Response Letter

June 27, 2015

Dr. Markus Ammann
Editor, Atmospheric Chemistry and Physics

RE: *Manuscript Number:* acp-2014-967R; *Manuscript Title:* Laboratory photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls.

Dear Dr. Ammann,

Thank you for your decision letter of May 26, 2015. According to your (and reviewer #2) comment, we revised the manuscript. Our responses and changes are detailed as below. We uploaded the revised MS with and without track changes. Please check them. We believe that the revised MS is now ready to be accepted for the publication.

We are looking forward to hearing from you soon.

Sincerely yours,

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Editor Comment

The reviewer of the revised version has still a major concern regarding the interpretation of your experiments in view of the 185 nm radiation and its impact on photolysis. I think this is a valid point. As he notes, it would be best, if you could provide results from control experiments. On the hand, I would also agree with a more quantitative assessment of the photolysis rates at 185 nm. In your present section 2.3 you are quoting appropriate references, but using cross sections for photolysis for the compounds of interest and using the irradiance you have in your experiment at 185nm as compared to 256 nm, you could substantiate your point more.

Response: Since we used atmospheric aerosol filter samples, which contain a complex mixture of organic and inorganic contents, it is difficult to conduct the control experiments to examine the potential photolysis of individual compounds of interest by the radiation of 185 nm in this study.

However, following the Editor's suggestion, we provided an additional discussion to substantiate our point that the photolysis of organics by 185 nm light is insignificant during our experiment as described below.

The photolysis of organics by the radiation of 185 nm, whose intensity is 100 times lower than that of 254 nm, should be insignificant during the experiment because the intensity of the 185 nm light emitted from UV lamp is small and is mostly absorbed by water due to its high absorption coefficient (1.8 cm^{-1} at 25 °C) (Weeks et al., 1963). It is well established that the photolysis rates of organics by the radiation of 185 nm are elevated only in the absence of dissolved oxygen (Shirayama et al., 2001) whereas in aerated solutions, mainly water undergoes photolysis under irradiation of 185 nm and produce the hydrogen atoms, which are scavenged by oxygen to form $HO_2^•$ radicals that finally converted to $HO^•$ (Chitose et al., 2003; Yang et al., 2008). These points are described in the revised MS. Please see section 2.3, lines 156-169.

Reviewer #2 Comment

The paper is now better but as a photochemist, I am not relay convinced by your answer on my first remark about the wavelength of irradiation. I really think that experiments at wavelength higher than 300 nm or experiments with the same lamp but with organic products alone in water could be very useful to confirm or infirm the mentioned results and the low effect of the shorter wavelengths (254 and 185 nm) on the photolysis of organic compounds.

Response: We agree with the reviewer's opinion that he use of UV light of solar spectrum and organic compounds alone is better to study the reaction pathways of specific compounds. However, the organic compounds alone in water do not reflect a complex mixture of organic and inorganic aerosol constituents in the atmosphere (Ervens et al., 2011). Therefore, we believe that the laboratory experiments on complex mixture of organic and inorganic compounds under atmospherically relevant conditions could provide more useful information on the photochemical formation and degradation processes of organics in the atmosphere with photochemical aging. These points are noted in introduction section of the MS (please see lines 70-76).

In fact, as detailed in section 2.3 of the revised MS, photolysis of the compounds of interest under the irradiance of both 254 nm and 185 nm lights in this study is insignificant. Hence, our results and interpretations are reasonable, which can significantly contribute to the community of atmospheric chemistry and relevant sciences.

Citations:

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Ervens, B., Turpin, B. J. and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos Chem Phys, 11, 11069-11102, doi:10.5194/Acp-11-11069-2011, 2011.

Shirayama, H., Tohezo, Y. and Taguchi, S.: Photodegradation of chlorinated hydrocarbons in the presence and absence of dissolved oxygen in water, Water Research, 35, 1941–1950, 2001.

Weeks, J. L., Meaburn, G. M. A. C. and Gordon, S.: Absorption Coefficients of Liquid Water and Aqueous Solutions in the Far Ultraviolet, Radiation Research, 19, 559-567, 1963.

Yang, L. M., Ray, M. B. and Yu, L. E.: Photooxidation of dicarboxylic acids- Part 1: effects of inorganic ions on degradation of azelaic acid, Atmos Environ, 42, 856-867, 2008.

Laboratory photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls

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Abstract. To better understand the photochemical processing of dicarboxylic acids and related polar compounds, we conducted batch UV irradiation experiments on two types of aerosol samples collected from India, which represent anthropogenic (AA) and biogenic aerosols (BA), for time periods of 0.5 h to 120 h. The irradiated samples were analyzed for molecular compositions of diacids, oxoacids and α-dicarbonyls. The results show that photochemical degradation of oxalic (C_2) and malonic (C_3) and other C_8-C_{12} diacids overwhelmed their production in aqueous aerosols whereas succinic acid (C_4) and C_5-C_7 diacids showed a significant increase (ca. 10 times) during the course of irradiation experiments. The photochemical formation of oxoacids and α-dicarbonyls overwhelmed their degradation during the early stages of experiment, except for ω-oxooctanoic acid (ωC_8) that showed a similar pattern to that of C_4. We also found a gradual decrease in the relative abundance of C_2 to total diacids and an increase in the relative abundance of C_4 during prolonged experiment. Based on the changes in concentrations and mass ratios of selected species with the irradiation time, we hypothesize that iron-catalyzed photolysis of C_2 and C_3 diacids dominates their concentrations in Fe-rich atmospheric waters, whereas photochemical formation of C_4 diacid (via ωC_8) is enhanced with photochemical processing of aqueous aerosols in the atmosphere. This study demonstrates that the ambient aerosols contain abundant precursors that produce diacids, oxoacids and α-dicarbonyls, although some species such as oxalic acid decompose extensively during an early stage of photochemical processing.

1 Introduction

Dicarboxylic acids and related polar compounds constitute a significant fraction of water-soluble organic aerosols in the atmosphere (Saxena and Hildemann, 1996; Kawamura and Sakaguchi, 1999; Pavuluri et al., 2010). They have a potential contribution to the formation of cloud condensation nuclei (CCN) due to their water-soluble and hygroscopic properties (Saxena and Hildemann, 1996; Giebl et al., 2002). Thus diacids and related compounds have an impact on the indirect radiative forcing and hydrological cycle (Twomey, 1977; Albrecht, 1989). They also involve in a series of reactions occurring in gas phase, aerosols and atmospheric waters (Chebbi and Carlier, 1996; Wang et al., 2010b). Although diacids, oxoacids and α-dicarbonyls can be directly emitted into the atmosphere from incomplete combustion of fossil fuels (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999), they are mainly formed by secondary processes of volatile organic compounds of anthropogenic and biogenic origin (Kawamura et al., 1996a; Kawamura and Sakaguchi, 1999; Kanakidou et al., 2005). They are further subjected to photochemical oxidation during long-range transport; e.g., carbonyls to carboxylic acids (Tilgner and Herrmann, 2010) and breakdown of higher to lower diacids (Kawamura and Sakaguchi, 1999; Matsunaga et al., 1999; Wang et al., 2010a).

Molecular distributions of diacids in atmospheric aerosols have generally been reported with a predominance of oxalic (C_2) acid followed by malonic (C_3) or succinic (C_4) acid in different environments (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Narukawa et al., 1999; Pavuluri et al., 2010). The predominance of C_2 in different environments is likely explained because it is an ultimate end product in the chain reactions of diacids and various precursors including aromatic hydrocarbons, isoprene, alkenes and α-dicarbonyls (Kawamura et al., 1996a; Warneck, 2003; Ervens et al., 2004b; Lim et al., 2005; Carlton et al., 2007; Charbouillot et al., 2012). In contrast, C_4 was reported to be more abundant than C_2 in some aerosol samples collected from Antarctica (Kawamura et al., 1996b), the Arctic (Kawamura et al., 2010) and over the Arctic Ocean (Kawamura et al., 2012) as well as in ice core samples from Greenland (Kawamura et al., 2001). In addition, a significant reduction in C_2 diacid concentration and an inverse relationship between C_2 and Fe has been reported in stratocumulus clouds over the northeastern Pacific Ocean (Sorooshian et al., 2013). The predominance of C_4 over C_2 in ice core samples and atmospheric aerosols from polar regions, particularly in the Arctic marine aerosol samples collected under overcast conditions with fog or brume event (Kawamura et al., 2012) and the reduction of C_2 in cloud water, suggest that photochemical formation of C_4 and/or degradation of C_2 (Pavuluri and Kawamura, 2012) should be enhanced in atmospheric waters.

