Atmos. Chem. Phys. Discuss., 15, C4172–C4174, 2015
www.atmos-chem-phys-discuss.net/15/C4172/2015/

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.

A. Bianco et al.

marcello.brigante@univ-bpclermont.fr

Received and published: 1 July 2015

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, 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:

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 in blue.

1. Pg. 13932, equation (1), RtHO = Y*RtTAOH is not right. It should be RtTAOH = Y*RtHO, 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 RtHO, RtTAOH should be divided by Y, namely RtHO = RtTAOH /Y.

Reply:The wrong equation form has been corrected. For RfOH calculations we used the right form.

2. Pg. 13932, equation (2) should be [OH]ss = (RtTAOH)/{kOH, TA*[TA]*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 kOH, TA*[TA] = 4.0*109*2*10-3 = 8*106 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.

Reply:Concerning equation (2) we have corrected our mistake reporting now the right equation. We agree with reviewer's comment concerning the [HO]ss calculations. In the presence of an excess of TA all photogenerated hydroxyl radicals are expected to react with TA (and not with other naturally occurring scavengers). Under such conditions the HO steady-state concentration values should be different from the values expected in cloud water due to the higher value of compared to the value found considering the reactivity of hydroxyl radical with naturally occurring scavengers present in cloud waters (indicated as CWSi) . The main goal of such measurement was to compare obtained values with those found in rain and cloud waters (see Table 3). Finally [HO]ss should be determined as RfHO/kHO,CWSi*[CWSi]. The use of different TA concentration would be needed in order to determine the concentration of [HO]ss in samples considering the value at [TA]→0 following the kinetic approach reported by Anastasion and McGregor (2001). For these reasons the data concerning the steady-state concentration of HO and related discussion were erased.

3. Pg.13929Line 19-20, in acidic solution (HCl 37%). Does it have to be very acidic? I wonder what the pH was.

Reply:HCl solution was used to obtain an acid pH as required for the nitrite detection method as reported by Kieber and Seaton. The reaction between ferrozine and nitrite was performed in acidic conditions.

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 Fe2+. I appreciate clarification of the sentence.

Reply:Detection method is based on the formation of a stable and strong absorbing complex between Fe(II) and ferrozine. Considering an excess of ferrozine in solution, we can argue that all free and complexed iron can be detected using this method. In other words, the adopted method allows us to determine all Fe(II) and Fe(III) considered as free, aquacomplexes and complexed with other organic compounds. In order to clarify this point a new sentence was added in section 2.3.
