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Identification of hydroxy and keto-dicarboxylic acids in remote marine aerosols: Implications for photochemical formation and transformation of water-soluble organic aerosols

（外洋エアロゾル中のヒドロキシおよびケトジカルボン酸の同定：水溶性有機エアロゾルの光化学的生成と変質への関係）

A Thesis submitted for the Degree of

Doctor of Environmental Science

By

DIVYAVANI

Institute of Low Temperature Science

Atmospheric and Organic Geochemistry Course

Graduate School of Environmental Science

Hokkaido University, Japan

September 2016

“Identification of hydroxy and keto-dicarboxylic acids in remote marine aerosols: Implications for photochemical formation and transformation of water-soluble organic aerosols”

A Thesis Submitted to Hokkaido University
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In

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By

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September 2016

Dedication

This dissertation is dedicated to my family; father Boralinge Gowda, mother Bhagya, younger sister Ramya, husband Dr. Siddabasave gowda, and my little angel Tanvi. S without their supports and encouragements, the study described herein would not have been successful.

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Abbreviations

GC	Gas chromatography
GC/MS	Gas chromatography/Mass spectrometry
GC-FID	Gas chromatography-flame ionization detection
GC/TOFMS	Gas chromatography/ time-of-flight mass Spectrometry
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
CCN	Cloud Condensation nuclei
IN	Ice nuclei
OC	Organic carbon
TC	Total carbon
WSOC	Water-soluble organic carbon
TMS	Trimethylsilyl
TSP	Total suspended particles
JAXA	Japan Aerospace Exploration Agency
MW	Molecular weight
RT	Retention time
POA	Primary Organic Aerosol
SOA	Secondary Organic Aerosol
EI	Electron ionization
C_2	Oxalic acid
C_3	Malonic acid
C_4	Succinic acid
hC_3	Tartronic acid
hC_4	Malic acid
hC_5	Hydroxyglutaric acid
hC_6	Hydroxyadipic acid
UV	Ultraviolet
AA	Anthropogenic aerosols
BA	Biogenic aerosols

Thesis abstract

Understanding the composition of atmospheric organic particulate matter is essential for predicting its effects on climate, air quality, and health. Dicarboxylic acids (diacids) are dominant components of organic aerosols in the atmosphere and have been extensively studied at many locations around the world. Because of their high water solubility and hygroscopic properties, particles enriched with diacids play an important role as cloud condensation nuclei (CCN) and ice nuclei (IN) affecting the radiative forcing of the Earth. In spite of their ubiquity in the Environment and their high reactivity, there are some diacids related compounds containing hydroxyl and keto groups that have been suggested to exist in the atmosphere but have never been identified in marine aerosols. Due to the enhanced polarity compared with diacids, these compounds should play a crucial role as CCN and IN. Identification of these compounds is important to a better understanding of the photochemical process and chemical composition of organic particulate matter, as this chemical composition is essential for predicting the effects on climate, air quality, and human health. In the present study, the author focused on identification, quantification, seasonal distribution and formation pathways of atmospherically important hydroxy and keto-diacids. The first chapter of this thesis is general introduction to diacids and related compounds, their significances in the atmosphere with recent scientific updates.

The second chapter of this thesis will focus on identification of hydroxy and keto-dicarboxylic acids in remote marine aerosol samples. Remote marine aerosols collected at Chichijima Island were studied for hydroxy and keto-diacids. A two-step derivatization technique was employed, using 14% BF_3/n-butanol for the butylation of carboxyl groups and acidic ketones followed by N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) for the trimethylsilylation of hydroxyl groups. Several new peaks were detected in the gas

chromatogram after trimethylsilylation of the dibutyl ester fraction. Based on mass spectral interpretation with authentic standards, the author successfully identified and quantified a homologous series of hydroxydiacids (hC_3–hC_6), includes tartronic acid, malic acid, 3-hydroxyglutaric acid, 2-hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydroxyadipic acid, and tartaric acid. Ketodiacids includes oxaloacetic acid (kC_4).

The third chapter of this thesis focused on seasonal variations of hydroxy and keto-diacids at Chichijima Island, shows maximum in spring followed by winter and autumn. Molecular compositions of hydroxy and keto-diacids show predominance of malic acid followed by tartronic acid. Total hydroxy and keto-diacids maximized in spring when air masses originated from the Asian Continent with westerly winds. Significant positive correlation was observed between hydroxydiacids and diacids compounds in all four seasons suggest that hydroxydiacids and diacids have similar sources. This study demonstrates that the ambient aerosols at Chichijima Island are strongly influenced by long-range atmospheric pollutants from East Asia in winter/spring and by photo-oxidation process they are converting into low molecular weight diacids through intermediates.

The fourth chapter describes about photochemical processing of hydroxy and keto-diacids, the author conducted batch UV irradiation experiments on two types of samples collected from India, which symbolize anthropogenic (AA) and biogenic aerosols (BA), for time periods of 0.5 to 120 h. The results show that photochemical degradation of tartronic (hC_3), malic (hC_4), 2-hydroxyglutaric (2-hC_5), and 2-hydroxyadipic acids (2-hC_6) and keto form of oxaloacetic acid overcome their production in aqueous aerosols. Whereas, 3-hydroxyglutaric acid (3-hC_5), tartaric acid, 3-hydroxyadipic acid (3-hC_6), enol form of oxaloacetic acid showed a significant increase during the course of irradiation experiment upto some extent then decrease. And also found a gradual decrease in the relative abundance of hC_4 to total hydroxy diacids and an increase in the relative abundance of enol form of oxaloacetic acid during prolonged experiment. Based on the changes in concentrations and mass ratios of selected species with the irradiation time, the author suggests that hydroxydiacids are the key intermediates in the degradation of smaller diacids. This study demonstrates that the ambient aerosols contain abundant precursors that produce diacids via intermediates such as hydroxy and keto-diacids.

In the fifth chapter the author describes about aqueous phase photooxidation of anthropogenic (toluene, Benzene) and biogenic precursors (isoprene and α-pinene) via laboratory experiments. The preliminary results of this study suggest the production of diacids and related compounds in aqueous phase by the photooxidation of anthropogenic and biogenic precursors are significant.

Chapter 1

General Introduction

1.1. Atmospheric aerosols

The word aerosol was introduced more than 80 years ago as an analogy to the term hydrosol, a stable liquid suspension of solid particles [Hinds et al., 1999]. Aerosols are colloid of fine solid minute particles or liquid droplets that are suspended in a gas, with particle diameters in the range of 10^{-9}-10^{-4} m [Seinfeld et al., 2005]. Some occur naturally, originating from volcanoes, dust storms, forest and grassland fires, and living vegetation. Human activities, such as the burning of fossil fuels, automobiles, power plants, wood burning, and the alteration of natural surface cover, also can generate aerosols. Averaged global aerosols made by human activities currently account for about 10% of the total amount of aerosols in the atmosphere. Most of that 10% is concentrated in the Northern Hemisphere, especially downwind of industrial sites, and overgrazed grasslands. Aerosols are of central importance for atmospheric chemistry and Physics, the Biosphere, climate, and Public health. The Earth's atmosphere contains thousands aerosols particles in every liter of air, but the exact type and number of particles is not the same in all locations around the world. The airborne solid and liquid particles in the nanometer to micrometer size range influence the energy balance of the Earth, the hydrological cycle, atmospheric circulation, and the abundance of greenhouse and reactive trace gases [Finlayson et al., 2000].

Moreover, they play important roles in the spreading of biological organisms; reproductive materials, pathogens (pollen, bacteria, spores, viruses etc.), and can cause or enhance respiratory, cardiovascular, infectious and allergic diseases [Finlayson-Pitts et al., 2000; Pitts, et al., 1997]. The primary parameters that determine the environmental and health effects of aerosol particles are their concentration, size, structure, and chemical composition. Aerosols have the potential to significantly influence our entire planet through their role in heterogeneous chemistry in the troposphere and stratosphere [Ravishankara et al., 1997; Finlayson-Pitts et al., 2000], as well as their effect on the Earth's climate as they scatter sunlight and serve as condensation nuclei for cloud droplet formation [Charlson et al., 1992; Ramanathan et al., 2001]. Aerosols also alter warm, ice and mixed-phase cloud formation processes by increasing droplet number concentrations and ice particle concentrations. They decrease the precipitation efficiency of warm clouds and thereby cause an indirect radiative forcing associated with these changes in cloud properties. An important characteristic of aerosols is that they have short atmospheric life times and therefore cannot be considered simply as a long-term offset to the warming influence of greenhouse gases. A better understanding of the formation, composition and transformation of aerosols in the atmosphere is of critical importance in order to better quantify these effects.

1.2 Sources and effects of atmospheric aerosols

Aerosols originate from a wide variety of natural and anthropogenic sources. Various aerosol particles are generated through a combination of physical, chemical and biological processes. Based on the formation processes, different source types can be distinguished (**Table 1**). Primary atmospheric aerosols: are particulates that emitted directly into the atmosphere as liquids or solids, through a wide range of processes (Bulk-to-Particle Conversion, BPC), from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt, and biological materials (plant fragments, microorganisms, pollen, etc.). Secondary atmospheric aerosols: particulates that formed in the atmosphere by nucleation and condensation of precursor gases (Gas-to-Particles Conversion, GPC) and reactions of dissolved substance in cloud droplets in the atmosphere.

Source	**Amount Tg/yr**	**Best estimate**
Natural		
• Soil dust	1000 - 3000	1500
• Sea salt	1000 - 10000	1300
• Botanical debris	26 - 80	50
• Volcanic dust	4 - 10000	30
• Forest fires	3 -150	20
• Gas-to-particle conversion	100 - 260	180
• Photochemical	40 - 200	60
• Total for natural sources	2200 - 24000	3100
Anthropogenic		
• Direct emissions	50 - 160	120
• Gas-to-particle conversion	260 - 460	330
• Photochemical	5 - 25	10
• Total for anthropogenic sources	320 - 640	460

Table 1: Sources and estimates of global emissions of atmospheric aerosols [Hinds et al., 1999].

Atmospheric aerosols are currently a subject of high scientific and political interest due to their important effects on climate, human health [Lighty et al., 2000], ecosystems and agricultural yields [acidification and eutrophication; Matson et al., 2002], as well as visibility [Watson et al., 2002]. Atmospheric aerosol particles play important role in radiation budget of the Earth's as they scatter and absorb both shortwave solar radiation and long wave terrestrial radiation [Twomey et al., 1974]. They are also highly involved in the formation of clouds and precipitation since they operate as cloud condensation and ice nuclei (CCN and IN), which also can reflect incoming light and results in the further reduction in solar radiation reaching the Earth's surface. Aerosols can form the abundance and distribution of atmospheric trace gases by complex chemical reactions, and can affect significantly the cycles of nitrogen, sulphur, and atmospheric oxidants.

Aerosol particles in the upper atmosphere, where the major part of atmospheric ozone forms, can modify the ozone removal [Mészáros et al., 2000]. Additionally, particles are major elements of lower tropospheric air quality, and can influence harmfully the environment and human health. Aerosol particles can deposit in the nose, mouth, and pharynx, larynx (the head airways region deeper within the respiratory tract or in the alveolar region. The deposition of aerosol particles within the respiratory system strong determines the health effects of exposure to such aerosols [Paur et al., 2011]. Aerosols play important role in the balance of the Earth's climate. Due to the increasing anthropogenic emission of aerosols since the industrial revolution, they can also effect the global climate change. However, the effects of aerosols on climate are not one-way, moreover excessively uncertain. The climate forcing by aerosols can be realized in two ways, basically: in direct and indirect radiative forcing (**Figure 1**).

Direct effects: direct radiative forcing due the scattering radiation. Aerosol particles reflected a part of shortwave solar radiation back into the space, cooling the Earth's atmosphere. This cooling effect of aerosols, especially by sulphate components may be compensated by the absorption of long wave terrestrial radiation primarily by elemental (black) carbon aerosols and dust particles. The global, annual mean radiative forcing still less certain and is estimated -0.4 ± 0.2 W m^{-2} for sulphate, -0.05 ± 0.05 W m^{-2} for fossil fuel organic carbon, +0.2 ± 0.15 W m^{-2} for fossil fuel black carbon, +0.03 ± 0.12 W $m^{-2}$for biomass burning, -0.1 ± 0.1 W m^{-2} for nitrate and -0.1 ± 0.2 W m^{-2} for mineral dust (IPCC, 2007). A large volcanic eruption can greatly increase the concentration of stratospheric sulphate aerosols, thereby increasing the negative radiative forcing. However, a single, large eruption can cool our atmosphere only for a few years.

Indirect effects: indirect radiative forcing through cloud formation effects. Aerosol particles can also affect the radiation balance by formation of cloud droplets. Cloud droplets are formed in the troposphere by condensation of water vapour onto aerosol particles (cloud condensation nuclei, or ice nuclei) when the relative humidity exceeds the saturation level. Without these particles, a very large super saturation (about 400%) would be necessary for the homogeneous condensation of water vapour. The properties and the number of particles can affect the formation and the characteristic of clouds and precipitation in many ways [Lohmann et al., 2005]. The increased number of aerosol particles, and therefore the increased cloud optical thickness decrease the net surface solar radiation. The more numerous smaller cloud particles reflect more solar radiation (called albedo effect or Twomey effect). Smaller particles decrease the precipitation efficiency, thereby prolonging cloud lifetime. The absorption of solar radiation by soot particles may cause evaporation of cloud particles (semi-direct effect). In mixed-phased clouds, smaller cloud droplets delay the beginning of freezing and decrease the riming efficiency. However, more ice nuclei increase the precipitation efficiency.

Light scattering by aerosols is measurable as well as calculable from measured aerosol size and composition. This permits comparisons, called closure studies, of the different measurements for consistency. An example is the comparison of the derived optical depth with directly measured or inferred optical depths from sun photometers or satellite radiometers. Indeed, various sorts of closure studies have been successfully conducted and lend added credibility to the measurements of the individual quantities [McMurry et al., 1996; Clarke et al., 1996; Raes et al., 2000]. Closure studies can also provide objective estimates of the uncertainty in calculating radiative quantities such as optical depth.

Aerosols in the accumulation mode, i.e., those with dry diameters between 0.1 and 1 μm [Schwartz et al., 1996] are of most importance. Accumulation mode aerosols not only have high scattering efficiency, they also have the longest atmospheric lifetime: smaller particles coagulate more quickly while nucleation to cloud drops or impaction onto the surface removes larger particles efficiently. Accumulation mode aerosols form the majority of cloud condensation nuclei (CCN). Hence, anthropogenic aerosol perturbations such as sulphur emissions have the greatest climate impact when, as is often the case, they produce or affect accumulation mode aerosols [Jones et al., 1994]. Indirect forcing by aerosols is broadly defined as the overall process by which aerosols perturb the Earth-atmosphere radiation balance by modulation of cloud albedo and cloud amount. It can be viewed as a series of processes linking various intermediate variables such as aerosol mass, cloud condensation nuclei (CCN) concentration, ice nuclei (IN) concentration, water phase partitioning, cloud optical depth, etc., which connect emissions of aerosols (or their precursors) to the top of the atmosphere radiative forcing due to clouds.

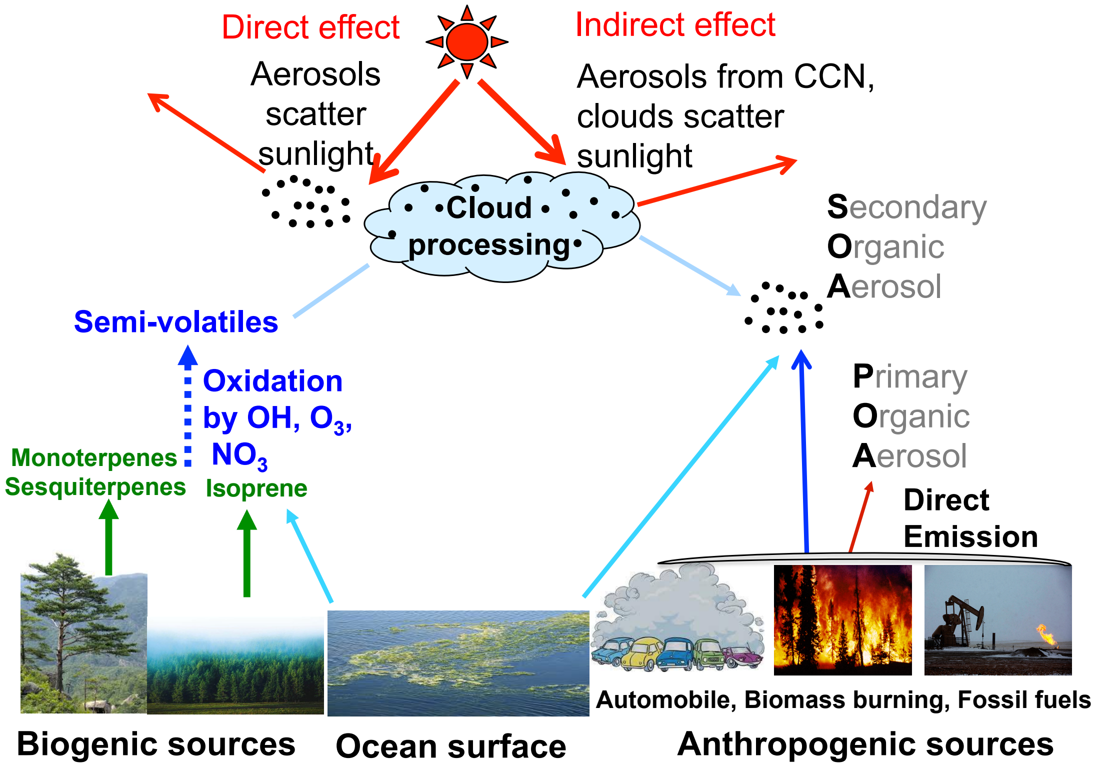

Figure 1: Sources and effects atmospheric aerosols

1.3 Chemical composition and analysis of atmospheric Aerosols

In general aerosol consists of a complex mixture of organic matter, inorganic salts, trace elements, mineral dust, elemental carbon and water suspended in the air. Detailed analyses of physicochemical properties and spatiotemporal variability are crucial to understand the mechanisms of aerosol toxicity and their role in climate change [IPCC, 2007]. Accurate determination of the chemical composition of air particulate matter is a formidable analytical task. Minute sample amounts are usually composed of several main constituents and hundreds of minor and trace constituents. Moreover, the composition of the individual particles can be fairly uniform (internally mixed aerosols) or very different from the ensemble composition (externally mixed aerosols), depending on the particle sources and atmospheric aging processes involved (coagulation, gas-particle partitioning, chemical reactions). Especially in populated environments, air particulate matter can be pictured as the result of an “exploded pharmacy”, comprising just about any non- or semivolatile chemical compound occurring in the biosphere, hydrosphere, and lithosphere, or released by human activity. Besides primary chemical components, which are directly emitted by natural and anthropogenic sources; air particulate matter mostly also contains secondary chemical components, which are formed by gas-phase reactions and subsequent gas-to-particle conversion or by chemical transformation of primary particle components in the atmosphere.

Earth’s atmosphere contains mainly several different gases and additionally aerosol particles. Atmospheric gases are generally classified by their amount and residence time. The residence time (or removal time or lifetime) is an average amount of time that a particle or substance spends in a particular system (as the atmosphere). The residence time can be defined as the amount of the compound in the atmosphere divided by the rate at which this compound removed from the atmosphere. Based on the quantity, major components and trace gases, while according to residence time, constant and variable (and sometimes highly variable) gases can be distinguished. A wide range of methods can be and have been applied for the physical and chemical analysis of aerosol particles and components [Finlayson-Pitts et al., 2000; Baron PA et al., 2001]. In practice, the selection and combination of analytical methods depend on the sample type and target parameters (single particles or particle ensembles, suspended or deposited particles, physical properties or chemical composition, etc.) and requires a trade-off between sensitivity and selectivity, time and size resolution, and equipment and labor expenses.

1.4 Organic aerosols: sources and effects

Atmospheric organics constitute a significant fraction (20-90%) of fine particulate mass [Kanakidou et al., 2005], which have a large impact on Earth's radiative balance directly by absorbing or scattering the sunlight and indirectly by acting as cloud condensation nuclei (CCN) [Novakov and Penner, 1993]. The concentration of organic carbon is highly dependent on the geographical location and surrounding sources. Significant amounts of carbonaceous aerosols are also observed in the middle troposphere [Huebert et al., 2004]. A substantial fraction of the organic component of atmospheric particles consists of water-soluble, possibly multifunctional compounds [Saxena and Hildemann, 1996; Facchini et al., 1999a]. The composition of the organic aerosol fraction is highly variable in time and space and the present knowledge on the chemical composition of the carbonaceous aerosol is still incomplete, since only a limited fraction of the organic carbon is usually identified on a molecular level [Turpin et al., 2000]. Carbonaceous species that exist in the aerosol phase tend to be identified according to the manner in which they entered the particulate phase. Organic compounds that are emitted directly in particulate form are referred to as Primary Organic Aerosol (POA). Many gas-phase organic compounds undergo oxidation in the gas phase to yield products, generally oxygenated, that have sufficiently low vapor pressures that they will partition themselves between the gas and aerosol phases. Such compounds are often referred to as semi- or non-volatile, and when residing in the aerosol phase, as Secondary Organic Aerosol (SOA).

Other classes of aerosol organic compounds exist that do not fit neatly into these two categories. One class is organic compounds emitted into the atmosphere in vapor form, which subsequently condense into the aerosol phase without undergoing gas-phase chemistry. Since these compounds can be identified with a particular source, it seems most appropriate that they fall into the POA category. Another class of compounds is gas phase organic species that are absorbed into cloud droplets and subsequently end up in the aerosol phase when the cloud droplets evaporate and leave residual aerosol. Again, the distinction can be drawn as to whether the compound was emitted directly by a source or resulted from chemical processing in the atmosphere, in terms of its categorization as POA or SOA, respectively. Despite their significant contribution to aerosol mass, the individually identified fractions of organic aerosols (OAs) are rather small (~10– 14%) [Fu et al., 2008; Roach et al., 2010]. However, the chemical characterization of continental OAs is more studied than that over the open ocean [Fu et al., 2008; Fu et al., 2013]. As in the marine atmospheric boundary layer (MABL) could be derived from either long-range atmospheric transport of chemical constituents from the continents or sea-to-air efflux of biogenic compounds [Kawamura and Sakaguchi, 1999; Miyazaki et al., 2011]. Among organic aerosol components, the water-soluble species have a greater significance due to their CCN activity and are also linked to the formation of secondary OAs [Miyazaki et al., 2011].

1.5 Dicarboxylic acids

Dicarboxylic acids (diacids) and related polar compounds are major contributors to organic aerosol mass [Kawamura and Usukura, 1993; Sempéré and Kawamura, 2003]. Due to their low vapor pressure, dicarboxylic acids are predominantly present in the aerosol phase

[Limbeck et al., 2001]. They are ubiquitous in the atmosphere; measurements are reported from urban [Kawamura and Ikushima, 1993], continental background [Limbeck and Puxbaum, 1999], remote marine [Kawamura and Sakaguchi, 1999] and Arctic [Narukawa et al., 2002] areas. Among diacids, oxalic acid (C_2) is generally the dominant organic species in aerosols followed by malonic (C_3) or succinic (C_4) acid [Kawamura and Sakaguchi, 1999]. The concentrations and relative abundance of diacids is controlled by primary sources and secondary formation by photooxidation processes. Primary sources include fossil fuel combustion [Kawamura and Kaplan, 1987], biomass burning [Narukawa et al., 1999] and meat cooking operations [Rogge et al., 1991]. Secondary processes in the atmosphere include photooxidation of unsaturated fatty acids [Kawamura et al., 1996] and cyclic alkenes [Hatakeyama et al., 1987]. The relative contribution of these sources and their temporal and spatial variability is still unclear [Mochida et al., 2003]. Photochemical oxidation and breakdown of relatively higher diacids and other precursors are important sources of lower diacids in the atmosphere [Kawamura et al., 2005]. The removal and mixing processes also affect the ambient concentrations of these compounds during long-range transport [Mochida et al., 2003].

Low molecular weight (LMW) diacids are the most abundant organic compound class in aerosols. They can contribute to 0.2-1.8% of total carbon (TC) in urban aerosols from Tokyo [Kawamura and Ikushima, 1993], and up to 16% of TC in remote marine aerosols from the central Pacific including the tropics [Kawamura and Sakaguchi, 1999]. Over the remote North Pacific, diacids and related compounds comprise 4-52% (av. 14%) of water-soluble organic carbon (WSOC) in marine aerosols [Bikkina et al., 2015b]. They have also been identified in cloud water samples collected at a high mountain range in central Europe [Puxbaum and Limbeck, 2000], in the condensed phase at a semi-urban site in the northeastern US [Khwaja, 1995] and in Arctic aerosol [Kawamura et al., 1996]. As a result of their hygroscopic properties, dicarboxylic acids can act as cloud condensation nuclei and have an impact on the radiative forcing at earth's surface [Kerminen et al., 2000]. Diacids also participate in many biological processes. They are important intermediates in the tricarboxylic acid and glyoxylate cycles and the catabolism and anabolism of amino acids [Tedetti et al., 2006].

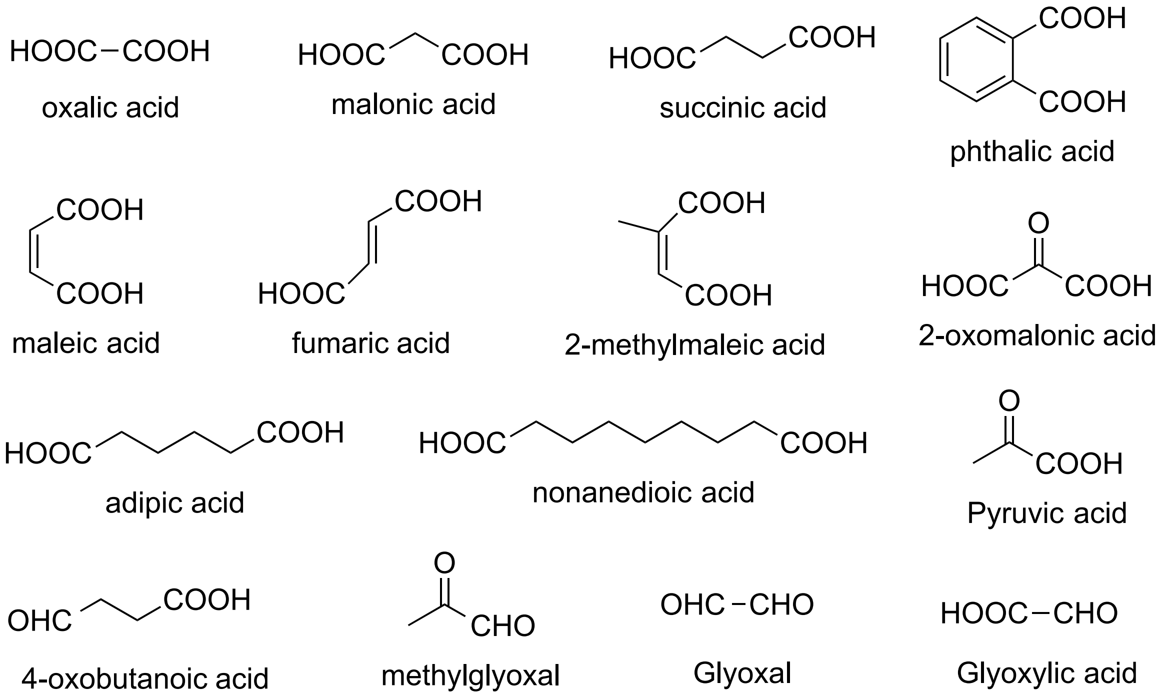

Figure 2: Chemical structures of representative dicarboxylic acids and related compounds detected in ambient aerosols.

