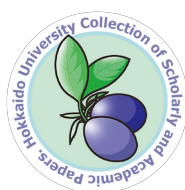




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1 **Seasonal variations of low molecular weight hydroxy-dicarboxylic acids and**
2 **oxaloacetic acid in remote marine aerosols from Chichijima Island in the**
3 **western North Pacific (December 2010 – November 2011)**

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ABSTRACT

Concentrations of homologous hydroxy-dicarboxylic acids (diacids) ($\text{hC}_3\text{-hC}_6$) and keto-diacid (oxaloacetic acid) were measured in the atmospheric aerosols collected at Chichijima Island (27.04°N , 142.13°E) in the western North Pacific from December 2010 to November 2011. The monthly averaged concentrations of hydroxy-diacids and oxaloacetic acid were significantly higher in spring followed by winter and autumn. Molecular distributions of hydroxy-diacids demonstrated that malic acid was the most abundant species in all four seasons, followed by tartronic acid in winter and spring and 3- and 2-hydroxyglutaric acids in summer and autumn. Hydroxy-diacids and keto-diacid maximized in spring and winter when air masses originated from the Asian continent with westerly winds. The concentrations of total hydroxy-diacids and oxaloacetic acid ranged from 0.1 to 27.3 ng m^{-3} and <0.005 to 2 ng m^{-3} , respectively. The enhanced concentrations of diacids and their intermediates in winter and spring are associated with a long-range atmospheric transport of pollutants from East Asia to remote Chichijima Island followed by photochemical processing of organic aerosols. Seasonal molecular distribution of hydroxy-diacids and oxaloacetic acid was found to be dependent on the source strengths and plausible photochemical processing to form smaller diacids. Moderate to strong correlations among hydroxy-diacids, oxaloacetic acid and low molecular weight (LMW) diacids suggest that hydroxy-diacids and oxaloacetic acid are the intermediates in the photochemical oxidation of LMW diacids. Hence, photochemical formation of the most abundant LMW diacids, i.e., oxalic acid, could be produced via hydroxy- and keto-diacid as intermediates.

1. Introduction

Atmospheric aerosols have received considerable attention with regard to their impact on radiative balance directly by absorbing or scattering the sunlight and indirectly by acting as cloud condensation nuclei (CCN), which is associated with a global climate change (O'Dowd et al., 2004). The organic compounds are a main fraction of the fine atmospheric aerosols and potentially control the chemical and physical properties of the particles. In particular, polar organic compounds are proposed to make the aerosol surfaces more hydrophilic, leading particles to act as CCN (Mochida et al., 2003). Although various studies have been performed in order to characterize individual species in organic aerosols (Kawamura and Ikushima, 1993; Simoneit et al., 2004), less than 20 % of organic aerosol mass has been quantified in the ambient aerosols and their complete chemical characterization is inadequate because each organic compound has its own complex behavior that is difficult to generalize (Neususs et al., 2000; Pandis et al., 2013).

Organic acids are one of the major compound classes in tropospheric organic aerosols. In particular, dicarboxylic acids (diacids) constitute a significant portion of water-soluble organic fraction in aerosols (Kawamura and Sakaguchi, 1999; Saxena and Hildemann, 1996). Diacids are mostly present as particles rather than in gas phase (Limbeck et al., 2005). Because they are highly water-soluble, their presence in the aerosols can alter the physicochemical properties of atmospheric particles and enhance the capability of aerosols as CCN (Saxena et al., 1995). Low molecular weight (LMW) diacids, oxocarboxylic acids and α -dicarbonyls are extensively studied over the marine and continental aerosols (Kawamura and Usukura, 1993; Pavuluri et al., 2010). Although diacids and related compounds can be generated by primary sources including fossil fuel combustion (Kawamura and Kaplan, 1987), meat cooking (Rogge et al., 1991) and biomass burning (Narukawa et al., 1999), they are mainly formed by secondary processes in the atmosphere via the photochemical oxidation of volatile organic compounds (VOCs) of both anthropogenic and biogenic origin (Charbouillot et al., 2012; Kawamura et al., 1996b; Pavuluri et al., 2010).

Photo-oxidation of higher diacids and other precursors are also important sources of LMW diacids in aerosols (Zuo and Hoigne, 1994), where oxalic acid (C_2) is generally the dominant species followed by malonic acid (C_3) or succinic acid (C_4) (Kawamura and Sakaguchi, 1999). Diacids and related polar compounds are also produced by photochemical chain reactions of unsaturated fatty acids as well as their oxidation products. These compounds are important in the climate changes of the earth (Kumar et al., 2003). In a

previous study, oxalic acid (C_2) is suggested to be formed by in-cloud oxidation of glyoxal (Gly), in which glyoxylic acid (ωC_2) is a key intermediate (Warneck, 2003). Further, laboratory investigation showed that aqueous phase oxidation of methylglyoxal (MeGly) derived from atmospheric oxidation of isoprene and toluene via pyruvic acid (Pyr) and acetic acid leads to result in C_2 (Lim et al., 2005). Subsequent studies demonstrated the formation of C_2 from Gly through ωC_2 as an intermediate (Carlton et al., 2006). However, the formation and removal processes of LMW diacids are still ambiguous.

Kawamura and Sakaguchi (1999) suggested that multifunctional diacids are the important intermediates in the formation of smaller diacids. However, studies focusing on multifunctional diacids (hydroxy-diacids and keto-diacid) are limited. Due to their enhanced polarity compared to diacids, they play an important role in enhancing the hygroscopicity of organic aerosols. It is also expected that studies of keto- and hydroxy-diacids provide useful information to better understand the oxidative reaction mechanisms of LMW diacids in the atmosphere during long-range transport. Recently, Gowda et al. (2016) have identified a homologous series of hydroxy-diacids and keto-diacid in marine aerosols collected over Chichijima Island. In this study, we analyzed marine aerosol samples collected for one year for molecular distributions of hydroxy-diacids and keto-diacid. Here, we report the first seasonal observation of a homologous series of hydroxy-diacids (hC_3 - hC_6) and keto-diacid with their concentration changes, and discuss their sources and photochemical formation mechanisms.

2. Experimental

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, 254 m above the sea level), an outflow region of the Asian dusts and polluted air masses from China and other neighboring countries. Total 53 samples were collected from 1 December 2010 to 30 November 2011 on pre-combusted (450 °C) quartz fiber filters using a high volume air sampler (Kimoto AS-810B) at a flow rate of $1.0 \text{ m}^3 \text{ min}^{-1}$ (Kumar et al., 2003). Sampling periods were five days. The sampling site is shown in Fig. 1. After the sampling, the filters were placed in precombusted glass jars with a Teflon-lined screw cap, transported to Hokkaido University in Sapporo, and stored in a freezer room at -20 °C prior to analysis.

2.2. Chemical analysis

The filter samples were analyzed for diacids, hydroxy-diacids and keto-diacid (as sum of their carboxylic acid and carboxylate) by the previously reported method (Gowda et al., 2016). Briefly, a part of the quartz-fiber filter (Pallflex, 2500 QUAT-UP) 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 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 (Büchi, R114) under a vacuum. A 14% BF₃/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 acidification during derivatization shifts the equilibrium between carboxylate and carboxylic acid to carboxylic acid. Hence, hereafter sum of carboxylate and carboxylic acid concentrations were referred as concentration of free carboxylic acid. 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 (10 mL x 2).