However, the photochemical formation and degradation of diacids and related compounds are not fully understood, particularly in aqueous phase because the composition of aqueous solutions used in laboratory experiments do not reflect the complex mixture of organic and inorganic aerosol constituents in the atmosphere and the experimental conditions are not necessarily atmospherically relevant (Ervens et al., 2011). Hence, it is required to investigate the fate of diacids and related polar compounds with photochemical processing in atmospheric waters. In this study, we conducted a laboratory experiment using two types of ambient aerosol samples collected from Chennai, India, which represent anthropogenic (AA) and biogenic aerosols (BA). The samples were exposed to UV irradiation in the presence of moisture for different time ranging from 0.5 h to 120 h and then analyzed for diacids, oxoacids and α-dicarbonyls. Here, we report their molecular compositions and discuss the photochemical formation and/or degradation of diacids as a function of the irradiation time. Based on the results obtained, we propose possible photochemical formation and degradation pathways of diacids and related compounds with atmospheric implications.

2 Materials and Methods

2.1 Atmospheric aerosol samples

In this study, we used two types of atmospheric aerosol (PM_{10}) samples that were collected in winter on January 28 (IND104) and in summer on May 25 (IND178), 2007 during daytime (ca. 06:00-18:00 h local time) from Chennai (13.03º N; 80.17º E), India using a high volume air sampler and pre-combusted (450 ºC, 4 h) quartz fiber filters. Sampling was conducted on the rooftop of the Mechanical Sciences building (~18 m a.g.l. (above the ground level)) at the Indian Institute of Technology Madras (IITM) campus. The details of sampling site and meteorology are described elsewhere (Pavuluri et al., 2010). The sample filter was placed in a preheated glass jar with a Teflon-lined screw cap and stored in darkness at -20°C prior to the experiment. Figure 1 presents ten-day backward air mass trajectories arriving in Chennai at 500 m AGL for every 6 h during the sampling periods of IND104 and IND178. Table 1 shows concentrations of elemental carbon (EC), organic carbon (OC), levoglucosan and sums of hopanes (specific biomarkers of petroleum and coal) and lipid class compounds: fatty acids and fatty alcohols, in IND104 and IND178 (Fu et al., 2010; Pavuluri et al., 2011).

The air mass trajectories showed that the air masses for the IND104 sample originated from the north Indian subcontinent passing over the Bay of Bengal (Fig. 1). In North India, anthropogenic emissions are mainly derived from fossil fuel combustion and forest fires (Lelieveld et al., 2001; Reddy and Venkataraman, 2002a). This sample is enriched with EC (Table 1). The anthropogenic signature of IND104 is further supported by high abundances of hopanes. In contrast, the air masses for the IND178 sample originated from the Arabian Sea passing over the south Indian subcontinent (Fig. 1), where the emissions from marine biota, combustion of biofuels (e.g., cow-dung) (Reddy and Venkataraman, 2002b) and livestock (Garg et al., 2001) are important. In addition, emission of volatile organic compounds (VOCs) from tropical plant species in India is enhanced in summer (Padhy and Varshney, 2005). This sample is enriched with OC but EC is less abundant (Table 1). The biogenic signature of IND178 is supported by high abundances of fatty acids and fatty alcohols (Table 1). Hence, we consider that IND104 represents anthropogenic aerosols (AA) whereas IND178 represents biogenic aerosols (BA).

2.2 Determination of trace elements, metals and water-soluble iron species

Trace elements and metals were determined using an inductively coupled plasma mass spectrometry (ICP-MS, Thermo Electron X Series) after the acid microwave digestion of samples (a filter disc of 1.8 cm in diameter) as reported by Theodosi et al. (2010b). Recoveries obtained with the use of certified reference materials ranged from 90.0 to 104.1%. Water-soluble iron (Fe_{WS}: sum of Fe^{2+} and Fe^{3+} species) was determined spectrometrically using the Ferrozine colorimetric method developed by Stookey (1970) as reported by Theodosi et al. (2010a). Fe^{2+} was measured using the same procedure without adding the reducing agent (hydroxylamine hydrochloride), and then Fe^{3+} was estimated indirectly as the difference between Fe_{WS} and Fe^{2+}. The recovery was ~98.3% for both Fe_{WS} and Fe^{2+}.

2.3 Irradiation experiment of aerosol samples

Batch UV irradiation experiments using two aerosol samples (AA and BA) were conducted separately for 0.5, 1.5, 3.0, 6.0, 12, 18, 24, 36, 48, 72, 96 and 120 h, because both primary and secondary chemical species that are associated with aerosols can be subjected for significant photochemical processing through out their stay (i.e., up to 12 days) in the atmosphere (Warneck, 2003). In each experiment, ~12 cm^2 (ca. 3 × 4 cm) of sample filter was cut into 3~4 pieces and placed vertically in a cleaned quartz reaction vessel (cylinder, 100 ml) with the sample surface facing to UV light as depicted in Fig. 2. The sample was fully wetted by injecting ~0.4 ml of ultra pure organic free Milli Q water and sealed with Teflon-lined screw cap under the ambient pressure. Further, the available excess Milli Q water (Fig. 2) may promote humid (RH = 100%) environment in the reaction vessel by equilibrium between water vapor and Milli Q water. The aqueous ambient aerosol sample was then irradiated with a low-pressure mercury lamp (Ushio, UL0-6DQ) that emits a UV, whose spectra are characterized by main peak at 254 nm and minor peak at 185 nm as well as broad peak at >254 nm. The experimental setup (Fig. 2) was covered with a cartoon box containing a hole on each side for the passage of ambient air, and placed in a draft chamber. The temperature around the experimental system (i.e. inside cartoon box) was equivalent to room temperature (25±1°C).

The main objective of UV irradiation with a wavelength primarily at 254 nm, rather than a solar spectrum, was to produce significant amount of hydroxyl radicals ($HO^{\bullet}$) from various sources described below that should be sufficient enough to act as the main oxidant in our experimental system. Although we do not preclude a minor photolysis of some organic compounds present in the aerosol samples by irradiation at ≤254 nm, it is well established that low molecular weight diacids, oxoacids and α-dicarbonyls including pyruvic acid and methylglyoxal have negligible absorbance at 254 nm and exhibit minimal photolysis, particularly when $HO^{\bullet}$ reactions of organics are significant (Carlton et al., 2006; Yang et al., 2008b; Tan et al., 2012). Because sulfate is abundant in non-irradiated AA and BA (Pavuluri et al., 2011), the production of organosulfates should be significant upon irradiation (Noziere et al., 2010) in both the samples. However, the sulfate contents may not have significant impact on the production rate of diacids and related compounds (Tan et al., 2009).

Further, the photolysis of organics by the radiation of 185 nm, whose intensity is 100 times lower than that of 254 nm, should be insignificant during the experiment because the 185 nm light intensity is small and is mostly absorbed by water due to its high absorption

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Deleted: is mostly absorbed by water to subsequently produce $HO^{\bullet}$ and thus minimize the photolysis of organics coefficient (1.8 cm^{-1} at 25 °C) (Weeks et al., 1963). It is well established that the photolysis rates of organics by the radiation of 185 nm are elevated only in the absence of dissolved oxygen (Shirayama et al., 2001) whereas in aerated solutions, mainly water undergoes photolysis under irradiation of 185 nm and produce the hydrogen atoms, which are scavenged by oxygen to form $HO_2^•$ radicals that finally converted to $HO^•$ (Chitose et al., 2003; Yang et al., 2008b). Thus, the minor 185 nm light emitted from UV source promotes the production of $HO^•$ during the experiment rather than the photolysis of the compounds of interest in this study. On the contrary, iron-dicarboxylate complexes (e.g., oxalate and malonate) can photolyze by absorbing both UV-C (254 nm) and UV-A light and their photolysis rate depends on the concentration of Fe in the given sample rather than the UV light wavelength (Zuo and Hoigne, 1994; Wang et al., 2010b; Pavuluri and Kawamura, 2012). In addition, radiation at 254 nm has been reported to impose only a marginal photolysis of most of the inorganic species, except for nitrate, which is one of the $HO^•$ sources (Yang et al., 2008b).