The water-soluble dicarboxylic acids, oxocarboxylic acids, and a-dicarbonyls are some of the most extensively studied OA components over the continents (**Figure 2**) [Miyazaki et al., 2009; Wang et al., 2012]. However, the studies on their chemical characterization over the open oceanic regions are mostly for the latitudinal distributions and the studies on longitudinal distributions are very limited [Bikkina et al., 2015; Kawamura and Sakaguchi, 1999; Kawamura and Usukura, 1993; Kunwar and Kawamura, 2014]. It has been suggested that atmospheric abundances of these water-soluble organic species could have significant influence on the regional radiative forcing through direct aerosol effect (via light scattering properties), as well as cloud or fog formation processes [Facchini et al., 1999].

1.6 Miscellaneous functional diacids

The diacids possessing highly hydrophilic functional groups such as hydroxy, keto, carboxylic acid, etc., are know to be miscellaneous functional diacids (**Figure 3**). For example, tartronic acid (2-hydroxymalonic acid), malic acid (2-hydroxysuccinic acid), 2/3-hydroxyglutaric acid, 2/3- hydroxyadipic acid, tartaric acid, and oxaloacetic acid. In spite of diacids ubiquity in the environment and their high reactivity, there are some miscellaneous diacids (hydroxy- and oxodicarboxylic acids) that have been suggested to exist in the atmosphere but have never been measured in marine atmosphere. 4-oxoheptanedioic acid (4-oxopimelic acid) was the first and foremost-identified oxodiacid in atmospheric aerosol from a suburban area near Tokyo [Yokouchi and Ambe 1986]. The same compound was also measured in aerosol over the Pacific Ocean [Sakaguchi and Kawamura, 1994] and the Arctic [Narukawa et al., 2002]. Followed by oxopropanedioic acid (ketomalonic acid) in atmospheric aerosol [Kawamura et al., 1996a; Kawamura and Sakaguchi, 1999]. Other includes a series of 4- and 5-oxodiacids reported in the aerosol field sample from Finokali [Rompp A. et al., 2006].

Due to the enhanced polarity compared with diacids, these compounds should play a crucial role as CCN and IN, and act as key intermediates in the formation of smaller diacids in the atmosphere [Kawamura and Ikushima, 1993]. It is also possible that they react further in the aerosol phase through esterification reactions and serve as precursors for oligomeric humic-like substances [Tolocka et al., 2004]. Miscellaneous diacids have a low volatility, are relatively strong acids, and can readily form complexes with transition metals, which are sensitive to photo-degradation [Okochi et al., 2002]. Trifunctional hydroxy- and keto-diacids can give rise to stable homo- and hetero-molecular clusters through hydrogen bonding, being similar to the clusters proposed for bifunctional compounds [Hoffmann et al., 1998]. They may as such participate in new particle formation and growth [Kulmala et al., 2003]. Since these compounds are highly oxygenated, their study should provide useful information to better understand the oxidative reaction mechanisms of organic matter in the marine atmosphere during long-range transport. Identification and quantification of these compounds will thus help identify the principal mechanisms for the chemical aging of organic aerosols in the marine atmosphere.

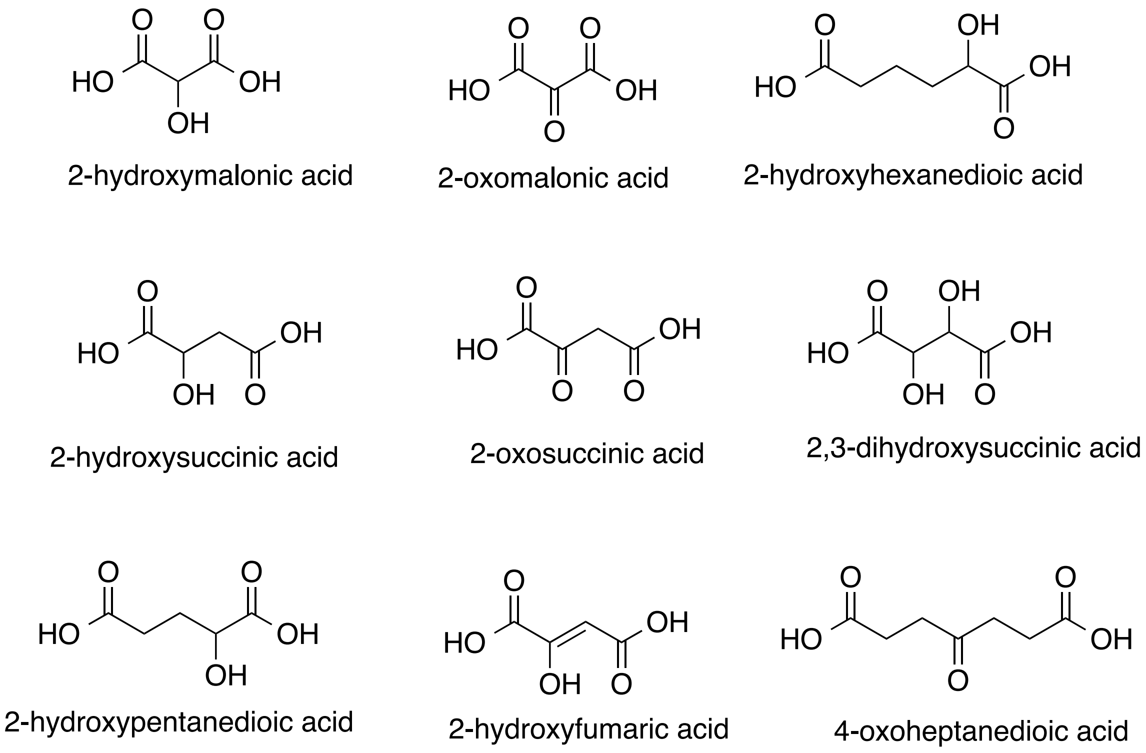
2-hydroxymalonic acid
2-oxomalonic acid
2-hydroxyhexanedioic acid
2-hydroxysuccinic acid
2-oxosuccinic acid
2,3-dihydroxysuccinic acid
2-hydroxypentanedioic acid
2-hydroxyfumaric acid
4-oxoheptanedioic acid

Figure 3: Chemical structures of representative miscellaneous dicarboxylic acids and related compounds detected in ambient aerosols.

1.7 Purpose of the study

Characterization of diacids and related compounds in organic aerosols were limited in the literature even though their contributions are highly significant to global climate change. Hence, in the current study the author will focusing on identification of homologous series of hydroxy and keto-diacids in the remote marine aerosols. Their seasonal changes, aqueous photochemical processes, and possible sources were discussed with an evidence of laboratory photooxidation experiments.

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Chapter 2

Identification of hydroxy and keto-diacids in remote marine aerosols using gas chromatography/quadruple and time of flight mass spectrometry

2.1 Introduction

Organic aerosols are present not only in the continental atmosphere, but also in the marine atmosphere [Fu et al., 2013]. They can significantly contribute to the global budget of atmospheric particles and thus have an impact on the Earth's albedo, climate, atmospheric chemistry, and biogeochemical cycles of carbon and nitrogen [Dowd et al., 2004]. The fate of hydrophilic organics in the marine atmosphere is highly uncertain. Organic compounds in marine aerosols may act as important precursors and a dominant sink for OH radicals, leading to the formation of various low molecular weight diacids by their degradation [Zhou et al., 2008]. However, water-soluble organic carbon in remote marine aerosols has not been well characterized at the molecular level [Rinaldi et al., 2010].

Diacids are dominant components of organic aerosols in the atmosphere and have been extensively studied at many locations around the world. [Wang et al., 2002; Ho et al., 2010; Mochida et al., 2003]. Because of their high water solubility and hygroscopic properties, particles enriched with diacids play an important role as cloud condensation nuclei (CCN) and ice nuclei (IN) affecting the radiative forcing of the earth [Cheng et al., 2013; Limbeck et al., 2001; Novakov and Penner 1993; Saxena et al., 1995]. Recent studies on marine aerosols have revealed high abundances of diacids with a predominance of oxalic acid followed by malonic and succinic acids [Sempéré et al., 1996]. Their concentrations and relative abundances are controlled by primary emissions and secondary formation in the atmosphere [Kawamura and Sakaguchi, 1999]. Diacids are scavenged from the atmosphere by dry and wet deposition [Grosjean and Seinfeld, 1989].

Previous studies from the western North Pacific showed that diacids contribute 1.6% of the total aerosol mass [Kawamura and Sakaguchi, 1999], suggesting that they are important constituents of marine organic aerosols. Furthermore, studies from different sites found average ratios of total diacid-C to organic carbon (OC) of 1.4% in 14 Chinese cities, [Wang et al., 2006] 0.95% in Tokyo, Japan [Kawamura et al., 2005], and 3.2% in the western Pacific [Mochida et al., 2003]. In spite of their ubiquity in the environment and their high reactivity, there are some diacid-related compounds containing hydroxyl and keto groups that have been suggested to exist in the atmosphere [Kawamura and Sakaguchi 1999; Kawamura and Ikushima, 1993], but have never been identified in marine aerosols. Due to the enhanced polarity compared with diacids, these compounds should play a crucial role as CCN and IN, and act as key intermediates in the formation of smaller diacids in the atmosphere [Kawamura and Ikushima, 1993]. It is also possible that they react further in the aerosol phase through esterification reactions and serve as precursors for oligomeric humic-like substances [Tolocka et al., 2004]. Diacids have a low volatility, are relatively strong acids, and can readily form complexes with transition metals, which are sensitive to photo-degradation [Okochi et al., 2002].

Trifunctional hydroxy and keto-diacids can give rise to stable homo- and hetero-molecular clusters through hydrogen bonding, being similar to the clusters proposed for bifunctional compounds [Hoffmann et al., 1998]. They may as such participate in new particle formation and growth [Kulmala et al., 2003]. Since, these compounds are highly oxygenated, their study should provide useful information to better understand the oxidative reaction mechanisms of organic matter in the marine atmosphere during long-range transport.

Identification and quantification of these compounds will thus help identify the principal mechanisms for the chemical aging of organic aerosols in the marine atmosphere. In this study, many unknown peaks were detected in the gas chromatograms obtained after trimethylsilyl (TMS) derivatization of the dibutyl ester fraction of remote marine aerosols. Mass spectral examination of the unknown peaks suggests that they belong to a homologous series of hydroxydiacids (hC_3di–hC_6di), including tartronic acid, malic acid, 3-hydroxyglutaric acid, 2-hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydroxyadipic acid, and tartaric acid. Some of these compounds have been individually detected in laboratory photo-oxidations [Hamilton et al., 2006] and ambient aerosol samples [Claeys et al., 2007], but there has been no report of the identification of the homologous series of hydroxyl diacids formed in marine aerosols. Many isomeric ketodicarboxylic acids have been identified in atmospheric aerosol particles [Rompp et al., 2006]. Oxaloacetic acid was suggested to exist in aerosols by the photo-oxidation of succinic acid, [Charbouilot et al., 2012] but has not previously been detected in ambient aerosols. Here, oxaloacetic acid was successfully identified as isomeric forms in marine aerosols. Tentative mass spectrometric fragmentation pathways are proposed for the derivatized unknown hydroxydiacids and oxaloacetic acid in marine aerosols.

2.2 Samples and analytical protocol

2.2.1 Reagents and chemicals

Special grade organic solvents and authentic malic, tartaric, and oxaloacetic acids were purchased from Wako Pure Chemical Industries (Tokyo, Japan). Tartronic acid and 3-hydroxyglutaric acid were purchased from Alfa Aesar (Heysham, UK) and Toronto Research Chemicals (Toronto, Canada), respectively. The purities of authentic standards are greater than 97%. All the organic solvents were redistilled in the laboratory prior to use. All the glassware was cleaned with soap solution, rinsed with tap water followed by distilled water, dried and baked at 450 °C overnight. Just before use, the glassware was rinsed three times with organic-free pure water, methanol, and dichloromethane.

2.2.2 Aerosol sampling

Total suspended particles (TSP) were collected on a weekly basis from 1 December 2010 to 30 November 2011 (n = 53) using pre-combusted (450 °C) quartz fiber filters and a high volume air sampler at a flow rate of 1.0 m^3 min^{-1} at the Ogasawara Downrange Station of the Japan Aerospace Exploration Agency (JAXA) at Chichijima Island (27°04'N; 142°13'E) (**Figure 1**) in the western North Pacific, an outflow region of the Asian dust and polluted air masses from China and other neighboring countries. The sampling periods were generally 5 days. After sampling, the filters were placed in precombusted glass jars with a Teflon-lined screw cap, sent to Hokkaido University in Sapporo (Japan), and stored in a freezer room at -20 °C prior to analysis.

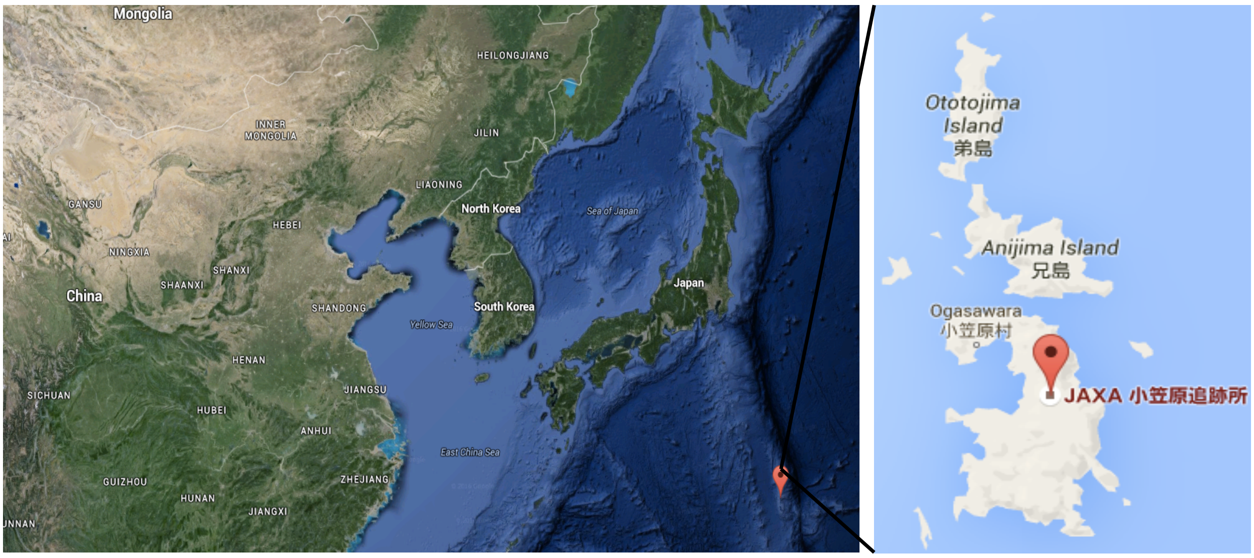


Figure 1. Map showing the geographical region of Chichijima Island, where aerosol sampling was performed.

2.2.3 Preparation of dibutyl esters

Filter aliquots were extracted three times with 10 mL organic free pure water under ultrasonication for 10 min. To remove insoluble particles and filter debris, the extracts were passed through a glass column (Pasteur pipette) packed with quartz wool into a pear-shaped flask. The water extracts were pH adjusted to 8.5-9.0 with 0.05 M aqueous KOH solution and concentrated almost to dryness using a rotary evaporator under a vacuum. A 14% BF_3/n-butanol solution was added to the concentrates in the flask to allow esterification to take place at 100 °C for 1 h. During the reaction, carboxyl groups are derivatized to their butyl esters, and keto groups to dibutoxy acetals. The derivatives were extracted with 10 mL of n-hexane after adding 10 mL of organic-free water and 0.5 mL of acetonitrile. Acetonitrile transfers the excess n-butanol into the aqueous phase efficiently. The hexane layer was further washed with organic-free water (2 Å~ 10 mL). Using a rotary evaporator under vacuum and a nitrogen blow-down system, the extracts were concentrated and then dissolved in 100 µL of n-hexane.

2.2.4 BSTFA derivatization

An aliquot of the dibutyl ester fraction containing hydroxyl diacids was dried under a gentle stream of nitrogen, and hydroxyl diacid dibutyl esters were derivatized to the corresponding TMS ethers with 50 µL of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) at 80 °C for 30 min. The derivatives were dried under a nitrogen stream, dissolved in n-hexane (50 µL) and analyzed using gas chromatography/quadrupole mass spectrometry (GC/QMS) and gas chromatography/time of- flight mass spectrometry (GC/TOFMS). Their concentrations were determined using gas chromatography–flame ionization detection (GC-FID). Known amounts of authentic standards (tartronic, malic, 3-hydroxyglutaric, tartaric, and oxaloacetic acids) were spiked on a precombusted quartz fiber filter and derivatized to butyl esters-TMS ethers by the procedure described above. We found that the recoveries of hydroxyl diacids were more than 80%. The analytical errors in duplicate analyses of the aerosol sample (QFF3769) for hydroxy- and keto-diacids are about 10%.

2.2.5 Instrumentation

GC/TOFMS analyses were performed using an Agilent Technologies model 7890A gas chromatograph system coupled to JEOL Accu TOF-GCv 4G mass spectrometer (JEOL, Tokyo, Japan). The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV and the mass analyzer was scanned in the range *m/z* 40 - 650. The mass spectrometer resolution is > 8000 at a mass range of *m/z* 4 - 5000. The gas chromatographic separation was carried out on an Agilent DB-5MS fused silica capillary column (30 m long, 0.25 mm i.d., 0.25 µm film thickness), (Agilent Technologies, Tokyo, Japan). For GC the temperature was programmed from 50 °C for 2 min, increased from 50 to 120 °C at 15 °C min^{-1}, then to 305 °C at 5 °C min^{-1} with a final isothermal hold. The splitless mode was used at an injection temperature of 280 °C and 16.3 psi pressure. This mass spectrometer provides high sensitivity, fast detection, and a high dynamic range.

GC-FID analyses were performed using a Hewlett Packard HP 6890 gas chromatograph system. GC/MS analyses were carried out on an Agilent 5975C mass spectrometer linked to an Agilent 7890A gas chromatograph system. The mass analyzer was scanned in the range *m/z* 50-650 and the ion source was in EI mode. In both systems, similar gas chromatographic conditions were maintained as described above. The GC/MS data were acquired and processed with the Agilent GC/MSD Chemstation software.

2.3 Chemical analysis by GC, GC/MS, and GC/TOFMS

In order to distinguish dicarboxylic acids with and without hydroxyl groups, the water extracts of marine aerosols were subjected to a two-step derivatization procedure, i.e., butylation followed by trimethylsilylation, by which carboxyl groups are converted to butyl esters whereas hydroxyl groups are converted to TMS ethers. Methylation TMS-derivatization has been often used for hydroxydicarboxylic acids [Rompp et al., 2006], but in this study the butylation TMS method was used because butyl ester derivatization is highly selective for bifunctional compounds [Bao et al., 2012] and the recoveries are high even for small diacids. On the other hand, methyl esters of diacids are sometimes highly volatile and thus are lost by evaporation during the analytical procedure [Haddada et al., 2009].

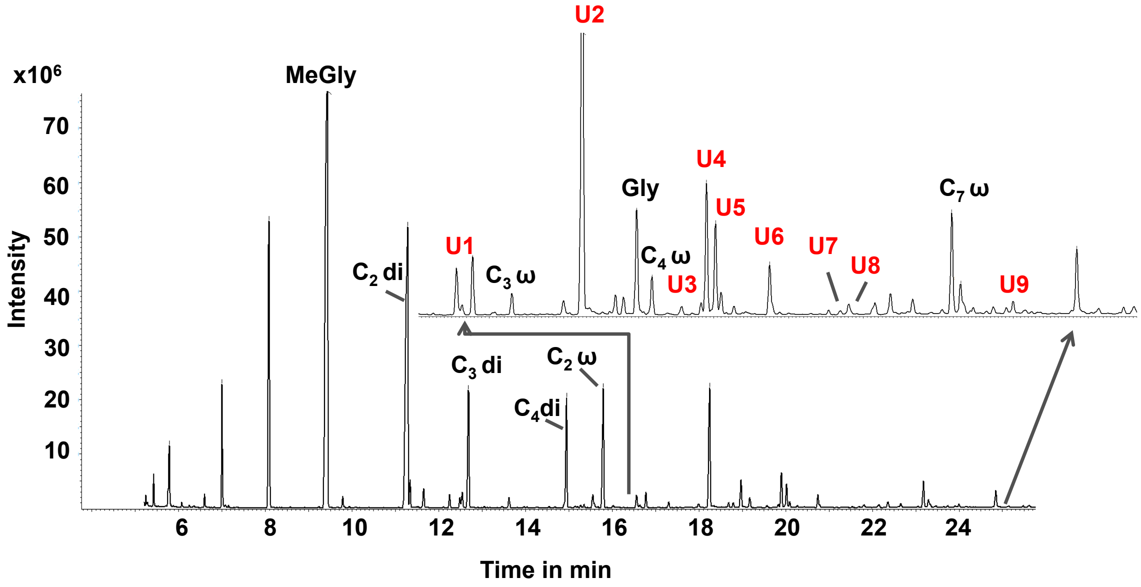


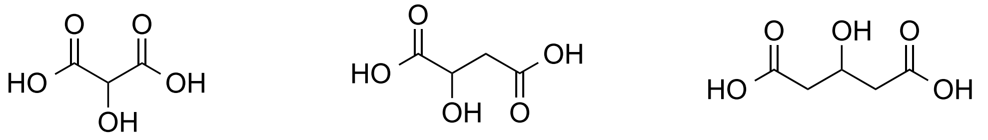
Figure 2. Reconstructed (GC/TOFMS) total ion chromatogram obtained for (a) butyl ester TMS-derivatized of the marine aerosol sample (QFF3769) obtained from Chichijima Island in the western North Pacific. Identification: methylglyoxal (MeGly), oxalic acid (C_2 di), malonic acid (C_3 di), succinic acid (C_4 di), pyruvic acid (Pyr), glyoxylic acid (C_2 ω), glutaric acid (C_5 di), methylglutaric acid (iC_6), 3-oxopropanoic acid (C_3 ω), adipic acid (C_6 di), glyoxal (Gly), 4-oxobutanoic acid (C_4 ω), pimelic acid (C_7 di), phthalic acid (Ph), 4-oxopimelic acid (kC_7), and 7-oxoheptanoic acid (C_7 ω). Chemical structures of the novel compounds identified in the present study: U1, tartronic acid; U2, malic acid; U3, enol oxoloacetic acid; U4, 3-hydroxyglutaric acid; U5, 2-hydroxyglutaric acid; U6, tartaric acid; U7, 2-hydroxyadipic acid; U8, 3-hydroxyadipic acid; and U9, keto oxoloaceticacid.

2.4 Characterization of Unknown Compounds U1-U9

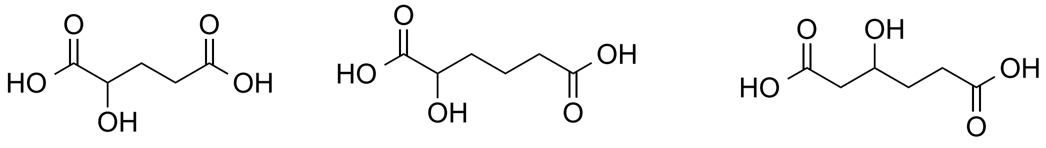
Figure 2 shows reconstructed total ion chromatogram of butylated-TMS derivatives from Chichijima Island in the western North Pacific (QFF3769). In the gas chromatogram (**Figure 2**, nine new peaks were observed after TMS derivatization of the diacid butyl ester fraction. They are unknown structures and thus named as compound U1 to U9, which are considered to contain additional hydroxyl- and keto- groups in their diacid structures. The detailed interpretation and characterization for unknown compounds U1 to U9 are presented below.

2.4.1 Tartronic acid

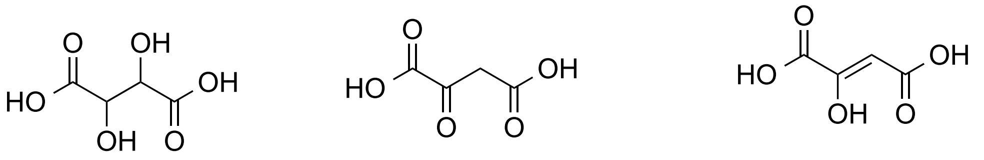
The EI mass spectra for the butyl ester TMS derivative of unknown compound U1 allow us to infer the molecular weight (MW) of the underivatized compound as 120 (retention time (RT): 16.5 min; MW of 304 for the butyl ester TMS derivative; $[M\text{-}CH_3]^+$ ion at m/z 289; $C_{13}H_{25}O_5Si$; measured mass: 289.14569, error: -5 ppm). These results suggest that U1 is tartronic acid (2-hydroxymalonic acid). Tartronic acid has been postulated to exist in marine aerosols following photo-oxidation of malonic acid [Grosjean and Seinfeld 1989], but no evidence has been provided for its presence in ambient aerosol samples. In the present study, we successfully identified tartronic acid (**Figure 3(a)**) in remote marine aerosols.



(a) tartronic acid (b) malic acid (c) 3-hydroxyglutaric acid



(d) 2-hydroxyglutaric acid (e) 2-hydroxyadipic acid (f) 3-hydroxyadipic acid

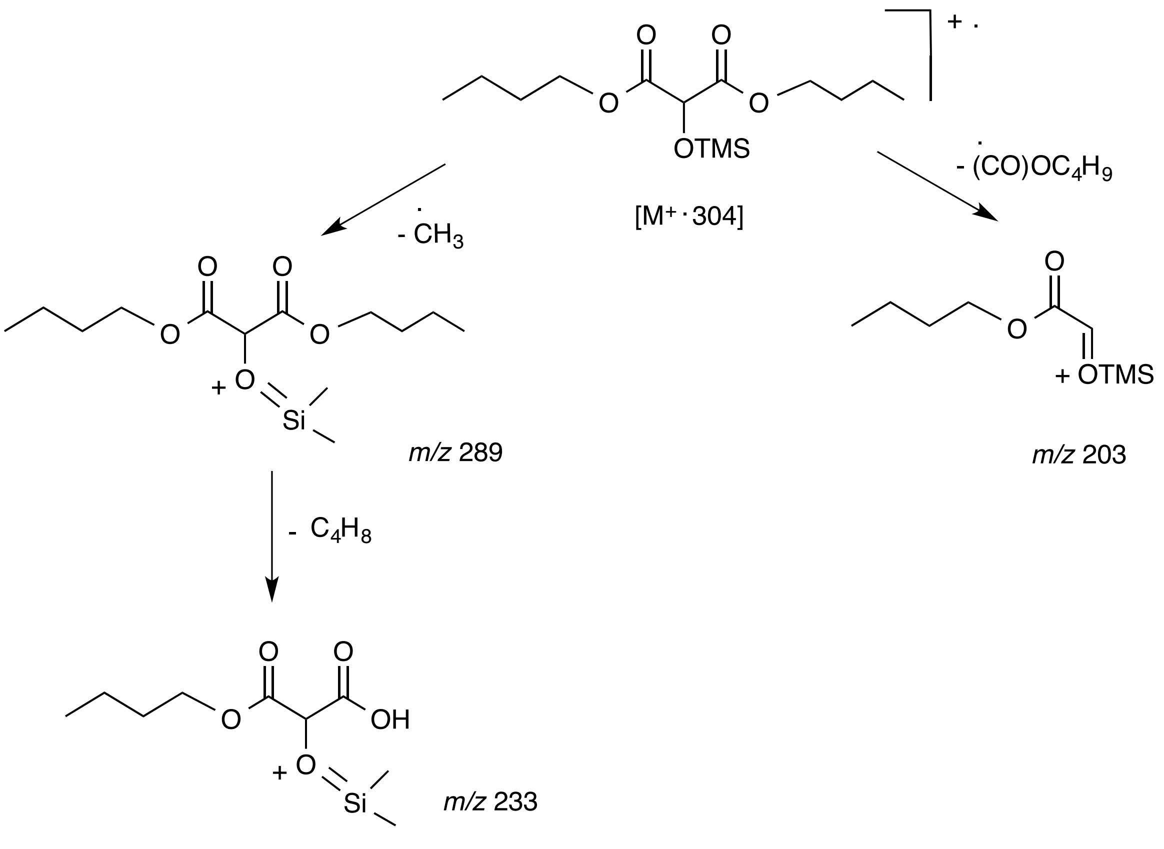


(g) tartaric acid (h) keto-oxaloacetic acid (i) enol-oxaloacetic acid

Figure 3. Chemical structures of hydroxy and keto-dicarboxylic acids identified in remote marine aerosols from the western North Pacific.

