

Authors' Responses to Referee #2 Comments

We thank the anonymous referee for his/her thoughtful comments, which are helpful to improve the publication. Based on the reviewer's comments, we revise the manuscript.

The manuscript "Laboratory photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls" submitted for publication by Pavuluri et al. describes the photochemical reactions of wetted atmospheric aerosols (PM10) collected in winter and summer during day time at Chennai (India). The authors performed irradiation experiments of the filter in the presence of moisture with low- pressure mercury lamp emitting mainly at 254 but also at 185 nm. Two types of ambient aerosols were collected and classified as anthropogenic and biogenic aerosols. This paper present many analysis results of the filters before and after irradiation and conclusions about the photochemical processes. However, I am also many concerns about the validity of such interpretation.

Response: We appreciate the critical comments.

Main remarks:

1) The most important concern is due to the use of such lamp with a wavelength emission at 185 nm. With this wavelength, the photolysis processes are present for many (all) compounds take into account in this study? How the authors can separate and evaluate the significance of photolysis processes and reactivity of HO• on the organic compounds? Experiments with such organic compounds in water and under irradiation with this kind of lamp seem very important to conclude about the photochemical processes. The wavelengths 254 and 185 nm are not present in the solar emission at the earth surface.

Response: We believe that the UV light, whose spectra are characterized by main peak at 254 nm and minor peak at 185 nm, does not cause a significant photolysis of the measured species in this study. As noted in section 2.3 of the MS, it is well established that the photolysis of diacids and related compounds by UV light at 254 nm is not significant in aqueous phase. Although some compounds, for example, pyruvic acid and methylglyoxal, can absorb UV light at 254 nm, their photolysis is minimal when OH radical reactions are significant. The UV light at 185 nm also does not cause a significant photolysis of organics because the radiation of 185 nm is mostly absorbed by water and subsequently utilized to produce OH radicals (Yang et al., Atmos. Environ., 42, 856-867, 2008). It is true that light at 254 nm is not present in the tropospheric UV spectrum (>300 nm). However, as noted in section 2.3, the UV light at 254 nm has been used to produce significant amount of OH radicals from various sources. The expected chemical reactions of organics with OH radicals during the experiment are relevant to those present in tropospheric aqueous aerosols. We added these points in the revised MS (please see section 2.3, lines 147-157).

2) Page 1204, lines 26 and 27. Could you explain why there is no sharp increase for the compound ω C3? There is a sharp increase for the compounds ω C2 and ω C4.

Response: Such trends are reasonable because ω C₂ is significantly produced from aliphatic olefins and aromatic hydrocarbons via glyoxal and methylglyoxal and ω C₄ is significantly produced from cyclic olefins and unsaturated fatty acids but not ω C₃ (Bandow et al., Bull. Chem. Soc. Jpn., 58, 2531-2540, 1985; Hatakeyama et al., Environ. Sci. Technol., 21, 52-57, 1987; Kawamura et al., Atmos. Environ., 30, 1709-1722, 1996; Lim et al., Environ. Sci. Technol., 39, 4441-4446, 2005; Warneck, Atmos. Environ., 37, 2423-2427, 2003). We added this point in the revised MS (please see section 3.4, lines 318-326).

3) Page 1205, lines 27-28. The authors mentioned that the concentration of water soluble iron species may increase upon UV irradiation. Did you control this affirmation? What is level of the increase of concentration? This information is very important to explain or not some phenomenon.

Response: Yes, the amounts of water-soluble Fe might have increased in the sample with irradiation time, which should have further promoted the degradation of C₂ and C₃ diacids with photochemical processing of aerosols. Unfortunately, there is no control on water-soluble Fe formation from the insoluble Fe and we did not measure the concentration levels of Fe species in irradiated samples. We noted this point in the revised MS (please see section 3.4, lines 357-358). However, the present study explores the importance of the Fe-catalyzed photolysis of C₂ and C₃ diacids in atmospheric aerosols during long-range transport. In fact, the quantitative analysis of Fe-catalyzed photolysis of C₂ diacid including kinetics has been reported in our previous publication (Pavuluri and Kawamura, 39, L03802, 2012).