The irradiation of wetted aerosol sample at 254 nm induces the formation of O_3 from the dissolved O_2 followed by generation of H_2O_2, and photolysis of H_2O, NO_3^-, NO_2^-, H_2O_2, $Fe(OH)^{2+}$ and certain organic compounds, and Fenton's reaction of photochemically formed Fe^{2+} and H_2O_2 to produce $HO^•$ in aqueous phase (Arakaki and Faust, 1998; Carlton et al., 2006; Yang et al., 2008b). In fact, high amount of Fe, including water-soluble Fe^{2+} and Fe^{3+} species, is available in both AA and BA samples (Table 1), which could promote the Fenton's reaction upon UV irradiation. In addition, O_3, H_2O_2, $HOO^•$ and NO_2 formed in aqueous phase reactions may be partitioned into gas phase and generate the gaseous $HO^•$ that should be re-partitioned into aqueous phase (Arakaki and Faust, 1998). These sources of $HO^•$ are similar to those of atmospheric waters: (i) gas/drop partitioning of $HO^•$ and (ii) gas/drop partitioning of O_3 followed by reaction with peroxy radical ($HOO^•$), (iii) photolysis of H_2O,

NO_3^-, NO_2^-, H_2O_2, $Fe(OH)^{2+}$ and certain organic compounds, and (iv) Fenton's reaction of Fe^{2+} and H_2O_2 (Arakaki and Faust, 1998).

Unfortunately, we could not approximate the actual concentrations of $HO^{\bullet}$ in our experiments because we did not add any chemical (e.g., a standard compound whose kinetics are known) in order to keep our experimental system as realistic as possible. Furthermore, the formation of O_3 from the initially available O_2 (~0.94 mM) in the reaction vessel may not cause the deficit of the O_2 that could potentially induce the polymerization of organics during the irradiation on aerosols for several hours, because the additional O_2 could be produced from the gaseous $HOO^{\bullet}$ formed by photolysis of organics and Fenton's reaction (Arakaki and Faust, 1998) during the experiment.

2.4 Measurements of diacids, oxoacids and α-dicarbonyls

Immediately after the irradiation, samples were analyzed for diacids, oxoacids and α-dicarbonyls using a method reported elsewhere (Kawamura, 1993; Kawamura and Ikushima, 1993). Briefly, the irradiated sample filter was extracted with Milli-Q water (10 mL x 3) under ultra sonication for 10 min and the extracts were concentrated to near dryness using a rotary evaporator under vacuum. The extracts were then derivatized with 14% BF_3/n-butanol at 100°C to butyl esters and/or butoxy acetals. Both the esters and acetals were extracted with *n*-hexane and then determined using a capillary GC (HP 6890) and GC-MS (Thermo Trace MS). Recoveries of authentic standards spiked to a pre-combusted quartz fiber filter were 73% for oxalic (C_2) acid and more than 84% for malonic (C_3), succinic (C_4) and adipic (C_6) acids (Pavuluri et al., 2010). The analytical errors in duplicate analysis of the aerosol filter sample are within 9% for major species. Gas chromatogram of the field and laboratory blanks showed small peaks for C_2, phthalic (Ph) and glyoxylic acids.

Concentrations of all the species reported here are corrected for the non-irradiated field blanks (Pavuluri et al., 2010).

2.5 Quality control

To examine the possible experimental errors, including the distribution of organic/inorganic constituents over the filter sample, we conducted replicate experiments (n = 3) for 18 h irradiation of AA sample by using the sample cut taken from different parts of the filter sample for each experiment because a deviation in the results of the irradiation experiment should become large if the impact of potential variance in chemical composition of aerosol at different parts of the single filter, size of the filter sample used (i.e., amount of aerosols) and the amount of Milli Q water added is significant. The experimental errors, including the analytical errors, were found to be within 11% for major species, except for C_3 diacid (19%). These results suggest that organic and inorganic constituents are well distributed over the filter sample and took up water evenly distributed upon wetting. In addition, two irradiation experiments were conducted to check the procedural blank by using a clean quartz filter for 1.5 h and 6.0 h. No peaks were detected, except for a small peak for C_2 and Ph. These results indicate that the occurrence of bias during the experiment is insignificant.

3 Results and discussion

3.1 Concentrations of trace elements, metals and water-soluble iron species

Concentrations of trace elements, metals and water-soluble Fe species (Fe^{2+} and Fe^{3+}) determined in non-irradiated AA and BA samples are presented in Table 1. The trace elements and metals in AA sample, which mainly originate from soil dust (e.g., P, Al, Ca and Fe), non-ferrous metallurgical industrial activities (Cd, Cu and Zn) and fossil fuel combustion (Cr, Pb and V) (Pacyna and Pacyna, 2001; Mahowald et al., 2008), are significantly more abundant than in BA (by up to several times higher), except for S, Ni and Sb (Table 1). The high abundances of trace metals in AA further suggest that the AA sample should contain high abundances of anthropogenic organic matter. The high abundances of S, Ni and Sb in BA than in AA may be due to high emissions of the S from intensive consumption of biofuels, particularly cow-dung that contains higher S content (Reddy and Venkataraman, 2002b), while Ni and Sb are from some specific industrial activities in southern India. Although water-soluble Fe^{2+} and Fe^{3+} species are abundant in both AA and BA, their concentrations in BA are 30-50% higher than in AA (Table 1). Further the fraction of water-soluble Fe (Fe_{WS}: sum of Fe^{2+} and Fe^{3+}) in total particulate Fe (Fe_{Tot}) is 2.77% in AA whereas it is 14.6% in BA.

3.2 Molecular compositions of diacids, oxoacids and α-dicarbonyls

A homologous series of normal (C_2-C_{12}) and branched chain (iso C_4-C_6) saturated α,ω-diacids were detected in both non-irradiated and irradiated AA and BA samples as well as aliphatic unsaturated diacids such as maleic (M), fumaric (F), and methylmaleic (mM) acids and aromatic diacids such as phthalic (Ph), isophthalic (*i*-Ph), and terephthalic (*t*-Ph) acids. Diacids with an additional functional group, i.e., malic (hydroxysuccinic, hC_4), ketomalonic (kC_3), and 4-ketopimelic (kC_7) acids, were detected, together with ω-oxoacids (ωC_2-ωC_9), pyruvic acid (Pyr), and α-dicarbonyls, i.e., glyoxal (Gly) and methylglyoxal (MeGly). ωC_6 will not be reported here due to the overlapping peak on GC chromatogram.

Oxalic (C_2) acid was found as the most abundant diacid in non-irradiated samples (accounting for 54% of total diacids in AA and 53% in BA), followed by Ph (10%), C_4 (9%), C_3 (8%) and C_9 (4%) in AA and by malonic (C_3) (9%), C_4 (6%) and *t*-Ph (6%) acids in BA. Branched chain diacids were significantly lower than the corresponding normal structures in both samples. Glyoxylic (ωC_2) acid is the most abundant oxoacid, comprising 64% and 57%

of total oxoacids in AA and BA, respectively, followed by Pyr (13%) and 4-oxobutanoic (ωC_4) acid (10%) in AA and ωC_4 (18%) and Pyr (13%) in BA. MeGly is more abundant than Gly in AA whereas their abundances are equivalent in BA.