Using a rotary evaporator under a vacuum and a home-made nitrogen blow-down system, extracts were concentrated and hydroxyl group were derivatized to corresponding trimethylsilyl (TMS) ethers with a 50 µL of BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) 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) (Agilent GC7890A and JEOL MS Accu TOF-GCv 4G) and quantified using a gas chromatography (GC/FID). Known amounts of authentic standards (malic, tartaric, and oxaloacetic acids from Wako Pure Chemical Industries (Tokyo, Japan), tartronic and 3-hydroxyglutaric acids from Alfa Aesar (Heysham, UK) and Toronto Research Chemicals (Toronto, Canada), respectively) were spiked to pre-combusted quartz fiber filter and derivatized to butyl esters/TMS ethers by the procedure described above (Gowda et al., 2016). The adjustment of pH may not alter the integrity of some organic species; this can be assessed by the analysis of spiked authentic standards and confirm their GC-MS profile. The recoveries were 80% for oxalic acid, better than 85% for malonic acid and greater than 80% for hydroxy-diacids. In the case of authentic oxaloacetic acid, GC retention time and the mass spectra are used to distinguish enol and keto forms; both species derivatize differently, and

provide a distinct mass spectrum. The recovery experiments suggest that they were quite stable during the extraction. However, their equilibrium was affected by several factors such as solvent, temperature, and pH, so it is difficult to predict the enol to keto conversion during extraction. For the purpose of evaluating artifacts during the experiment, we conducted repeated analysis of a same filter sample with the analytical errors of less than 10 %. Concentrations of diacids and hydroxy-diacids reported in this study were corrected against the field blanks.

3. Results and Discussion

3.1. Molecular distributions of diacids, hydroxy-diacids and oxaloacetic acid

A homologous series of diacids (C_2 - C_6), hydroxy-diacids (tartronic, malic, 3-hydroxyglutaric, 2-hydroxyglutaric, tartaric, 2-hydroxyadipic, 3-hydroxyadipic acids), and two tautomeric forms of oxaloacetic acid (enol & keto) were detected in marine aerosol samples. Table 1 summarizes the concentrations of diacids, hydroxy-diacids and oxaloacetic acid in winter, spring, summer, and autumn, with concentration ranges, average and standard deviations for each season and the abbreviations of each compounds. Concentrations of total diacids (C_2 - C_6) range from 5.36 to 423 $ng\ m^{-3}$, whereas those of total hydroxy diacids (hC_3 - hC_6) range from 0.1 to 30 $ng\ m^{-3}$ and those of oxaloacetic acid range from BDL to 2.0 $ng\ m^{-3}$. Among diacids, oxalic acid (C_2) was found as the most abundant species followed by malonic acid (C_3) or succinic acid (C_4) in all the seasons. Among hydroxy diacids, malic acid (hC_4) was found as the dominant species in all four seasons followed by tartronic acid (hC_3) in winter and spring, whereas 3-hydroxyglutaric acid ($3-hC_5$) was the second most abundant species in summer, and 2-hydroxyglutaric acid ($2-hC_5$) in autumn.

3.2. Seasonal variations of hydroxy-dicarboxylic acid and oxaloacetic acid

Figure 2 shows seasonal variations in the concentrations of hydroxy-diacids and oxaloacetic acid measured in the Chichijima aerosols from December 2010 to November 2011. Monthly averaged concentrations of diacids, hydroxy-diacids and keto-diacids clearly show significant seasonal variations with springtime maxima and summertime minima. Highest average concentration of malic acid (6.5 $ng\ m^{-3}$) was observed in spring, whereas lowest concentration (0.65 $ng\ m^{-3}$) was found in summer on a seasonally averaged basis. Similar seasonal variations can be seen for tartronic, hydroxyglutaric and hydroxyadipic acids. Although concentrations of hydroxy-diacids are generally higher in spring and lower in summer, this significant difference could be explained by a difference in the emission of their precursors or atmospheric processing.

Chichijima is a remote island located in the western North Pacific, which is frequently influenced by westerly-driven continental outflow from the Asian continent (Duce et al., 1980). From January to April the wind is strong, with wind circulation of westerly (from the Asian continent to the Pacific) and the observation site experiences long-range transport of continental aerosols (anthropogenic and dust). The winds are weakening by May/June and the wind direction changes to southeasterly and continues until August/September. The observation site gets pristine marine air masses, low wind speed and also much rainfall during the southeasterly regime. Again, the wind starts shifting from southeasterly to northwesterly by October and becomes stronger towards December. Therefore, on the basis of major synoptic meteorological conditions as stated above, one year is divided into four seasons, i.e., winter (December-February), spring (March-May), summer (June-August) and autumn (September-November) over Chichijima (Boreddy et al., 2017). Air mass back trajectories are given in Figure 3. The large variations in the concentrations of hydroxy-diacids and keto-diacids in autumn to spring may also 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 for diacids and hydroxy-diacids imply that their formation processes are linked each other.

3.3. Correlation analyses between diacids and hydroxydiacids

In order to find the source and formation pathways of hydroxy-diacids we performed a correlation analysis among diacids, hydroxy-diacids and oxaloacetic acid for four seasons. Table 2 shows the results of correlation analyses of LMW diacids and its intermediate compounds in winter, spring, summer and autumn. Correlation coefficient (r) is classified as strong ($r > 0.80$), moderate to strong (0.7-0.80), moderate (0.4-0.65), weak to moderate (0.2-0.4) and weak (< 0.2) (Rubin, 2012).

As seen in Table 2a, a weak correlation between diacids and hydroxy-diacids (except for malic and 3-hydroxyglutaric acids) was obtained in winter. The weak correlations may suggest that sources or formation mechanisms of hydroxy-diacids from diacids are different in winter season. In spring (Table 2b), moderate to strong correlations were obtained between oxalic acid (C_2) and hydroxy-diacids such as hC_3 ($r = 0.70$), 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). These hydroxy diacids also show good correlations with ωC_2 , 3-oxopropanoic acid (ωC_3), pyruvic acid (Pyr), glyoxal (Gly), methylglyoxal (MeGly), and adipic acid (C_6). C_6 is produced by incomplete combustion of aromatic hydrocarbons (e.g., naphthalene)

(Kawamura and Ikushima, 1993) and cyclic olefins (Hatakeyama et al., 1985). Gly and MeGly are emitted from myriad sources, such as biomass burning (Schauer et al., 2001) and noncatalyst equipped gasoline-powered motor vehicles (Schauer et al., 2002), additionally, gas-phase oxidation products of VOCs such as benzene, toluene, xylene, isoprene, ethylene, and naphthalene (Ervens et al., 2004; Volkamer et al., 2001). These results suggest that photochemical chain reactions are involved in the formation of hydroxy-diacids and keto-diacids as intermediate compounds for the production of small diacids in spring season.

In summer, moderate to strong 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) (see Table 2c). Azelaic acid (C_9) also shows good correlations with $3-hC_5$ (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 containing a double bond predominantly at C_9 position, which are emitted from marine phytoplankton to the atmosphere (Kawamura and Gagosian, 1987). These correlations suggest that LMW diacids may be formed through intermediate compounds such as hydroxy-diacids and keto-diacids in summer. We found moderate to strong correlations in autumn (Table 2d) between oxalic acid (C_2) and hydroxy-diacids such as hC_3 ($r = 0.95$), hC_4 (0.91), enol oxaloacetic acid (0.89), keto oxaloacetic acid (0.79), $3-hC_5$ (0.93), $2-hC_5$ (0.95), Tart (0.97), $2-hC_6$ (0.71), and $3-hC_6$ (0.97).

Deshmukh et al. (2018) reported that correlation of C_2/C_2-C_{12} diacids ratios with solar radiation could be used as an indicator for the photochemical production of C_2 from higher homologous diacids. And they found strong correlation between C_2/C_2-C_{12} diacids ratios with solar radiation suggesting that C_2 in Alaskan region is produced by photooxidation of homologous diacids under high solar radiation. In this study, hydroxy-diacids show good correlations each other in all four seasons, suggesting that they may be strongly connected to each other in the chain reactions. Many studies have been conducted to interpret the production of diacids, e.g., Kawamura and Sakaguchi (1999); Lim et al. (2005); Warneck (2003). However, this is the first time to quantify homologous hydroxy diacids as intermediates in order to examine their source and formation mechanism. Additionally, no statistically significant correlation was found between total hydroxy-diacids and Na^+ in all the seasons even in summer when most air masses originated from the western North Pacific (Figure S1). This suggests even though malic acid can be emitted from primary sources such as biomass burning (Kundu et al., 2010) but they are largely formed in the atmosphere through secondary oxidation processes.

