

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

Anonymous Referee #1

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This paper describes a detailed analysis of measured HO_x (OH, HO₂, RO₂) levels, obtained during the MEGAPOLI experiments in 2009. A large number of ground level in situ observations are used to constrain analytical and model simulations of radical levels, for comparison with observations and identification of the dominant source, sink and interconversion processes. Discrepancies between observed and modelled / calculated values are assessed in terms of the potential role of unmeasured species, and (to an extent) uncertainties in the observations and model analysis. This paper adds to a number of other similar studies in which the broad characteristics of ground level HO_x seem to be reasonably well understood, but in which quantitative agreement between measurements and models is elusive. The topic of the paper is suitable for publication in ACP, and the manuscript is generally clearly written, and figures, graphics are well presented. The paper is quite long, and I would encourage the authors to consider if

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section 4.4 in particular could be shortened.

I have one substantial reservation over an aspect of the analysis, which needs to be addressed before the paper can be considered for publication in ACP, and several other comments :

Problems with the PSS approach

A PSS approach is presented to calculate OH levels for comparison with measurements. However, the approach used mixes OH and HO₂/RO₂ sources and sinks, and neglects partitioning between OH, HO₂ and RO₂. As presented, combining equations 1 and 2/3 would determine the sum of [OH] + [HO₂] + [RO₂], not [OH] (if it is assumed that HO_x loss is dominated by OH + NO₂). Equations 4 and 5 are therefore not correct, and the quantity Pr/Lr should be compared with [OH]+[HO₂]+[RO₂], if this approach is to be followed. In practice the much longer lifetime of HO₂ and RO₂, compared with OH, begins to make such an analysis, using point observations, problematic.

To obtain a steady state level for OH, you need to consider OH sources and sinks – this will need to include HO₂+NO and probably HO₂+O₃, from either measured or calculated HO₂. Total radical (HO_x) termination may be dominated by OH + NO₂, but OH removal is dominated by OH + VOC (ca. 80 %, as shown by your radical budget analysis, section 4.4), so this term should feature in any PSS calculation for comparison with observed OH.

Model mechanism. This is something of a matter of opinion but it may not be desirable to construct “hybrid” mechanisms (as has been done here, mixing reactions from the MCM and from SAPRC), rather than using a single, well-defined, auditable, mechanism to facilitate comparison with other work. Does the new mechanism reproduce e.g. chamber data to a similar level to the original mechanisms ? If so, why bother with the change – if not, what are the consequences for confidence in the model simulations ? (There is also the issue that some mechanisms, such as SAPRC, are tuned to chamber datasets, so while reactions may look like fundamental processes, other dependencies

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within the mechanism mean that direct changes to single parameters are not, strictly, valid – without re-tuning the whole mechanism. This does not however apply for the near-explicit MCM).

Other Comments

-Abstract, minor points: Clarify if RO₂ includes HO₂, and ensure this usage is consistent with the rest of the manuscript. “Various modelling procedures” and “two extremes” both undefined are not very helpful here – these either need to be specified, or this section re-worded more generally. Give % contributions for the various “significant” pathways mentioned.

-Introduction: NO₃ reactions represent another HO_x initiation route

-p.15888 L5 need to specify the rate constant for X with RO₂, HO₂. Include Fuchs et al. (AMT 2011) reference for the HO₂ – RO₂ interference.

-p.15889 L19: The other cause for model-observation discrepancy is of course error in the measurements. This should be considered, for example with reference to the recent papers by Mao et al (ACPD 2012) and Fuchs et al. (AMT 2012) – especially given that in this work a different technique (CIMS) is used for the OH measurements.

-p.15891 L8 please ensure consistent usage of RO₂, to include or exclude HO₂ throughout the paper – it would be better to refer to “HO₂ + RO₂” for clarity. The term “RO_x” appears later in the paper – is this OH+HO₂+RO₂ ??

-p.15891 L25 Would it be useful to estimate the systematic uncertainty in the mean OH and HO₂+RO₂ levels also – e.g. the uncertainty that might be expected in the mean diurnal profiles shown in figs 5, 11 ?

-p.15892 the description of the albedo treatment is not clear, what values were used for e.g. jHONO or jHCHO ? Is the 25% uncertainty in jHONO 2 s.d. ? This seems rather high. -p.15893 Please specify if the NO₂ measurement used a thermal (heated Mo catalyst) or photolytic NO₂ converter.

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-Equation 4 $k(\text{OH}+\text{NO}_2)$ not $k(\text{NO}+\text{NO}_2)$

-p.15896 You say that all alkenes except methylpropene were below DL, but then that measurements of isoprene, α/β -pinene, limonene were made ??

-p.15898 the description of the spin-up process is a little confusing.

-p.15899 would a dilution loss with 1-2 hours timescale be expected, in a well-mixed boundary layer ?

-p.15095 It would be useful to refer back to the observational uncertainty for NO₂, in particular considering the type of NO₂ converter used and potential for retrieval of other NO_y as NO₂.

-p.15907 please include (briefly) the quantitative outcome (ie. % change in HO_x) of the aerosol loss sensitivity runs.

-p.15910 Do the calculated role of alkenes relate to the observed alkene concentrations, or the runs in which 100 ppt was assumed for various species, or ?? Similarly, for the overall budget figures presented on p.15911.

-Graphs, several subscripts missing in captions and legends.

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

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