

Interactive comment on “Comparison of OH reactivity measurements in the atmospheric simulation chamber SAPHIR” by Hendrik Fuchs et al.

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Received and published: 25 September 2017

We thank the reviewer for the helpful comments.

Comment: In Table 4, the corrections for non-pseudo first-order conditions for the CRM instruments is given and appear to depend only on the overall reactivity. However, as discussed in Michoud et al. (2015), the correction also depends on the reactivity of the individual VOCs. It appears that the instruments always used an average correction factor for a range of reactive VOCs based on laboratory calibrations regardless of the VOC mixture in the chamber. This should be clarified. Could an inappropriate correction factor explain some of the discrepancies in the CRM measurements when specific

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VOCs were added to the chamber, such as the terpene mixture?

Response: The reviewer raises an important point: Indeed the corrections were made based on an average correction factor (typical of normal operating conditions), rather than based on the specific chamber mixture. The CRM systems have been developed for conditions prevalent in ambient air whereas in the chamber, artificial mixtures were used to test performance under simplified conditions (e.g. only CO or only monoterpenes). Instead of calibrating for the specific chemicals in the chamber, the CRM operators choose to apply their usual correction methods (average correction factor from the single component calibration bottles available to each group). This will indeed lead to a discrepancy particularly for situations where the reactivity of the injected compounds are significantly different from this average value as also discussed in the manuscript.

The correction for non-pseudo first-order conditions shown in Table 4 was calculated from the parameterization presented in Michoud et al. (2015) at a pyrrole-to-OH ratio of 2 for the MDOUAI instrument. This parameterization provides an average correction factor for trace gases exhibiting a bimolecular rate constant with OH ranging from 2.4×10^{-13} (ethane) to 10^{-10} (isoprene) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The 1σ variability observed experimentally on this correction factor (when the different gases were used) is approximately 9%. As a consequence, the measured OH reactivity could deviate from the true reactivity by 9% (1σ) if a VOC (or group of VOCs) exhibiting OH rate constants close to the two bounds mentioned above were used in the chamber, with an overestimation and an underestimation of the OH reactivity for the less reactive and the most reactive compounds, respectively. The monoterpenes used in SAPHIR experiments exhibit rate constant ranging from 5.3×10^{-11} (α -pinene) to 2.1×10^{-10} (myrcene) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Part of the discrepancy observed between the measurements of the MDOUAI instrument and the true OH reactivity in the chamber may therefore be due to an underestimation of the correction for non-pseudo first-order conditions. Since the rate constants of some of the monoterpenes used in SAPHIR are larger than the upper bound tested on the MDOUAI instrument, it is not straightforward to estimate the

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underestimation due to a miscorrection for non-pseudo first-order conditions. It would require testing compounds such as myrcene on the CRM instrument.

Comment: For the FT-LIF instrument, it was found that the measurements displayed greater deviations for more chemically complex mixtures, and the authors suggest that issues related to this particular flow tube instrument configuration may be responsible. What aspects of this particular instrument and its operation were significantly different from the normal PSU instrument?

Response: The Penn State group shipped their OH reactivity instrument to Juelich for the intercomparison, but had other obligations for the OH-measuring system, including the electronics, the drive controller for the OH reactivity instrument's movable wand, and the data collection system. Fortunately, Hartwig Harder's group at MPI Mainz was able to lend a laser system and to build a drive system. But this meant that new software had to be written to reduce the data. Also, the drive system had issues and needed to be reset often. The Penn State group also had to borrow a dye laser from Ron Cohen's group from UC Berkeley, which was similar to the one that Hartwig's group and we normally use, but not identical. In addition, the Penn State instrument normally pulls 100 LPM, but it could not do that in the chamber. So they had to use a large dilution, which amplifies small systematic deviations and small day-to-day variations in the dilution flows by a factor of five or so.

Between the occasional problems with the laser and drive systems and the amplified variability due to the dilution, the instrument precision and the day-to-day accuracy was degraded somewhat from normal operation.

A more concise version of this response can already be found in the manuscript.

Comment: Two of the LP-LIF instruments observed bi-exponential behavior due to misalignment of the photolysis laser. How sensitive is the observed decay to the laser alignment? Is this sensitivity common to all LP-LIF instruments?

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Response: The alignment of the photolysis laser in the flow tube is critical as shown in the results. Laboratory tests with the FZJ instruments, for example, have shown, that experimental parameters like laser beam diameter, beam profile, geometry of gas sampling by the LIF cell (head-on or sideways) have an influence on the decay curve. Once these geometrical parameters are properly fixed, the decay curves are usually reproducible over time and have a single exponential behavior. Deviations from this exponential behavior can be recognized, if the quality of the decay curve is checked, for example, by plotting on a logarithmic scale or by inspection of the residuum of the fit. On the other hand, reasonable corrections can be applied by post-processing as shown by the good agreement of all LP-LIF instruments in this campaign.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-231, 2017.

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