3.4. Concentration ratios of diacids, hydroxy- and keto-diacids: implications for sources and formation mechanisms

Studies have been conducted to interpret the formation mechanisms of C₂, C₃, C₄ and C₅ from their higher homologues (Kawamura and Sakaguchi, 1999). LMW diacids have been proposed to result from atmospheric photo-oxidative chain reactions, that is, C₂ can be produced by the oxidation of ωC₂, Pyr, Gly, C₃ and C₄ (Kawamura et al., 1996a). Further, it has been suggested that C₂ and C₃ are likely produced in the marine atmosphere by the photooxidation of C₄ through intermediates such as malic acid (hC₄) and keto-malonic acid (kC₃) (Kawamura and Sakaguchi, 1999). However, the detailed formation pathways of LMW diacids in the atmosphere are still unclear. It has been suggested that maleic acid (M), a photo-oxidation product of aromatic hydroxycarbons such as benzene and toluene, may be isomerized to fumaric acid (F) under high solar radiation in the atmosphere (Kawamura, 1993). Therefore, F/M mass ratio may be a good indicator of photochemical processing. Kawamura and Bikkina (2016) suggest that higher F/M ratio in summer can be explained by the enhanced photo-isomerization of maleic to fumaric acid. In the current study, F/M ratio shows an increasing trend from winter to autumn along with an increase in ambient temperature (Fig. 4 i and j).

On the other hand, mass ratio of adipic acid to azelaic acid (C₆/C₉) and phthalic acid to azelaic acid (Ph/C₉) ratio can be used as tracer to evaluate contribution of biogenic versus anthropogenic source contribution to dicarboxylic acids (Kawamura et al., 2013). In the atmosphere, adipic acid and phthalic acids are mainly formed by the photochemical oxidation of cyclic olefins and naphthalens, respectively, whereas azelaic acid is a specific photochemical oxidation product of biogenic unsaturated fatty acids that contain a double bond predominantly at C₉ position (Kawamura and Gagosian, 1987). Based on C₆/C₉ and Ph/C₉ mass ratio, we can clearly differentiate between different seasons. Additionally, we can differentiate the long-range transport from marine emissions. In this study, C₆/C₉ and Ph/C₉ mass ratios show higher values in winter and/or spring and lower values in summer and /or autumn, suggesting that winter and spring samples are influenced by anthropogenic emissions and summer samples by marine air masses. In this study, we found an increase in the trend of mass concentration ratios of C₃/C₄ (except for April) and C₂/C₃ (except for May) from winter to autumn. Additionally, mass ratio of kC₄ (keto form of oxaloacetic acid)/hC₄ and kC₃/hC₃ showed an increase from winter to autumn. These observations suggest that C₂ could be largely produced by the photochemical degradation of C₃ and C₄ diacids through the

production of intermediates such as hydroxy- and keto-diacids.

4. Summary and Conclusions

Homologous series of hydroxy-diacids ($\text{hC}_3\text{-hC}_6$) and oxaloacetic acid were identified in marine aerosols collected from Chichijima Island in the western North Pacific. Based on a year-round data set, we found that malic acid is the most abundant hydroxy diacid species followed by tartronic acid in winter and spring, 3-hydroxyglutaric acid in summer and 2-hydroxyglutaric acid in autumn. The hydroxy diacids showed a strong seasonal trend with concentration maxima in spring and minima in summer, suggesting that an important anthropogenic emission from East Asia followed by long-range atmospheric transport over the western North Pacific is an important source. Mass ratios and strong correlation between LMW diacids and hydroxy-diacids ($\text{hC}_3\text{-hC}_6$) in spring and autumn indicate that they are internally linked in photochemical oxidative chain reactions in the atmosphere to produce oxalic acid. This study may suggest that photochemical formation of oxalic acid from their higher homologous ($\text{C}_3\text{-C}_5$) through the production of intermediates such as hydroxy- and keto-diacids. These results demonstrate that the increased concentrations of LMW diacids over the western North Pacific are probably due to the photochemical processing during long-range atmospheric transport from the Asian continent in winter and spring and during the transport of pristine marine air masses in summer and autumn.

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References

- Boreddy, S.K.R., Kawamura, K., Tachibana, E., 2017. Long-term (2001-2013) observations of water-soluble dicarboxylic acids and related compounds over the western North Pacific: trends, seasonality and source apportionment, *Sci. Rep.* 7, 8518. <http://dx.doi.org/10.1038/s41598-017-08745-w>.
- Carlton, A.G., Turpin, B.J., Lim, H.J., Altieri, K.E., Seitzinger, S., 2006. Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.* 33, (06). <http://dx.doi.org/10.1029/2005gl025374>.
- Charbouillot, T., Gorini, S., Vyard, G., Parazols, M., Brigante, M., Deguillaume, L., Delort, A.M., Mailhot, G., 2012. Mechanism of carboxylic acid photooxidation in atmospheric aqueous phase: Formation, fate and reactivity, *Atmos. Environ.* 56, 1-8.
- Deshmukh, D.K., Haque, M.M., Kawamura, K., Kim, Y., 2018. Dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls in fine aerosols over central Alaska: implications for sources and atmospheric processes. *Atmos. Res.* 202, 128-139.
- Duce, R.A., Unni, C.K., Ray, B.J., Prospero, J.M., Merrill, J.T., 1980. Long-range atmospheric transport of soil dust from Asia to the tropical North Pacific: Temporal variability, *Science* 209, 1522-1524.
- Ervens, B., Feingold, G., Frost, G.J., Kreidenweis, S.M., 2004. A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.* 109, (D15), 1984-2012. <http://dx.doi.org/10.1029/2004jd004575>.
- Gowda, D., Kawamura, K., Tachibana, E., 2016. Identification of hydroxy- and keto-dicarboxylic acids in remote marine aerosols using gas chromatography/quadrupole and time-of-flight mass spectrometry, *Rapid Commun. Mass Spectrom.* 30 (7), 992-1000.
- Hatakeyama, S., Tanonaka, T., Weng, J. H., Bandow, H., Takagi, H., Akimoto, H., 1985. Ozone cyclohexene reaction in air - quantitative-analysis of particulate products and the reaction-mechanism, *Environ. Sci. Technol.* 19, 935-942.
- Kawamura, K., 1993. Identification of C₂-C₁₀ ω -oxocarboxylic acids, pyruvic acid, and C₂-C₃ α -dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC/MS, *Anal. Chem.* 65, 3505-3511.
- Kawamura, K., Bikkina, S., 2016. A review of dicarboxylic acids and related compounds in atmospheric aerosols: molecular distributions, sources and transformation. *Atmos. Res.* 170, 140-160.
- Kawamura, K., Gagosian, R.B., 1987. Identification of α -oxocarboxylic acids as acetal esters in aerosols using capillary gas-chromatography mass-spectrometry, *J. Chromatogr.* 390, 371-377.
- Kawamura, K., Ikushima, K., 1993. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.* 27, 2227-2235.
- Kawamura, K., Kaplan, I.R., 1987. Motor Exhaust Emissions as a Primary Source for Dicarboxylic-Acids in Los-Angeles Ambient Air, *Environ. Sci. Technol.* 21, 105-110.
- Kawamura, K., Kasukabe, H., Barrie, L.A., 1996a. Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.* 30, 1709-1722.
- Kawamura, K., Sakaguchi, F., 1999. Molecular distributions of water soluble dicarboxylic acids in marine

- aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.* 104, (D3), 3501-3509.
- Kawamura, K., Sempéré, R., Imai, Y., Fujii, Y., Hayashi, M., 1996. Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, *J. Geophys. Res.* 101, (D13), 18721-18728.
- Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S., Kanaya, Y., Wang, Z., 2013a. High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in the mountaintop aerosols over the North China Plain during wheat burning season, *Atmos. Chem. Phys.* 13, 8285-8302.
- Kawamura, K., Usukura, K., 1993. Distributions of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, *J. Oceanogr.* 49, 271-283.
- Kumar, P., Broekhuizen, K., Abbatt, J., 2003. Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.* 3, 509-520.
- Kundu, S., Kawamura, K., Lee, M., 2010. Seasonal variations of diacids, ketoacids, and α -dicarbonyls in aerosols at Gosan, Jeju Island, South Korea: Implications for sources, formation, and degradation during long-range transport, *J. Geophys. Res.* 115, D19307. <http://dx.doi.org/10.1029/2010JD013973>.
- Lim, H.J., Carlton, A.G., Turpin, B.J., 2005. Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.* 39, 4441-4446.
- Limbeck, A., Kraxner, Y., Puxbaum, H., 2005. Gas to particle distribution of low molecular weight dicarboxylic acids at two different sites in central Europe (Austria), *J. Aeros. Sci.* 36, 991-1005.
- Mochida, M., Umemoto, N., Kawamura, K., Uematsu, M., 2003. Bimodal size distribution of C₂-C₄ dicarboxylic acids in the marine aerosols, *Geophys. Res. Lett.* 30 (13). <http://dx.doi.org/10.1029/2003GL017451>.
- Narukawa, M., Kawamura, K., Takeuchi, N., Nakajima, T., 1999. Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.* 26, 3101-3104.
- Neususs, C., Pelzing, M., Plewka, A., Herrmann, H., 2000. A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: Methods and first results, *J. Geophys. Res.* 105 (D4), 4513-4527. <http://dx.doi.org/10.1029/1999JD901038>.
- O'Dowd, C.D., Aalto, P.P., Yoon, Y.J., Hameri, K., 2004. The use of the pulse height analyser ultrafine condensation particle counter (PHA-UCPC) technique applied to sizing of nucleation mode particles of differing chemical composition, *J. Aeros. Sci.* 35(2), 205-216.
- Pandis, S.N., Donahue, N. M., Murphy, B. N., Riipinen, I., Fountoukis, C., Karnezi, E., Patoulias, D., Skyllakou, K., 2013. Introductory lecture: atmospheric organic aerosols: insights from the combination of measurements and chemical transport models, *Faraday Discuss* 165, 9-24.
- Pavuluri, C.M., Kawamura, K., Swaminathan, T., 2010. Water-soluble organic carbon, dicarboxylic acids, ketoacids, and α -dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.* 115(D11). <http://dx.doi.org/10.1029/2009JD012661>.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., Source of fine organic

- aerosols: 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.* 25 (6), 1112-1125.
- Rubin, A., 2012. *Statistics for Evidence-Based Practice and Evaluation*. Cengage Learning (3), 201-215.
- Saxena, P., Hildemann, L.M., 1996, Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.* 24, 57-109.
- Saxena, P., Hildemann, L.M., McMurry, P.H., Seinfeld, J.H., 1995. Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.* 100, 18755-18770.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 2001. Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.* 35, 1716-1728.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 2002. Measurement of emissions from air pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles, *Environ. Sci. Technol.* 36, 1169-1180.
- Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K., Huebert, B.J., 2004. Aerosol particles collected on aircraft flights over the northwestern Pacific region during the ACE-Asia campaign: Composition and major sources of the organic compounds, *J. Geophys. Res.* 109, (D19). <http://dx.doi:10.1029/2004JD004565>.
- Volkamer, R., Platt, U., Wirtz, K., 2001. Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, *J. Phys. Chem. A* 105 (33), 7865-7874.
- Warneck, P., 2003. In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.* 37(17), 2423-2427.
- Zuo, Y.G., Hoigne, J., 1994. Photochemical decomposition of oxalic, glyoxalic and pyruvic-acid catalyzed by iron in atmospheric waters, *Atmos. Environ.* 28, 1231-1239.

Table 1. Concentrations (ng m^{-3}) of hydroxy-diacids 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). Below detection limit (BDL) was 5 pg m^{-3}

	<u>Abbr.</u>	<u>Winter (n = 13)</u>		<u>Spring (n = 13)</u>		<u>Summer (n = 13)</u>		<u>Autumn (n = 13)</u>	
		Range	av $\pm$ SD	Range	av $\pm$ SD	Range	av $\pm$ SD	Range	av $\pm$ SD
Oxalic acid	C ₂	35.8-334	97.4 $\pm$ 74.1	4.74-181	89.7 $\pm$ 65.1	5.27-43.9	17.2 $\pm$ 10.5	6.49-158	50.4 $\pm$ 49.7
Malonic acid	C ₃	5.79-44.5	13.5 $\pm$ 9.68	0.46-28.0	14.1 $\pm$ 9.85	1.17-12.0	4.12 $\pm$ 2.83	0.46-28.1	7.80 $\pm$ 8.52
Succinic acid	C ₄	3.49-35.3	8.18 $\pm$ 8.29	0.16-22.3	10.1 $\pm$ 7.85	0.49-4.71	1.43 $\pm$ 1.30	0.27-12.0	3.25 $\pm$ 3.75
Glutaric acid	C ₅	0.59-5.97	1.72 $\pm$ 1.37	BDL-3.17	1.47 $\pm$ 1.09	0.07-0.66	0.22 $\pm$ 0.17	0.03-2.67	0.55 $\pm$ 0.76
Adipic acid	C ₆	0.39-2.66	0.91 $\pm$ 0.16	0.16-1.02	0.43 $\pm$ 0.25	0.13-0.41	0.27 $\pm$ 0.09	0.02-1.65	0.46 $\pm$ 0.37
Azelaic acid	C ₉	0.10-0.68	0.27 $\pm$ 0.60	0.01-1.33	0.60 $\pm$ 0.44	0.04-0.30	0.14 $\pm$ 0.09	0.01-1.25	0.33 $\pm$ 0.38
Phthalic acid	Ph	0.62-12.82	2.97 $\pm$ 3.32	0.03-4.72	1.35 $\pm$ 1.40	0.01-0.24	0.10 $\pm$ 0.07	0.02-1.95	0.38 $\pm$ 0.61
Tartronic acid	hC ₃	0.53-3.4	1.52 $\pm$ 0.79	0.02-5.27	1.88 $\pm$ 1.66	0.01-0.29	0.13 $\pm$ 0.08	BDL-1.85	0.58 $\pm$ 0.61
Keto-malonic acid	kC ₃	0.17-1.62	0.55 $\pm$ 0.42	BDL-1.86	0.60 $\pm$ 0.53	0.01-0.10	0.04 $\pm$ 0.03	0.01-0.68	0.20 $\pm$ 0.22
Malic acid	hC ₄	2.61-7.1	4.37 $\pm$ 1.50	0.03-14.75	6.50 $\pm$ 4.91	0.11-1.75	0.65 $\pm$ 0.57	0.11-10.22	2.28 $\pm$ 3.00
3-Hydroxyglutaric acid	3-hC ₅	0.36-1.7	0.89 $\pm$ 0.42	0.01-4.98	1.77 $\pm$ 1.52	0.01-0.67	0.12 $\pm$ 0.19	0.01-2.38	0.50 $\pm$ 0.75
2-Hydroxyglutaric acid	2-hC ₅	0.80-2.8	1.56 $\pm$ 0.57	0.03-4.79	2.31 $\pm$ 1.69	0.05-0.55	0.18 $\pm$ 0.14	0.06-2.52	0.69 $\pm$ 0.78
Tartaric acid	Tart	0.47-1.2	0.78 $\pm$ 0.22	0.01-2.65	0.98 $\pm$ 0.91	0.01-0.41	0.09 $\pm$ 0.12	0.01-1.42	0.39 $\pm$ 0.51
2-Hydroxyadipic acid	2-hC ₆	0.04-0.5	0.28 $\pm$ 0.14	BDL-0.73	0.32 $\pm$ 0.26	BDL-0.05	0.02 $\pm$ 0.01	BDL-0.36	0.09 $\pm$ 0.12
3-Hydroxyadipic acid	3-hC ₆	0.19-0.6	0.38 $\pm$ 0.13	BD -0.82	0.40 $\pm$ 0.28	BDL-0.13	0.03 $\pm$ 0.03	BDL-0.39	0.11 $\pm$ 0.13
Enol oxaloacetic acid	Enol	0.14-0.7	0.36 $\pm$ 0.16	BDL-1.52	0.57 $\pm$ 0.48	0.01-0.12	0.04 $\pm$ 0.03	0.01-0.78	0.23 $\pm$ 0.26
Keto oxaloacetic acid	Keto	0.05-0.4	0.14 $\pm$ 0.09	BDL-0.51	0.17 $\pm$ 0.16	0.01-0.05	0.03 $\pm$ 0.02	0.01-0.23	0.08 $\pm$ 0.06

Table 2. Correlation coefficients (r) among selected diacids, hydroxy- and keto-diacids in (a) winter, (b) spring, (c) summer and (d) autumn (Correlation is significant at $p=0.01$ where $r \geq 0.69$, and $p=0.05$ where r is $0.68 - 0.56$).