The mass spectrum of the tartronic acid derivative (**Figure 4(a)**) shows fragment ions at *m/z* 289, 233, 203, 177, 147,131, 73, 57 and 41. Structurally informative ions include *m/z*

289 [M-15]$^+$, due to loss of a methyl radical from the TMS moiety, [Petersson et al., 1972] while the peak at *m/z* 203 [M-101]$^+$ could be explained by loss of a butoxycarbonyl radical ((CO) OC_4H_9) via an α-cleavage, which is not detectable in the EI mode, [Kawamura et al., 1990] and the peak at *m/z* 233 [M-15-56]$^+$ may be due to elimination of butene (C_4H_8, 56 u) by a McLafferty rearrangement. Proposed fragmentation pathways those are structurally informative for the butyl ester TMS derivative of unknown U1 (tartronic acid) are summarized in **Scheme 1**. The TOFMS spectrum of a tartronic acid standard was compared with that of the unknown compound U1 (**Figure 4(b)**) and showed good agreement and a similar retention time, allowing us to confirm U1 as tartronic acid.



Scheme 1. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U1, which is identified as tartronic acid.

To our knowledge, this is the first identification of tartronic acid in ambient aerosols. We found that the measured concentration of tartronic acid ranged from 0.01 to 5.27 ngm^{-3} in total suspended particles collected at Chichijima Island during the period of 1 December 2010 to 30 November 2011 (n = 53). This wide range is due to seasonal changes in the air masses. The sampling site is strongly influenced by westerly winds in winter to spring, oceanic clean air masses in summer, and both oceanic and continental air masses in autumn, [Mochida et al., 2003] affecting the concentration of tartronic acid in remote marine aerosols.

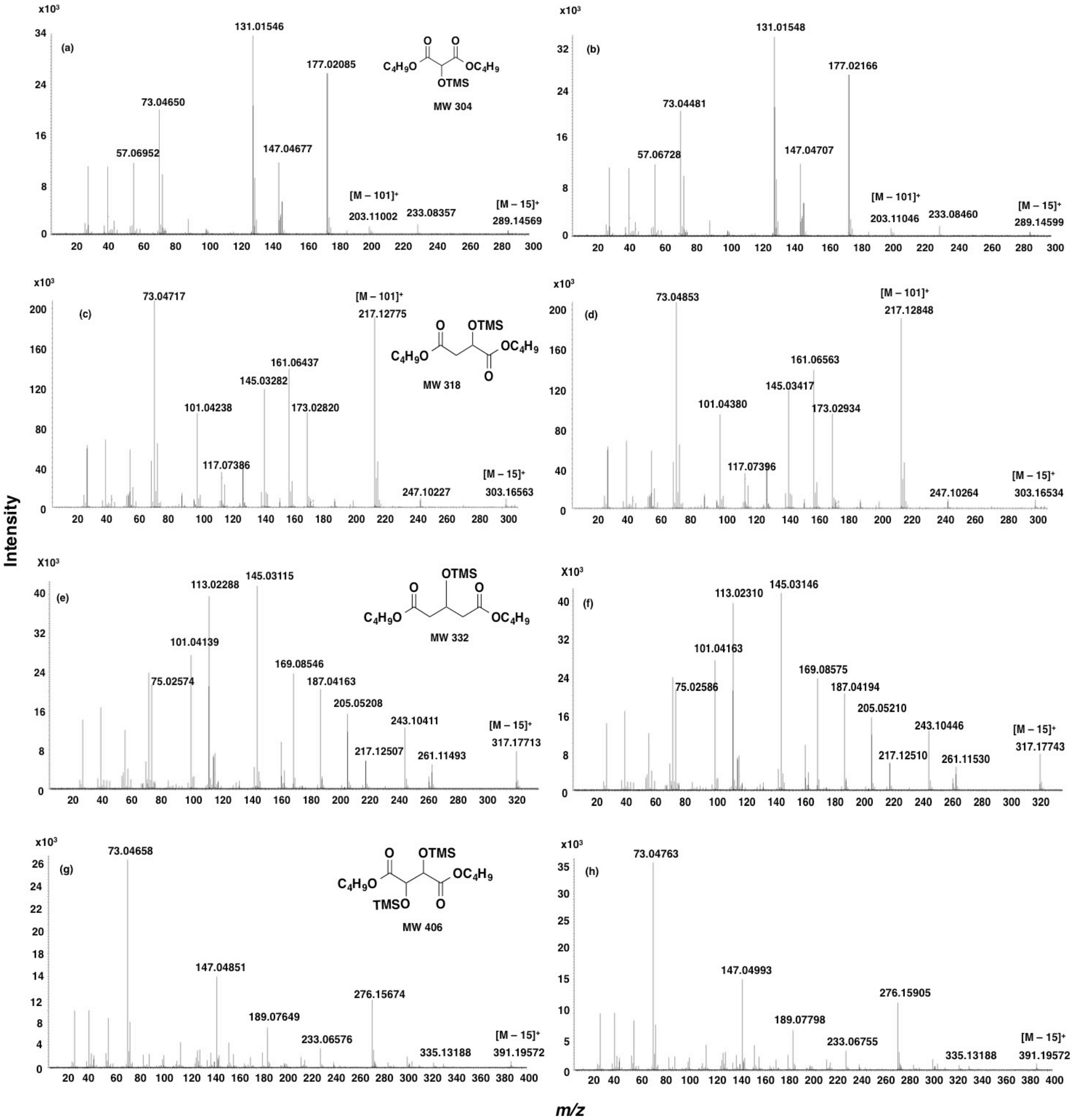
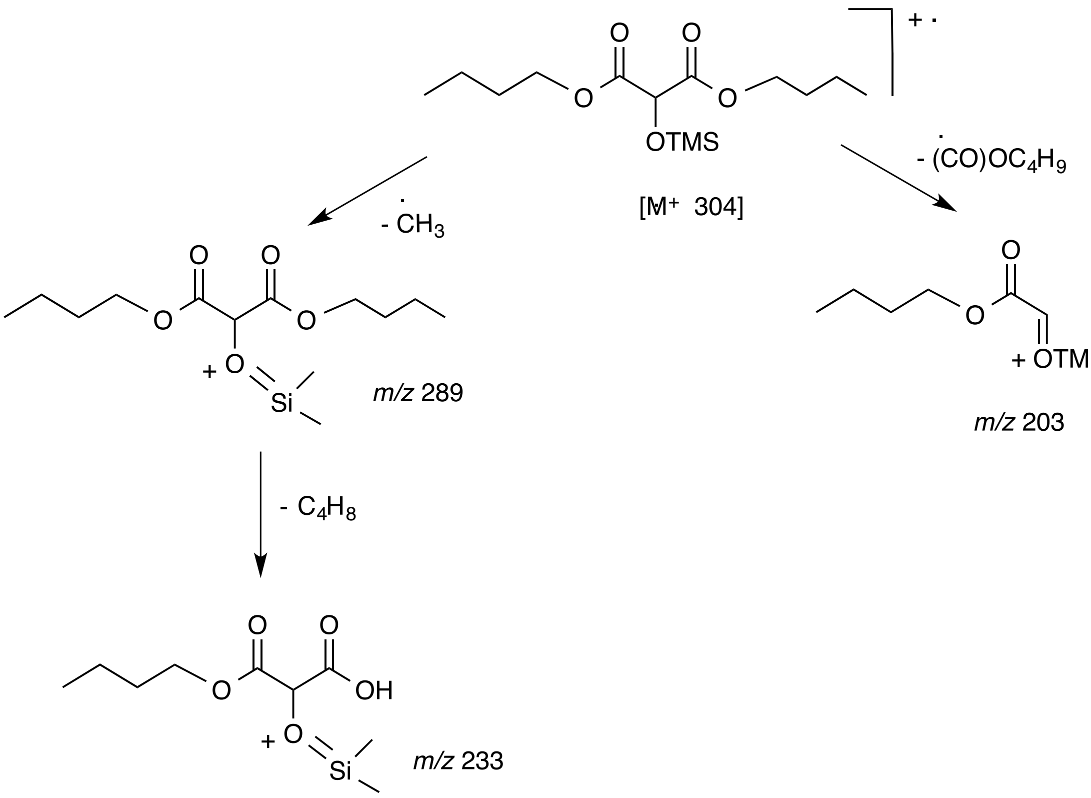


Figure 4. Mass spectra of dibutyl ester TMS-derivatives of (a) tartronic acid (U1), (b) tartronic acid (standard), (c) malic acid (U2), (d) malic acid (standard), (e) 3-hydroxyglutaric

acid (U4), (f) 3-hydroxyglutaric acid (standard), (g) tartaric acid (U6), (h) tartaric acid (standard).

2.4.2 Malic acid

The EI mass spectral data for the butyl ester TMS derivative of unknown compound U2 allow us to infer that the MW of the underivatized compound is 134 (RT: 18.2 min; MW of 318 for the butyl ester TMS derivative; $[M\text{-}CH_3]^+$ ion at *m/z* 303; $C_{14}H_{27}O_5Si$; measured mass: 303.16563, error: 9 ppm). These results suggest that compound U2 is malic acid (2-hydroxysuccinic acid) (**Figure 3(b)**). Malic acid has been proposed to result from the hydroxylation of succinic acid in marine aerosols using 14% BF_3/n-butanol as the derivatizing agent [Kawamura and Sakaguchi 1999]. We found that it was the most abundant hydroxyl diacid in marine aerosols. Because the hydroxyl group was underivatized in the previous technique for diacid dibutyl ester derivatization, malic acid dibutyl ester often showed peak tailing in the chromatogram, which may lead to underestimation of the concentrations of this compound [Rohrl and Lammel 2002]. Here, we addressed this problem by derivatizing the hydroxyl groups to TMS ethers with BSTFA. The malic acid concentration in all the measured samples (n = 53) ranged from 0.03 to 14.7 ng m^{-3}, which is ca 3 times higher than those reported in previous studies without TMS derivatization.



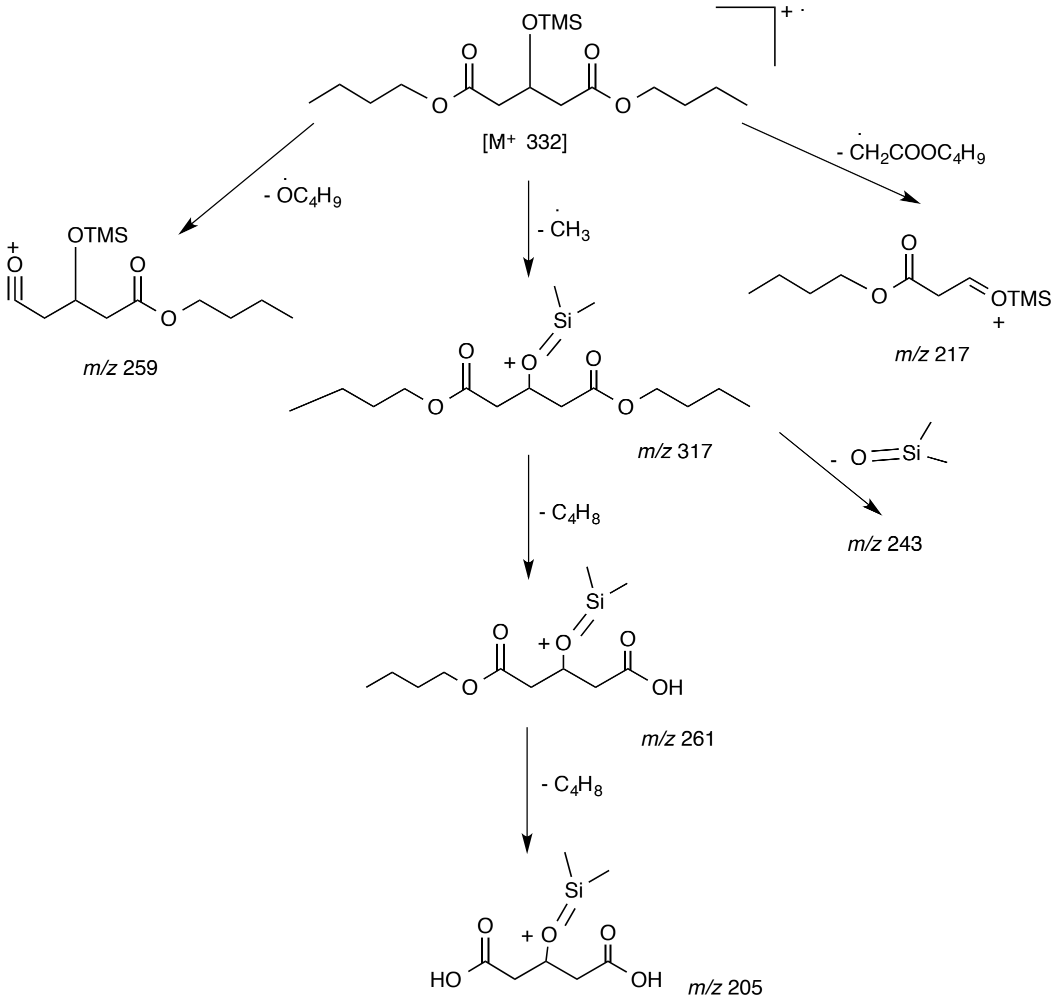
Scheme 2. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U2, which is identified as malic acid.

The mass spectrum of the malic acid derivative shows fragment ions at *m/z* 303, 247, 217, 173, 161, 145, 117, 101, 73, 57 and 41 (**Figure 4(c)**). Structurally informative ions include m/z 303 $[M-15]^+$, *m/z* 217 $[M-101]^+$ and the peak at *m/z* 247 $[M-15-56]^+$, which could be explained by a similar pathway to that described above for the dibutyl ester TMS derivative of tartronic acid. Proposed fragmentation pathways for the butyl ester TMS derivative of unknown U2 (malic acid) are summarized in **Scheme 2**. A malic acid standard TOFMS spectrum was obtained (**Figure 4(d)**) and compared with that of the unknown compound U2, showing good agreement and a similar retention time, allowing the confirmation of U2 as malic acid.

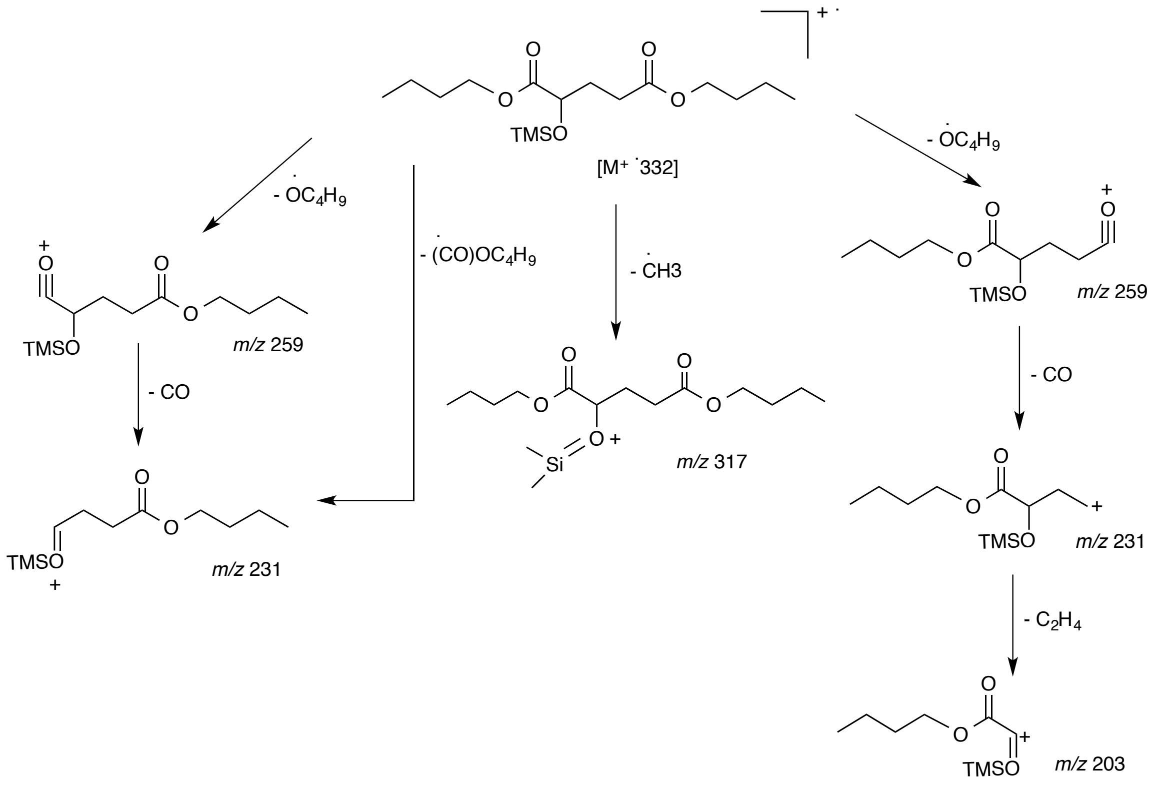
2.4.3 3-and 2-hydroxyglutaric acids

The EI mass spectra for the butyl ester TMS derivatives of both unknown compounds U4 and U5 suggest that the MW of the underivatized compounds is 148 with a MW of 332 for butyl ester TMS derivatives and *m/z* 317 for $[M-CH_3]^+$ ion. The RTs of U4 and U5 are 19.1 min and 20.03 min, and the measured *m/z* values of $C_{15}H_{29}O_5Si$ are 317.17713 and 317.17765 with errors of -4 ppm and -2 ppm, respectively. These results suggest that U4 and U5 are positional isomers, which we have assigned to 3-hydroxyglutaric and 2-hydroxyglutaric acids (**Figures. 3(c) and 3(d)**). Based on the mass spectral fragmentation patterns we could distinguish both isomers. 3-hydroxy- and 2-hydroxyglutaric acids have been reported in fine PM2.5 aerosols from rural K-puszta, Hungary, as photo-oxidation products of α-pinene [Claeys et al., 2007]. The butyl ester TMS derivative of compound U4 shows fragment ions at m/z 317, 261, 259, 243, 217, 205, 187, 169, 145, 113, 101, 73, 57 and 41 (**Figure 4(e)**).

Structurally informative ions Include *m/z* 317 $[M-15]^+$ and *m/z* 261 $[M-15-56]^+$, while the peak at *m/z* 259 $[M–73]^+$ may be due to the loss of a butoxy radical (OC_4H_9) from the molecular ion by α-cleavage. The *m/z* 217 ion ($[M-115]^+$) could be explained by loss of a butyl ethanoate radical [$CH_2COOC_4H_9$] from the molecular ion by β-cleavage, suggesting that the hydroxyl group is situated on the third carbon [Zaikin and Halket 2009]. The 3-hydroxyglutaric acid standard TOFMS spectrum was obtained (**Figure 4(f)**) and compared with that of U4 (**Figure 4(e)**).



Scheme 3. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U4, which is identified as 3-hydroxyglutaric acid.



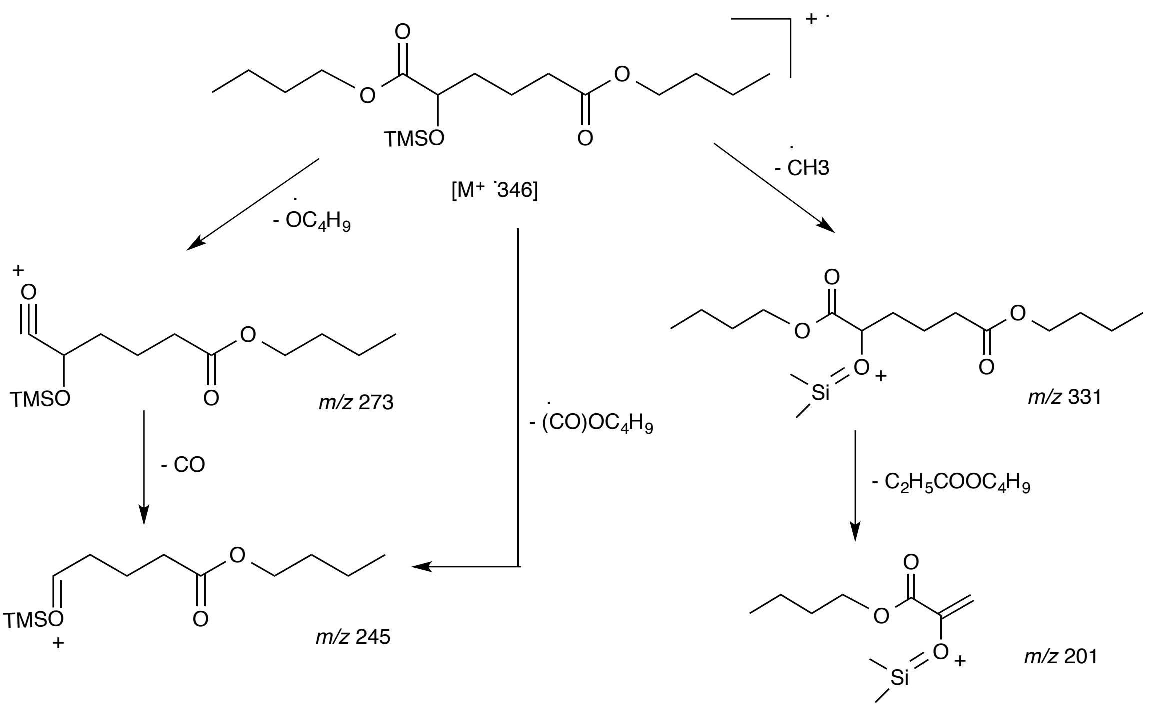
Scheme 4. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U5, which is identified as 2-hydroxyglutaric acid.

The results showed a good agreement and similar retention time allowing confirmation of U4 as 3-hydroxyglutaric acid. Proposed fragmentation pathways for the butyl ester TMS derivative of 3-hydroxyglutaric acid are summarized in **Scheme 3**. The atmospheric concentration of 3-hydroxyglutaric acids in all measured samples (n = 53) ranged from 0.01 to 4.98 ng m^{-3}. The butyl ester TMS derivative of compound U5 shows fragment ions at *m/z* 317, 259, 231, 203, 187, 175, 159, 129, 85, 73, 57 and 41 (Fig. 5(a)). Structurally informative ions include *m/z* 317 $[M-15]^+$ and *m/*z 259 $[M-73]^+$. The peak at *m/z* 231 $[M-101]^+$ or via $[M-73-28]^+$ could be due to loss of a molecule of carbon monoxide (CO, 28 u) from the $[M-73]^+$ ion, and *m/z* 203 could be explained by the elimination of a molecule of ethene (C_2H_4, 28 u) from the ion of *m/z* 231. Tentative fragmentation pathways for the butyl ester TMS derivative of unknown U5 (2-hydroxyglutaric acid) are summarized in **Scheme 4**.

The fragment ion of *m/z* 231 $[M-101]^+$ suggests that the hydroxyl group is situated at the second carbon, thus helping us to distinguish 2-hydroxyglutaric acid from 3-hydroxyglutaric acid. Based on these experimental observations, U5 is assigned to 2-hydroxyglutaric acid. The atmospheric concentration of 2-hydroxyglutaric acids in all the measured samples (n = 53) ranged from 0.03 to 4.79 ng m^{-3}.

2.4.4 2- and 3-hydroxyadipic acids

The EI mass spectra for the butyl ester TMS derivatives of both U7 and U8 implied that the MW of the underivatized compounds is 162 with a MW of 346 for the butyl ester TMS derivatives and with a $[M-CH_3]^+$ ion at *m/z* 331. The RTs of U7 and U8 are 21.7 min and 21.8 min and the measured *m/z* values of $C_{16}H_{31}O_5Si$ are 331.19289 and 331.19226 with errors of -4 ppm and -5 ppm, respectively. Thus, the mass spectral information indicates that compounds U7 and U8 are positional isomers, attributed to 2-hydroxyadipic and 3-hydroxyadipic acids, respectively (**Figures. 3(e) and 3(f)**). Based on the mass spectral fragmentation patterns we could distinguish the two isomers. 2-hydroxyadipic and 3-hydroxyadipic acids have not been identified in marine aerosols. On the other hand, 3-hydroxyadipic acid has been identified as a reaction product during laboratory photo-oxidation of cyclohexane [Kalberer et al., 2000].



Scheme 5. Proposed fragmentation pathways of the butyl ester TMS-derivative of unknown compound U5, which is identified as 2-hydroxyadipic acid.

The butyl ester TMS derivative of compound U7 shows fragment ions at *m/z* 331, 273, 245, 201, 173, 129, 99, 73, 57 and 41 (**Figure 5 (b)**). Structurally informative ions include *m/z* 331 $[M-15]^+$, m/z 273 $[M-73]^+$ and *m/z* 245 $[M-73-28]^+$ or $[M-101]^+$. Tentative fragmentation pathways for the butyl ester TMS derivative of U7 (2-hydroxyadipic acid) are summarized in **Scheme 5**.

The butyl ester TMS derivative of compound U8 shows fragment ions at *m/z* 331, 273, 231, 217, 201, 157, 127, 85, 73, 57, and 41 (**Figure 5 (c)**). Structurally informative ions include *m/z* 331 $[M-15]^+$ and *m/z* 273 $[M-73]^+$. The peak at *m/z* 217 may be due to neutral loss of CO (28 u) and ethene (C_2H_4, 28 u) from the $[M-73]^+$ ion whereas *m/z* 231 $[M-115]^+$ could be explained by loss of a butyl ethanoate radical [$CH_2COOC_4H_9$] from the molecular ion by β-cleavage, suggesting that the hydroxyl group is situated at the third carbon. Tentative fragmentation pathways for the butyl ester TMS derivative of unknown U8 (3-hydroxyadipic acid) are summarized in **Scheme 6**. The fragment ions at *m/z* 245 $[M-101]^+$

and *m/z* 231 $[M\text{-}115]^+$ in U7 and U8 indicate the location of the hydroxyl group [Zaikin and Halket 2009]. Based on these experimental observations, U7 and U8 are assigned to 2-hydroxyadipic and 3-hydroxyadipic acid, respectively. The concentrations of 2-hydroxyadipic and 3-hydroxyadipic acid in all the measured samples (n = 53) ranged from 0.04 to 0.73 ng m^{-3} and from 0.19 to 0.82 ng m^{-3}, respectively.