3.3 Changes in concentrations of diacids and related compounds as a function of UV irradiation time

Changes in concentrations of individual and total diacids as a function of UV irradiation time in AA and BA are depicted in Fig. 3, while those of oxoacids and α-dicarbonyls as well as total oxoacids and α-dicarbonyls in Fig. 4. Concentrations of C_2 diacid were sharply decreased by a factor of 3-9 (from 553 ng m^{-3} to 61.7 ng m^{-3} in AA and from 339 to 118 ng m^{-3} in BA) within 6 h and 12 h of UV irradiation, respectively (Fig. 3a). Then, the concentrations started to increase to maximize at 24 h (292 ng m^{-3}) in AA and 18 h (306 ng m^{-3}) in BA on further irradiation. They gradually decreased toward the end (120 h) of the experiment (Fig. 3a). Interestingly, C_3 diacid showed a temporal variation similar to C_2 in both AA and BA, except for few points (Fig. 3b). Relative abundances of C_2 in total diacids gradually decreased from non-irradiated samples (54% in AA and 53% in BA) toward the end (120 h) of the experiment (3.2% in AA and 9.2% in BA, Fig. 5).

Concentrations of ωC_2, an immediate precursor of C_2 (Kawamura et al., 1996a; Warneck, 2003; Lim et al., 2005), increased with irradiation time up to 18 h in both AA and BA, except for two cases (3 and 6 h) of AA, and then gradually decreased until the end (120 h) of the experiment, except for one case (36 h) in AA (Fig. 4a). Pyr, Gly and MeGly, which are the precursors of ωC_2 acid, are all produced by the oxidation of VOCs of anthropogenic and biogenic origin (Warneck, 2003; Ervens et al., 2004b; Lim et al., 2005; Carlton et al., 2006). They also increased with irradiation time up to 18~24 h in both samples and then gradually decreased (except for MeGly in AA) until the end (120 h) of the experiment (Fig.

4g, i, j). However, the other precursor of C_2 diacid, kC_3 diacid (Kawamura et al., 1996a), showed a decrease with irradiation time throughout the experiment, except for few cases (Fig. 3v) whereas hC_4, a precursor of C_3 diacid (Kawamura et al., 1996a), increased up to 18 h in BA and 24 h in AA and remained relatively high until 72 h and then gradually decreased until the end (120 h) of the experiment (Fig. 3u).

In contrast, concentrations of C_4 diacid showed a gradual increase with irradiation time up to 72 h in BA and 96 h in AA followed by a slight decrease in the AA and a sharp decrease in BA (Fig. 3c). Relative abundance of C_4 diacid in total diacids also increased from 8.9% (non-irradiated) to 82% (120 h) in AA and from 6.4% to 88% in BA (Fig. 5). Similarly, C_5 diacid in AA (Fig. 3d) showed a gradual increase with irradiation up to 36 h and stayed almost constant until 96 h followed by a slight decrease. Similar trend was found in BA (Fig. 3d). Both C_6 and C_7 diacids showed an increase with irradiation up to 6~36 h and then a gradual decrease until the end (120 h) of the experiment (Fig. 3e,f). Concentrations of iC_4 diacid also increased with irradiation up to 18 h in BA and 36 h in AA and stayed relatively constant until 72 h or 96 h. Then, the concentrations gradually decreased until the end (120 h) of the experiment (Fig. 3l). iC_5 and iC_6 diacids (Fig. 3m,n) showed very similar trend with their corresponding normal diacids (Fig. 3d,e).

Long-chain (C_8-C_{12}) diacids showed a sharp decrease with irradiation up to 12 h and then a gradual decrease until the end (120 h) of the experiment (Fig. 3g-k). C_8, C_9 and C_{12} diacids became below the detection limit within several hours, particularly in BA. On the other hand, unsaturated aliphatic (M, F, mM, and Ph) and aromatic diacids (*i*-Ph and *t*-Ph) showed a gradual decrease with irradiation, except for few cases during the early stages of the experiment (Fig. 3o-t). Concentrations of kC_7 increased with irradiation time up to 18 h and then decreased gradually until 120 h (Fig. 3w) whereas oxoacids: ωC_3, ωC_7 and ωC_9 acids, showed a gradual decrease with irradiation, except for few cases (Fig. 4b,d,f). On the other hand, ωC_4 acid showed a sharp increase up to 12 h and then a sharp decrease toward 24 h (Fig. 4c). Interestingly, temporal pattern of ωC_8 acid (Fig. 4e) was similar to that of C_4 diacid (Fig. 3c).

Thus the changes in the concentrations of individual diacids, oxoacids and α-dicarbonyls as well as relative abundances of individual diacids in total diacids and mass ratios of selected species in AA and BA found to be similar (Figs. 3-6), although significant differences are recognized between AA and BA samples during irradiation. Such similarities in the temporal variations of diacids and related polar compounds infer that their photochemical formation and degradation pathways in aqueous aerosols (Fig. 7) are almost same between anthropogenic and biogenic aerosols. However, there were significant differences in the rate of formation and/or degradation of diacids and related compounds between AA and BA, which might have been driven by the differences in the abundances of the diacids and related compounds as well as their precursor compounds in the original (non-irradiated) AA and BA samples. In fact, total diacids, oxoacids and α-dicarbonyls were higher in non-irradiated AA than in BA. On the contrary, OC that contains several precursor compounds (including fatty acids) of diacids and related polar compounds is higher in BA than in AA (Table 1).

3.4 Production and decomposition of short-chain diacids and related compounds

A sharp increase was observed in the concentrations of ωC_2, ωC_4, Pyr, Gly and MeGly, but not ωC_3, with irradiation up to 18~24 h following a gradual decrease (Fig. 4), demonstrating an enhanced photochemical production of short-chain ($\leq C_4$) oxoacids and α-dicarbonyls during an early stage of photochemical processing. It is likely because ωC_2, Pyr, Gly and MeGly are significantly produced by photochemical oxidation of aliphatic olefins and aromatic hydrocarbons whereas ωC_4 from cyclic olefins and unsaturated fatty acids (Bandow et al., 1985; Hatakeyama et al., 1987; Kawamura et al., 1996a; Warneck, 2003; Lim et al., 2005) but ωC_3 may not be significantly produced from any of these precursor compounds (Fig. 7). On the other hand, the increasing trends of mass ratios of C_2 to its precursor compounds: ωC_2, Pyr, Gly and MeGly as well as C_3 (but not C_4) diacid (Kawamura et al., 1996a; Warneck, 2003; Ervens et al., 2004b; Lim et al., 2005; Carlton et al., 2007), were found for BA toward to 120 h (Fig. 6a-e and f). It is noteworthy that $C_3/\omega C_7$ ratios also showed a slight increase, although they are not clear in the later stages of experiment (Fig. 6g), suggesting a potential formation of C_3 diacid via ωC_7 that is derived from unsaturated fatty acids and/or cyclic olefins. In addition, F/M ratios showed an increase with irradiation up to 48 h in AA and 18 h in BA followed by a gradual decrease until the end of experiment (Fig. 6i), indicating a significant photochemical transformation during an early stage of experiment and decomposition in a later stage.

Photochemical degradation of C_2 and C_3 diacids should have overwhelmed their photochemical production even in an early stage of experiment, except for few cases (Fig. 3a,b). Diacids and other compounds containing a carbonyl group can form stable carboxylate salts with amines upon photochemical oxidation. However, based on laboratory studies, C_2 and C_3 diacids have been reported to decompose in aqueous phase in the presence of Fe^{3+} (and C_2 diacid even in the presence of Fe^{2+}) under UV irradiation at 254 nm as well as at a solar spectrum (>300 nm) (Zuo and Hoigne, 1994; Wang et al., 2010b; Pavuluri and Kawamura, 2012), but C_2 diacid (and maybe C_3 diacid) is relatively stable in the absence of Fe species (Pavuluri and Kawamura, 2012). It is well documented that both C_2 and C_3 diacids have the strongest chelating capacity with Fe^{3+} among all diacids and tend to form mono, di and tri oxalato (equilibrium constant $\log_{10}(b) = 9.4$, 16.2 and 20.4, respectively) and malonato (equilibrium constant $\log_{10}(b) = 7.5$, 13.3 and 16.9, respectively) complexes by acting as ligands in aqueous phase, which exhibit a strong light absorbing ability (Wang et al., 2010b).

Although the equilibrium constant of Fe^{3+}-malanato complex is slightly lower than that of Fe^{3+}-oxalato, both diacids photolyze upon the absorption of UV light to result in Fe^{2+} and CO_2 (Zuo and Hoigne, 1994; Wang et al., 2010b).