(a) Winter

	hC ₃	hC ₄	Enol	Keto	3-hC ₅	2-hC ₅	Tart	2-hC ₆	3-hC ₆	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉
hC ₃	1														
hC ₄	0.31	1													
Enol	0.81	0.31	1												
Keto	0.90	0.28	0.70	1											
3-hC ₅	0.23	0.94	0.25	0.16	1										
2-hC ₅	0.66	0.87	0.68	0.62	0.82	1									
Tart	0.70	0.75	0.73	0.65	0.73	0.91	1								
2-hC ₆	0.76	0.76	0.75	0.68	0.68	0.94	0.85	1							
3-hC ₆	0.72	0.69	0.61	0.68	0.65	0.85	0.86	0.91	1						
C ₂	-0.13	0.61	-0.36	0.10	0.57	0.34	0.19	0.21	0.29	1					
C ₃	-0.16	0.6	-0.38	0.07	0.58	0.34	0.19	0.19	0.26	0.99	1				
C ₄	-0.10	0.58	-0.36	0.1	0.57	0.34	0.18	0.23	0.31	0.99	0.98	1			
C ₅	0.10	0.59	-0.22	0.35	0.56	0.43	0.28	0.36	0.45	0.95	0.93	0.97	1		
C ₆	0.13	0.51	-0.23	0.37	0.45	0.38	0.24	0.36	0.38	0.93	0.92	0.94	0.97	1	
C ₉	-0.29	-0.2	-0.03	-0.34	-0.1	-0.14	0.05	-0.22	-0.16	-0.27	-0.23	-0.32	-0.39	-0.35	1

(b) Spring

	hC ₃	hC ₄	Enol	Keto	3-hC ₅	2-hC ₅	Tart	2-hC ₆	3-hC ₆	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉
hC ₃	1														
hC ₄	0.78	1													
Enol	0.83	0.89	1												
Keto	0.7	0.65	0.69	1											
3-hC ₅	0.71	0.95	0.91	0.49	1										
2-hC ₅	0.7	0.90	0.77	0.51	0.87	1									
Tart	0.8	0.85	0.95	0.48	0.93	0.76	1								
2-hC ₆	0.8	0.88	0.94	0.56	0.90	0.87	0.95	1							
3-hC ₆	0.88	0.88	0.88	0.69	0.81	0.87	0.83	0.94	1						
C ₂	0.70	0.93	0.73	0.70	0.81	0.77	0.65	0.69	0.77	1					
C ₃	0.76	0.97	0.82	0.68	0.90	0.86	0.78	0.82	0.85	0.97	1				
C ₄	0.56	0.87	0.69	0.52	0.82	0.97	0.65	0.78	0.78	0.79	0.86	1			
C ₅	0.73	0.89	0.68	0.71	0.76	0.85	0.61	0.70	0.82	0.95	0.95	0.86	1		
C ₆	0.68	0.80	0.60	0.74	0.62	0.70	0.51	0.61	0.76	0.93	0.90	0.73	0.96	1	
C ₉	-0.36	-0.38	-0.51	-0.4	-0.42	-0.52	-0.45	-0.54	-0.48	-0.2	-0.32	-0.47	-0.33	-0.24	1

Table 2 (Continued).

(c) Summer															
	hC ₃	hC ₄	Enol	Keto	3-hC ₅	2-hC ₅	Tart	2-hC ₆	3-hC ₆	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉
hC ₃	1														
hC ₄	0.46	1													
Enol	0.36	0.56	1												
Keto	0.20	0.68	0.72	1											
3-hC ₅	0.56	0.76	0.52	0.59	1										
2-hC ₅	0.58	0.83	0.68	0.67	0.96	1									
Tart	0.62	0.78	0.58	0.60	0.97	0.95	1								
2-hC ₆	0.66	0.51	0.20	0.21	0.68	0.63	0.72	1							
3-hC ₆	0.46	0.65	0.35	0.55	0.94	0.89	0.86	0.61	1						
C ₂	0.42	0.74	0.48	0.47	0.83	0.82	0.88	0.48	0.71	1					
C ₃	0.42	0.68	0.36	0.38	0.83	0.79	0.87	0.54	0.75	0.96	1				
C ₄	0.47	0.74	0.61	0.50	0.95	0.95	0.94	0.59	0.84	0.86	0.85	1			
C ₅	0.34	0.74	0.21	0.29	0.75	0.75	0.73	0.45	0.76	0.77	0.80	0.80	1		
C ₆	0.29	0.84	0.36	0.39	0.64	0.68	0.66	0.28	0.53	0.80	0.72	0.71	0.88	1	
C ₉	0.37	0.47	0.03	0.21	0.83	0.72	0.75	0.68	0.90	0.65	0.74	0.74	0.78	0.49	1
(d) Autumn															
	hC ₃	hC ₄	Enol	Keto	3-hC ₅	2-hC ₅	Tart	2-hC ₆	3-hC ₆	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉
hC ₃	1														
hC ₄	0.86	1													
Enol	0.89	0.88	1												
Keto	0.80	0.70	0.93	1											
3-hC ₅	0.86	0.99	0.86	0.68	1										
2-hC ₅	0.88	0.98	0.93	0.79	0.97	1									
Tart	0.92	0.89	0.93	0.85	0.91	0.93	1								
2-hC ₆	0.67	0.61	0.83	0.92	0.59	0.74	0.77	1							
3-hC ₆	0.92	0.82	0.89	0.84	0.85	0.89	0.98	0.75	1						
C ₂	0.95	0.91	0.89	0.79	0.93	0.95	0.97	0.71	0.97	1					
C ₃	0.84	0.96	0.86	0.72	0.94	0.96	0.85	0.70	0.80	0.90	1				
C ₄	0.83	0.94	0.81	0.66	0.93	0.94	0.81	0.66	0.76	0.88	0.99	1			
C ₅	0.81	0.74	0.60	0.50	0.79	0.77	0.80	0.52	0.82	0.87	0.78	0.81	1		
C ₆	0.86	0.77	0.71	0.66	0.80	0.82	0.86	0.67	0.89	0.92	0.83	0.84	0.97	1	
C ₉	-0.19	-0.06	-0.01	-0.01	0.01	-0.01	-0.07	-0.06	-0.01	0.02	0.10	0.03	-0.04	-0.04	1