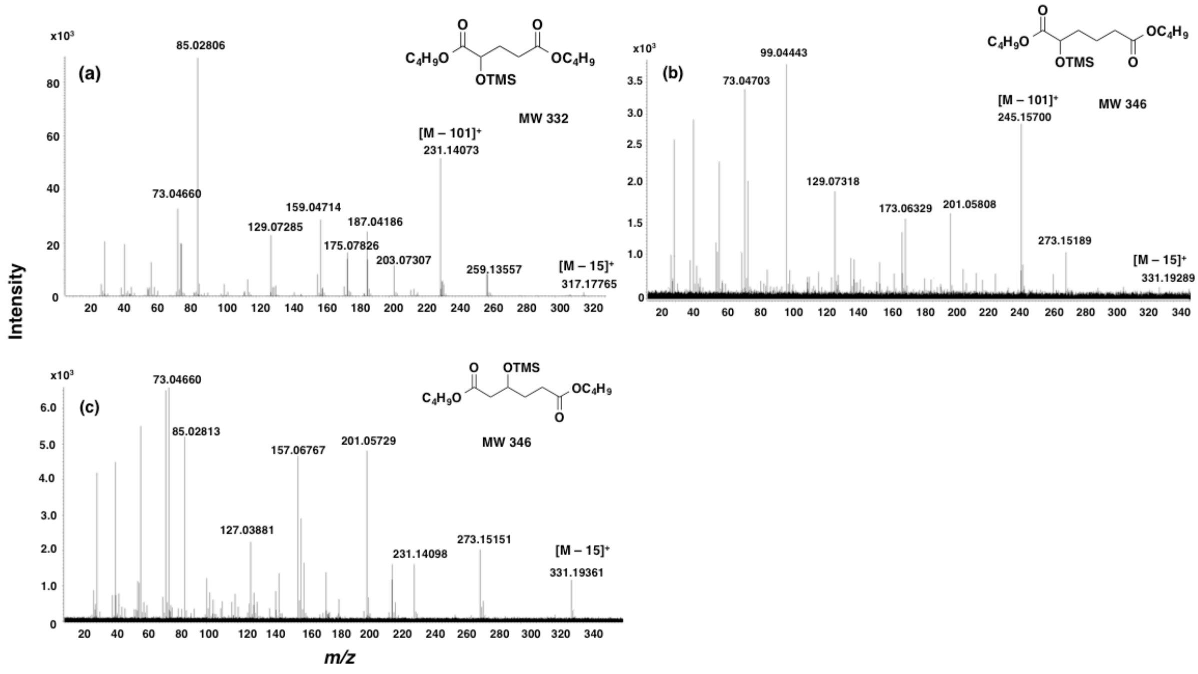
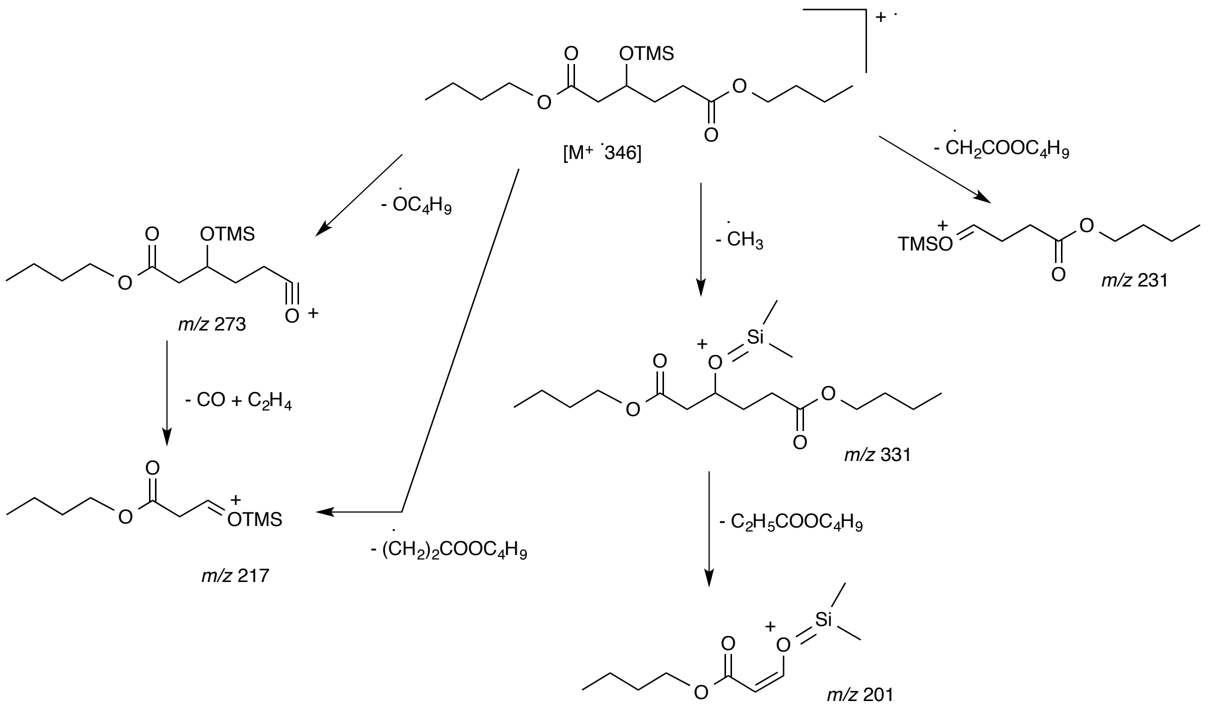


Figure 5. Mass spectra of dibutyl ester TMS-derivatives of (a) 2-hydroxyglutaric acid, (b) 2-hydroxyadipic acid, (c) 3-hydroxyadipic acid, isolated from the remote marine aerosol samples collected in the western North Pacific.



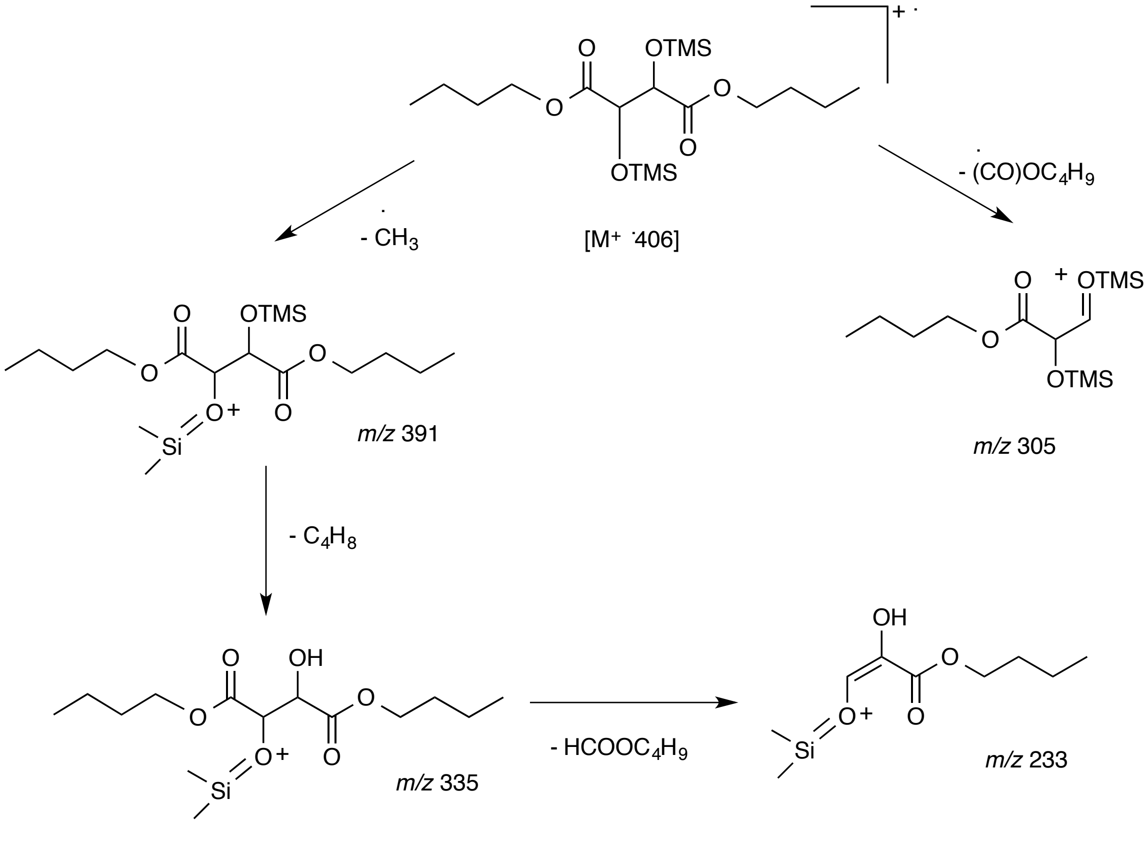
Scheme 6. Proposed fragmentation pathways of the butyl ester TMS-derivative of unknown compound U6, which is identified as 3-hydroxyadipic acid.

2.4.5 Tartaric acid

The EI mass spectra for the butyl ester TMS derivative of unknown compound U6 suggested that the MW of the underivatized compound is 150 (RT 20.7 min) and the MW is 406 for the butyl ester TMS derivative with a $[M-CH_3]^+$ ion of *m/z* 391. The measured *m/z* value of $C_{17}H_{35}O_6Si_2$ is 391.19572 with an error of -4 ppm. This information suggests that compound U6 is tartaric acid (2,3-dihydroxysuccinic acid) (**Figure 3 (g)**). Tartaric acid has been reported in continental aerosols [Rohrl and Lammel 2002], however, there is no report of its presence in marine aerosols. This is the first report of the presence of tartaric acid in continentally influenced remote marine aerosols.

The mass spectrum of the butyl ester TMS derivative of tartaric acid presents characteristic fragment ions at *m/z* 391, 335, 305, 276, 233, 189, 147 and 73 (**Figure 4 (g)**).

Structurally informative ions include *m/z* 391 $[M-15]^+$, m/z 335 $[M-15-56]^+$ and m/z 305 $[M-101]^+$. The peak at *m/z* 233 could be caused by the combined loss of a butoxycarbonyl ((C = O) OC_4H_9) and hydrogen radical by α-cleavage from the ion of *m/z* 335. The abundant fragment ions at *m/z* 147 and 73 are commonly seen in trimethylsilylethers [Rontani et al., 2004; Hoffmann and Stroobant 2007]. The tartaric acid standard TOFMS spectrum was obtained (**Figure 3(h)**) and compared with that of U6 (**Figure 3(g)**), showing good agreement and a similar retention time, allowing the confirmation of U6 as tartaric acid. Proposed fragmentation pathways for the butyl ester TMS derivatives of tartaric acid are summarized in **Scheme 7**. The concentration of tartaric acid in all the studied samples (n = 53) ranged from 0.01 to 2.65 ng m^{-3}.



Scheme 7. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U6, which is identified as tartaric acid.

2.4.6 Oxaloacetic acid

Many isomeric keto-dicarboxylic acids were reported in a previous study of atmospheric particles with their sources and formation mechanisms [Romp et al., 2006]. However, oxaloacetic acid (3-oxodicarboxylic acid) has not been detected in atmospheric aerosols, possibly due to its rapid decarboxylation. In the present study, we successfully identified unknown compounds U3 and U9 as isomers of oxaloacetic acid in the remote marine aerosol samples. The EI mass spectra for the butyl ester TMS derivatives of the two unknown compounds, U3 and U9, suggest that the MW of the underivatized compounds is 132. The RTs of U3 and U9 are 19.5 min and 24.0 min, respectively. The derivative of U3 provides a fragment ion at *m/z* 301 $[M-CH_3]^+$ with a measured *m/z* value of $C_{14}H_{25}O_5Si$ of 301.14764 with an error of 2 ppm, whereas U9 provides a fragment ion of *m/z* 273 $[M-101]^+$ with a measured *m/z* value of $C_{15}H_{29}O_4$ at 273.20609 with an error of -2 ppm. This mass spectral information indicates compounds U3 and U9 are isomers of oxaloacetic acid: U3 is the enolic form of oxaloacetic acid whereas U9 is the keto form of oxaloacetic acid (**Figures. 3(h) and 2(i)).**

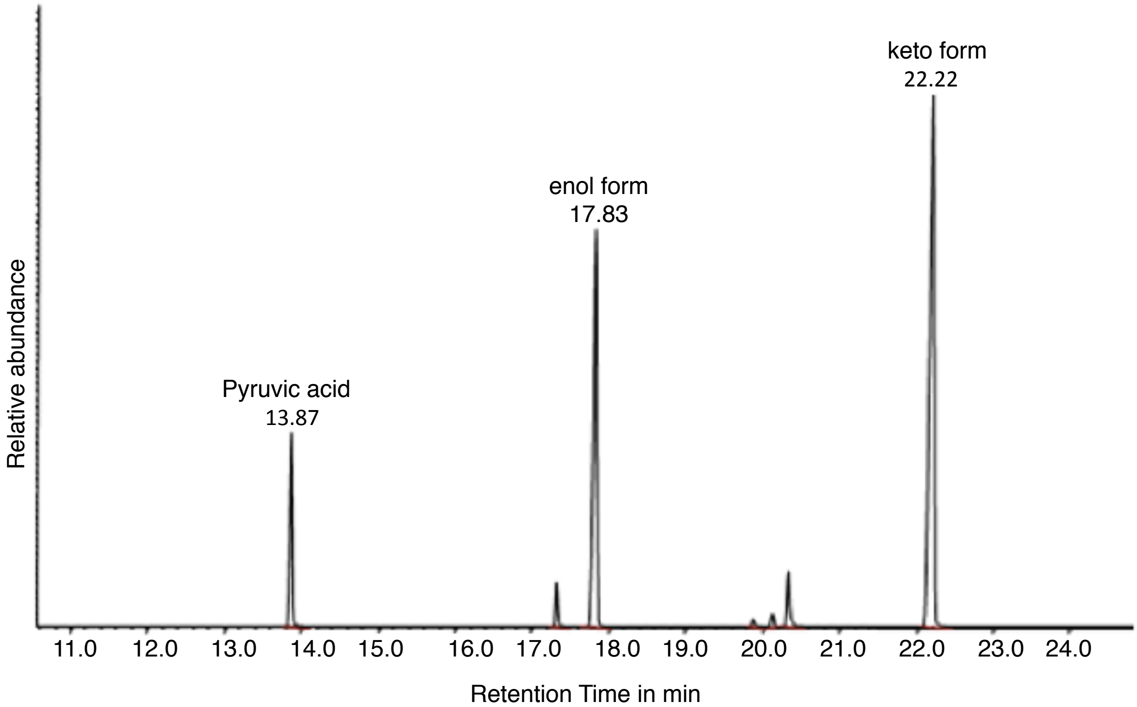


Figure 6. Gas chromatogram of butyl ester TMS-derivatized authentic oxaloacetic acid, which exists in three forms.

Authentic oxaloacetic acid was derivatized by the procedures described above, followed by GC/MS measurements. The gas chromatogram shows three peaks (Fig. 6). The mass spectral analysis of these peaks demonstrated that two of the peaks are the keto and enolic forms of oxaloacetic acid. The third peak was confirmed as the butyl ester of pyruvic acid. Based on the comparison of QMS and TOFMS spectra for authentic oxaloacetic acid with those of unknowns U3 and U9, we confirmed that oxaloacetic acid may exist in atmospheric aerosols as three different forms: the keto form (U9), the enolic form (U3) and its decarboxylated form (pyruvic acid). The transformation of oxaloacetic acid in aqueous solution may be possible because of the presence of a highly acidic α-hydrogen, which exhibits keto-enol isomerism, with the enol form being more stable than the keto form due to the intermolecular forces of attraction. Dicarboxylic acids with the keto group at the β-position undergo spontaneous decarboxylation in the aqueous phase to result in pyruvic acid that can be detected in ambient aerosols [Frosch et al., 2010].

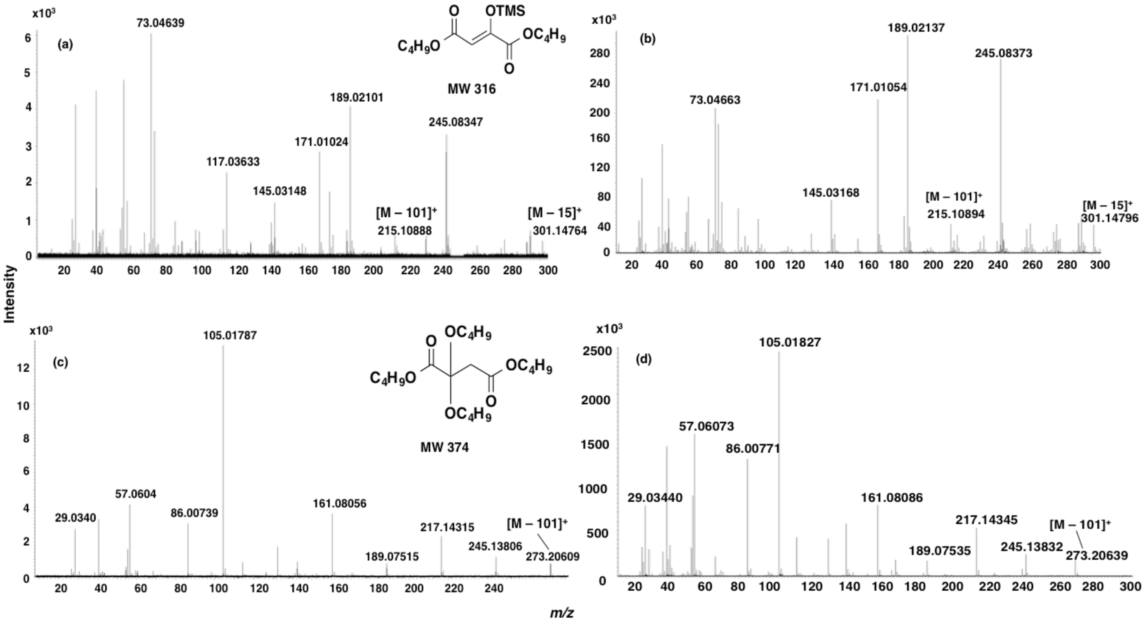
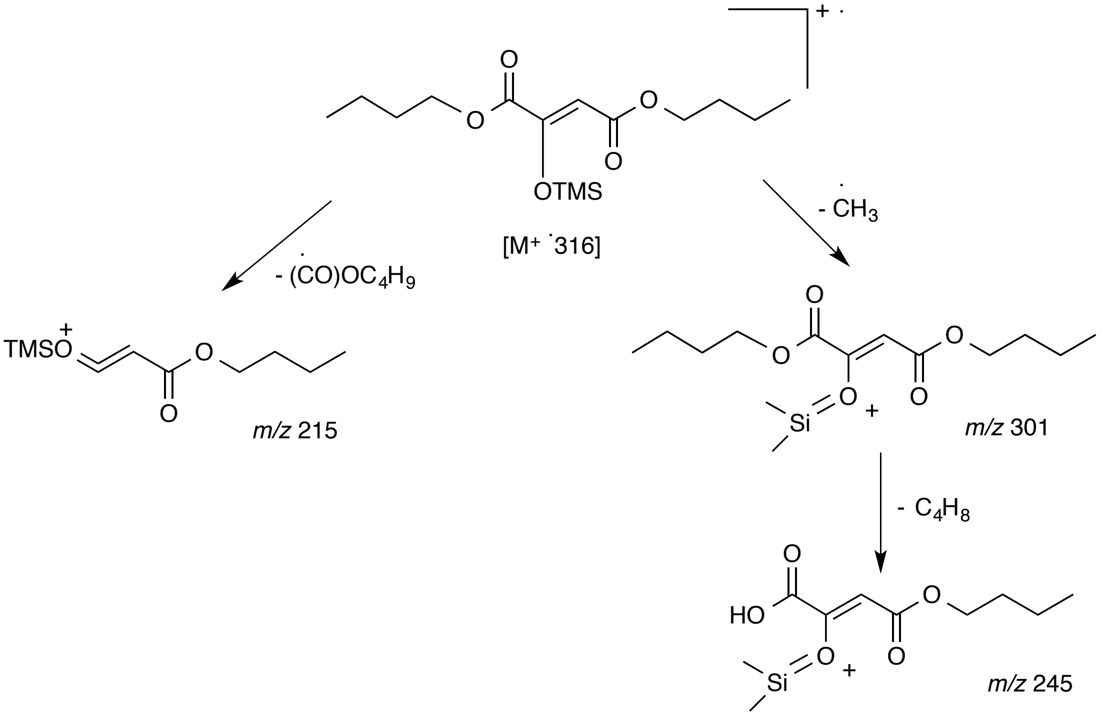


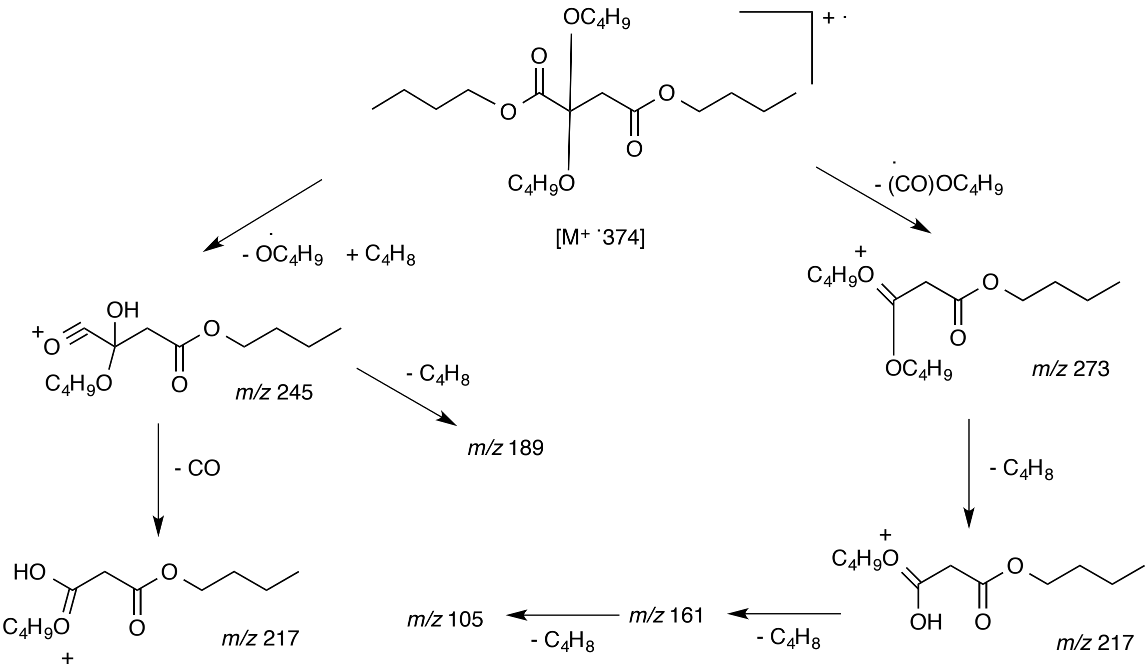
Figure 7. Mass spectra of dibutyl ester TMS-derivatives of (a) enol-oxaloacetic acid (U3),

(b) enol-oxaloacetic acid (standard), (c) keto-oxaloacetic acid (U9), and (d) keto-oxaloacetic acid (standard).



Scheme 8. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U3, which is identified as enol-oxaloacetic acid.

Detailed interpretation of the high-resolution mass spectra led to the proposal that this compound is oxaloacetic acid resulting in enolic fragment ions at *m/z* 301, 245, 215, 189, 171, 145, 117, 73, 57 and 41 (**Figure 7 (a)**). Structurally informative ions include *m/z* 301 $[M-15]^+$, *m/z* 245 $[M-15-56]^+$ and *m/z* 215 $[M–101]^+$. Proposed fragmentation pathways for the butyl ester TMS derivative of unknown U3 (enol-oxaloacetic acid) are summarized in **Scheme 8**. The proposed structure was subsequently confirmed by comparison of its GC and MS data (**Figure 7 (a)**) with those of an authentic standard (**Figure 7 (b)**).



Scheme 9. Proposed fragmentation pathways for the butyl ester TMS-derivative of the unknown compound U9, which is identified as keto-oxaloacetic acid.

The derivative of the keto form of oxaloacetic acid (U9) shows fragment ions at m/z 273, 245, 217, 189, 161, 105, 57 and 41 (**Figure 7 (c)**). Structurally informative ions include *m/z* 273 $[M-101]^+$. The peak at m/z 245 $[M-73-56]^+$ could be explained by the loss of a butoxy radical (C_4H_9O) and butene (C_4H_8, 56 u) from the molecular ion by α-cleavage followed by a McLafferty rearrangement. The fragment ion of *m/z* 217 was derived from loss of CO from the ion of *m/z* 245. Proposed fragmentation pathways for the butyl ester derivative of unknown U9 (keto-oxaloacetic acid) are summarized in Supplementary **Scheme 9**. The proposed structure was subsequently confirmed by comparison of its GC and MS data with those of an authentic standard (**Figure 7 (d)**). This is the first report of the existence of two forms of oxaloacetic acid in marine aerosols. Oxaloacetic acid may be the intermediate in the oxidation of dicarboxylic acids such as succinic acid to yield pyruvic acid, which is further oxidized to oxalic acid. The concentrations of the enol and keto forms of oxaloacetic acid in all the samples (n = 53) ranged from 0.01 to 1.52 ng m $^{-3}$ and 0.01 to 0.51 ng m $^{-3}$, respectively.

2.5 Summary and conclusions

Unknown intermediates of diacid formation have been successfully identified in remote marine aerosols as tartronic acid, malic acid, 3-hydroxyglutaric acid, 2-hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydoxyadipic acid, tartaric acid and the enol and keto forms of oxaloacetic acid by detailed analysis of chromatographic and mass spectral data. All the identified compounds were further quantified, indicating that malic acid is the most abundant hydroxydiacid followed by tartronic acid in the remote marine atmosphere. This is the first report of the identification and quantification of a homologous series of hydroxydiacids (hC_3di–hC_6di) including tartaric acid. We also demonstrated that oxaloacetic acid is present as two forms and is in part converted into pyruvic acid in remote marine aerosol samples. A further study is required to better understand the seasonal variations in hydroxydiacids in remote marine aerosols and their sources and transformation pathways.

2.6 References

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Chapter 3

Seasonal distributions of hydroxy and keto-diacids in the atmospheric aerosols over western North Pacific

3.1 Introduction

Atmospheric aerosols have received considerable attention with regard to their impact on radiative forcing [Charlson et al., 1992], which is associated with global climate change. Organic compounds in aerosol particles are highlighted because they account for a substantial portion of atmospheric aerosols, and potentially control the chemical and physical properties of the particles. Moreover polar organics are assumed to make the aerosol surfaces hydrophilic, leading the particles to act as cloud condensation nuclei (CCN). Organic acids are one of the most abundant compound classes in the tropospheric organic aerosols. In particular dicarboxylic acids (diacids) having two carboxylic groups are major constituents of the water-soluble organic fraction in aerosols [Saxena and Hildemann, 1996]. Diacids are present predominantly as atmospheric particles rather than in the gas phase [limbeck et al., 2001]. They are water-soluble; their presence in the aerosols can alters the chemical and physical properties of the atmospheric aerosols and enhances the capability of aerosols as CCN [Saxena et al., 1995]. The vapour pressures of diacids are several orders of magnitude than those of monoacids having same number of carbon [Jacobson et al., 2000] and their Henry's constant to water are much higher.

Although diacids and related compounds can be generated by primary sources including fossil fuel combustion [Kawamura and Kalpa, 1987], biomass burning [Narukawa et al., 1999], mainly formed by secondary processes in the atmosphere [Satsumabayashi et al., 1990]. Photo-oxidation of higher diacids and other precursors are important sources of low molecular diacids in the atmosphere [zuo and hoigne, 1994]. Low molecular weight diacids and relative compounds are extensively studied organic carbon over the marine and continents [Kawamura, Usukura 1993; Kawamura and Pavuluri, 2010]. The particle size distribution of diacids in aerosols is showed considerable amount of diacids are present in the submicron mode, suggesting a long-range atmospheric transport of diacids [Mészáros et al., 1997; Kerminen et al., 2000]. However, in the atmosphere diacids possessing additional hydroxy and keto functional group are suggested to be exist and were identified recently by the author in marine atmosphere as discussed in chapter 2. These hydroxy and keto diacids has enhanced polarity compare to diacids, hence they play an important role in hygoscopysity of organic aerosols. Trifunctional hydroxy and keto-diacids can give rise to stable homo-and hetero-molecular clusters through the formation of hydrogen bonding, being similar to the clusters proposed for bifunctional compounds [Hoffmann et al., 1998], and may as such participate in new particle formation and growth [Kulmala, 2003]. Since they are highly oxygenated, it is expected that studies of hydroxy and keto-diacids provide useful information to better understand the oxidative reaction mechanisms of organic matter in the marine atmosphere during long-range atmospheric transport.

More attention has been paid to East Asia and its outflow region with regard to influence of human activities on climate. The population in East Asia and Southeast Asia is almost one-third of world population. Because of rapid industrialization and changes in land use and life style, atmospheric changes are concerned to be significant in the Asian-Pacific region regarding atmospheric oxidizing capability, aerosol composition and concentrations, and acidity of rain. Chichijima Island is located on the outflow region of East Asia and has been regarded as an ideal site to study the chemical processes (production and transformation and degradation) of organic aerosols in the East Asia. At Chichijima Island variation studies have been conducted for Diacids [Mochida et al., 2003], Biomass burning traces [Verma et al., 2015], hygroscopic studies [Boreddy et al., 2014] and inorganic ions [Boreddy et al., 2015]. Howere, there are no studies on hydroxy and keto diacids at this site. This chapter describes about, seasonal variation of previously identified hydroxy- and keto-diacids such as tartronic, malic, 3-hydroxyglutaric, 2-hydroxyglutaric, 2-hydroxyadipic, 3-hydroxyadipic, tartaric, and oxaloacetic acid over the western North Pacific. Temporal variations of hydroxy and keto diacid concentrations were further analyzed with a that of air mass backward trajectories.