We found that non-irradiated AA and BA samples contain significant amounts of water-soluble Fe^{2+} and Fe^{3+} species (Table 1). Because high abundance of particulate Fe is present in both AA and BA (Table 1), the concentrations of water-soluble Fe^{2+} and Fe^{3+} species in both AA and BA samples may increase upon UV irradiation; the water-insoluble Fe can be transformed into water-soluble forms by photochemical processing of mineral aerosols (Solmon et al., 2009; Srinivas et al., 2012). However, we did not measure the concentrations of Fe^{2+} and Fe^{3+} species in the irradiated samples. In fact, the mass ratio of C_2 diacid to Fe^{3+} is 15:1 in non-irradiated AA and 7:1 in BA, which are close to the ratio (10:1) used in laboratory experiments conducted by Pavuluri and Kawamura (2012) for Fe-catalyzed photolysis of C_2 diacid in aqueous phase, in which the photolysis of C_2 is very fast ($k = 206\ L\ mol^{-1}\ s^{-1}$) and 99% of the C_2 is degraded in 0.5 h. Therefore, available water-soluble Fe^{3+} (and Fe^{2+}) in AA and BA should be enough to promote the catalytic photochemical degradation of C_2 (and C_3) upon UV irradiation (Fig. 7) and thus the degradation rate of C_2 (and C_3) should have increased with the prolonged experiment due to enhancement in Fe^{3+} (and Fe^{2+}) levels in the given sample.

The concentration of C_2 diacid in AA decreased by 30% in 1.5 h and continued to decline by 90% until 12 h (Fig. 3a). On the other hand, the experiment of BA showed that the concentration of C_2 decreased by 47% and 51% in 0.5 h and 1.5 h, respectively, and then gradually declined. The concentrations of C_3 also showed similar trends with C_2 (Fig. 3b). Although C_2 and C_3 diacids decreased sharply during early stages of experiment, they decreased gradually in the later stages, despite possibly enhanced levels of water-soluble Fe^{2+} and Fe^{3+} species. These trends imply that photolysis of C_2 and C_3 diacids is highly significant in the presence of water-soluble Fe^{3+} (and Fe^{2+}) (Fig. 7). On the other hand, the formation of both C_2 and C_3 diacids is also intensive with the photochemical processing of their precursor compounds in AA and BA. However, the net rate of production or degradation of C_2 and C_3 diacids in each experiment (Figs. 3a,b) should depend on the abundances of water-soluble Fe^{2+} and Fe^{3+} species and their precursors in AA and BA.

We found an increase in the mass ratios of MeGly to Gly with irradiation toward the end of the experiment, except for an early stage of experiment (up to 6 h) in AA, whereas in BA they remained relatively constant up to 36 h and then increased gradually up to 72 h followed by a rapid decrease (Fig. 6n). As noted earlier, concentrations of Gly and MeGly increased with experiment up to 18~24 h in both AA and BA. Thereafter, Gly decreased toward the end of experiment in both AA and BA whereas MeGly remained relatively constant in the AA, but decreased in BA (Fig. 4i,j). Such differences should be caused by the difference in their production rates depending on the concentrations of potential precursors and their oxidation products in AA and BA: benzene and glycolaldehyde for Gly, acetone and higher alkanes ($>C_3$) and alkenes ($>C_2$) for MeGly (Fu et al., 2008), rather than the reaction rates of the Gly (1.1×10^9 M^{-1} S^{-1}) and MeGly (6.44×10^8 M^{-1} S^{-1}) with $HO^\bullet$ in aqueous phase (Tan et al., 2012). Therefore, the high abundance of MeGly in AA than Gly can be attributed to its enhanced production than the later species during photochemical processing of aqueous aerosols derived from anthropogenic sources. Further, the oligomerization of Gly and MeGly (Tan et al., 2009; Lim et al., 2010; Tan et al., 2012) might have also played an important role on the changes in their concentrations with irradiation time, however, we did not focus on the measurements of oligomers here because of the analytical limitations.

3.5 Possible photochemical pathways of long-chain diacids and oxoacids

Enhanced concentrations of normal and branched C_4-C_7 diacids during an early stage (18~36 h) (Fig. 3c-f), despite degradation of C_2 and C_3 and longer-chain >C_7) diacids (Fig. 3a, b, g-k), may be caused by photochemical oxidation of the first generation products derived from the oxidation of anthropogenic and/or biogenic VOCs (e.g., cycloalkenes, monoterpenes, and sesquiterpenes) and unsaturated fatty acids (Kalberer et al., 2000; Gao et al., 2004) (Fig. 7). In addition, the photochemical oxidation of the polymers of polyunsaturated fatty acids, if available, can significantly produce the long-chain ($\geq C_4$) diacids (Harvey et al., 1983), a subject of future research. In fact, polyunsaturated fatty acids (e.g., linolenic acid ($C_{18:3}$)) can undergo free radical oxidative cross-linking in the air and produce high molecular weight organic compounds (e.g., fulvic acid) (Wheeler, 1972; Harvey et al., 1983). Harvey et al. (1983) found a series of C_4-C_9 diacids by oxidizing the marine fulvic acid in a laboratory study. On the other hand, the chelating capability of succinate (equilibrium constant $\log_{10}(b) = 7.5$ (Wang et al., 2010b)) and other long-chain diacids with Fe^{3+} is weak and hence, their photolysis is insignificant. However, they should be further oxidized to result in lower diacids (Kawamura et al., 1996a; Matsunaga et al., 1999). The degradation of these diacids should be increased with increasing chain length because the oxidation rate of C_4 to C_9 diacids is increased with increasing carbon number (Yang et al., 2008a).

The relatively constant levels of C_5, iC_4 and iC_5 during 36 h and 72~96 h (Fig. 3d, l, and m) may be due to the balance between photochemical production and degradation. The increases in the concentrations of C_4 with a prolonged irradiation up to 72 h in BA and 96 h in AA further demonstrate its formation from higher diacids and other precursors in aqueous aerosols (Kawamura and Sakaguchi, 1999; Charbouillot et al., 2012) (Fig. 7). In fact, total diacids stayed relatively constant from 24 h to 72~96 h (Fig. 3x). In addition, mass ratios of C_4 to C_5-C_7 showed a gradual increase throughout the experiment (until 120 h) in both AA and BA (Fig. 6k-m). These results support a photochemical breakdown of longer-chain ($\geq C_5$)

diacids resulting in C_4 (Matsunaga et al., 1999; Yang et al., 2008a; Charbouillot et al., 2012). Yang et al. (2008a) reported that the production of C_4 diacid is predominant followed by C_5 diacid during a laboratory photochemical oxidation of C_6-C_9 diacids.

In addition, ωC_8 acid, which can be produced by the oxidation of cyclic olefins and unsaturated fatty acids (Kawamura and Sakaguchi, 1999; Gao et al., 2004), showed a gradual increase (Fig. 4e) similar to that of C_4 diacid (Fig. 3c) in both AA and BA, suggesting a significant photochemical production of C_4 via ωC_8 until the consumption of the precursor compounds derived from anthropogenic and biogenic VOCs and biogenic unsaturated fatty acids (Kalberer et al., 2000; Gao et al., 2004). In fact, ratios of C_4 to C_5-C_7 were 10 times higher in BA than in AA whereas those of $C_4/\omega C_8$ were similar in both the BA and AA (Fig. 6j). However, their temporal profiles with irradiation time are similar in both AA and BA. These results suggest that the formation of C_4 and ωC_8 is much higher in biogenic aerosols than in anthropogenic aerosols compared to C_5-C_7 diacids, but their formation/degradation processes may be similar irrespective of the origin of precursors. However, it is not clear from this study if C_4 is mainly derived (via ωC_8) from cyclic olefins or unsaturated fatty acids (Fig. 7).