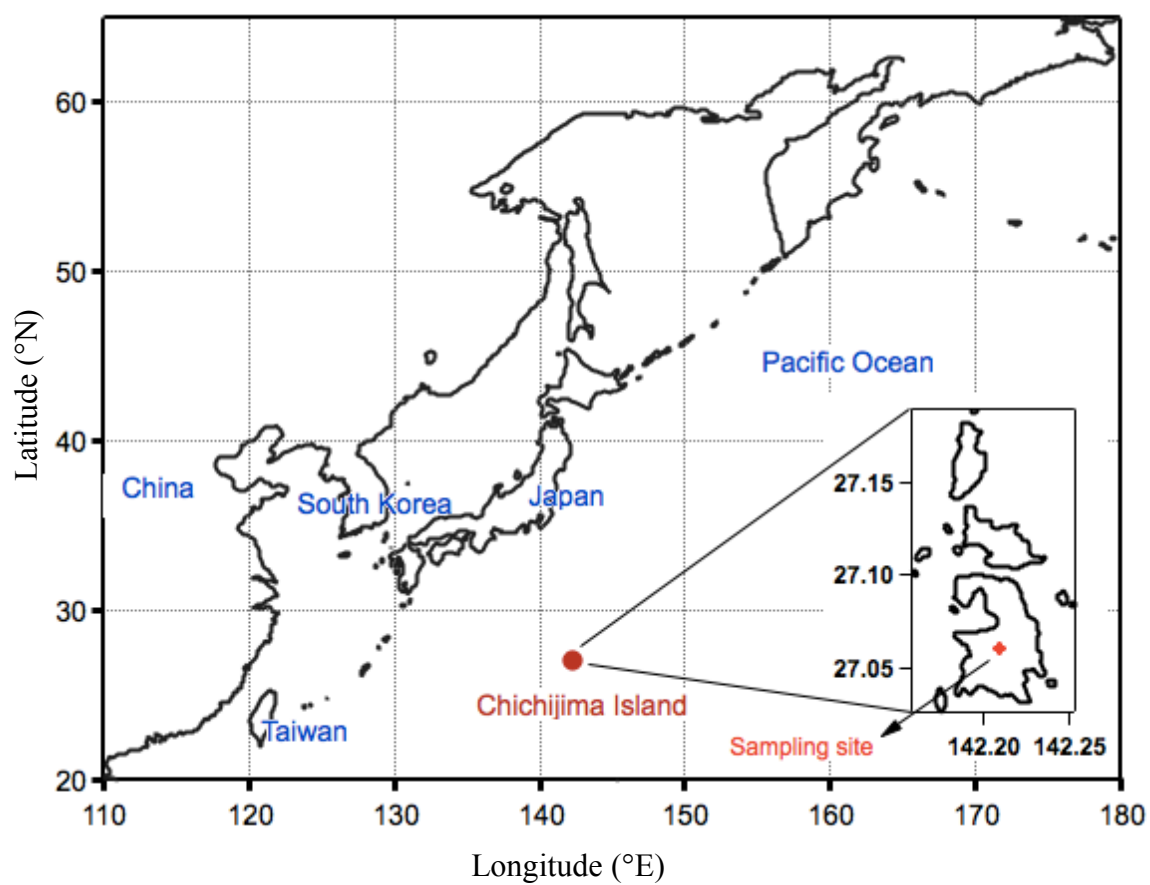


Figure 1. A map of the western North Pacific with the location of Chichijima Island.

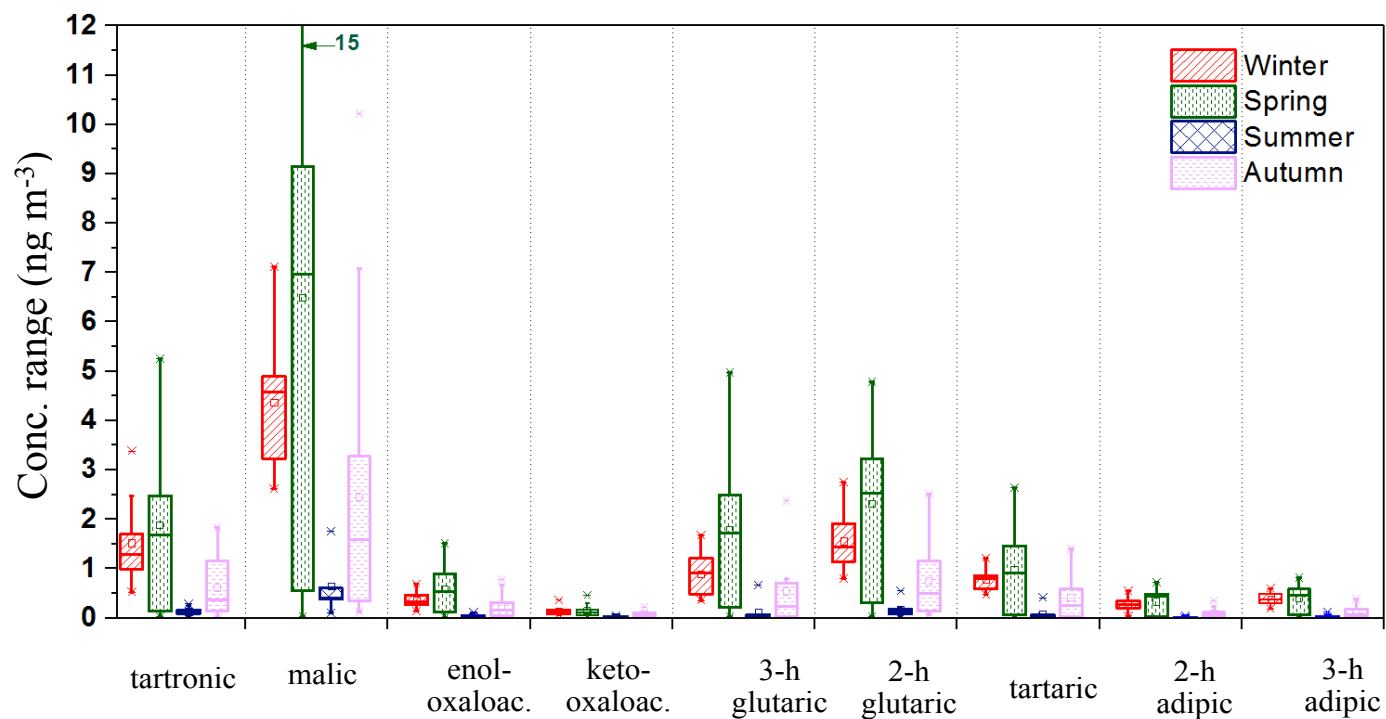


Figure 2. Box plot showing the seasonally variation in hydroxy-diacids (hC₃-hC₆) and keto-diacid (oxaloacetic acid) in aerosols collected from Chichijima Island.

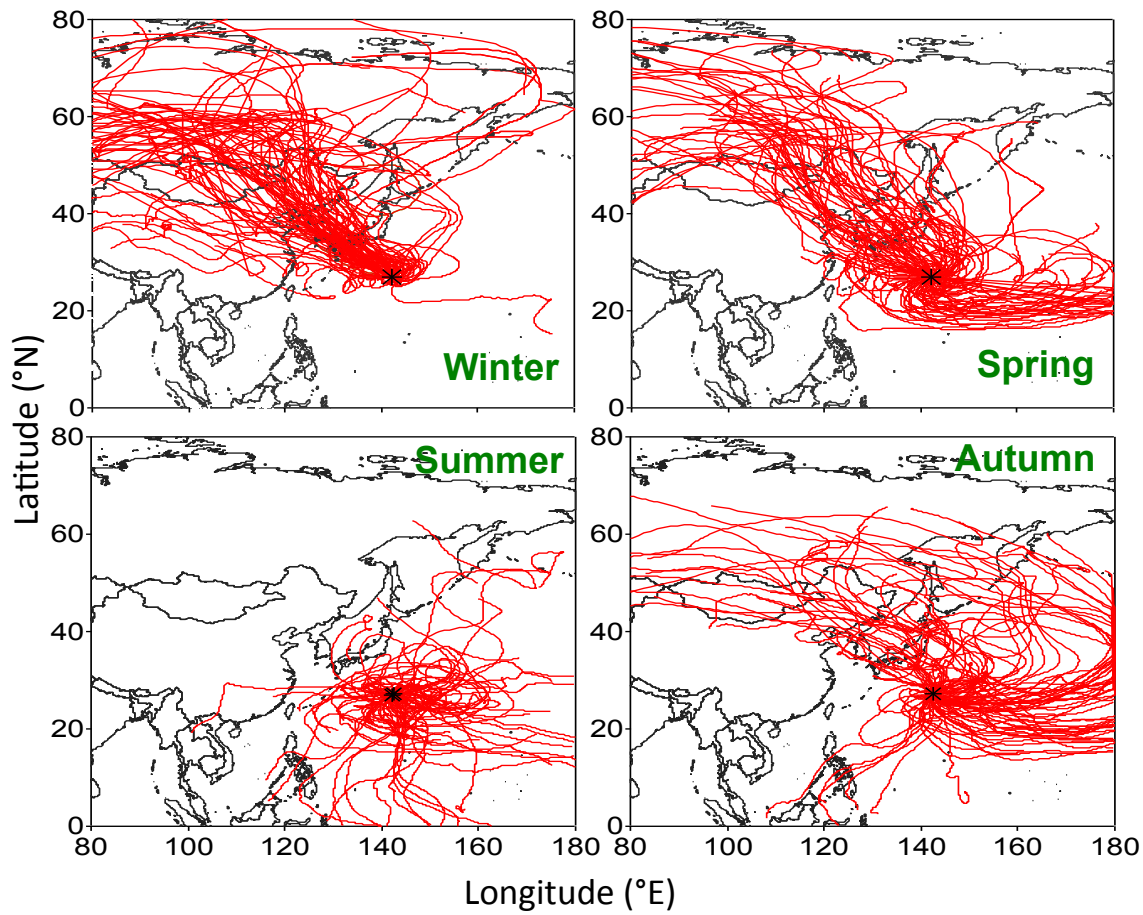


Figure 3. NOAA HYSPLIT 10 days air mass backward trajectories at 500 m a.g.l. for each season over Chichijima Island during December 2010 to November 2011.

