Authors' Responses to Referee #1 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.

It is now well accepted that water soluble organic compounds undergo aqueous chemistry in atmospheric waters and form secondary organic aerosol (SOA). Moreover, aqueous chemistry could be a chemical aging process of hygroscopic wet aerosols at high RH, yet largely unexplored. The manuscript by Pavuluri et al. demonstrates this aging process through aqueous photochemistry. Pavuluri et al. sampled two types of ambient aerosols (i.e., biogenic aerosols (BA) and anthropogenic aerosols (AA)), conducted UV-photolysis after wetting BA and AA samples, presented real-time measurements of organic compounds (carbonyls and diacids) and discussed photochemical degradation and formation of these organic compounds. Most of degradation and formation were due to OH radical formed from various sources (e.g., Fenton reactions, H2O2, and photosensitizers), whereas the degradation of C2/C3 diacids was due to Fe species, which form strong light absorbing Fe ligands. I think this manuscript is well written and suitable for the readership of Atmospheric Chemistry and Physics, so I recommend it for publication. Following comments are provided for authors' consideration.

Response: We consider all the comments and revise the manuscript accordingly.

[Page 1198, Line 14-16] Authors should mention the phase of ambient aerosol samples. Were they liquid and all the organic/inorganic constituents well distributed? And were they hygroscopic so they took up water evenly by wetting? Since authors conducted separate photochemical reaction vessel experiments, not only the reaction time but the phase, the hygroscopicity and the morphology of aerosols should matter.

Response: We agree with the reviewer's opinion that, in addition to the reaction time, the phase, hygroscopicity and morphology of aerosols play an important role in photochemical reactions of organics. In this study, we have focused only on reaction time and phase of aerosols. In fact, the injected Milli Q water (~0.4 mL) onto the filter sample was higher than the required quantity of water to fully wet the sample. The excess amount of water available after wetting the sample is present at the bottom of the reaction vessel (see Fig. 2 in the MS), which could create the humid (RH = 100%) environment in the reaction vessel. Therefore, the ambient aerosol sample in our experiments is in aqueous phase. These points are included in the revised MS (please see section 2.3, lines 133-137). We consider that water contents should be evenly distributed in the aerosol samples used in the experiments, although there may be different microstructures of aerosol particles.

As noted in section 2.5, the experimental errors, including analytical errors, in replicate experiments (n = 3) conducted by using the sample cuts taken from different parts of the sample filter for each experiment are within 11% for major species. Therefore, we believe that the organic/inorganic constituents should have well distributed over the filter sample. The non-irradiated filter samples used in this study contain significant amounts of hygroscopic components: inorganic ions and water-soluble organic compounds (Pavuluri et al., Atmos. Chem. Phys., 11, 8215-8230, 2011). As noted above, these components should have well distributed over the filter and hence the filter sample should be hygroscopic and take up water evenly upon wetting. These points are added in the revised MS (please see section 2.5, lines 203-212).

[Page 1198, Line 28-Page 1200, Line 7] Pyruvic acid and methylglyoxal do absorb 254 nm UV, and radical reactions take place. But UV photolysis of these is minor when OH radical reactions of these occur. In addition to Fe-catalyzed UV photolysis and NO3 photolysis, authors should discuss photochemical effects of sulfates. Although authors did not measure sulfate concentrations, in Table 1 substantial amounts of S were found. Noziere et al., Geophys. Res. Lett. (2009) measured organosurfates formed by the UV photolysis of organic compounds.

Response: Yes, the photolysis of pyruvic acid and methylglyoxal is minimal when HO radical reactions are significant. We included this point in the revised MS (please see section 2.3, lines 148-151).

As noted by the reviewer, organosulfates can be produced when organics such as isoprene, methyl vinyl ketone, methacrolein, and α-pinene are irradiated in sulfate solutions (Noziere et al., Geophys. Res. Lett., 37, L05806, 2009). However, the presence of sulfate may not have significant influence on the formation/degradation processes of diacids and related compounds. Tan et al. (Environ. Sci. Technol., 43, 8015-8112, 2009) reported that presence of acidic sulfate in the range of 0 to 840 μM does not alter the production rate of oxalic acid from glyoxal significantly. We added these points in the revised MS (please see section 2.3, lines 152-155).

[Page 1205, Line 12-23] Authors claim that Fe-catalyzed photolysis is the main decomposition reaction of C2 & C3 diacids since these diacids form strong light absorbing Fe ligands. Is this still true for the photolysis of tropospheric UV (>300 nm)? Besides, C2/C3 diacids form stable and low volatile carboxylate salts with amines. Is still Fe the major sink when amines are present? By the way, photochemical reactions were conducted up to 120 hrs. I am not sure why reactions exceed daytime 12 hrs? There should occur other reactions (e.g., NO3, O3 reactions, acid catalysis) during the night-time. Besides, using 254 nm UV should represent daytime photochemistry in less than 12 hrs.

Response: Yes, as evidenced from laboratory studies, the photolysis of C_2 (Zuo and Hoigne, Atmos. Environ., 28, 1231-1239, 1994) and C_3 (Wang et al., Environ. Sci. Technol., 44, 263-268, 2010), diacids can be decomposed under the solar UVA spectrum (>300 nm). This point is included in the revised MS (please see section 3.4, lines 339-342).

We agree with the reviewer's opinion that diacids can form salts with amines. However, because the oxalate and malonate have the strongest chelating capacity with Fe^{3+} among all diacids, they are expected to preferably form a complex with Fe^{3+} and can easily be photolyzed. These points are added in the revised MS (please see section 3.4, lines 338-351)

Because aerosols can reside up to 12 days (Warneck, Atmos. Environ. 37, 2423-2427, 2003) in the atmosphere and both primary and secondary organic aerosols can be subjected for photochemical processing during daytime during their stay in the atmosphere, we conducted the irradiation experiments up to 120 h in order to understand the photochemical processing of diacids and related compounds during long-range atmospheric transport. This point is added in the revised MS (please see section 2.3, lines 128-131).

[Page 1207, Line 6-7] Shouldn't author mention rate constants of the OH radical reaction in the aqueous phase? What they have is the gas-phase rate constants. By the way, in the aqueous phase, the glyoxal rate constant is bigger. To me, methylglyoxal production in AA is just sufficient to maintain "the steady state."

Response: Yes, the rate constant (1.1×10^9 M^{-1} S^{-1}) of glyoxal with OH radical in aqueous phase is higher than that (6.44×10^8 M^{-1} S^{-1}) of methylglyoxal (Tan et al., Atmos. Chem. Phys. 12, 801-813, 2012). However, higher abundances of methylglyoxal than glyoxal in the anthropogenic aerosol samples suggest more production of the former than the latter species during photochemical processing of aqueous aerosols derived from anthropogenic sources. We modified the text and replaced the gas-phase rate constants with those of aqueous phase in the revised MS (please see section 3.4, lines 385-392).

[Page 1209, Line 22-23] Did authors find any evidence of photochemical oligomerization (i.e., organic radical-radical reaction) when the concentrations of organic precursors are high (mM or above)? Tartaric acid is the major dimer product of glyoxal + OH (Lim et al., Atmos. Chem. Phys., 2010) and C6H10O6 (m/z-177) is the major dimer product of methylglyoxal + OH (Tan et al., Atmos. Chem. Phys., 2012).

Response: In fact, we did not focus on oligomerization of the studied organic species and dihydroxy diacids in this study. We briefly noted this point in the revised MS (please see section 3.4, lines 392-395).