It is well established that long-chain (C_8-C_{12}) diacids are formed by photochemical oxidation of unsaturated fatty acids (e.g., oleic acid) (Kawamura and Gagosian, 1987; Matsunaga et al., 1999) (Fig. 7). However, unsaturated fatty acids were not abundant (e.g., oleic acid was 0.89 ng m^{-3} in AA and below detection limit in BA) in non-irradiated samples (Fu et al., 2010). Hence, photochemical formation of long-chain diacids from the oxidation of unsaturated fatty acids should be less important during the experiment, although chemical forms of polymerized and/or partially oxidized unsaturated fatty acids may be abundant in the aerosols. On the other hand, photooxidation rate constant of diacids increases with an increase in carbon number of individual diacids ($\geq C_4$) (Yang et al., 2008a). Hence, photochemical breakdown of C_8-C_{12} diacids to lower diacids (Matsunaga et al., 1999; Yang et al., 2008a) should be very likely (Fig. 7). The gradual decreases of aliphatic unsaturated diacids, aromatic diacids, and oxoacids, except for ωC_8, with irradiation are likely caused by the photochemical degradation (Fig. 7).

3.6 Atmospheric implications

As discussed above, this study reveals that photochemical degradation of C_2 and C_3 (due to Fe-catalyzed photolysis) in aqueous aerosols overwhelmed their production whereas C_4 diacid showed photochemical formation. These results are consistent with the recent atmospheric observations: a significant reduction in C_2 diacid concentration and an inverse relationship between the C_2 and Fe in cloud water (Sorooshian et al., 2013), and the replacement of the predominance of C_2 by C_4 in the Arctic aerosols (Kawamura et al., 2010; Kawamura et al., 2012). It was also reported that C_4 and C_5 diacids are most abundant among C_3-C_8 diacids determined during the photochemical oxidation of C_6-C_9 diacids in a laboratory experiment (Yang et al., 2008a).

On the contrary, enhanced degradation of C_2 and C_3 and formation of C_4 diacid upon prolonged irradiation, are not consistent with previous laboratory, observation and model studies on photochemical production and degradation of diacids and related compounds in aqueous phase (e.g., cloud processing) (Kawamura et al., 1996a; Kawamura and Sakaguchi, 1999; Warneck, 2003; Ervens et al., 2004b; Lim et al., 2005; Carlton et al., 2007; Charbouillot et al., 2012). In fact, previous studies did not consider Fe-catalyzed photolysis of C_2 diacid, which is significant at least in Fe-rich atmospheric waters. On the other hand, the formation processes and potential precursor compounds of C_4 diacid have not been fully explored yet. Moreover, previous laboratory experiments on aqueous solutions of specific species did not consider the mixing state of organic and inorganic constituents in atmospheric aerosols (Ervens et al., 2011), although simplified experiments sometimes provide useful information on mechanisms.

Generally, it has been considered that the anthropogenic contributions of α-dicarbonyls to organic aerosols are minor: 8% for Gly and 5% for MeGly (Fu et al., 2008). To the best of our knowledge, their production in atmospheric waters has not well been recognized yet. Our laboratory experiments indicate that the photochemical production of Gly and MeGly is significant in aqueous aerosols. The production of MeGly is more pronounced compared to Gly with prolonged photochemical processing of aqueous anthropogenic aerosols. Finally, our findings based on the batch laboratory experiment emphasize the importance of the photolysis of C_2 and C_3 diacids and photochemical production of C_4 diacid and α-dicarbonyls in aqueous aerosols to reconcile the current atmospheric model(s) such as cloud parcel model (Ervens et al., 2004a), and to better understand the secondary organic aerosol budget and its climatic impacts.

4 Summary and conclusions

In this study, we conducted batch UV irradiation experiments on anthropogenic (AA) and biogenic (BA) aerosol samples collected from Chennai, India in the presence of moisture for the reaction time of 0.5 h to 120 h. The irradiated samples were analyzed for molecular compositions of diacids, oxoacids and α-dicarbonyls. Concentrations of C_2 and C_3 and C_8-C_{12} diacids decreased with an increase in 12-24 h. In contrast, C_4 diacid (and C_5-C_7) showed a significant increase with reaction time up to 72 h in BA and 96 h in AA. Oxoacids and α-dicarbonyls showed a significant increase during an early stage of irradiation followed by a gradual decrease in the prolonged experiment, except for ωC_8 acid that showed a pattern similar to C_4 diacid and for methylglyoxal that remained relatively abundant from 24 h to the end of the experiment in AA. The mass ratios of C_2 diacid to its precursors: glyoxylic acid, pyruvic acid, α-dicarbonyls (glyoxyal and methylglyoxal) and C_3, showed a considerable increase with irradiation, while those of C_4 to C_5-C_7 diacids and ωC_8 acid and methylglyoxal to glyoxal in AA showed a significant increase with irradiation. These results demonstrate that degradation of C_2 and C_3 (and C_8-C_{12}) and formation of C_4 (and C_5-C_7) is enhanced with photochemical processing of aqueous aerosols. This study further infers that iron-catalyzed photolysis of C_2 and C_3 diacids and photochemical formation of C_4 diacid via ωC_8 acid derived from cyclic olefins and/or unsaturated fatty acids play an important role in controlling their abundances in the atmosphere with photochemical processing of aqueous aerosols. This study also suggests that photochemical production of α-dicarbonyls, in particular methylglyoxal, in anthropogenic aerosols is significant.

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Table 1. Concentrations of carbonaceous components, organic molecular tracer compounds, diacids and related compounds, trace elements, metals and water-soluble iron species in non-irradiated IND104 (anthropogenic aerosols: AA) and IND178 (biogenic aerosols: BA) aerosol samples collected from Chennai, India.

	Concentrations (ng m^{-3})	
	IND104 (AA)	IND178 (BA)
Organic carbon[a]	6400	9820
Elemental carbon[a]	4810	1810
Levoglucosan[b]	79.1	158
Hopanes (C_{27}-C_{35}) [b]	11.8	3.9
Fatty acids (C_{8}-C_{34}) [b]	167	297
Fatty alcohols (C_{14}-C_{34}) [b]	93.3	178
Total diacids	1030	640
Total oxoaxids	110	62.2
Total α-dicarbonyls	10.9	11.6
Al	15100	914
Ca	1640	0.00
Cd	10.7	1.73
Co	1.07	0.00
Cr	5.33	0.00
Cu	796	13.9
Fe	2070	553
K	1220	893
Mg	679	90.2
Mn	129	19.1
Na	1890	408
Ni	58.7	106
P	62.9	0.00
Pb	133	39.9
S	4640	5820
Sb	13.9	29.5
V	9.60	0.00
Zn	2030	137
Fe_{WS}[c]	57.0	78.3
Fe^{2+}	20.5	30.0
Fe^{3+}	36.6	48.4

[a]: Data is obtained from Pavuluri et al. (2011), [b]: Data is obtained from Fu et al. (2010), [c]: Fe_{WS} is water-soluble Fe.

Figure Captions

Fig. 1. A map of South Asia with sampling site, Chennai (13.04°N; 80.17°E), India together with plots of 10-day air mass trajectories arriving at 500 m a.g.l. over Chennai, India.

Fig. 2. Schematic of experimental setup for irradiation of atmospheric aerosol filter sample.

Fig. 3. Changes in concentrations of individual dicarboxylic acids and total diacids as a function of UV irradiation time in anthropogenic (AA) and biogenic aerosols (BA).

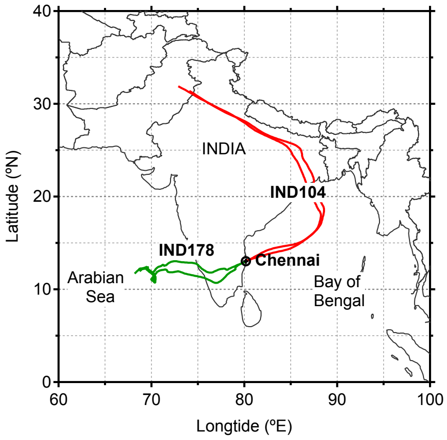
Fig. 4. Changes in concentrations of individual oxoacids and α-dicarbonyls and total oxoacids and α-dicarbonyls as a function of UV irradiation time in AA and BA.

Fig. 5. Changes in relative abundances of straight chain diacids (C_2-C_{10}) to total diacids as a function of UV irradiation time in AA and BA.

Fig. 6. Changes in mass ratios of selected diacids, oxoacids and α-dicarbonyls as a function of UV irradiation time in AA and BA.