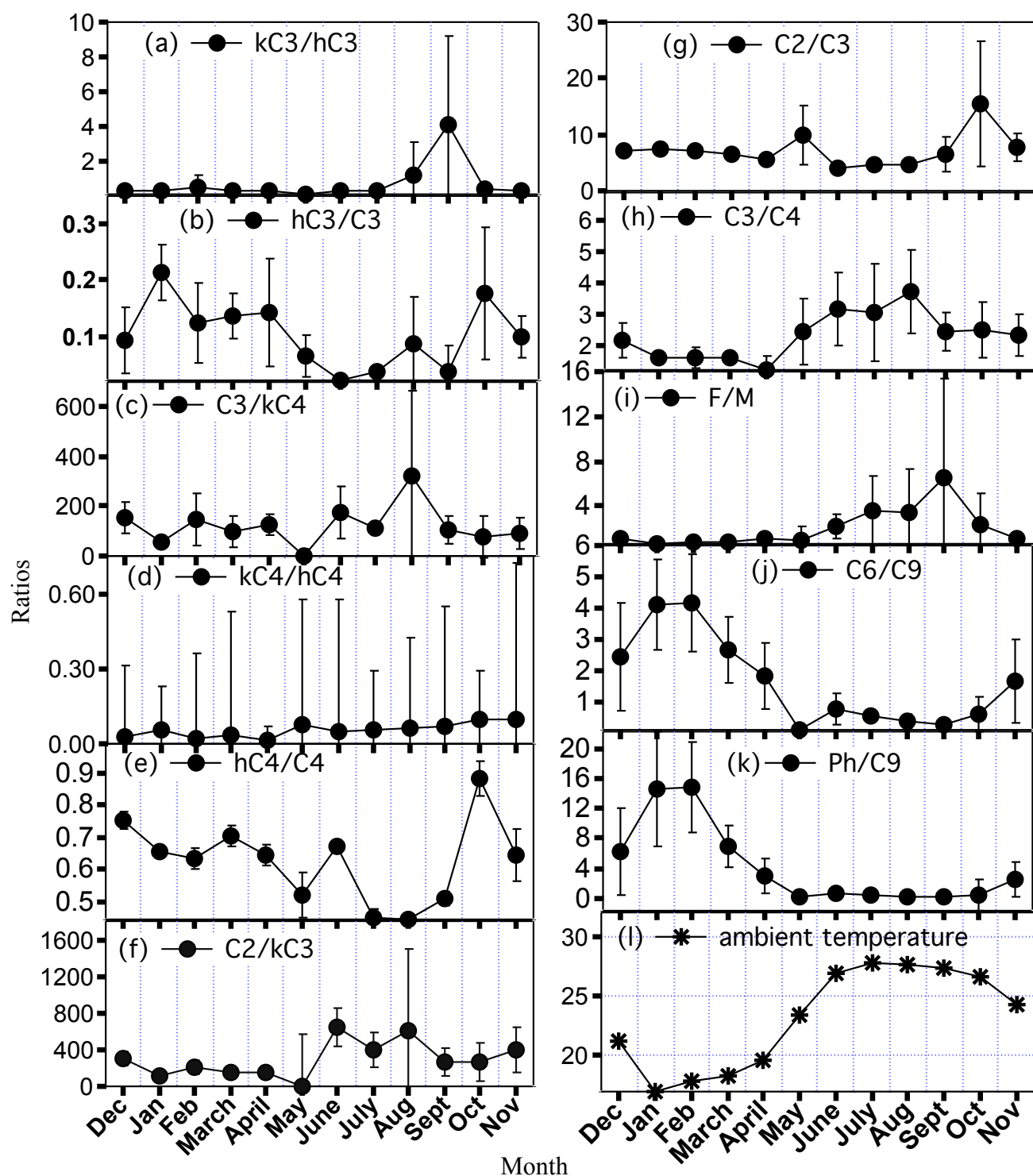


Figure 4. Seasonally variations in the mass concentration ratios of (a) kC_3/hC_3 , (b) hC_3/C_3 , (c) C_3/kC_4 , (d) kC_4/hC_4 , (e) hC_4/C_4 , (f) C_2/kC_3 , (g) C_2/C_3 , (h) C_3/C_4 , (i) F/M , (j) C_6/C_9 , (k) Ph/C_9 and (l) ambient temperature.

Table S1. Correlation coefficients (r) among selected α -dicarbonyls, hydroxy- and keto-diacids in winter, spring, summer and autumn season (Correlation is significant at $p=0.01$ where r is ≥ 0.69 and 0.05 where r is $> 0.68 - 0.56$).

