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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.

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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.

We would like to thank the reviewer for her/his interest in our work and the valuable remarks. In the revised manuscript all the corrections are indicated by the blue colour.

1. 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.

Reply: In a first step we compared experimental and modelled RfHO founding discrepancies. In order to better simulate and assess individually the contribution of the main photochemical sources to the generation of HO, new photolysis rates for nitrite, nitrate and hydrogen peroxide were determined experimentally. Originally, the photolysis rates for these compounds are calculated by the model using experimental quantum yields, absorption cross-sections extracted from the literature and the experimental actinic flux of the lamp. The calculated value is then subject to uncertainties and can present some differences to what is observed in the aqueous photochemical reactor. The experimental values were implemented in the M2C2 model instead of the original calculated ones. This lead to better agreement between simulated and modelled RfHO. Nevertheless higher differences estimated calculating the bias error ((mod - exp) / exp in (%)) were found in samples with iron concentrations > 0.1 μM where the median of the bias error was > 61%. In fact, the model considers only iron species under aqua-complexes or iro-oxalate complexes (in the case of Fe(III)). In the case of aqua-complexes, their photolysis represent a strong sources of hydroxyl radical. Nevertheless iron is expected to be complexed by organic compounds in cloud waters that are still not characterized. In order to support this hypothesis iron photoreactivity was considered as negligible (as expected for iron complexes) and a good agreement between experimental and modelled results was found.

2. 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)?

Reply: The M2C2 model calculates the photolysis rates using experimental quantum yields, absorption cross-sections extracted from the literature and the experimental actinic flux of the lamp. These data considered in the model are subject to uncertainties. The experimental J values correspondto the effective photodegradation of H2O2, NO2- and NO3- in the reactor; therefore, we think that the experimental photolysis rates better represent the experimental conditions than the calculations by the model. However, the photolysis rates calculated by the model are realistic since they are in the same range of order (model : 1.52 × 10-6 s-1 vs. experiment: 2.5 × 10-6 s-1 for the H2O2

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photolysis rates for example).

3. There is no discussion why such a simple experiment should be representative of what occurs in a chemically-complex cloud drop.

Reply: The main objective of the experimental photolysis rates calculations is to assess the contribution of each photochemical source to the hydroxyl radical formation. The next step is to consider these experimental values in the M2C2 model that considers explicit aqueous phase chemistry (see table SM1) to simulate cloud water chemistry.

3. Another analyses could be to assume the original model photolysis rates are correct for NO2-, NO3-, H2O2 and adjust the free Fe levels (i.e., 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.

Reply: Ferrozine method allows us to determine all Fe(II) and Fe(III) considered as free, aquacomplexes and complexed with other organic compounds. To assess the impact of iron complexation on hydroxyl radical rates, new simulations are performed. In the model, we consider 0%, 25%, 50%, 75% and 100% of the initial concentrations of iron. Part of the iron is therefore free or complexed by oxalate. The simulations are performed with the original model photolysis rates.

As shown on Figure 1, decreasing the iron amount from 100% to 0% leads to an underestimation by the model of hydroxyl radical formation rates in comparison with experimental data (median of the bias error from 22% to 42%, respectively for the iron amount equal to 100% and 0%). The figure suggests that iron photoreactivity cannot be considered as the main sources driving the hydroxyl formation rates in our cloud water samples. For this reason, the adopted approach was to modify the photolysis rates in the model that present uncertainties in their calculations. Moreover, with this new approach, the strong overestimation by the model of the hydroxyl formation rates due to the iron photolysis is neglected. The main uncertainties in the hydroxyl radical formation are related to the iron photoreactivity that strongly depends on its complexation. In fact, actually, only iron-oxalate complexes are considered in cloud chemistry models (Weller et al., 2014). Considering the around 90% of the organic matter in real cloud samples are unknown, the presence of other organic complexes is expected with various photochemical stability. However, it is quiet difficult to correlate the iron photoreactivity with the TOC due to the lack of the characterization of the organic matter.

Weller, C., Tilgner, A., Brauer, P., and Herrmann, H.: Modeling the impact of iron-carboxylate photochemistry on radical budget and carboxylate degradation in cloud droplets and particles, Environ. Sci. Technol., 48, 5652-5659, 10.1021/es4056643, 2014.

Figure 1 caption: Distribution of the bias error for the whole cloud water samples for the reference case (100%) and considering different level of iron amounts (from 75% to 0%). The bias error is defined by the ratio (mod - exp) / exp in (%). The bottom and top lines correspond to the 25th and 75th percentiles, respectively. The full line represents the median values. The ends of the whiskers are the 10th and 90th percentiles.

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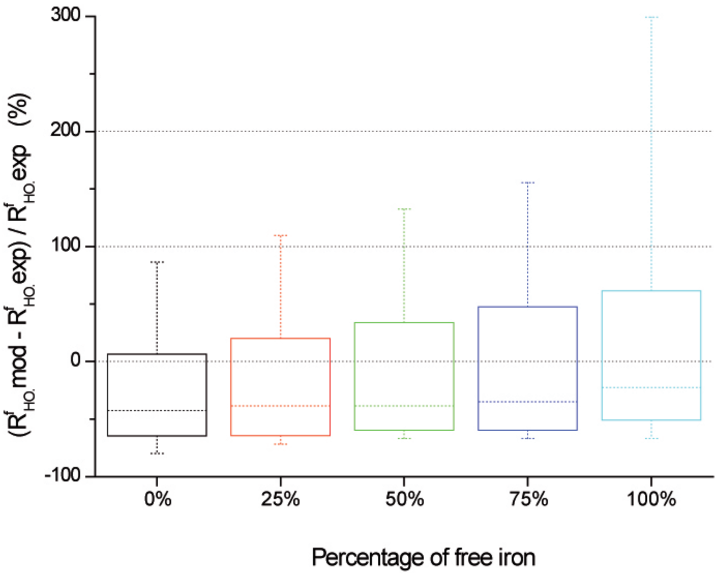
300
200
100
0
-100
$(R^f_{HO.}mod - R^f_{HO.}exp) / R^f_{HO.}exp$ (%)
0%
25%
50%
75%
100%
Percentage of free iron

Fig. 1.