

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 #2

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Overall comments:

Bianco et al. collected cloud waters (mostly marine origin) at a relatively high mountain site and studied their chemical compositions and photochemical formation of hydroxyl radical (OH). The measurements of chemical species were done within 24 hours after collection of those samples, which is pretty impressive. A fair number of samples were also studied to discuss the OH formation and their sources. The reviewer believes that the results presented in the manuscript, such as OH formation rates, OH sources,

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contribution of different OH sources and Fe(II) measurements are interesting and add valuable information to the atmospheric chemistry community. However, the reviewer also found several mistakes and mis-interpretation of the results in the manuscript. Thus, the reviewer recommends publication of this manuscript in Atmos. Chem. Phys. after the comments as listed below are incorporated in the revised manuscript.

Detailed comment: 1. Pg. 13932, equation (1), $R_tHO = Y \cdot R_tTAOH$ is not right. It should be $R_tTAOH = Y \cdot R_tHO$, since Y is the reaction yield between OH and TA, forming a fluorescent TAOH, and has a value between 0.15-0.25. To obtain R_tHO , R_tTAOH should be divided by Y, namely $R_tHO = R_tTAOH / Y$.

2. Pg. 13932, equation (2) should be $[OH]_{ss} = (R_tTAOH) / \{k_{OH}, TA \cdot [TA] \cdot Y\}$. Actually, calculation of $[OH]_{ss}$ by this equation is fundamentally a mistake. This $[OH]_{ss}$ is for the conditions with added TA (2 mM), not for the cloud water samples by themselves. Since OH formation rates are different among cloud water samples, $[OH]_{ss}$ appears to show some variation, but the major sink for the OH is always TA for all the samples. Thus, OH scavenging rate constant for the experimental condition is always $k_{OH}, TA \cdot [TA] = 4.0 \cdot 10^9 \cdot 2 \cdot 10^{-3} = 8 \cdot 10^6 \text{ s}^{-1}$. It is not possible to calculate $[OH]_{ss}$ from a single OH formation rate study when high concentration of TA or any probe is added to the samples. So, please re-consider the discussion on $[OH]_{ss}$.

3. Pg. 13929, Line19-20, in acidic solution (HCl 37%). Does it have to be very acidic? I wonder what the pH was.

4. Pg. 13929, Line28, (free or complexed). The sentence was not somehow clear to me. Do authors suggest Fe(II) is free but Fe(III) is complexed? I would guess both Fe(II) and Fe(III) can have complexed species, not just Fe^{2+} . I appreciate clarification of the sentence.

End of comments.

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

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