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Atmospheric Measurement Techniques Discussions

Interactive comment on "Intercomparison of the comparative reactivity method (CRM) and pump-probe technique for measuring total OH reactivity in an urban environment" *by* R. F. Hansen et al.

Anonymous Referee #2

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This manuscript presents the first formal intercomparison of total OH reactivity measurements, via two of the three currently used instrumental techniques. Observations of total OH reactivity are becoming widespread due to their unique constraint on local atmospheric chemistry, and have thus far provided significant insight into our understanding of oxidation processes in a range of environments. The inclusive nature of OH reactivity observations unfortunately makes it difficult to compare with other established observational techniques, as it is expected that in ambient air OH reactivity instruments are sensitive to compounds currently missed by other techniques. The development of

three separate techniques to measure OH reactivity provides an excellent opportunity to check for instrument interferences and artefacts, and thus improve confidence in observed total OH reactivity. The direct comparison of two of these techniques presented in this paper is thus a useful contribution to the atmospheric chemistry observational and modelling communities.

The paper provides significant detail on both the comparative reactivity and pump-probe instruments compared, as well as on instrument operating procedures. Further detail on the comparison experiments themselves would, however, be of significant benefit to the reader (minor comment 1).

The conclusions drawn from the experiments appear sound, although the attribution of a constant 2 s-1 discrepancy during the ambient comparison to the pump-probe instruments zero needs stronger evidencing (minor comments 3-4). Analysis of the comparison of ambient OH reactivity observations with that calculated using measured OH sinks would also increase the contribution of this work (minor comment 4). Finally, the conclusions would benefit from a statement on the relevance of this work to previous observations and analysis of OH reactivity.

Overall the manuscript is well written and makes a valuable contribution to the field. I therefore recommend publication in AMT after the following minor comments have been addressed.

Minor comments:

1) Although significant instrument detail is provided, more information on the instrument set up during the experiments would be useful (sections 3.1 and 3.2). The inclusive nature of OH reactivity observations means that inlet losses need to be considered. Hence, differences in instrument inlets and sampling in both the synthetic VOC and ambient comparisons should be discussed. The short lifetimes of many components of total OH reactivity also means that the proximity of all the observations (OH reactivity and ancillary) during the ambient comparison should be provided.

2) Lines 226 – 236 describe the use of platinum wool heated to 350 °C to remove volatile organic compounds (VOCs) from a humid airflow. As OH reactions often show significant temperature dependencies, the authors should note any effect of this approach on the gas temperature within the reactor and a calculated effect on the OH + pyrrole rate constant if non-negligible.

3) Possible impurities in the air used for measuring zeros on the pump- probe instrument are highlighted as the likely cause of a 2 s-1 discrepancy between the two instruments during the ambient observations period (section 3.2.2). Similar impurities in the air used to measure the zero on the comparative reactivity instrument (step C2, Fig. S3), however, are not discussed or quantified. In order to minimise humidity effects in the comparative reactivity instrument the air used for step C2 is ambient air that has been passed through a Purafil media and activated charcoal trap to remove VOCs and NOx. The effectiveness of this process needs to be evidenced and discussed, as it seems likely that it is not 100% and if so the possible impact on the reported numbers needs to be quantified. Also, if this process is more effective at providing a clean air supply than the cylinder supply used for the pump-probe instrument, was a Purafil media and activated charcoal trap tested on the zero air supply for the pump- probe instrument also?

4) It is apparent that possible uncertainties in the zero obtained for both instruments could impact the comparison, but the evidence provided for a 2 s-1 error in the pump-probe instrument zero is not compelling. The diel average data in fig. 8 does suggest that increasing the pump- probe OH reactivity observations by 2 s-1 would improve agreement with the comparative reactivity observations and the calculated OH reactivity. However, the same conclusion is not as obvious from the data shown in figs. 5 and 6. Would an error of 2 s-1 in the pump-probe instrument zero not also be expected to be visible in the measurements of the synthetic VOC mixtures, which currently agree well with calculations (fig. S8)? It appears to the reader that a zero offset has been suggested to reconcile the two instruments, but that direct evidence that this can be

attributed to the pump-probe zero is lacking. The authors should provide evidence that this is the likely cause of the 2 s-1 offset, or make it obvious to the reader that it is a speculative explanation, especially in the conclusions section.

5) Further analysis of the agreement between the observed total OH reactivity and that calculated using the ancillary observations would be a nice addition to the paper. Although a detailed analysis is likely outside the scope of this work, the authors should at least comment on how the calculated vs. observed OH reactivity compares to previous studies in similar environments, and on the potential sources of disagreement. Comparison with previous studies will provide a context with which to asses the relevance of the work presented.

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