO₂ formation at a non negligible fraction.” Please be quantitative

P15909 L11-27 and P15910 L18-21: The radical budget of HO₂ and RO₂ radicals are discussed in detail. However, there is no information about HO₂+RO₂ concentrations at night in Figs.10 and 11. It would be interesting for the reader to display the nighttime modeled concentrations of RO₂+HO₂ as it was done for OH in Figs. 5 and 8.

P15914 Lines 27-29: “The total initiation and termination rates were in balance and similar to other ones found during previous studies in suburban or remote areas but far lower than other ones found in previous urban field campaigns.” Please be quantitative

P15927 Table 3: Please indicate the time period used to perform these sensitivity tests

P15932 Fig.5: Wrong caption

P15937 Fig. 10 and P15938 Fig. 11: The labels of the vertical axes indicate RO_x radicals. Did you really plot OH+HO₂+RO₂? Or did you plot RO₂+HO₂?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15883, 2012.

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