3.2. Samples and analytical protocol

3.2.1 Aerosol sampling

Total suspended particles (TSP) were collected at the Ogasawara Downrange Station of the Japan Aerospace Exploration Agency (JAXA) at Chichijima Island (27°04′N; 142°13′E) in the western North Pacific, 254 m above the sea level, an outflow region of the Asian dusts and polluted air masses from China and other neighboring countries. From 1 December 2010 to 30 November 2011 (n = 53) using pre-combusted (450 °C) quartz fiber filters and a high volume air sampler at a flow rate of 1.0 m^3 min^{-1}. Sampling periods were five days. The sampling site is described in detail in the chapter 2. After the sampling, the filters were placed in precombusted glass jars with a Teflon-lined screw cap, sent to Hokkaido University in Sapporo, and stored in a freezer room at -20 °C prior to analysis.

3.2.2 Derivatization of hydroxy and keto-dicarboxylic acids.

The filter samples were analyzed for hydroxydiacids and oxaloacetic acid, a part of the quartz-fiber filter were extracted three times with 10 ml organic-free pure water under ultrasonication for 10 min. To remove insoluble particles and filter debris, the extracts were passed through a glass column (Pasteur pipette) packed with quartz wool into a pear-shaped flask. The pH of the extracts were adjusted to 8.5-9.0 with 0.05 M aqueous KOH solution and concentrated almost to dryness using a rotary evaporator under a vacuum. A 14% BF_3/n-butanol was added to the concentrates in the pear-shaped flask to allow the esterification at 100 °C for 1 h. During the reaction, carboxyl groups were derivatized to their butyl esters, and keto groups to dibutoxy acetals.

The derivatives were extracted with 10 mL of n-hexane after adding 10 mL of organic free-water and 0.5 mL of acetonitrile. Acetonitrile transfers the excess n-butanol into the aqueous phase more efficiently. The hexane layer was further washed with organic free-water (10 mL x 2). Using a rotary evaporator under a vacuum and a nitrogen blow-down system, extracts were concentrated and hydroxyl group were derivatized to corresponding TMS ethers with a 50 μL of BSTFA at 80 °C for 30 min. The derivatives were dried under a nitrogen stream, dissolved in n-hexane (50 μL) and analyzed using gas chromatography/mass spectrometer (GC/MS), and gas chromatography/time of flight mass spectrometer (GC/TOFMS) and quantified using a gas chromatography (GC/FID). Known concentration of authentic standards were spiked to pre-combusted quartz fiber filter and derivatized to butyl esters/TMS ethers by the procedure described above. We found that the recoveries are more than 80%. The analytical errors in duplicate analysis of the aerosol sample (QFF3769) for hydroxy- and keto-diacids are about 10%.

3.3 Molecular distributions and concentrations of hydroxy-diacids and oxaloacetic acid

A homologous series of diacids (C_2-C_6), hydroxydiacids (tartronic, malic, 3-hydroxyglutaric, 2-hydroxyglutaric, tartaric, 2-hydroxyadipic, 3-hydroxyadipic acids), and two forms of oxaloacetic acid (enol & keto) were detected in marine aerosol samples. Their concentrations are summarized in **Table 1** together with the abbreviations of each compound. Concentrations of total diacids (C_2-C_6) ranges from 5.36 to 423 ng m^{-3}, total hydroxy diacids (hC_3-hC_6) ranges from 0.1 to 30 ng m^{-3} and oxaloacetic acid ranges from 0 to 2 ng m^{-3}. Among the diacids oxalic acid (C_2) was found as the most abundant species followed by malonic acid (C_3) or succinic acid and among hydroxy diacids malic acid (hC_4) was the most abundant species in all four seasons, followed by tartronic acid (hC_3) in winter and spring. 3-hydroxyglutaric acid (3-hC_5) becomes second most abundant species in summer, and 2-hydroxyglutaric acid (2-hC_5) in autumn.

Compounds	Winter (n = 13)		Spring (n=13)		Summer (n=13)		Autumn (n=13)	
	Range	av ± SD	Range	av ± SD	Range	av ± SD	Range	av ± SD
Oxalic acid, C_2	35.8-334	97.4± 74.1	4.74-181	89.7± 65.1	5.27-43.9	17.2± 10.5	6.49-158	50.4± 49.7
Malonic acid, C_3	5.79-44.5	13.5± 9.68	0.46-28.0	14.1± 9.85	1.17-12.0	4.12± 2.83	0.46-28.1	7.80± 8.52
Succinic acid, C_4	3.49-35.3	8.18± 8.29	0.16-22.3	10.1± 7.85	0.49-4.71	1.43± 1.30	0.27-12.0	3.25± 3.75
Glutaric acid, C_5	0.59-5.97	1.72± 1.37	0.00-3.17	1.47± 1.09	0.07-0.66	0.22± 0.17	0.03-2.67	0.55± 0.76
Adipic acid, C_6	0.39-2.66	0.91± 0.60	0.01-1.33	0.60± 0.44	0.04-0.30	0.14± 0.09	0.01-1.25	0.33± 0.38
Tartronic acid, hC_3	0.53-3.4	1.52 ± 0.79	0.02-5.27	1.88 ±1.66	0.01-0.29	0.13±0.08	0.00-1.85	0.58±0.61
Malic acid, hC_4	2.61-7.1	4.37 ± 1.50	0.03-14.75	6.50 ± 4.91	0.11-1.75	0.65±0.57	0.11-10.22	2.28±3.00
3-Hydroxyglutaric acid, 3-hC_5	0.36-1.7	0.89 ± 0.42	0.01-4.98	1.77 ±1.52	0.01-0.67	0.12±0.19	0.01-2.38	0.50±0.75
2-Hydroxyglutaric acid, 3-hC_5	0.80-2.8	1.56 ± 0.57	0.03-4.79	2.31±1.69	0.05-0.55	0.18±0.14	0.06-2.52	0.69±0.78
Tartaric acid, tart	0.47-1.2	0.78 ± 0.22	0.01-2.65	0.98±0.91	0.01-0.41	0.09±0.12	0.01-1.42	0.39±0.51
2-Hydroxyadipic acid, 2-hC_6	0.04-0.5	0.28 ± 0.14	0.00-0.73	0.32±0.26	0.00-0.05	0.02±0.01	0.00-0.36	0.09±0.12
3-Hydroxyadipic acid, 3-hC_6	0.19-0.6	0.38 ± 0.13	0.00-0.82	0.40±0.28	0.00-0.13	0.03±0.03	0.00-0.39	0.11±0.13
Enol oxaloacetic acid, enol	0.14-0.7	0.36 ± 0.16	0.00-1.52	0.57±0.48	0.01-0.12	0.04±0.03	0.01-0.78	0.23±0.26
Keto oxaloacetic acid, keto	0.05-0.4	0.14 ± 0.09	0.00-0.51	0.17±0.16	0.01-0.05	0.03±0.02	0.01-0.23	0.08±0.06

Table 1. Concentrations (ng m^{-3}) of hydroxydiacids and oxaloacetic acid measured in the remote marine aerosols collected at Chichijima Island in the western North Pacific during 2010-2011. [av: average concentration, SD: standard deviation, winter: December to February, spring: March to May, summer: June to August, autumn: September to November]

Sampling site	Sampling period	Aerosol Type	hC3	hC4	3-hC5	2-hC5	Tart	2-hC6	3-hC6	Reference
Chichijima Island	Dec- Nov 2011	TSP	0.0-5.2	0.0-14	0.0-4.9	0.0-3.9	0.0-2.6	0.0-0.7	0.0-0.81	Present study
Xinken, China	23 Oct-30 Oct 2004	PM 1.8 PM1.8-5.6	11.1 0.45	18.8 0.25						T. Gnauk et al., 2008
Changbai, Chongming, Dinghu, China	23-29 July 2007 12-19 June 2006 2-14 Aug 2006	PM 2.5		31-63 37-88 4.1-62	7.7-27 - -	13-18 - -				W.Wang et al., 2008
Yaan, Baima, China	14-22 June 2010 18-30 July 2010	TSP		45.7-111 0.9-137	3.6-6.1 0.3-6.6	7.5-15.7 0.4-21.8				Li et al., 2013
Mt. Tai, China	May-June 2006	TSP		10.2-236			0.65-25.9			Fu et al., 2008
Mt. Tai, China	22-28 June 2006	PM 2.5 day Night time		3.7-45 3.5-25			1.5-37 BDL-4.9			G. Wang et al., 2009
Cruise near Western North pacific	30 Oct 1989-3 March 1990	TSP		3.3 and 1.5			0.3 and 0.17			Fu et al., 2011

Table 2. Concentration range of hydroxydiacids determined in this work and literature data for comparable from different site. All data are given in ng m^{-3}. For Xinken site, average

concentrations are given and cruise near western North Pacific; two different samples concentrations are given.

To better understand the atmospheric processes during long-range transport of these compounds, concentrations of hydroxy diacids are compared with those reported for different sites are summarized in **Table 2**. Among the hydroxydiacids, the predominance of malic acid followed by tartronic acid has been reported from biomass burning influence aerosols (T. Gnauk et al., 2008), rural site and traffic-impacted site (D. van Pinxteren et al., 2014). Data from different sites suggest that near the continent concentrations of hydroxydiaicds are high when comparing with remote area. Asian outflows of pollutant air mass are the important sources for hydroxydiaicds precursors over the remote Chichijima Island.

3.4 Seasonal variation of hydroxydiacids and oxaloacetic acid

Figure 1 shows monthly averaged concentrations of total hydroxydiacid and oxaloacetic acid measured from December 2010 to November 2011 on Chichijima Island. Monthly averaged concentrations of diacids, hydroxy and keto diacids show a peak in winter to spring and lower in summer. Large bars (presented as one standard deviation, Figure 1) indicate significant variations of the concentrations within one-month periods. Although concentrations of hydroxy diacids are generally higher in spring and lower in summer, the different seasonal variations should be caused by a difference in the emission of their precursors or atmospheric processing.

Air mass back trajectories (**Figure 2)**, the marine atmosphere over a wide area of the northwestern Pacific are frequently influenced by continental outflow [e.g., Duce et al., 1980]. In winter to spring the westerlies blow from Asian continent. It is known that in the summer season, a maritime high-pressure system dominates over the western North Pacific in which the air mass is less influenced by the continental outflow from Asia. The large variations of hydroxy and keto diacids concentrations in autumn to spring may be due to the frequent passages of low- and high-pressure systems, leading to changes in air mass origins and the extent of wet deposition processes of atmospheric aerosols. Similar monthly trends between diacids and hydroxy diacids imply that their formation processes are similar or related to each other.

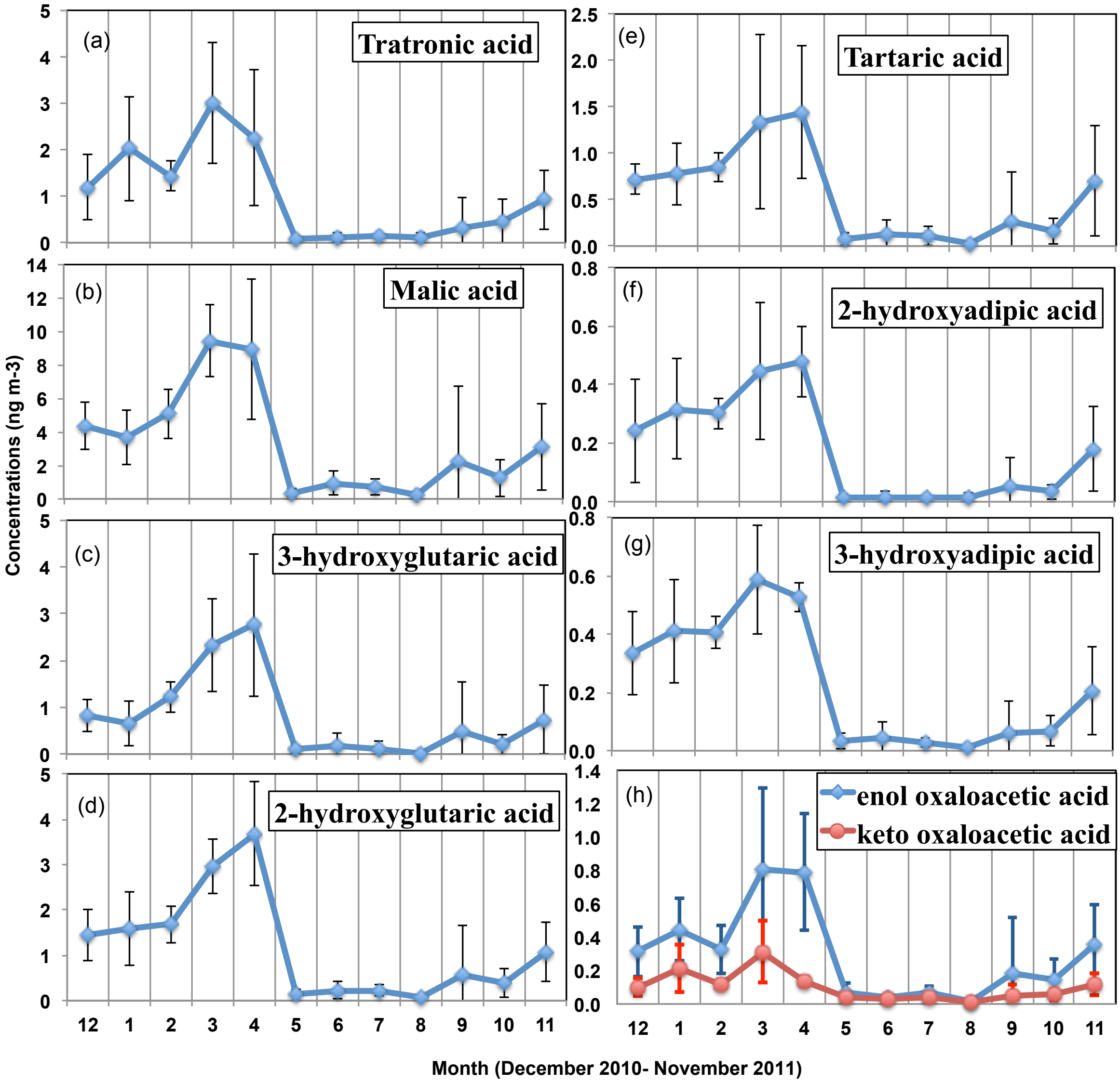

Figure 1. Monthly averaged concentrations of hydroxydicarboxylic acids and oxaloacetic acid measured from December 2010- November 2011 at Chichijima Island. The averages are calculated on the basis of the numbers of samples and standard deviation is shown as error bars in the figure.

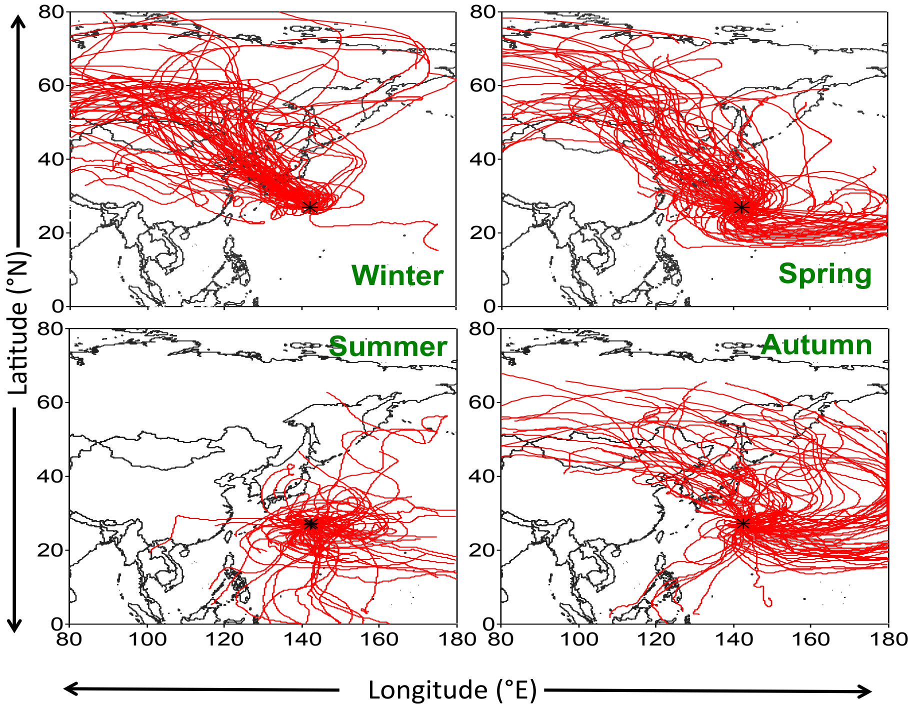

Figure 2. Seven days air mass backward trajectories at Chichijima Island.

3.5 Possible sources of hydroxydiacids and oxaloacetic acid in marine aerosols

Winter	hC3	hC4	enol	keto	3-hC5	2-hC5	Tar	2-hC6	3-hC6	C2	C3	C4	C5	C6
hC3	1													
hC4	0.31	1												
enol	0.81	0.3	1											
keto	0.90	0.28	0.7	1										
3-hC5	0.23	0.94	0.25	0.16	1									
2-hC5	0.66	0.87	0.68	0.62	0.82	1								
Tar	0.70	0.75	0.73	0.65	0.73	0.91	1							
2-hC6	0.76	0.76	0.75	0.68	0.68	0.94	0.85	1						
3-hC6	0.72	0.69	0.61	0.68	0.65	0.85	0.86	0.91	1					
C2	-0.13	0.6	-0.36	0.1	0.57	0.34	0.19	0.21	0.29	1				
C3	-0.16	0.6	-0.38	0.07	0.58	0.34	0.19	0.19	0.26	0.99	1			
C4	-0.10	0.58	-0.36	0.1	0.57	0.34	0.18	0.23	0.31	0.99	0.98	1		
C5	0.10	0.59	-0.22	0.3	0.56	0.43	0.28	0.36	0.45	0.95	0.93	0.97	1	
C6	0.13	0.51	-0.23	0.37	0.45	0.38	0.24	0.3	0.38	0.93	0.92	0.94	0.97	1

Table 3. Correlation coefficients (r) among selected diacids, hydroxy and keto-diacids in winter (Correlation is significant at 0.01 where r is ≥ 0.69, 0.05 where r is > 0.68 - 0.56).

In winter, week correlation was obtained between oxalic acid (C_2) and tartronic acid (hC_3) (r = -0.16), malic acid (hC_4) (0.61), enol oxaloacetic acid (-0.36), keto oxaloacetic acid (0.08), 3-hydroxyglutaric acid (3-hC_5) (0.57), 2-hydroxyglutaric acid (2-hC_5) (0.34), tartaric acid (tart) (0.19), 2-hydroxyadipic acid (2-hC_6) (0.21) and 3-hydroxyadipic acid (3-hC_6) (0.29). Same kind of weak correlation was obtained between C_3, C_4, $C_{2\omega}$, and $C_{3\omega}$ as shown in **Table 3**. The weak correlations may suggest that sources or formation mechanism of hydroxydiacids are different from diacids in winter season.

Spring	hC3	hC4	enol	keto	3-hC5	2-hC5	Tar	2-hC6	3-hC6	C2	C3	C4	C5	C6
hC3	1													
hC4	0.78	1												
enol	0.83	0.89	1											
keto	0.7	0.65	0.69	1										
3-hC5	0.71	0.95	0.91	0.49	1									
2-hC5	0.7	0.9	0.77	0.51	0.87	1								
Tar	0.8	0.85	0.95	0.48	0.93	0.76	1							
2-hC6	0.8	0.88	0.94	0.56	0.9	0.87	0.95	1						
3-hC6	0.88	0.88	0.88	0.69	0.81	0.87	0.83	0.94	1					
C2	0.7	0.93	0.73	0.7	0.81	0.77	0.65	0.69	0.77	1				
C3	0.76	0.97	0.82	0.68	0.9	0.86	0.78	0.82	0.85	0.97	1			
C4	0.56	0.87	0.69	0.52	0.82	0.97	0.65	0.78	0.78	0.79	0.86	1		
C5	0.73	0.89	0.68	0.71	0.76	0.85	0.61	0.7	0.82	0.95	0.95	0.86	1	
C6	0.68	0.8	0.6	0.74	0.62	0.7	0.51	0.61	0.76	0.93	0.9	0.73	0.96	1

Table 4. Correlation coefficients (r) among selected diacids, hydroxy and keto diacids in spring (Correlation is significant at 0.01 where r is ≥ 0.69, 0.05 where r is > 0.68 - 0.56).

In spring, good correlations was obtained between C_2 and hydroxydiacids such as hC_3 (0.70), hC_4 (0.93), enol oxaloacetic acid (0.73), keto oxaloacetic acid (0.70), 3-hC_5 (0.81), 2-hC_5 (0.77), tart (0.65), 2-hC_6 (0.69), and 3-hC_6 (0.77) they also show good correlation with C_3, C_4, $C_{2\omega}$, $C_{3\omega}$, pyr, Gly, Megly, and C_6 are produced by incomplete combustion of aromatic hydroxycarbons (e.g. naphthalene) and cyclic olefins (Kawamura and Kasukabe, 1996a,) as shown in **Table 4**. These results suggest that formation mechanism between hydroxydiacids and diacids are similar in spring season.

Summer	hC3	hC4	enol	keto	3-hC5	2-hC5	Tar	2-hC6	3-hC6	C2	C3	C4	C5	C6
hC3	1													
hC4	0.46	1												
enol	0.36	0.56	1											
keto	0.2	0.68	0.72	1										
3-hC5	0.56	0.76	0.52	0.59	1									
2-hC5	0.58	0.83	0.68	0.67	0.96	1								
Tar	0.62	0.78	0.58	0.6	0.97	0.95	1							
2-hC6	0.66	0.51	0.2	0.21	0.68	0.63	0.72	1						
3-hC6	0.46	0.65	0.35	0.55	0.94	0.89	0.86	0.61	1					
C2	0.42	0.74	0.48	0.47	0.83	0.82	0.88	0.48	0.71	1				
C3	0.42	0.68	0.36	0.38	0.83	0.79	0.87	0.54	0.75	0.96	1			
C4	0.47	0.74	0.61	0.5	0.95	0.95	0.94	0.59	0.84	0.86	0.85	1		
C5	0.34	0.74	0.21	0.29	0.75	0.75	0.73	0.45	0.76	0.77	0.8	0.8	1	
C6	0.29	0.84	0.36	0.39	0.64	0.68	0.66	0.28	0.53	0.8	0.72	0.71	0.88	1

Table 5. Correlation coefficients (r) among selected diacids, hydroxy and keto diacids in summer (Correlation is significant at 0.01 where r is ≥ 0.69, 0.05 where r is $> 0.68 - 0.56$).

In summer, good correlations were obtained between oxalic acid (C_2) and hC_4 (0.74), 3-hC_5 (0.83), 2-hC_5 (0.82), tart (0.88), and 3-hC_6 (0.71). Azelaic acid (C_9) also shows good correlation between 3-hC_5 (0.83), 2-hC_5 (0.72), tart (0.75), 2-hC_6 (0.68), and 3-hC_6 (0.90). C_9 is a specific oxidation product of biogenic unsaturated fatty acids emitted from marine phytoplankton to the atmosphere (Kawamura and Gagosian 1987). Strong correlation may suggest that sources or formation pathways of hydroxydiacids, diacids and C_9 are very similar in summer season (**Table 5**).

Autumn	hC3	hC4	enol	keto	3-hC5	2-hC5	Tar	2-hC6	3-hC6	C2	C3	C4	C5	C6
hC3	1													
hC4	0.86	1												
enol	0.89	0.88	1											
keto	0.8	0.7	0.93	1										
3-hC5	0.86	0.99	0.86	0.68	1									
2-hC5	0.88	0.98	0.93	0.79	0.97	1								
Tar	0.92	0.89	0.93	0.85	0.91	0.93	1							
2-hC6	0.67	0.61	0.83	0.92	0.59	0.74	0.77	1						
3-hC6	0.92	0.82	0.89	0.84	0.85	0.89	0.98	0.75	1					
C2	0.95	0.91	0.89	0.79	0.93	0.95	0.97	0.71	0.97	1				
C3	0.84	0.96	0.86	0.72	0.94	0.96	0.85	0.7	0.8	0.9	1			
C4	0.83	0.94	0.81	0.66	0.93	0.94	0.81	0.66	0.76	0.88	0.99	1		
C5	0.81	0.74	0.6	0.5	0.79	0.77	0.8	0.52	0.82	0.87	0.78	0.81	1	
C6	0.86	0.77	0.71	0.66	0.8	0.82	0.86	0.67	0.89	0.92	0.83	0.84	0.97	1

Table 6. Correlation coefficients (r) among selected diacids, hydroxy and keto-diacids in autumn (Correlation is significant at 0.01 where r is ≥ 0.69, 0.05 where r is > 0.68 - 0.56).

The author also found a strong correlation in autumn between oxalic acid (C_2) and hydroxydiacids such as hC_3 ($r = 0.75$), hC_4 (0.98), enol oxaloacetic acid (0.88), keto oxaloacetic acid (0.80), 3-hC_5 (0.95), 2-hC_5 (0.97), tart (0.98), 2-hC_6 (0.95), and 3-hC_6 (0.94) (Table 6). Hydroxydiacids shows good correlation with each other in all four season, suggest that they are strongly connected to each other in the chain reactions as shown in **Table 6**.

3.6 Temporal variation of hydroxydiacids with specific tracer

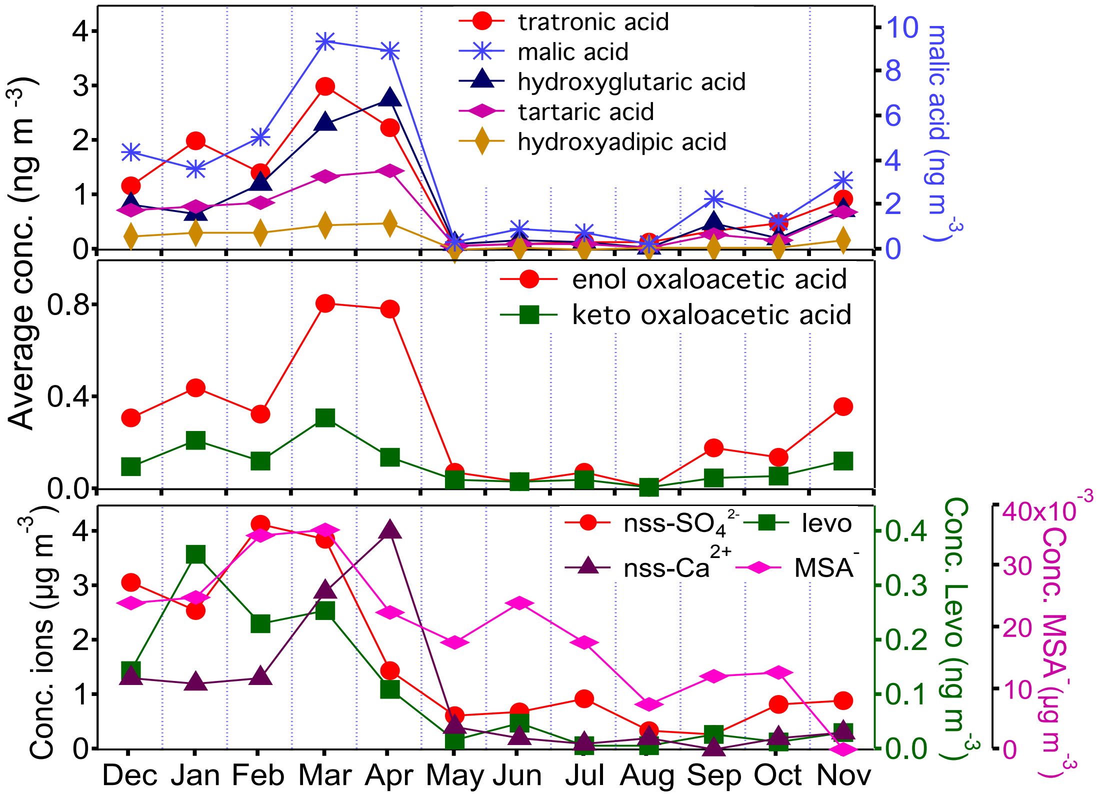

Figure 3. Temporal variation of hydroxydiacids with specific traces in aerosols samples collected from Chichijima Island.