Winter	hC ₃	hC ₄	Enol	Keto	3hC ₅	2hC ₅	Tart	2hC ₆	3hC ₆	ω C ₂	ω C ₃	ω C ₄	ω C ₅	Pyr	Gly	MeGly
hC ₃	1															
hC ₄	0.31	1														
Enol	0.81	0.30	1													
Keto	0.90	0.28	0.70	1												
3hC ₅	0.23	0.94	0.25	0.16	1											
2hC ₅	0.66	0.87	0.68	0.62	0.82	1										
Tart	0.70	0.75	0.73	0.65	0.73	0.91	1									
2hC ₆	0.76	0.76	0.75	0.68	0.68	0.94	0.85	1								
3hC ₆	0.72	0.69	0.61	0.68	0.65	0.85	0.86	0.91	1							
ω C ₂	0.17	0.58	-0.13	0.40	0.49	0.47	0.30	0.43	0.51	1						
ω C ₃	0.03	0.56	-0.28	0.26	0.52	0.39	0.22	0.29	0.38	0.97	1					
ω C ₄	0.03	0.52	-0.27	0.27	0.50	0.36	0.21	0.28	0.38	0.96	0.99	1				
ω C ₅	0.10	0.58	-0.19	0.35	0.53	0.44	0.29	0.35	0.44	0.96	0.98	0.98	1			
Pyr	0.31	0.52	0.01	0.54	0.45	0.50	0.36	0.49	0.57	0.96	0.92	0.94	0.94	1		
Gly	0.41	0.51	0.11	0.64	0.38	0.54	0.43	0.55	0.65	0.94	0.85	0.85	0.87	0.95	1	
MeGly	0.16	0.56	-0.07	0.19	0.40	0.43	0.18	0.44	0.37	0.72	0.65	0.57	0.57	0.58	0.66	1
Spring	hC ₃	hC ₄	Enol	Keto	3hC ₅	2hC ₅	Tart	2hC ₆	3hC ₆	ω C ₂	ω C ₃	ω C ₄	ω C ₅	Pyr	Gly	MeGly
hC ₃	1															
hC ₄	0.78	1														
Enol	0.83	0.89	1													
Keto	0.70	0.65	0.69	1												
3hC ₅	0.71	0.95	0.91	0.49	1											
2hC ₅	0.70	0.90	0.77	0.51	0.87	1										
Tart	0.80	0.85	0.95	0.48	0.93	0.76	1									
2hC ₆	0.80	0.88	0.94	0.56	0.90	0.87	0.95	1								
3hC ₆	0.88	0.88	0.88	0.69	0.81	0.87	0.83	0.94	1							
ω C ₂	0.67	0.80	0.61	0.83	0.63	0.63	0.47	0.53	0.69	1						
ω C ₃	0.55	0.76	0.52	0.76	0.61	0.61	0.37	0.44	0.61	0.98	1					
ω C ₄	0.64	0.89	0.66	0.72	0.82	0.82	0.54	0.64	0.76	0.93	0.94	1				
ω C ₅	0.67	0.82	0.63	0.79	0.70	0.70	0.51	0.55	0.68	0.97	0.97	0.94	1			
Pyr	0.70	0.86	0.69	0.80	0.70	0.70	0.57	0.60	0.73	0.99	0.97	0.95	0.98	1		
Gly	0.61	0.69	0.46	0.71	0.55	0.55	0.36	0.45	0.66	0.93	0.93	0.86	0.88	0.90	1	
MeGly	0.41	0.61	0.27	0.51	0.53	0.53	0.16	0.22	0.41	0.85	0.91	0.86	0.87	0.85	0.82	1
Summer	hC ₃	hC ₄	Enol	Keto	3hC ₅	2hC ₅	Tart	2hC ₆	3hC ₆	ω C ₂	ω C ₃	ω C ₄	ω C ₅	Pyr	Gly	MeGly
hC ₃	1															
hC ₄	0.46	1														
Enol	0.36	0.56	1													
Keto	0.20	0.68	0.72	1												
3hC ₅	0.56	0.76	0.52	0.59	1											
2hC ₅	0.58	0.83	0.68	0.67	0.96	1										
Tart	0.62	0.78	0.58	0.60	0.97	0.95	1									
2hC ₆	0.66	0.51	0.20	0.21	0.68	0.63	0.72	1								
3hC ₆	0.46	0.65	0.35	0.55	0.94	0.89	0.86	0.61	1							
ω C ₂	0.45	0.67	0.79	0.57	0.85	0.90	0.85	0.50	0.70	1						
ω C ₃	0.43	0.62	0.72	0.50	0.86	0.87	0.87	0.49	0.71	0.93	1					
ω C ₄	0.41	0.73	0.61	0.69	0.94	0.93	0.93	0.50	0.90	0.84	0.84	1				
ω C ₅	0.41	0.55	0.33	0.31	0.84	0.79	0.87	0.90	0.79	0.66	0.66	0.75	1			
Pyr	0.68	0.90	0.60	0.68	0.86	0.88	0.87	0.42	0.75	0.78	0.82	0.89	0.57	1		
Gly	0.35	0.74	0.74	0.74	0.84	0.89	0.86	0.39	0.74	0.85	0.88	0.92	0.62	0.90	1	
MeGly	0.28	0.55	0.84	0.62	0.68	0.78	0.67	0.32	0.61	0.85	0.88	0.72	0.47	0.67	0.79	1
Autumn	hC ₃	hC ₄	Enol	Keto	3hC ₅	2hC ₅	Tart	2hC ₆	3hC ₆	ω C ₂	ω C ₃	ω C ₄	ω C ₅	Pyr	Gly	MeGly
hC ₃	1															
hC ₄	0.86	1														
Enol	0.89	0.88	1													
Keto	0.80	0.70	0.93	1												
3hC ₅	0.86	0.99	0.86	0.68	1											
2hC ₅	0.88	0.98	0.93	0.79	0.97	1										
Tart	0.92	0.89	0.93	0.85	0.91	0.93	1									
2hC ₆	0.67	0.61	0.83	0.92	0.59	0.74	0.77	1								
3hC ₆	0.92	0.82	0.89	0.84	0.85	0.89	0.98	0.75	1							
ω C ₂	0.89	0.89	0.86	0.78	0.90	0.94	0.92	0.79	0.90	1						
ω C ₃	0.93	0.87	0.87	0.77	0.89	0.92	0.97	0.69	0.98	0.92	1					
ω C ₄	0.79	0.94	0.81	0.63	0.97	0.95	0.90	0.60	0.85	0.90	0.91	1				
ω C ₅	0.83	0.90	0.82	0.69	0.93	0.92	0.94	0.67	0.90	0.92	0.92	0.65	1			
Pyr	0.92	0.91	0.83	0.71	0.93	0.94	0.94	0.67	0.93	0.97	0.94	0.94	1	1		
Gly	0.74	0.73	0.73	0.74	0.72	0.81	0.76	0.84	0.74	0.94	0.76	0.74	0.77	0.84	1	
MeGly	0.50	0.34	0.55	0.62	0.32	0.52	0.51	0.79	0.55	0.65	0.56	0.42	0.43	0.54	0.77	1

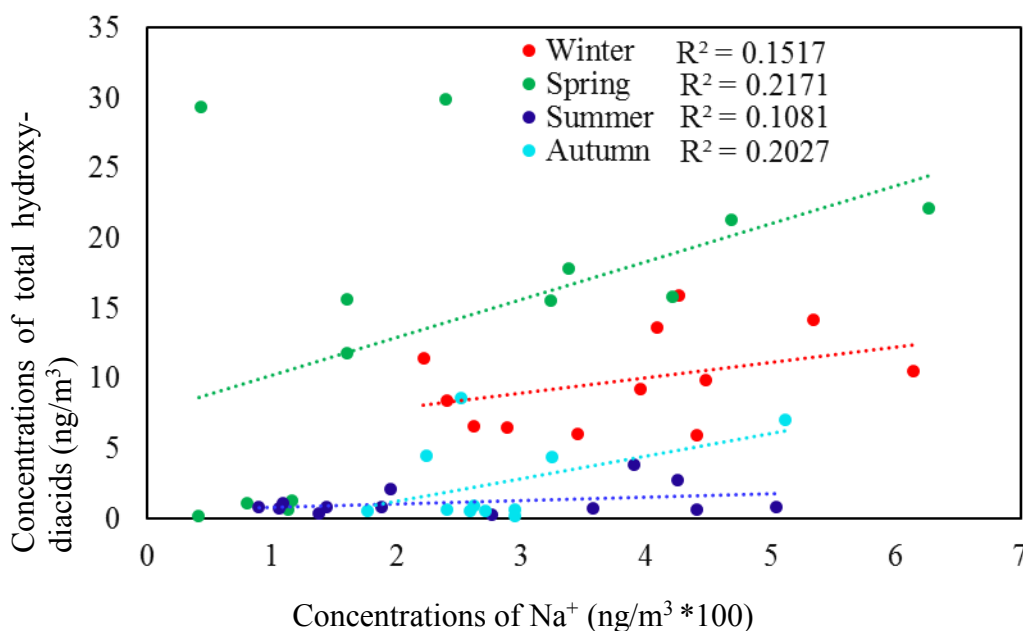


Figure S1. Correlations between Na^+ and total hydroxy-diacids in winter, spring, summer and autumn.

Reference:

- Fu, P., Kawamura, K., Miura, K., 2011. Molecular characterization of marine organic aerosols collected during a round-the-world cruise, *J. Geophys. Res.-Atmos.* 116 (D13), doi: 10.1029/2011JD015604.
- Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G., Kanaya, Y., Wang, Z., 2008. Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain, *J. Geophys. Res.-Atmos.* 113, (D19) doi:10.1029/2008JD009900.
- Gnauk, T., Müller, K., van Pinxteren, D., He, L.Y., Niu, Y., Hu, M., Herrmann, H., 2008. Size-segregated particulate chemical composition in Xinken, Pearl River Delta, China: OC/EC and organic compounds, *Atmos. Environ.* 42 (25), 6296-6309.
- Li, L., Dai, D., Deng, S., Feng, J., Zhao, M., Wu, J., Liu, L., Yang, X., Wu, S., Qi, H., 2013. Concentration, distribution and variation of polar organic aerosol tracers in Yaàn, a middle-sized city in western China, *Atmos. Res.* 120, 29-42.
- Wang, G., Kawamura, K., Umemoto, N., Xie, M., Hu, S., Wang, Z., 2009. Water-soluble organic compounds in $\text{PM}_{2.5}$ and size-segregated aerosols over Mount Tai in North China Plain, *J. Geophys. Res.-Atmos.* 114 (D19), doi:10.1029/2008JD011390.
- Wang, W., Wu, M.H., Li, L., Zhang, T., Liu, X.D., Feng, J.L., Li, H.J., Wang, Y.J., Sheng, G.Y., Claeys, M., Fu, J.M., 2008. Polar organic tracers in $\text{PM}_{2.5}$ aerosols from forests in eastern China, *Atmos., Phys.* 8 (24), 7507-7518.