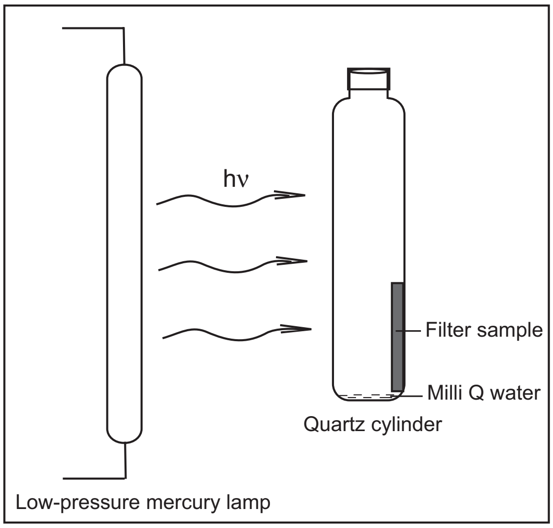
Fig. 7. Possible photochemical formation and/or degradation pathways of diacids, oxoacids and α-dicarbonyls in aqueous aerosols.

741 **Fig. 1.**


INDIA
IND104
IND178
Chennai
Arabian Sea
Bay of Bengal
Latitude (ºN)
Longtide (ºE)
0
10
20
30
40
60
70
80
90
100

742

743 **Fig. 2.**


hν
Filter sample
Milli Q water
Quartz cylinder
Low-pressure mercury lamp

744

Fig. 3.

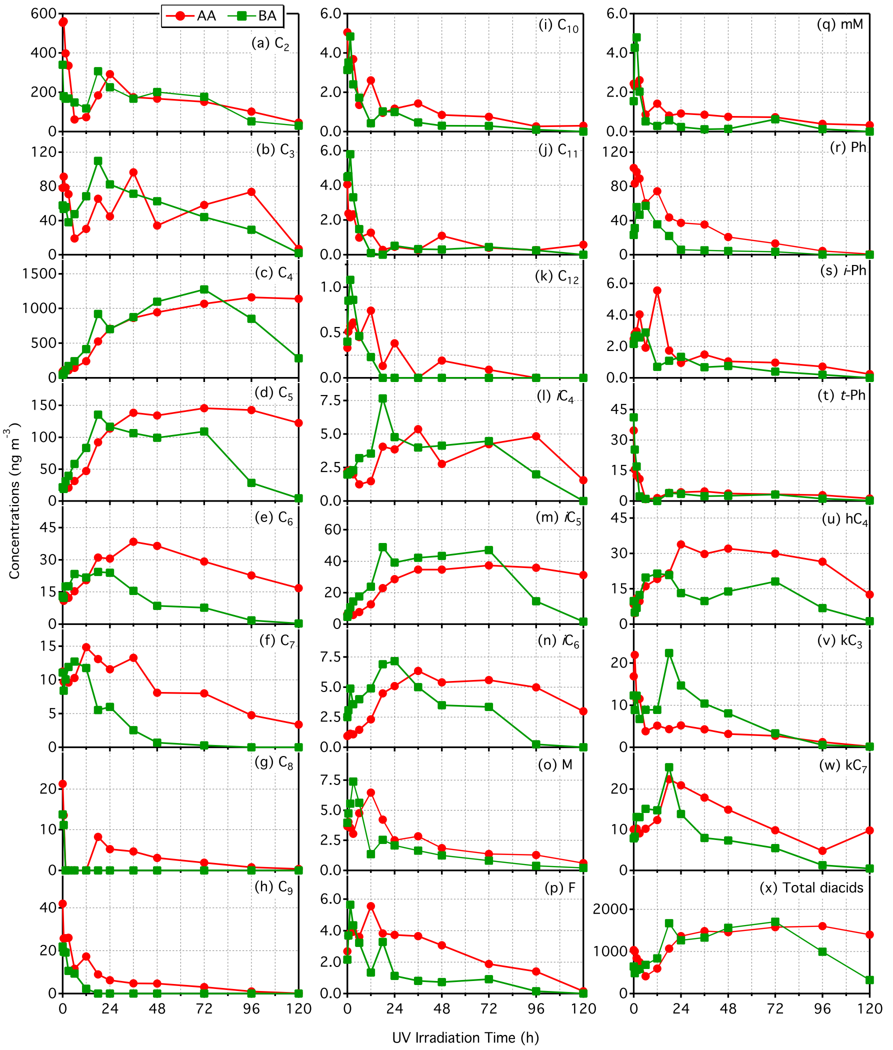
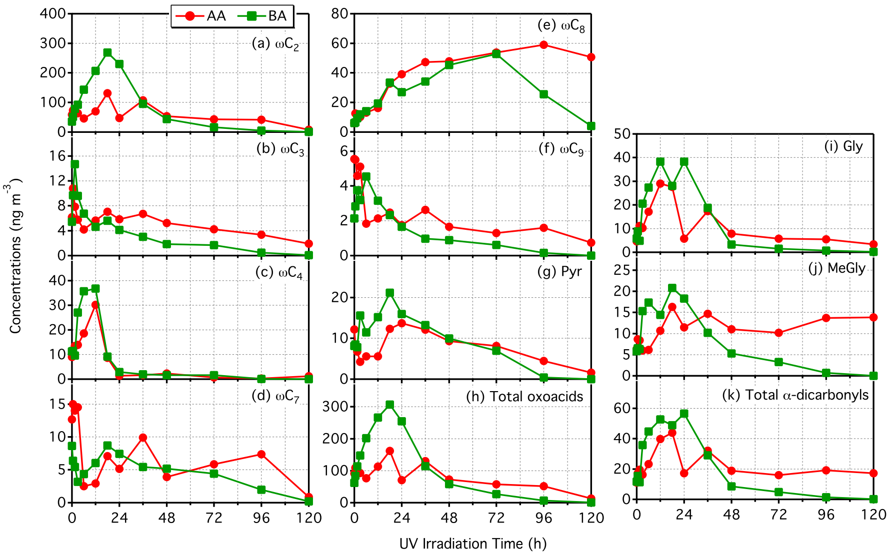
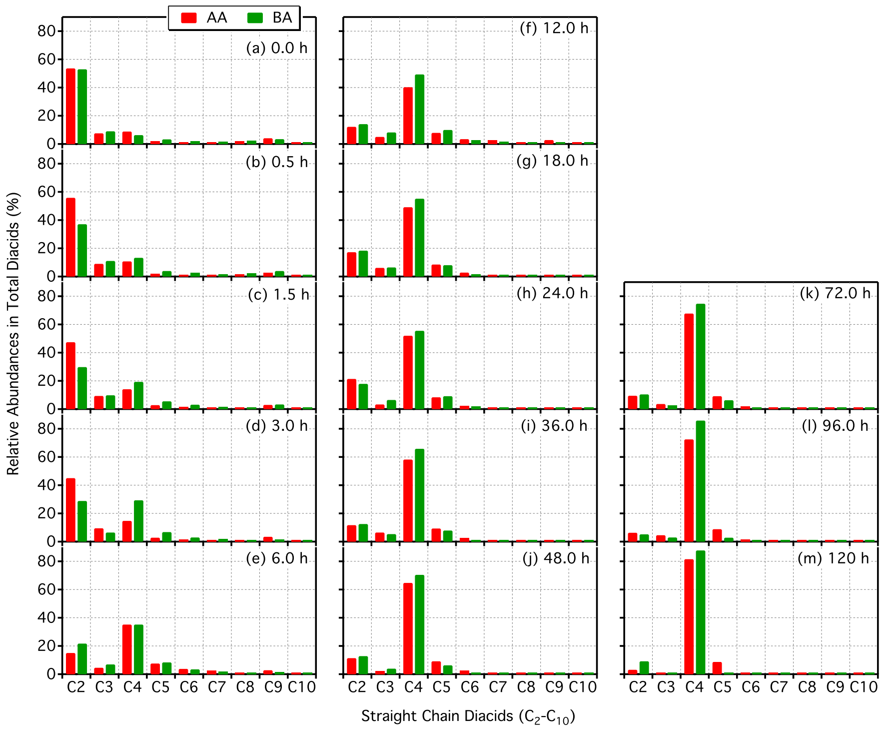

AA
BA
(a) C_2
(b) C_3
(c) C_4
(d) C_5
(e) C_6
(f) C_7
(g) C_8
(h) C_9
(i) C_{10}
(j) C_{11}
(k) C_{12}
(l) iC_4
(m) iC_5
(n) iC_6
(o) M
(p) F
(q) mM
(r) Ph
(s) i-Ph
(t) t-Ph
(u) hC_4
(v) kC_3
(w) kC_7
(x) Total diacids
Concentrations (ng m^{-3})
UV Irradiation Time (h)
0
24
48
72
96
120

Fig. 4.