Hydroxy and keto-diacids shows similar temporal variation with anthropogenic (nss-SO_4^{2-}), biomass burning (levoglucosan), and dusts tracers (nss-Ca^{2+}) from Dec to Apr, suggest they are originated from anthropogenic pollutants and biomass burning. Minimum conc. from May to August, suggest due to pristine air mass from ocean. Concentrations of hydroxydiacids and tracers starts to increase from September to November, when air mass are shifting towards the continent, suggest that the long-range atmospheric pollutants are the important sources for hydroxy and keto-diacids and its precursors at Chichijima Island.

3.7 Continental sources: Anthropogenic or terrestrial biogenic sources are important for hydroxy diacids?

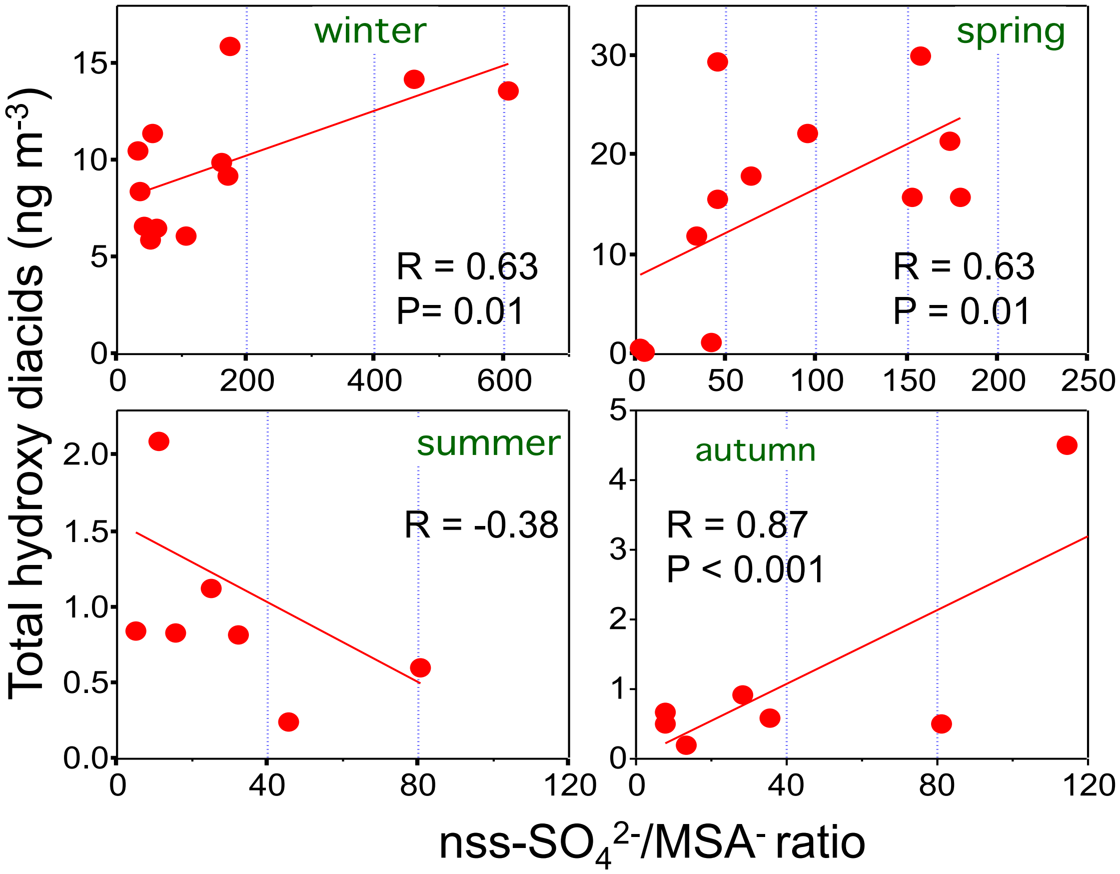

Figure 4. Correlation analysis between total hydroxy diacids and nss-SO_4^{2-}/MSA^- ratio in aerosols samples collected from Chichijima Island.

To better understand the sources of hydroxy and keto-diacids and its precursors, author examine anthropogenic (nss-SO_4^{2-})/ biogenic (MSA^-) ratio with total hydroxy diacids, it shows positive correlation in winter, spring, autumn, suggest major fraction are originated from anthropogenic sources. In summer, nss-SO_4^{2-}/MSA^- ratio decrease with increase in total hydroxy diacids, suggest they are originated from biogenic sources.

3.8 Possible formation mechanism of low molecular weight hydroxy diacids.

The formation of low molecular weight hydroxy diacids (hC_3-hC_6) can be formally explained by further photo-oxidation reactions of adipic acid, which is formed from unsaturated fatty acid, cyclic olefins, and incomplete combustions of aromatic hydroxycarbons. Oxalic and malonic acid likely produced in the atmosphere by photo-oxidation of longer chain diacids (>C_4) through intermediates such as hydroxydiacids and ketodiacids. In the present study, we identified homologous series of hydroxydiacids (hC_3-hC_6) and ketodiacid in marine aerosols. No statistically significant correlation was found between hydroxydiacids and Na^+ in all the seasons even in summer when most air masses originated from the pacific. This suggests that hydroxydiacids are not emitted directly from ocean but are largely formed in the atmosphere through secondary oxidation processes.

3.9 Summary and conclusions

Homologous series of hydroxydiacids (hC_3-hC_6) and oxaloacetic acid were identified in marine aerosols collected from December 2010-November 2011 over Chichijima Island, in the western North Pacific. A year-round data set showed that malic acid (hC_4) was the most abundant species in all four seasons, followed by tartronic acid (hC_3) in winter and spring. 3-hydroxyglutaric acid (3-hC_5) becomes second most abundant species in summer, and 2-hydroxyglutaric acid (2-hC_5) in autumn. The hydroxydiacids showed a strong seasonal trend with a maximum in spring, suggesting that an important anthropogenic emission from East Asia followed by long-range atmospheric transport over Chichijima Island is an important source. Correlation analysis between total hydroxydiacids and nss-SO_4^{2-}/MSA^- ratio, suggest in winter, spring, autumn, precursors of hydroxydiacids and ketodiacids are originated from anthropogenic sources and in summer lower nss-SO_4^{2-}/MSA^- ratio suggest they are originate from biogenic sources. No significant correlation between Na^+ and total hydroxy and keto diacids in all season, suggest hydroxy and keto-diacids are not directly emitted as primary sources but are largely formed in the atmosphere through secondary photo-oxidation process as an intermediates for diacids.

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Chapter 4

Photochemical processing of aqueous aerosols: Formation and degradation of hydroxy and keto-dicarboxylic acids

4.1 Introduction

Organic aerosols (OC) account for a substantial fraction of ambient submicron aerosols mass in urban, rural or remote environments [Putaud et al., 2004]. Since the 19th centaury considerable scientific attention has focused on chemical processes of organic compounds in the atmospheric aqueous phase including fog, rain, and wet aerosols. Dicarboxylic acid and relative compounds constitute a significant fraction of water-soluble OC in the atmosphere [Kawamura and Sakaguchi, 1999, Saxena and Hildemann, 1996]. Due to their water-soluble properties they have a potential contribution in the formation of cloud condensation nuclei (CCN), ice nuclei (IN) and hygroscopic properties [Giebl et al., 2002]. They are involved in a series of reactions such as gas phase, aerosols, cloud, and fog water [Wang et al., 2010].

Although diacids and relative compounds can be emitted into the atmosphere by direct sources such as incomplete combustions of fossil fuels [Kawamura and Kaplan, 1987], and biomass burning [Narukawa, 1999], but, they are mainly formed by secondary processes of volatile organic compounds of anthropogenic and biogenic origin [Kanakidou et al., 2005, Kawamura et al., 1996a, Kawamura and Sakaguchi, 1999]. They under go photochemical oxidation during long-range transport to form small diacids [Kawamura and Sakaguchi, 1999, Wang et al., 2010a]. Recent studies have revealed high abundances of diacids with a predominance of oxalic acid followed by malonic and succinic acids. While many gas phase oxidation schemes for diacids exist, databases for aqueous processes are much more limited.

Previous studies have postulated that long-chain diacids can be the precursors for smaller diacids [Kawamura and Ikushima, 1993]; the hypothesized mechanisms for diacids were subsequently employed by Ervens *et al.* to show that diacids can be formed in cloud droplets through OH radical oxidation [Ervens et al., 2004]. Photochemical oxidation of higher to lower diacids and its precursors have been proposed via intermediates [Kawamura and sakaguchi 1999] such as hydroxy and keto-diacids. These intermediate products also have finite lifetimes and thus might contribute to the organic aerosol mass. Hydroxy and keto-diacids are highly hygroscopic, plays a crucial role as CCN, IN, and serve as precursors for oligomeric humic-like substance. Furthermore, due to their strong hydrogen bonding interactions, readily forms homo and hetereonuclear clusters and may as such participate in new particle formation and growth.

Aqueous phase chemical processes of organic compounds in atmosphere have received increasing attention, partly due to their potential contribution to the formation of SOA. Due to the significant lack of studies on the photochemical formation, degradation of diacids and its intermediates particularly in aqueous phase. Hence, it is required to investigate the fate of diacids and related polar compounds with photochemical processing in atmospheric waters. In this study, author conducted 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 range 0.5 to 120 h and then analyzed for diacids, oxoacids, dicarbonyls [Pavuluri et al., 2015] and hydroxy and keto-diacids. Here, the author report their molecular compositions and discuss the photochemical formation and/or degradation of diacids and related compounds as a function of the irradiation time. Based on the results obtained, the author proposes possible photochemical formation and degradation pathways of diacids and related compounds with atmospheric implications.

4.2 Atmospheric aerosol samples

In this study, the author used two types of atmospheric aerosol (PM10) samples that were collected in winter on 28 January (IND104) and in summer on 25 May (IND178), 2007 during daytime (ca. 06:00-18:00 LT) from Chennai (13.03 ºN; 80.17 ºE), India using 25 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 (18ma.g.l. 1196 (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 ºC prior to the experiment. 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 (**Figure 1**). In North India, anthropogenic emissions are mainly derived from fossil fuel combustion and forest fires [Reddy and Venkataraman, 2002a]. 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, 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. The biogenic signature of IND178 is supported by high abundances of fatty acids and fatty alcohols [Pavuluri et al., 2010], as well as enhanced emission of volatile organic compounds from tropical plant in summer [Padhy and Varshney, 2005]. Hence, the author considers that IND104 represents anthropogenic aerosols (AA) and IND178 represents biogenic aerosols (BA).

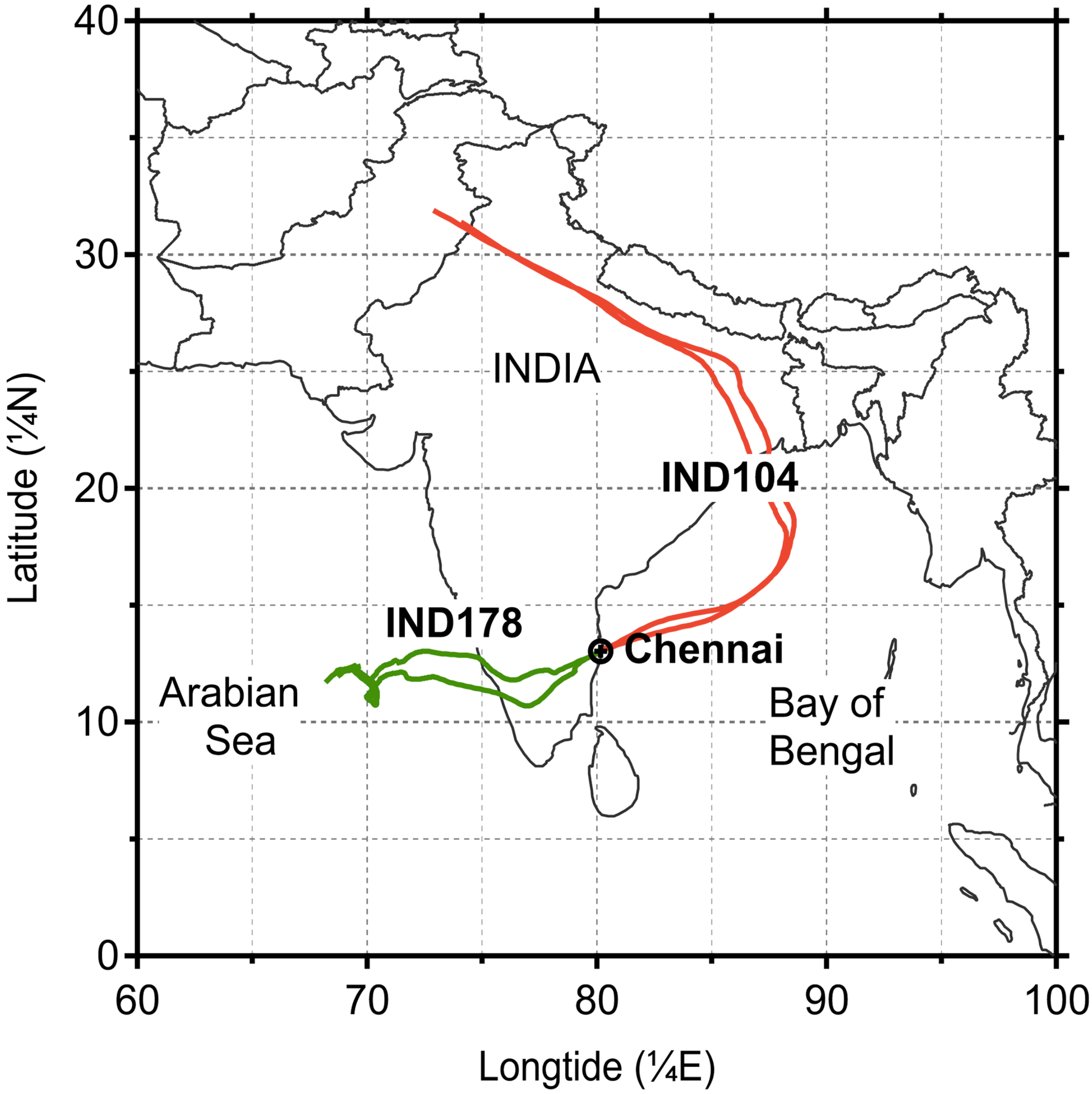


Figure 1. A map of South Asia with sampling site, Chennai (13.04 ºN; 80.17 ºE), India together with plots of 10 day air mass trajectories arriving at 500 ma.g.l. over Chennai, India.

4.3 Photo 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. In each experiment, 12 cm^2 (ca. 3 cm~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 **Figure 2**. The sample was wetted by injecting 0.4mL of ultra pure organic free Milli Q water and sealed with Teflon-lined screw cap under the ambient pressure and 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 185nm as well as broad peak at > 254 nm. The experimental setup (Fig. 2) was covered with a cardboard 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 ºC). The necessity of UV irradiation with a wavelength primarily at 254 nm, rather than a solar spectrum, was to produce significant amount of hydroxyl radicals from hydrogen peroxide, which should be sufficient enough to act as a principle oxidant in the experimental system. Also, when hydroxyl radicals are significant, it is well established that low molecular diacids have negligible absorbance at 254 nm and exhibit minimal photolysis [Carlton et al., 2006; tan et al., 2012].

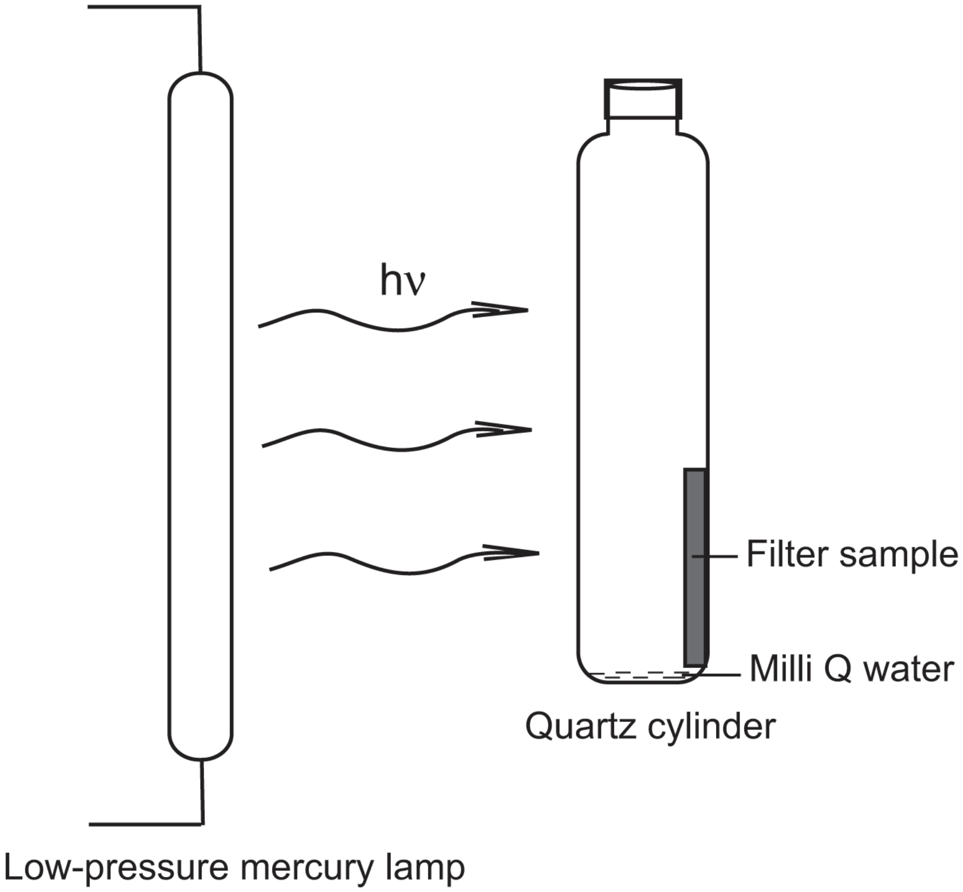


Figure 2. Schematic experimental setup for irradiation of atmospheric aerosol filter sample [Pavuluri et al., 2015].

Furthermore, the photolysis of organics by the radiation of 185 nm (intensity: 100 times < that of 254 nm), is to be insignificant, because it is mostly absorbed by water due to its high absorption coefficient (1.8 cm^{-1} at 25 ºC) [Weeks et al., 1963]. Due to the low intensity of UV source of wavelength 185 nm, it can able produce only hydroxyl radical rather the photolysis of desired compounds. Moreover hydroxydiacids suggested to be exists in the atmosphere as complexes with transition metals such as iron, copper etc., for example iron-dicarboxylate complexes of oxalate and malonate. These complexes readily undergo photolysis by absorption of both UV-C (200-290 nm) and UV-A (320-400 nm) light and their rates depend on concentration of iron [Zuo and Hoigne, 1994; Wang et al., 2010; Pavuluri and Kawamura, 2012]. Hence to produce significant photolysis in the current study the author employed a UV source of wavelength 254 nm.

4.4 Measurement of hydroxy and keto-diacids

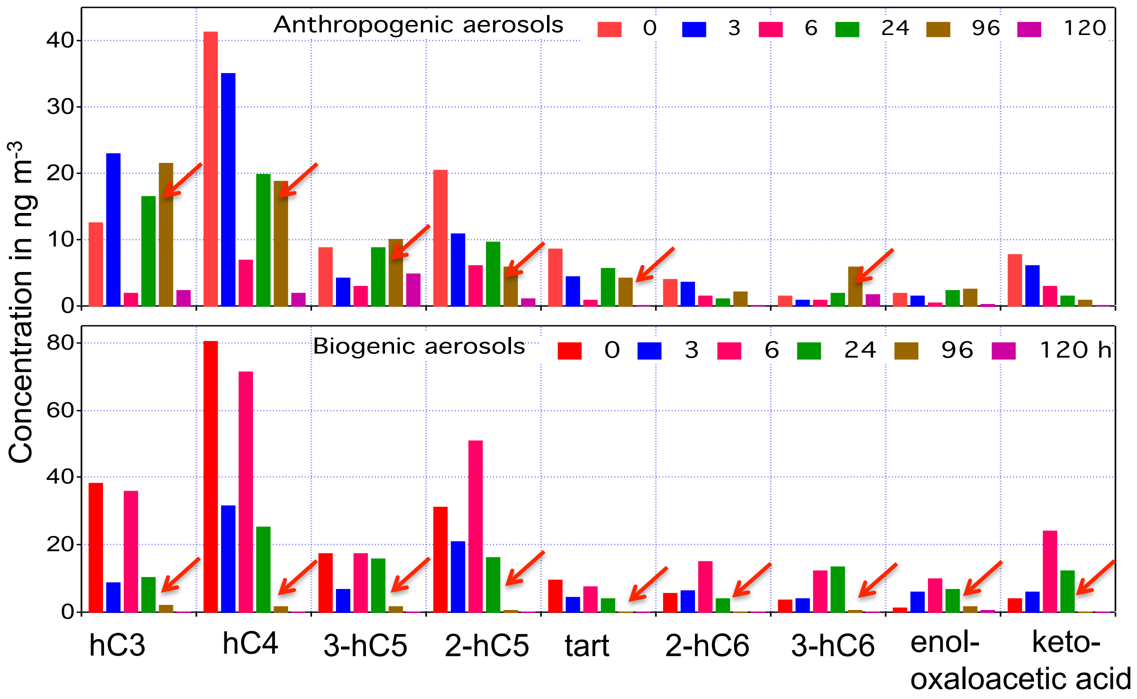
Immediately after the irradiation, samples were analyzed for hydroxy and keto-diacids using a method as described in chapter 1. Briefly, the irradiated sample filter was extracted three times with 10 mL organic free pure water under ultrasonication for 10 min. To remove insoluble particles and filter debris, the extracts were passed through a glass column (Pasteur pipette) packed with quartz wool into a pear-shaped flask. The water extracts were pH adjusted to 8.5-9.0 with 0.05 M aqueous KOH solution and concentrated almost to dryness using a rotary evaporator under a vacuum. A 14% BF_3/n-butanol solution was added to the concentrates in the flask to allow esterification to take place at 100 °C for 1 h. During the reaction, carboxyl groups are derivatized to their butyl esters, and keto groups to dibutoxy acetals. The derivatives were extracted with 10 mL of n-hexane after adding 10 mL of organic-free water and 0.5 mL of acetonitrile. Acetonitrile transfers the excess n-butanol into the aqueous phase efficiently. The hexane layer was further washed with organic-free water (2 ~ 10 mL). Using a rotary evaporator under vacuum and a nitrogen blow-down system, the extracts were concentrated and then dissolved in 100 μL of n-hexane.

An aliquot of the dibutyl ester fraction containing hydroxyl diacids was dried under a gentle stream of nitrogen, and hydroxyl diacid dibutyl esters were derivatized to the corresponding TMS ethers with 50 μL of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) at 80 °C for 30 min. The derivatives were dried under a nitrogen stream, dissolved in n-hexane (50 μL) and analyzed using gas chromatography/quadrupole mass spectrometry (GC/QMS) and gas chromatography/time of- flight mass spectrometry (GC/TOFMS). Their concentrations were determined using gas chromatography–flame ionization detection (GC-FID). Known amounts of authentic standards (tartronic, malic, 3-hydroxyglutaric, tartaric, and oxaloacetic acids) were spiked on a precombusted quartz fiber filter and derivatized to butyl esters-TMS ethers by the procedure described above. We found that the recoveries of hydroxyl diacids were more than 80 %.

To examine the possible experimental errors, including distribution of organic constituents over the filter paper, the author conducted replicate experiments (n=3) for 18 h irradiation of the AA sample by using the sample cut taken from different parts of the filter sample for each experiment, in order to keep the error minimum. The analytical errors in duplicate analyses of the aerosol sample (QFF3769) for hydroxy and keto-diacids are about 10%. These results suggest that organic 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 and 6.0 h. No peaks were detected, except for a small peak for C_2. These results indicate that the occurrence of bias during the experiment is insignificant.

4.5 Molecular distributions of hydroxy and keto-diacids

In searching for diacids with additional hydroxyl- and keto functional groups, a homologous series of hydroxydiacids (hC_3-hC_6), oxaloacetic acid (kC_4-keto, kC4-enol) were detected in both non-irradiated and irradiated AA and BA samples. Even though higher hydroxydiacids (C>7) were detected on the gas chromatograph, they were not reported here due to their very low abundance. The hydroxydiacids includes, tartronic acid (hydroxy malonic, hC3), malic acid (hydroxysuccinic, hC4), 2-hydroxyglutaric acid (2-hC5), 3-hydroxyglutaric acid (3-hC5), 2-hydroxyadipic acid (2hC6), 3-hydroxyadipic acid (3hC6), and additionally tartaric acid (2,3-dihydroxysuccinic). Malic acid (hC4) was found to be the most abundant hydroxydiacids in non-irradiated samples having 38 % of total hydroxydiacids in AA and 42 % in BA, followed by 2-hC_5 (19 %), hC_3 (12 %), 3-hC_5 (8 %), tartaric acid (8 %), 2-hC_6 (3%), 3-hC_6 (1.6%) and by hC_3 (20 %), 2-hC_5 (16 %), 3-hC_5 (9 %), tartaric acid (5 %), 2-hC_6 (3%), 3-hC_6 (2%), acids in BA. Oxaloacetic acid, kC_4-keto is slightly abundant than kC_4-enol in AA, whereas their abundances are equivalent BA. Rate of photo degradation of hydroxy and keto-diacids from anthropogenic aerosols is longer when compare to biogenic aerosols, due to the presence of enhanced levels of chelating ions [**Figure 3**]. Chelation makes the hydroxy diacids much stable and hence they exist for longer time.



Chelating ions:

Con. (ng/m^3)	AA	BA
Fe	2070	553
Al	15100	914
Ca	1640	0

[Pavuluri et al., 2015]

Figure 3. Molecular distributions and temporal changes in hydroxy and keto-diacids upon UV irradiation.

4.6 Change in concentrations of hydroxy and keto diacids as a function of UV irradiation time

Change in concentration of hydroxydiacids (hC_3-hC_6) and oxaloacetic acid are shown in **Figure 4.** Concentrations of hC_3 shows decreasing treand until 6 h and then, concentration start to increase upto 12 h for BA and 48 h for AA and shows gradual decrease towards to end of the experiment upon irradiation. Relative abundances of hC_3 in total hydroxydiacids gradually decreased from non-irradiated samples until 48 h later show sharp increase.

Concentrations of keto form of oxaloacetic acid increase upto 12 h and then gradual decreases towards end of the experiment for BA and for AA it decreases upto 6 h then increases upto 18 h then gradual decreases towards the end of the experiment.

