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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "A better understanding of hydroxyl radical photochemical sources in cloud waters collected at the puy de Dôme station: experimental vs. modeled formation rates" *by* A. Bianco et al.

Anonymous Referee #1

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This is a very nice paper that should be published. I have minor suggestions.

This work reposts on results of experiments where production rates of the OH radical (R(OH)) are measured in cloud water samples. Air mass source regions for the cloud water samples are identified. Major chemical species thought to contribute to R(OH) are also measured and used in a model to calculate R(OH). These results are then compared to the measurements. Additionally, the authors use the same experimental setup employed to measure cloud water R(OH) to measure OH production in samples

of single components (i.e., NO-, NO2- and H2O2) in pure water. The results from these synthetic experiments are then used in the model and compared to the measured production rates.

The measurements being made are complex and tricky and it appears the authors have done the experiments with great care. The data analyses are thorough. The data quality seems reasonable; the results are in general agreement with other studies, but there is limited data to assess the quality of these experiments.

The data interpretation is somewhat confusing and the logic of the Discussion section was somewhat unclear. I had to read through it a few times to understand the analyses approach. I suggest an attempt should be made to clarify this section. I also don't really see the logic of it; which I would summarize as follows: -measure R(HO) in real cloud water samples. -compare to model that was run using measured NO2-, NO3-, H2O2, and Fe -based on the finding that the discrepancy between model and observations is highest for cloud samples with highest Fe, the authors conclude the large range in discrepancy is due to the model over-predicting R(HO) from Fe. The reason? The model does not correctly simulate Fe-organic complexes (only considers oxalate, but much more Fe is likely complexed with unidentified organic species, whereas Ferrozine analytical method includes all Fe-org complexes in the measurement of Fe, which is used in the model). -rerun the model with no Fe contribution at all to predict R(HO) -find model R(OH) is too low. -rerun the model with new synthetic (single species) photolysis rate measurements for NO2-, NO3-, H2O2, but still without Fe contributions. -Conclude better agreement between model – measured R(OH) suggests that model over-predicts Fe contribution and most important species is H2O2.

The last two steps in the sequence are interesting, but the logic is not clear to me. Why, for example, do the authors believe their photolysis rates, which were based on overly simple experiments, versus what was originally in the model (is there a reason)? There is no discussion why such a simple experiment should be representative of what occurs in a chemically-complex cloud drop.

Another analyses could be to assume the original model photolysis rates are correct for NO2-, NO3-, H2O2 and adjust the free Fe levels (ie, the fraction of ferrozine-determined Fe(II)+Fe(III) that is not complexed) to achieve good agreement between modeled and measured R(OH). Data on both oxalate and TOC is available and could be included in this type of analysis.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 13923, 2015.