AA
BA
(a) ωC$_2$
(b) ωC$_3$
(c) ωC$_4$
(d) ωC$_7$
(e) ωC$_8$
(f) ωC$_9$
(g) Pyr
(h) Total oxoacids
(i) Gly
(j) MeGly
(k) Total α-dicarbonyls
Concentrations (ng m^{-3})
UV Irradiation Time (h)
0
24
48
72
96
120

749 **Fig. 5.**



AA
BA
(a) 0.0 h
(b) 0.5 h
(c) 1.5 h
(d) 3.0 h
(e) 6.0 h
(f) 12.0 h
(g) 18.0 h
(h) 24.0 h
(i) 36.0 h
(j) 48.0 h
(k) 72.0 h
(l) 96.0 h
(m) 120 h
0
20
40
60
80
Relative Abundances in Total Diacids (%)
C2 C3 C4 C5 C6 C7 C8 C9 C10
Straight Chain Diacids (C2-C10)

750

Fig. 6.

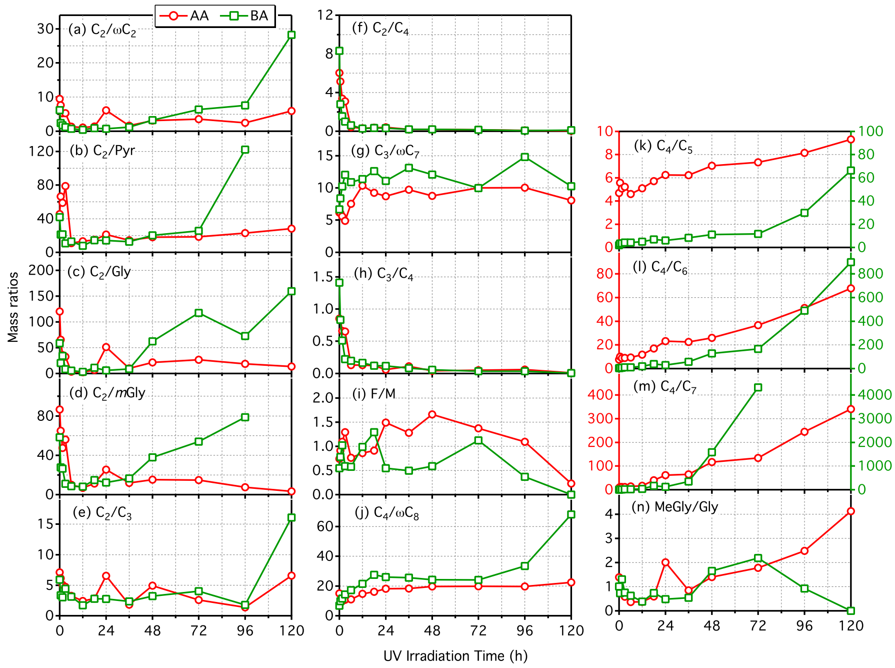
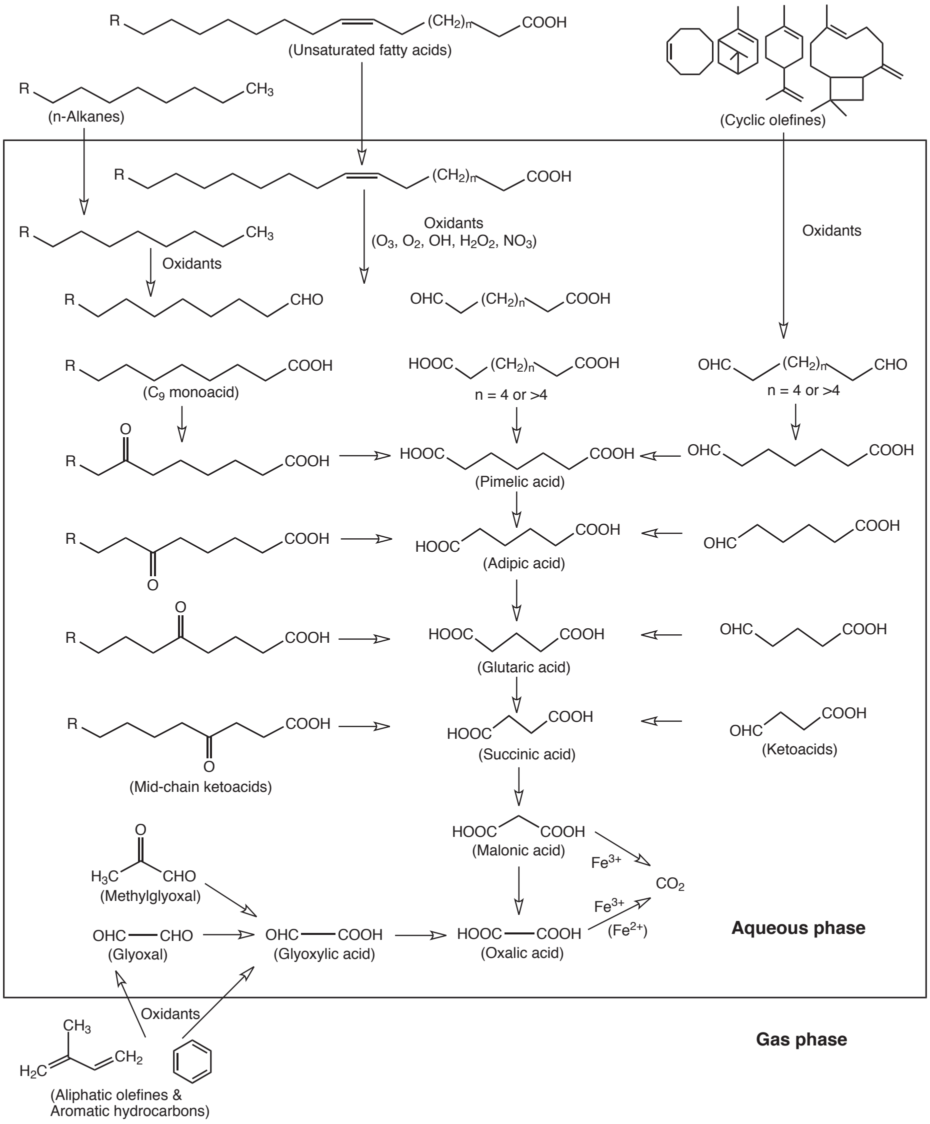

AA
BA
(a) $C_2/\omega C_2$
(b) C_2/Pyr
(c) C_2/Gly
(d) C_2/mGly
(e) C_2/C_3
(f) C_2/C_4
(g) $C_3/\omega C_7$
(h) C_3/C_4
(i) F/M
(j) $C_4/\omega C_8$
(k) C_4/C_5
(l) C_4/C_6
(m) C_4/C_7
(n) MeGly/Gly
Mass ratios
UV Irradiation Time (h)
0
24
48
72
96
120

Fig. 7.


(Unsaturated fatty acids)
(n-Alkanes)
(Cyclic olefines)
Oxidants
(O$_3$, O$_2$, OH, H$_2$O$_2$, NO$_3$)
Oxidants
Oxidants
(C$_9$ monoacid)
n = 4 or >4
n = 4 or >4
(Pimelic acid)
(Adipic acid)
(Glutaric acid)
(Succinic acid)
(Ketoacids)
(Mid-chain ketoacids)
(Malonic acid)
(Methylglyoxal)
Fe^{3+}
CO$_2$
Fe^{3+}
(Fe^{2+})
(Glyoxal)
(Glyoxylic acid)
(Oxalic acid)
Aqueous phase
Oxidants
Gas phase
(Aliphatic olefines &
Aromatic hydrocarbons)