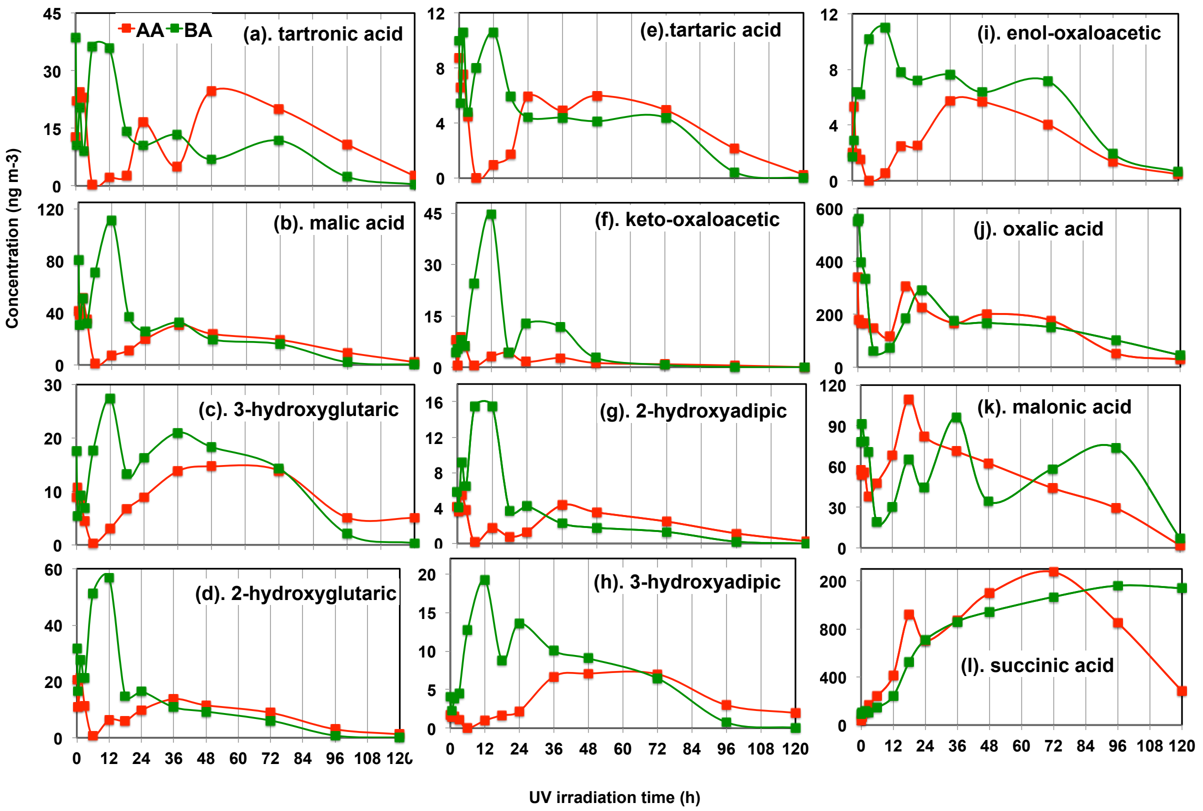


Figure 4. Changes in concentrations of individual hydroxydiaicds and oxaloacetic acid as a function of UV irradiation time in AA and BA.

Concentrations of enol form of oxaloacetic acid increase upto 12 h then gradual decreases towards the end of the experiment for BA and for AA concentrations decreases upto 6 h then shows increasing treand upto 36 h then gradual decrease towards the end of the experiment. Concentration of malic acid shows increasing treand upto 12 h except few points later shows gradual decreases towards the end of the experiment for AA and for BA it decreases upto 6h later shows increasing treand upto 36 h later shows gradual decreasing treand towards the end of the experiment. Relative abundance of hC_4 to total hydroxy diacids shows decreasing treand towards the end of experiment in AA and BA.

In contrast, concentration of 2-hC_5 and 2-hC_6 show increasing treand upto 12 h and then gradual decreasing treand towards the end of the experiment for BA and for AA concentration decreases upto 6h and shows increasing treand upto 36 h later on decreases towards the end of the experiment. Concentration of 3-hC_5 and 3-hC_6 shows increasing treand upto 12 h and shows gradual decreasing treand towards the end of the experiment for BA and for AA initial it shows decreasing treand upto 6 h and shows sharp increasing treand upto 36 h and stayed almost constant upto 96 h later on shows decreasing treand towards the end of the experiment.

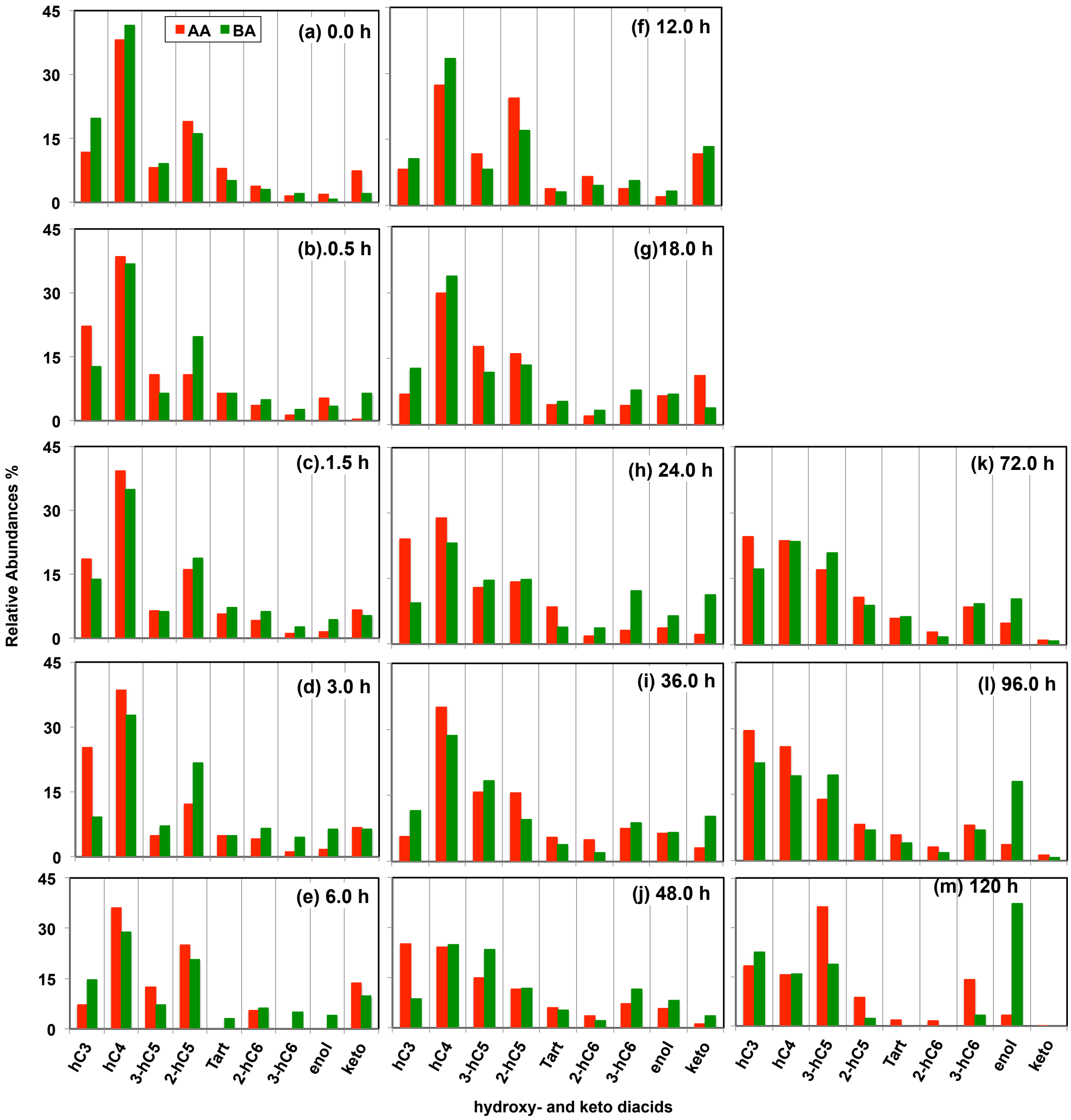


Figure 5. Changes in relative abundance of individual hydroxydiaicds and oxaloacetic acid as a function of UV irradiation time in AA and BA (hC_3: tartronic, hC_4: malic, 2-hC_5: 2-hydroxyglutaric, 3-hC_5: 3-hydroxyglutaric, 2-hC_6: 2-hydroxy adipic, 3-hC_6: 3-hydroxy adipic acid, Tart: tartaric acid, enol: enol form of oxaloacetic acid, keto: keto form of oxaloacetic acid).

Concentration of 2-hC_5 and 2-hC_6 shows increasing treand upto 12 h later gradual decreases towards the end of the experiment for BA and for AA concentration shows decreasing treand upto 6 h later shows increases upto 36 h later shows decreasing treand towards the end of the experiment. Tartaric acid shows higher concentration in the initial stage of experiment upto 12 h later shows gradual decrease towards the end of the experiment for BA and for AA initial it shows decreasing treand upto 6 h later increases upto 24 h and continue to maintain more or less same concentration upto 96 h and then decreases.

Relative abundance of hC_3 diacid in total diacids shows a slight increase from 19.8% (non-irradiated) to 22.4% (120 h) in BA and from 11.8 to 18.2 % in AA. Whereas, relative abundance of enol form of oxaloacetic acid significantly increased from 0.8% (non-irradiated) to 37.2% (120 h) in BA but no significant change in case of AA. Similarly 3-hydroxyadipic acid increased from 1.6% to 14% in AA whereas no significant change in BA (**Figure 5**).

The author found decrease in the mass ratios of succinic to malic and malic to keto-oxaloacetic with irradiation time toward the end of the experiment, except for an early stage of experiment in AA and BA (**Figure 6**). As noted earlier, concentrations of succinic and malic acid increased with experiment, up to 36 h for malic in both AA and BA. Thereafter, malic decreased toward the end of experiment in both AA and BA whereas succinic remained relatively constant in the BA, but decreased in AA (**Figure 4 b and l**). Mass ratios of keto-oxaloacetic to malonic increase with irradiation time indicating a significant photochemical transformation of intermediate keto-oxaloacetic acid to malonic acid. Mass ratio of malonic to tartronic and tartronic to ketomalonic decreases with irradiation time, whereas, mass ratio of ketomalonic to oxalic increase with irradiation time indicating a significant photochemical transformation of ketomalonic to oxalic acid. These results demonstrate that degradation of malic, oxaloacetic and tartronic, keto malonic and formation of malonic and oxalic is enhanced with photochemical processing of aqueous aerosols.

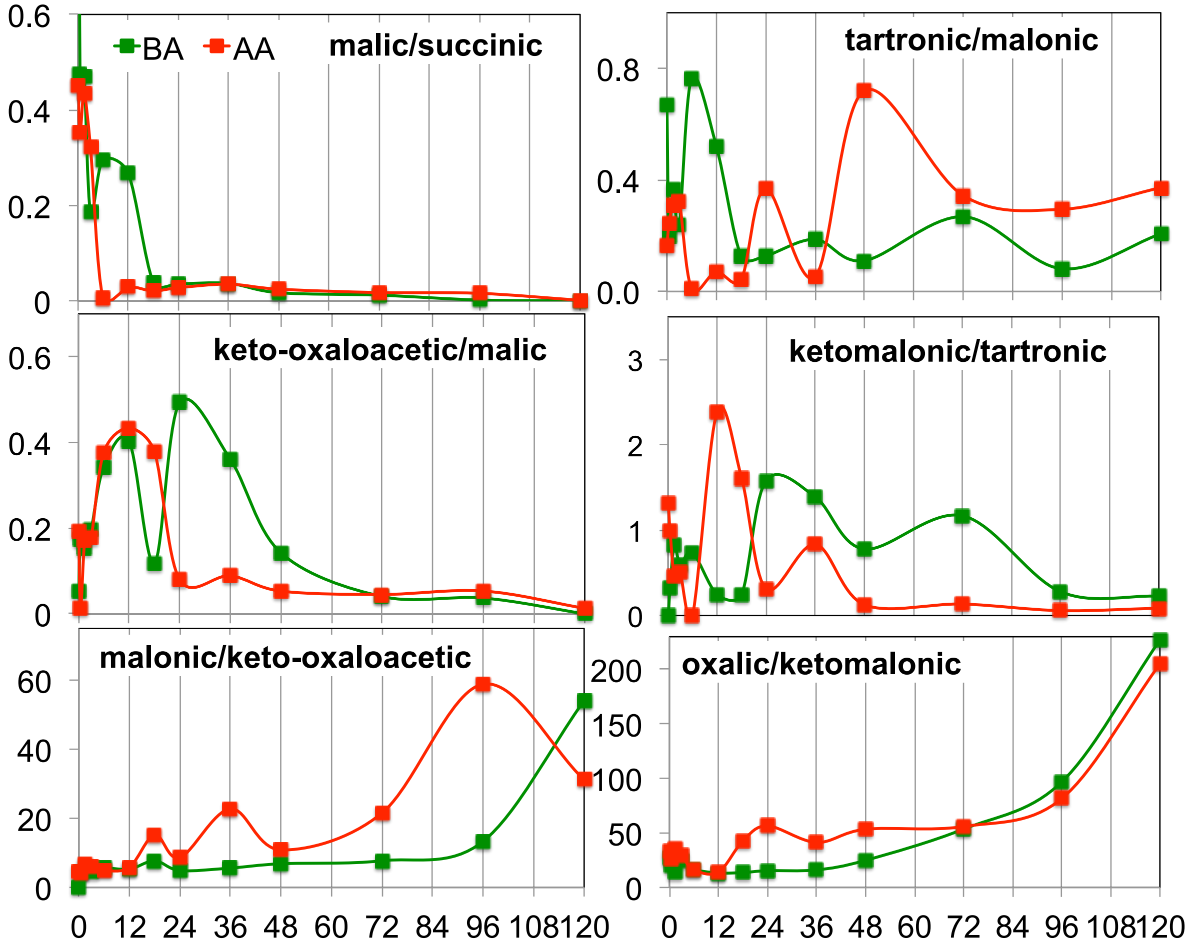


Figure 6. Changes in mass ratios of selected diacids, hydroxydiaicds and oxaloacetic acid as a function of UV irradiation time in AA and BA.

4.7 Production and decomposition of hydroxy and keto-diacids.

A sharp increase was observed in the concentrations of tartronic, malic, 2/3-hydroxyglutaric acids, 2/3- hydroxyadipic acids and oxaloacetic acids. Concentration of C_2 di and kC_3 sharply decrease upto 12 h later on start to increase 18 and gradual decrease towards the end of the experiment except few points [Pavuluri et al., 2015]. Whereas, concentration of hC_3 sharply increases upto 12 h later shows decrease treand indicates that hC_3 is converting into C_2 di via kC_3 hence the concentration of hC_3 decrease and C_2 and kC_3 increase at 18 h in BA. Initial stage of experiment concentration C_2 and hC_3 shows increase treand from 6 h to 18 h and shows gradual decrease treand for C_2 whereas hC_3 shows increase and decrease treand in the case of AA.

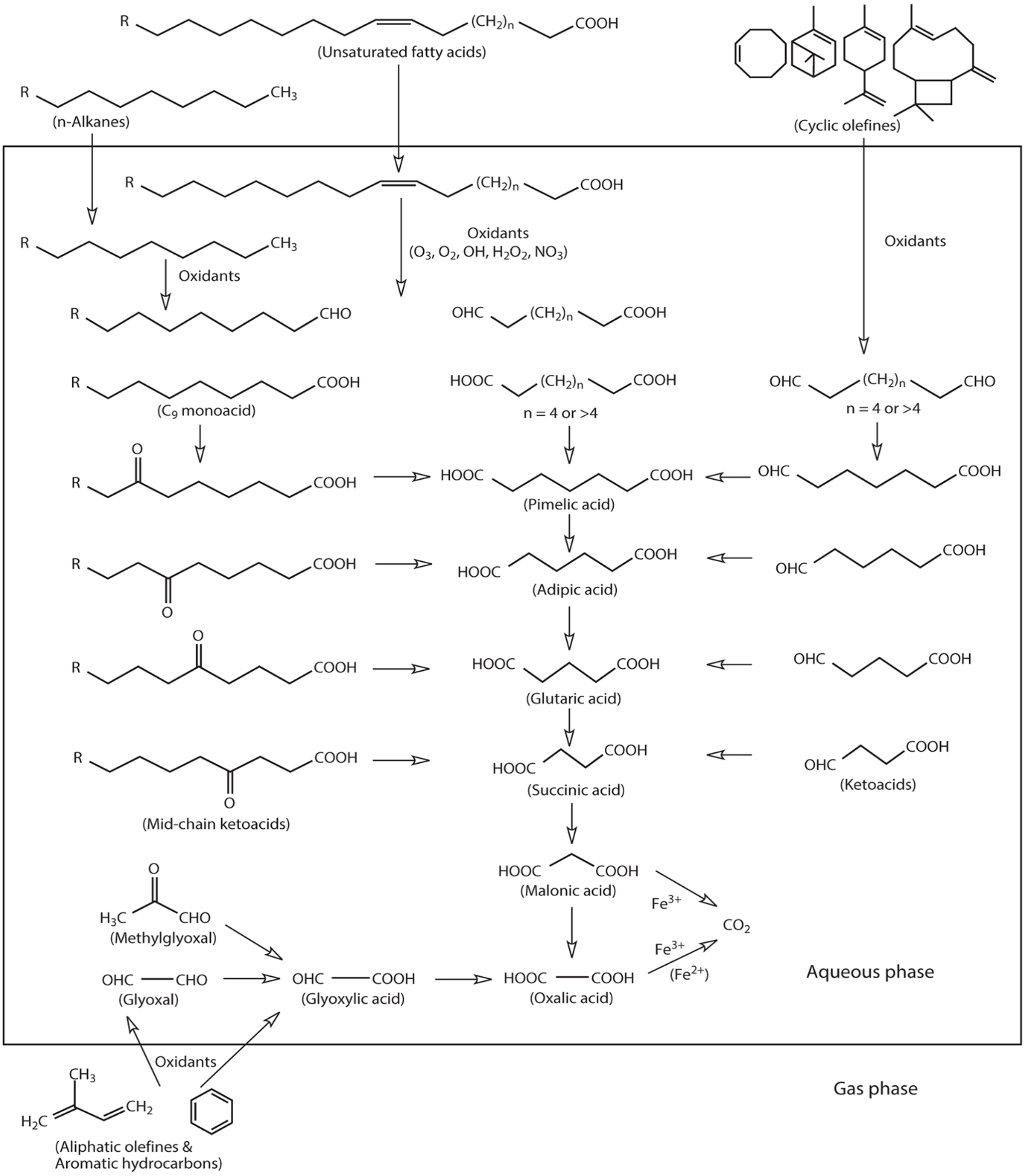


Figure 7. Previously proposed photochemical formation and /or degradation pathways of diacids and related compounds in aqueous aerosols [Pavuluri et al., 2015].

In compare, concentration of C_3 decrease until 6 then shows increase until 18 h and then shows decreasing treand upto 24 h whereas, in the case of hC_3 shows opposite treand to C_3 in

AA indicated that photo-degradation of C_3 leads to formation of hC_3 hence concentration of hC_3 is increase whereas, concentration of C_3 decrease upon photo irradiations. As shown in **Figure 3** (Anthropogenic sample conversation of C_3 to hC_3 is significant), photo-degradation higher to lower diacids shows different treand compare to AA and BA. In biogenic influence sample conversation of hC_3 to C_2 via kC_3 is important.

In previously proposed photochemical pathways formation of oxalic acid as been described via malonic acid from succinic acid (**Figure 7**). But, based on the obtained results and experimental evidences of the current study the author applied correction to the previously proposed schemes of Pavuluri et al., the newly proposed photochemical formation of oxalic acid from succinic acid as been shown in **Figure 8.**

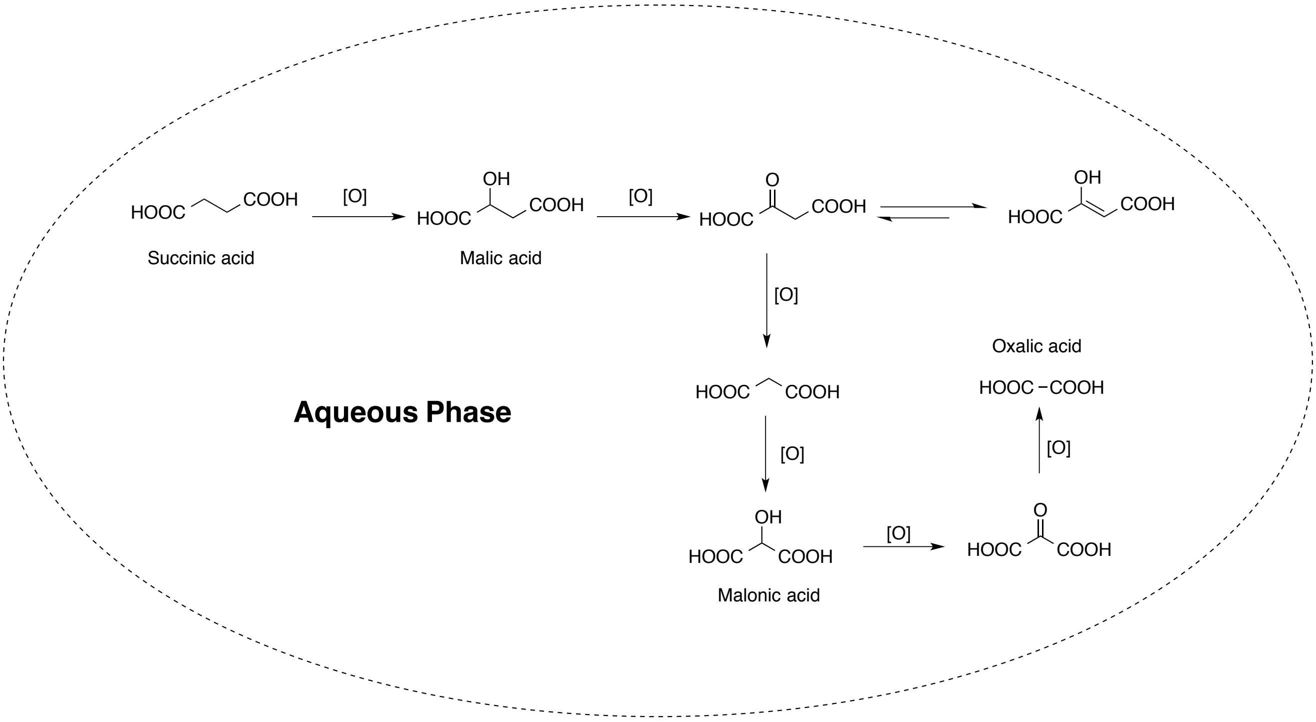


Figure 8. Proposed photochemical pathways for formation of oxalic acid from succinic via intermediates such as hydroxy and keto diacids.

4.8 Summery and conclusions

In this study, author 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 to 120 h. The irradiated samples were analyzed for hydroxy and keto diacids. Concentrations of hC_3, hC_4, 3-hC_5, 2-hC_5, 2-hC_6, 3-hC_6, tart, and oxaloacetic acid increased with an increase in irradiation time upto 12 h in BA followed by gradually decrease in the prolonged experiment. In AA concentration of hydroxy and keto-diacids showed significant decrease upto 6 h later start to increase upto 48h then decrease except few points. The mass ratio of C_2 to keto-malonic acid and malonic/ keto-oxaloacetic acid showed considerable increase with irradiation. These results demonstrate that degradation of hC_5, hC_4, hC_3 and formation of C_2 is enhanced with photochemical processing of aqueous aerosols. In general, rate of photochemical degradation of hydroxy and keto diacids in anthropogenic influenced aerosols takes place for prolonged time, due to the enhanced levels of chelating ions. Whereas, in biogenic aerosols, rate of photochemical degradation of hydroxy and keto diacids takes place rapidly, due to lesser amount of chelating ions. Photochemical processing studies suggest that formation and degradation of diacids through intermediates such as hydroxy and keto-diacids are significant in both anthropogenic and biogenic aerosols.

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Chapter 5

Hydroxyl radical mediated aqueous phase photooxidation of atmospherically significant biogenic and anthropogenic precursors

5.1 Introduction

In recent years, scientific consideration has focused on chemical processes of organic compounds found in the atmospheric aqueous phase of clouds, fogs, and wet aerosols, which affects global environmental health (e.g., climate, air quality). [Huang et al., 2011, Nielsen et al., 2012; Ervens et al., 2013; Herckes et al., 2013]. A significant number of laboratory, field, and modeling studies have shown that chemistry in atmospheric waters [Legrand and Puxbaum, 2007; Zhang et al., 2010] and it change the mass and properties of organic aerosols. Aqueous-phase photochemistry can transform organic compounds into more functionalized and oxygenated forms, contributing to the formation and aging of secondary organic aerosols (SOA) with the significant impact to air quality and global climate [Aljawhary et al., 2015]. However, nearly half of organic matter dissolved in atmospheric waters remains uncharacterized and its chemistry unexplored [Robinson et al., 2007]. To improve model predictions and implement appropriate policies, we must identify and include more detailed chemistry taking place in the atmosphere, specifically in atmospheric waters.

Formation of SOA through aqueous-phase chemistry is not considered in the established SOA formation pathway which involving only the gas-particle partitioning of semivolatile organic compounds [Odum et al., 1996] and it has been proposed as an alternative SOA formation pathway. It is known that the reactivity of organic compounds can be very different in the aqueous phase compared to the gas phase [Altieri et al., 2006 and 2008; Carlton et al., 2007; El Haddad et al., 2009; Sun et al., 2010]. And it is possible that the aging of SOA through aqueous phase results in very different physical and chemical composition than the aging under dry conditions. The aqueous phase formation SOA can occur through both thermal and photochemical reactions. For photochemical reactions, OH radical is typically used dominant oxidant for aqueous organics and thus the dominant source of SOA from the aqueous phase [Herrmann et al., 2010]. A number of recent studies have focused on the ability of aqueous phase reactivity of some single organic compounds to form oligomers, and potentially new SOA [Altieri et al., 2006 and 2008; Carlton et al., 2006 and 2007; Perri et al., 2009; El Haddad et al., 2009; Tan et al., 2009 and 2010; Zhang et al., 2010; Ortiz-Montalvo et al., 2012].

Benzene is a major aromatic hydrocarbon air pollutant with an emission rate of 11 Tg y^{-1}, and it plays a critical role in atmospheric chemistry. Atmospheric studies on benzene acquired greater relevance when this volatile organic compound (VOC) became established as a petrol additive, thus increasing its direct emission. Other benzene sources are the chemical industry, biomass burning, cracking of aromatic hydrocarbons, solvent usage and industries related to vegetable oil processing. Its atmospheric degradation mainly initiated by adding the OH radical to the aromatic ring to form OH-adduct. However, there is considerable uncertainty regarding its degradation pathways [Klotz et al., 2002; Berndt and Böge, 2001; 2006]. Benzene seems to behave differently from other aromatic hydrocarbons (Kroll and Seinfeld, 2008). Benzene can from condensable material using a high-volume photo-reactor with a natural sunlight [Martin-Reviejo and Wirtz, 2005], it can form SOA in a small smog chamber in the presence or absence of seed aerosol [Ng et al., 2007: Sato et al., 2010].

Toluene is also an important aromatic hydrocarbons emitted into the atmosphere from various anthropogenic sources. Sources of toluene are similar to benzene. Formation of OH adduct is not clearly integrated, as it is assumed that the subsequent reaction with oxygen is sufficiently fast leading to oxygenated ring cleavage products [Ervens et al., 2004]. SOA formation from the photooxidation of toluene is investigated using NO_x condition [Ng et al., 2007]. In addition, SOA formation in the presence of submicron ammonium sulfate aerosol also investigated in literature [Kleindienst et al., 1999]. Gas-phase photochemical oxidation was reported [(Borras et al., 2012), (Hoshino et al., 1978]). Several studies have shown that methylglyoxal and glyoxal are formed with average yields of 65 % and 67 % respectively [Ervens et al., 2004].

Isoprene, a volatile organic compound (VOC) produced by deciduous plants, comprises the single most abundant atmospheric nonmethane hydrocarbon by emission to the atmosphere, with estimates near 500 Tg C y^{-1} [Guenther et al., 2006]. It was not considered as a significant contributor to SOA until recently. The rapid oxidation of isoprene by OH radicals (k = 1.0 X 10^{-10} cm^3 $molecule^{-1}$ s−1) makes it an important driver in tropospheric chemistry, particularly in forested regions. Attack of isoprene by ozone and the OH radical both lead to the oxidation products methyl vinyl ketone and methacrolein with different yield for the two-reaction channel are more direct precursors of SOA [Hallquist et al., 2009]. Because most of the photooxidation products of isoprene are water soluble, it is likely that their aqueous phase processing has an important influence on SOA aging.

α-pinene is also a most important non-methane hydrocarbons emitted in the atmosphere from vegetation. Gas-phase photochemical oxidation was studied for the production of organic acid [Winterhalter et al., 2003]. Many proposed reaction product are oxygenated and expected to be sufficiently water-soluble to under go aqueous-phase processing [Aljawhary et al., 2015]. α-pinene average residence time adsorbing onto the aqueous interface was more than 0.1ns [Yu et al., 2008]. New models for the oxidation of α-pinene, which results in the formation of SOA show that ozonolysis has double the contribution to SOA formation compared with oxidation by OH [Capouet et al., 2008].