4) About the formation of complexes between iron species and the organic compounds, the authors mentioned only the possible formation with C₂ and C₃ compounds. This complexation phenomenon increases a lot the photolysis processes and explain the sharp decrease of these two compounds. However, for the C₄ compounds the value of the stability constant with Fe³⁺ is very similar. Why in this case a formation of C₄ is observed at the beginning of the irradiation? The comment is the same for C₅.

Response: Oxalate (C₂) and malonate (C₃) have the strongest chelating capability with with Fe³⁺ among all dicarboxylates including succinate (C₄) and glutarate (C₅) and monocarboxylates. Further, C₂ and C₃ diacids are capable of forming mono, di and tri oxalato (equilibrium constant log₁₀(β) = 9.4, 16.2 and 20.4, respectively) and malonato (equilibrium constant log₁₀(β) = 7.5, 13.3 and 16.9, respectively) complexes with Fe³⁺ whereas C₄ diacid can form only monosuccinate (equilibrium constant log₁₀(β) = 7.5) (Wang et al., Environ. Sci. Technol., 44, 263-268, 2010). Therefore, the photolysis of C₂ and C₃ diacids is significant but not other species such as C₄ and C₅ diacids. We noted these points in the revised MS (please see sections 3.4 and 3.5 and lines 344-351 and 409-411).

5) In the same experiments could you explain more in detail why the authors observed an increase of the C₄, C₅ and C₆ while the concentrations of all other diacids compounds decrease?

Response: Polyunsaturated fatty acids can undergo free radical oxidative cross-linking in the air, especially in sunlight and in the presence of transition metals, and produce high molecular weight organic compounds (Kirschenbauer, Anal. Chim. Acta., 76, 97-106, 1960). For example, Wheeler (J. Geophys. Res., 77, 5302-5306, 1972) reported that organic compound(s) resulted from the irradiation of linolenic acid (C_{18:3}) in sterilized seawater absorb the UV light of 270-300 nm, whose chemical structure is similar to that of marine fulvic acid (Harvey et al., Mar. Chem., 12, 119-132, 1983) and can produce the particle matter. Interestingly, oxidation of fulvic acid can significantly produce the low-molecular weight (C₄-C₉) diacids in aqueous phase (Harvey et al., Mar. Chem., 12, 119-132, 1983). Therefore, the production of C₄ to C₉ diacids should be increased with photochemical processing of aqueous aerosols, if polyunsaturated fatty acids are abundantly polymerized in the irradiated samples. However, the oxidation rate of C₄ to C₉ diacids is increased with increasing carbon number (Yang et al., Atmos. Environ., 42, 868-880, 2008) and hence, the photochemical breakdown of the long-chain diacids upon irradiation is more likely. Further, the photochemical breakdown of long-chain (C₆-C₉) diacids preferably produce the C₄ and C₅ diacids (Yang et al., Atmos. Environ., 42, 868-880, 2008). Because of these reasons, the concentrations of C₄ to C₆ diacids might have increased in our experiments, despite the decrease in the cases of other species, which is a subject of future research. We described these points in the revised MS (please see section 3.5, lines 398-425).

Minor remarks:

1) Replace “direct photolysis” by “photolysis”. 2) Page 1198 lines 3, replace Stooky by Stookey. 3) Page 1199 line 2 254 nm instead of 245 nm. 4) Replace “•OH” by “HO•” IUPAC Recommendations 2000. 5) The graphs are too small and it is difficult to appreciate the beginning of kinetics. Example page 1203, line 3 “except two cases (3 and 6h) of AA”. 6) Page 1205 line 1. I think that it is not Fig.7 but Fig.6?

Response: Following the reviewer's suggestions, we corrected all the remarks, except for #5, in the revised MS (please see section 2.3; and lines 121 and 321). Because the difference between the irradiation time periods of each experiment below 12 h is small and the x-axis tick increment is 24 h, few data points are overlapped in few cases. However, the increasing and decreasing trends of all the species are reasonably clear in Figures 3, 4 and 6.

In conclusion, this paper presents many results to understand the photochemistry at the wetted aerosol surface. But I recommend to perform more control experiments and to give more explanations to consolidate the early conclusions.

Response: We strongly believe that our responses to the reviewer's concerns noted above are satisfactory and do not think that there is a need of any further experiments to support the conclusions drawn from this study.