Our goal is to investigate the aqueous phase photo-oxidation products of benzene, toluene, isoprene, and α-pinene to form organic acids in the presence of OH radicles. Organic acids include dicarboxylic acids, α-dicarbonyls, oxoacids, hydroxydiacids, and ketodiacids.

5.2 Photo irradiation experiment

Batch UV irradiation experiments were conducted using 4 precursors separately for 0, 1, 4, and 6h. In each experiment, 1 mM precursors was taken into the 100 ml of quartz reactor and 2 mM of H_2O_2 was added and quartz reaction vessel was placed surface facing to UV light as depicted in Fig. 1 and sealed with Teflon-lined screw 15 cap under the ambient pressure and 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 185nm as well as broad peak at > 254 nm. The experimental setup (**Figure 1**) 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 experiment system (i.e. inside cartoon box) was equivalent to room temperature (25±1 ºC). 10 ml of sample was taken and catalase was added to stop the reaction.

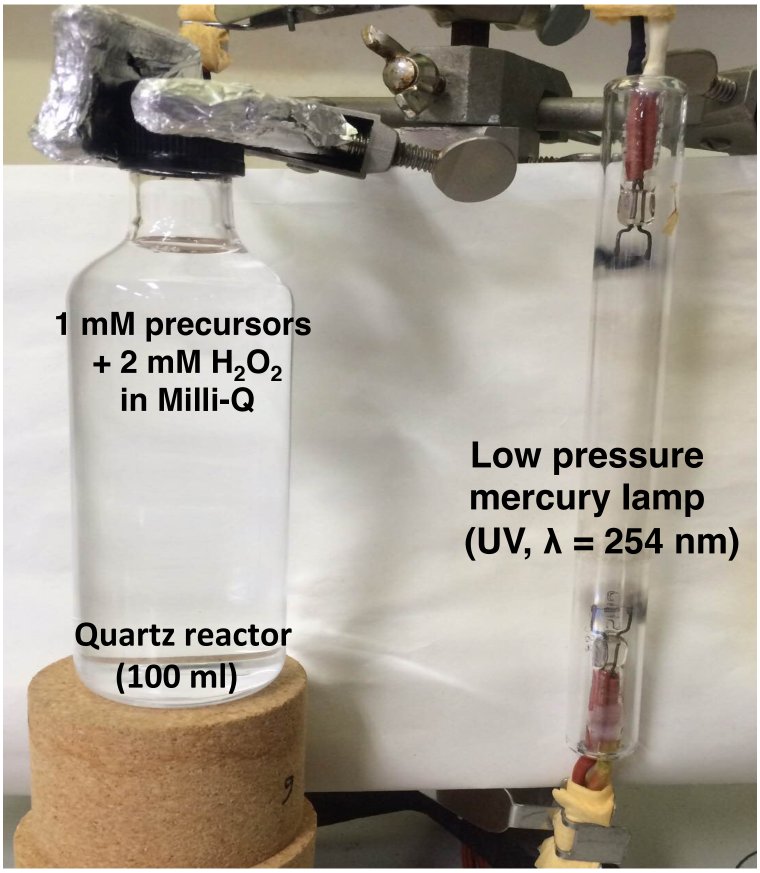

Figure1. Experiment setup for UV irradiation.

5.3 Extraction protocols for hydroxy and keto diacids

Immediately after the irradiation, samples were analyzed for Diacids and related compounds, hydroxy and keto diacids using a method as described in chapter 1. Briefly, the irradiated samples pH was adjusted to 8.5-9.0 with 0.05 M aqueous KOH solution and concentrated almost to dryness using a rotary evaporator under a vacuum. A 14% BF_3/n-butanol solution was added to the concentrates in the flask to allow esterification to take place at 100 °C for 1 h. During the reaction, carboxyl groups are derivatized to their butyl esters, and keto groups to dibutoxy acetals. The derivatives were extracted with 10 mL of n-hexane after adding 10 mL of organic-free water and 0.5 mL of acetonitrile. Acetonitrile transfers the excess n-butanol into the aqueous phase efficiently. The hexane layer was further washed with organic-free water (2 times ~10 mL). Using a rotary evaporator under vacuum and a nitrogen blow-down system, the extracts were concentrated and then dissolved in 100 μL of n-hexane.

An aliquot of the dibutyl ester fraction containing hydroxy diacids was dried under a gentle stream of nitrogen, and hydroxy diacid dibutyl esters were derivatized to the corresponding TMS ethers with 50 μL of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) at 80 °C for 30 min. The derivatives were dried under a nitrogen stream, dissolved in n-hexane (50 μL) and analyzed using gas chromatography/quadrupole mass spectrometry (GC/QMS) and gas chromatography/time of- flight mass spectrometry (GC/TOFMS). Their concentrations were determined using gas chromatography-flame ionization detection (GC-FID).

5.4 Molecular distributions of diacids and relative compounds from anthropogenic precursors

A homologous series of normal diacids (C_2-C_5), and diacids with addition functional groups were detected. i.e., α-dicarbonyls (glyoxal and methylglyoxal), pyruvic acids were detected together with ω-oxoacids (ωC_2-ωC_4) from photo-oxidation of anthropogenic precursors. In early stage of photo-oxidation experiment (1h) oxalic acid was found as dominant reaction product from toluene, and glyoxal from benzene. However, with the prolonged reaction, glyoxal became the most abundant species in the photo-oxidation of benzene and toluene, followed by oxalic acid in toluene and methyl glyoxal in benzene. Glyoxal, methyl glyoxal, oxalic, malonic, and succinic acid concentrations were found to be high at 4h in toluene photo-oxidation, whereas, in benzene glyoxal concentrations were high at 2h. Figure 2 presents molecular distribution of diacids, α-dicarbonyls, and oxoacids

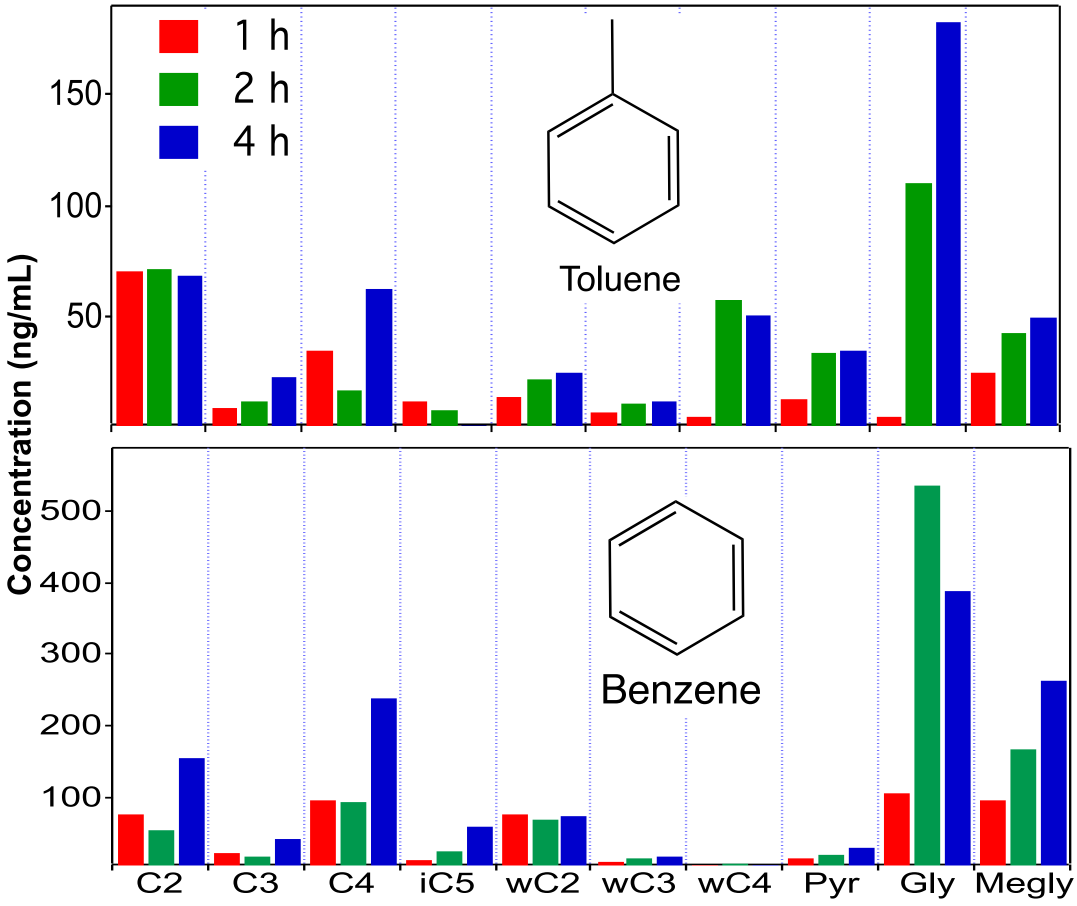

Figure 2. Molecular distribution of diacids, α-dicarbonyls, and oxoacids from toluene and benzene in aqueous phase UV irradiation experiments.

5.5 Change in concentrations of diacids and related compounds from anthropogenic precursors as a function of UV irradiation time

Concentrations of diacids, α-dicarbonyls and oxoacids increased with reaction time (selected species figure 3). Oxalic acid, malonic acid, and adipic acid concentration increase from 0 to 1h, further photo-oxidation remains more or less constant. Concentrations of glyoxal and methylglyoxal show gradual increasing treand upon photo-irradiation from both toluene and benzene.

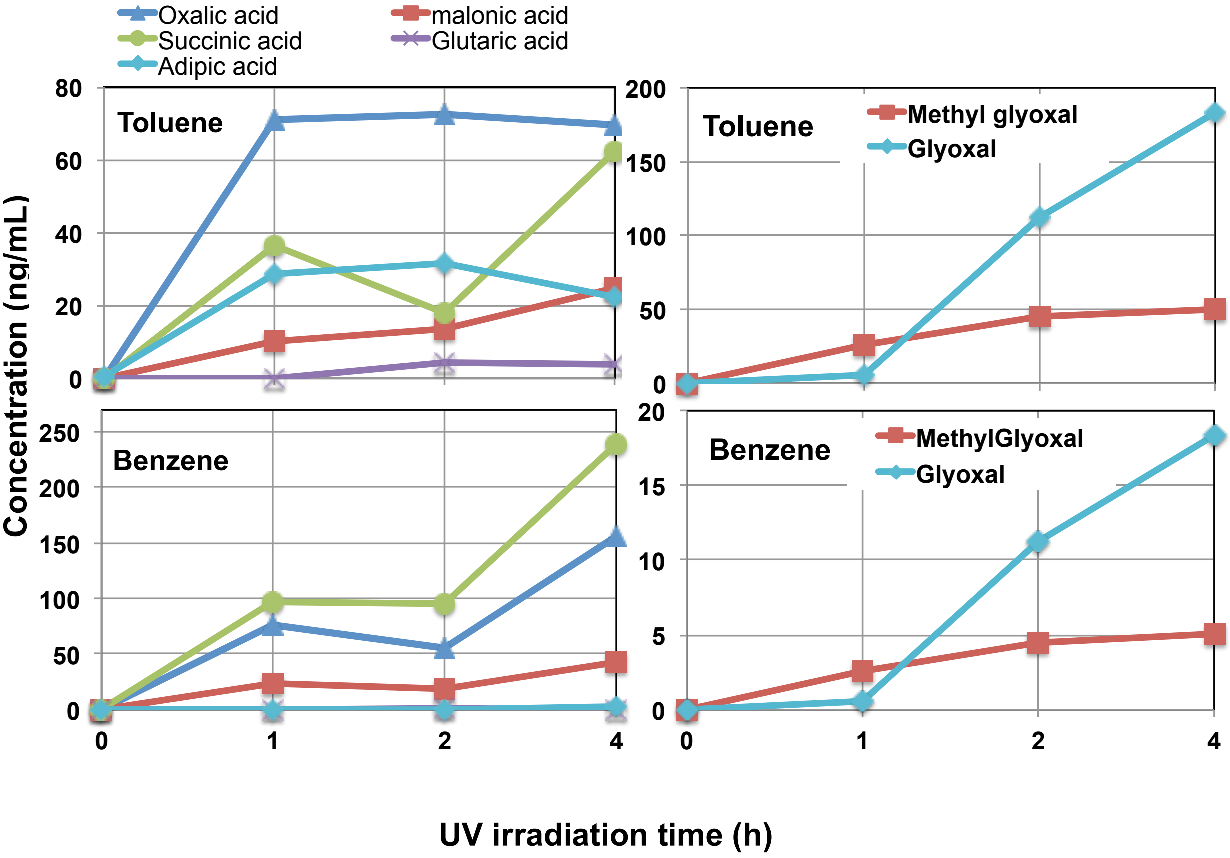

Figure 3. Concentrations of selected species from photo-oxidation of toluene and benzene.

5.6 Molecular distributions of diacids and related compounds from biogenic precursors

A homologous series of diacids (C_2-C_5), α-dicarbonyls, and oxoacids from photo-oxidation of biogenic precursors. Methyl succinic acid was found as the most abundant species followed oxalic acid in isoprene. In early stage of photo-oxidation experiment (1h) oxalic acid was found as dominant reaction product from isoprene and α-pinene. However, with the prolonged reaction, methyl succinic acid becomes most abundant species from photo-oxidation of isoprene and oxalic acid from α-pinene. Concentrations of methyl succinic and oxalic acids increase as a function of UV irradiation time. In α-pinene, molecular distributions are characterized by the predominance of oxalic acid followed by malonic and succinic acid, whose characteristics are similar to the ambient aerosols reported in urban and marine aerosols (Kawamura et al., 2013). Figure 4 presents molecular distribution of diacids, α-dicarbonyls, and oxoacids.

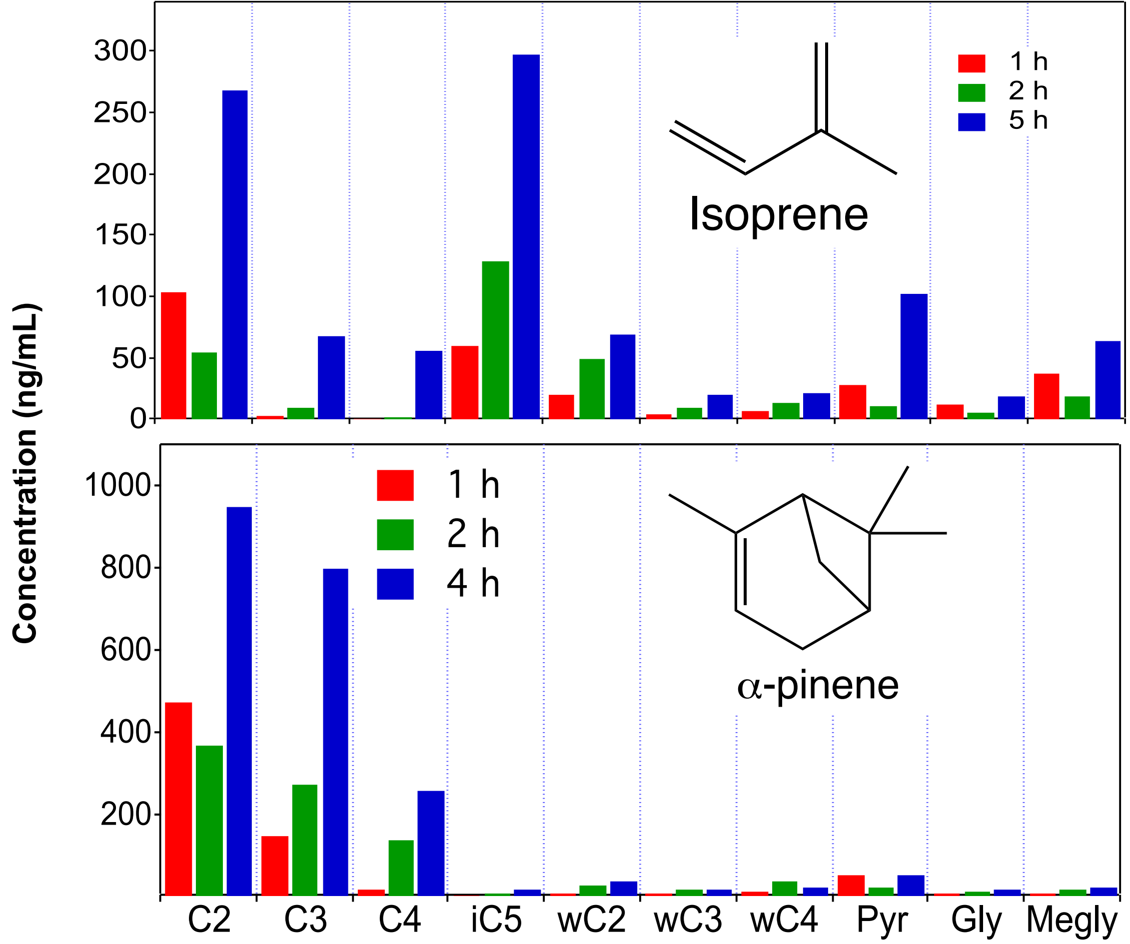

Figure 4. Molecular distributions of diacids, α-dicarbonyls, and oxoacids from isoprene and α- pinene in aqueous phase UV irradiation experiments.

5.7 Concentrations of diacids and related compounds from biogenic precursors

Concentrations of diacids, α-dicarbonyls and oxoacids increased with reaction time (selected species figure 6). Oxalic acid, malonic acid, and succinic acid concentration increase as a function of UV irradiation in both α-pinene and isoprene. Concentrations of glyoxal and methylglyoxal show gradual increasing treand upon photo-irradiation from both toluene and benzene.

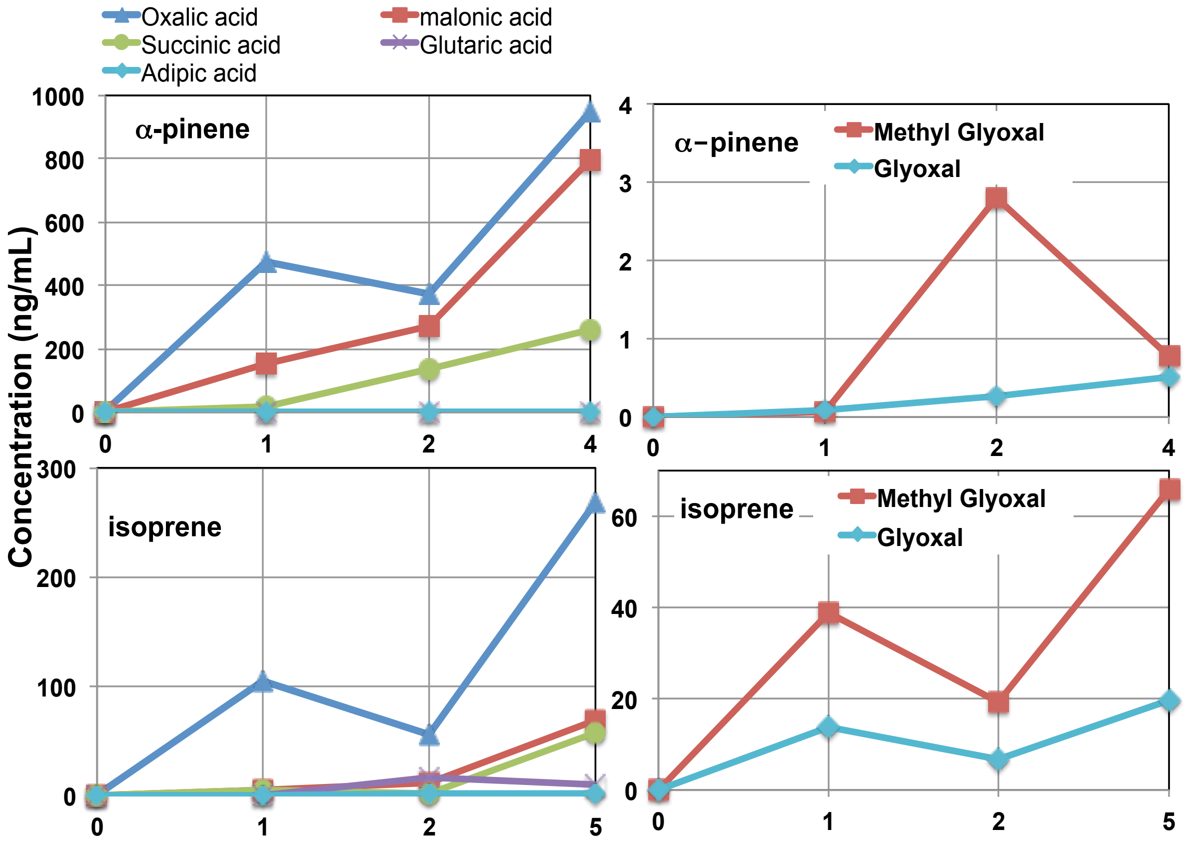

Figure 6. Concentrations of selected species from photo-oxidation of α- pinene and isoprene.

5.8 Molecular distributions and change of concentrations of hydroxy diacids and oxaloacetic acid from toluene and α- pinene.

Molecular distributions of hydroxy and oxaloacetic acid shows that tartaric acid was the most abundant species followed by 3-hydroxyglutaric acid from toluene photo-oxidation experiment (Figure 7). Concentrations of tartaric acid and 3-hydroxyglutaric acids start to increase to maximum at 2 h then start to decrease as a function of UV irradiation time.

In α- pinene, tartaric acid was the most abundant species followed by tartronic acid from α-pinene photo-oxidation experiment. Concentrations of tartronic acid shows maximum at 1 h then start to decrease as a function of UV irradiation time.

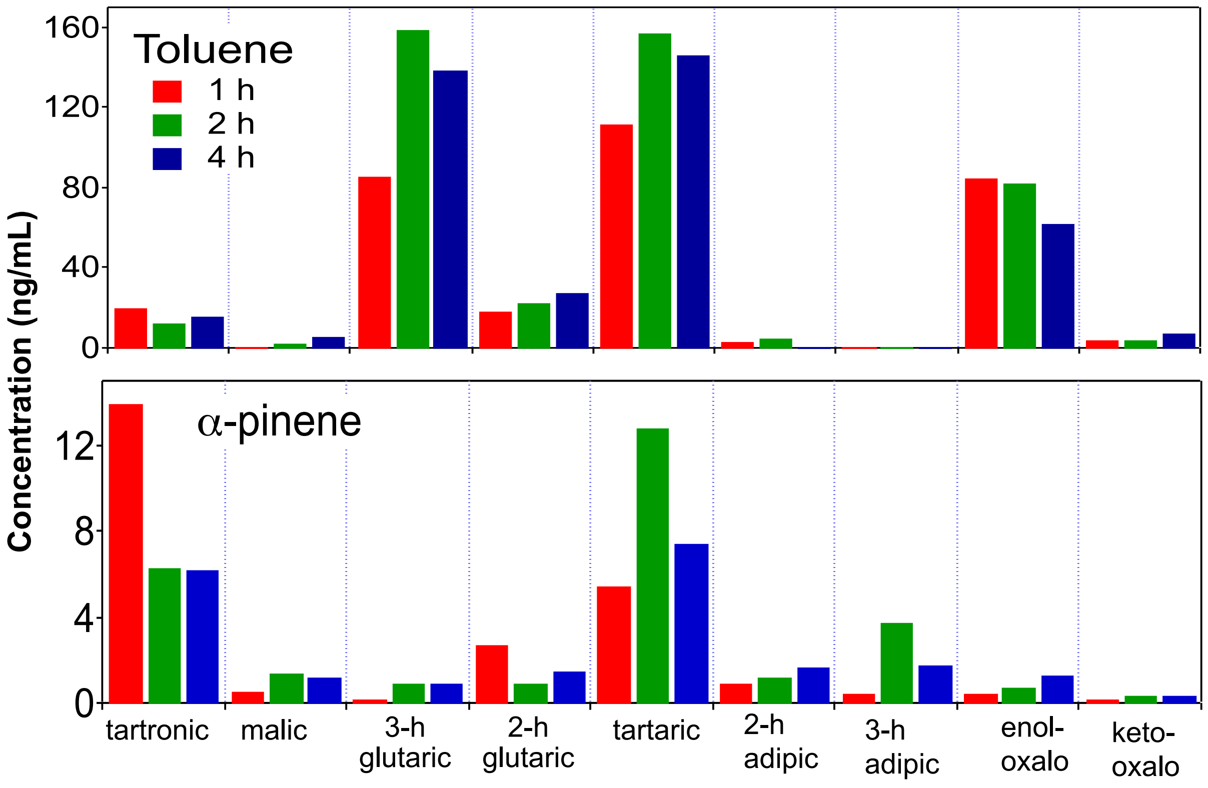

Figure 7. Molecular distribution of diacids, α-dicarbonyls, and oxoacids from toluene and α-pinene in aqueous phase UV irradiation experiments.

5.9 Summery and conclusions

Batch UV irradiation experiments were conducted on anthropogenic and biogenic precursors, the reaction time was 0, 1, 2, 4h. The irradiated samples were analyzed for Diacids and related compounds. Formation of diacids, α-dicarbonyls, and oxoacids from benzene is significant when compare with toluene in aqueous phase. In biogenic precursors, formation of diacids, α-dicarbonyls, and oxoacids is significant from α-pinene when compare with isoprene. Formation of hydroxy diacids and oxaloacetic acid from toluene and α-pinene in aqueous phase is significant. Oxalic acid and glyoxal are abundantly produced from photo-oxidation of toluene, glyoxal and methyl glyoxal from benzene, methyl succinic acid and oxalic acid from isoprene, and oxalic acid and malonic acid from α-pinene. Molecular distributions of diacids in the aqueous phase photo-oxidation of α-pinene are similar to those of ambient aerosols.

This work provides evidence for aqueous processing of VOC (toluene, benzene, isoprene, and α-pinene) resulting in the important organic acids. Identification of reactive organic precursors in aqueous phase is a first step towards more in depth investigation of the importance of these various effects.

5. 10 References

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Concluding Remarks

- ✓ For the first time, a homologous series of hydroxydiacids (tartronic acid, malic acid, 3-hydroxyglutaric acid, 2-hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydroxyadipic acid, tartaric acid), and oxaloacetic acid was identified and quantified in the remote marine aerosols collected from Chichijima Island. And existence of oxaloacetic acid was described in three different forms in the atmosphere.
- ✓ The seasonal variation of tartronic acid, malic acid, 3-hydroxyglutaric acid, 2-hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydroxyadipic acid, tartaric acid, and oxaloacetic acid showed winter to spring maxima. In which, malic acid was the most abundant species followed by 2-hydroxyglutaric acid and tartronic acid in all seasons. Most important contributors for hydroxy diacids and oxaloacetic acid in winter and spring at Chichijima Island are long-range transport of Asian dusts, anthropogenic pollutants, biomass burning products, and vehicular emissions. In summer, significant biological emissions from the ocean are important.
- ✓ Photochemical degradation of hydroxy and keto-diacids in anthropogenic aerosols takes place with prolonged irradiation due to the enhanced levels of chelate-forming metals. In biogenic aerosols, photochemical degradation of hydroxy and keto-diacids takes place rapidly due to lesser amount of chelate-forming metals. Studies of photochemical processing suggest that formation and degradation of diacids through intermediates such as hydroxy and keto-diacids are significant in both anthropogenic and biogenic aerosols.
- ✓ Aqueous phase laboratory study reveals that photochemical production of diacids and related compounds from benzene, toluene, isoprene and α-pinene in aqueous phase is significant. Concentrations of low molecular weight diacids and related compounds increases with irradiation time in all precursors, suggest that photo-oxidation of precursors in aqueous phase is important. And photochemical production of glyoxal from benzene and toluene in

aqueous phase is significant.

✓ Previously, formation pathways of hydroxydiacids as intermediates were proposed, in this study, those pathways were confirmed by identifying and quantifying the intermediates.

Finally, this study will be helpful in understanding the key chemical processes of shorter diacids occurring in the atmosphere. And hence it will beneficial for organic geochemists to explore further chemical processes occurring in the atmosphere.