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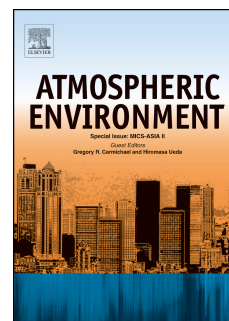
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Authors: Linfa Bao, Mariko Matsumoto, Tsutomu Kubota, Sekiguchi Kazuhiko, Qingyue Wang, Kazuhiko Sakamoto



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Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan

Linfa Bao, Mariko Matsumoto, Tsutomu Kubota, Sekiguchi Kazuhiko, Qingyue Wang, Kazuhiko Sakamoto*

Department of Environmental Science and Technology, Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

*Corresponding author. Tel/Fax: +81-48-858-9542, Email: sakakazu@env.gse.saitama-u.ac.jp (K. Sakamoto)

Abstract

Low-molecular-weight dicarboxylic acids (diacids) exhibit semivolatile behavior in the atmosphere, but their partitioning between the gaseous and particulate phases is still unclear. An annular denuder–filter pack system with a cyclone PM_{2.5} was employed to investigate the gaseous and particulate phase concentrations of diacids, with high collection efficiency of most target compounds. Saturated diacids, unsaturated diacids, ketocarboxylic acids, and dicarbonyls were determined in gaseous and particulate samples collected from a suburban site in Japan, during 2007 summer, 2008 late-winter and early-winter. The concentrations of gaseous and particulate diacids in early-winter were lower than those in summer, but higher than those in late-winter. Individual diacid in gaseous phase showed a relatively good correlation with ambient oxidants, but a low correlation with a primary pollutant (NO gas). Particulate fraction to the total amount (F_P) of individual acid was larger in winter than in summer, and also was larger at night than in the daytime. In the same sample, individual diacid and ketocarboxylic acid had higher particulate phase occurrence ($F_P > 56\%$ in summer), whereas unsaturated diacid had higher gaseous phase occurrence ($F_P < 18\%$ in summer). In

summer, gas/particle partitioning of diacids varied diurnally; F_p values of oxalic and glyoxylic acids increased from their lowest values in the morning to their highest values at night, exhibiting the similar diurnal variation of relative humidity in the atmosphere. The higher humidity at night may lead to the formation of droplets in which water-soluble gaseous phases can dissolve, thus promoting gas-to-particle conversion. These results suggest that gas/particle partitioning of diacids depends not only on the concentration in the gaseous phase by photochemical oxidation, but also on the characteristics of the atmosphere (e.g., temperature, sunlight, and relative humidity) and the aerosol (e.g., acidity, alkaline composition, and water content).

Keywords: Gas/particle partitioning, Dicarboxylic acids, Oxygenated organic aerosol, Atmospheric sampling, Collection efficiency

1. Introduction

Water-soluble dicarboxylic acids (diacids) may affect an aerosol's hygroscopic and cloud-nucleating properties (Cruz and Pandis, 1998; Peng et al., 2001; Abbatt et al., 2005). Diacids are considered to be principally associated with the particulate phase, owing to their relatively low vapor pressures and their hygroscopic behavior (Saxena and Hildemann, 1996). However, recent investigations have shown that low-molecular-weight (LMW) diacids display semivolatile behavior (Limbeck et al., 2001, 2005; Erdakos and Pankow, 2004; Ray and McDow, 2005). Thus, the collection of particulate diacids may be complicated by potential interference from the gaseous phase. Sampling artifacts related to interactions with vapor-phase compounds can occur in two ways: by adsorption of gaseous organic acids onto the sampling filter, inducing a positive artifact; and by volatilization of particulate organic acids collected on the filter,

which causes a negative artifact. A suitable approach to the correction of these artifacts is the use of a denuder–filter-adsorbent system for sample collection (Limbeck et al., 2005).

Several studies have reported the use of annular denuder–filter systems to determine both gaseous and particulate semivolatile organic species: for example, polycyclic aromatic hydrocarbons in indoor laboratory room air (Gundel et al., 1995); semivolatile ozone oxidation of monoterpenes in smog chamber experiments (Yu et al., 1999; Kalberer et al., 2000); semivolatile carbonyls in the atmosphere (Matsunaga et al., 2005; Ortiz et al., 2006, 2009); and carboxylic acids over the Atlantic Ocean (Baboukas et al., 2000). So far, few investigations of gas/particle partitioning of LMW diacids in the atmosphere have been reported (Arai and Sakamoto, 1999; Limbeck et al., 2005). Following Ye et al. (1991), Arai and Sakamoto (1999) developed an annular denuder–filter pack system to measure gaseous and particulate oxalic acid (C_2 diacid) in the atmosphere. Since the handling and instrumental setup of denuder–filter systems are very complex in most studies, Limbeck et al. (2005) collected C_2 – C_9 dicarboxylic acids in the gaseous phase by adsorption onto Teflon filters, with less effort than is necessary for the comparison with denuder systems.

In this study, we investigated the concentrations of saturated and unsaturated diacids as well as those of ketocarboxylic acids and dicarbonyls in gaseous and particulate phases at a suburban site using an annular denuder–filter pack (AD-FP) system. We evaluated the collection efficiency of the AD-FP system, and investigated in detail the gas-to-particle partitioning of diacids, including its diurnal variation and seasonal differences.

2. Experimental

2.1 Sampling

Atmospheric samples were collected at Saitama University, which is located in a suburban area of Saitama, about 30 km northwest of central Tokyo and about 4 km east of the business center of Saitama City. The sampling site was located on top of a 10-story office building at the university, about 37 m above the ground level, to avoid possible interference from local emission sources. Ambient air samples in summer were taken in summer (24–27 July 2007, $n = 13$), late-winter (30 January–2 February 2008, $n = 8$), and early winter (7–13 December 2008, $n = 14$), with four times a day (00:00–05:30, 06:00–11:30, 12:00–17:30, and 18:00–23:30 Japan Standard Time [JST]) in summer and two times a day (07:00–18:30 and 19:00–06:30 JST) in winter.

An AD-FP system was used to collect semivolatile organic acids in gaseous and particulate phases (Fig. 1). The AD-FP system consisted of a $PM_{2.5}$ cyclone (URG-2000-30EN, University Research Glassware, North Carolina, USA), followed by three annular denuders (URG-2000-30B) in series, and a filter pack with three quartz filters (Pallflex 2500 QAT-UP). The first denuder was coated with a 5 wt % solution of potassium iodide (KI) in a 1:1 mixture of methanol:water to remove ozone; the next two denuders were coated with 1 wt % potassium hydroxide (KOH) in a 1:1 mixture of methanol:water to collect gaseous phase organic acids. The first filter was a quartz fiber filter for collection of fine particles ($PM_{2.5}$); the next two quartz filters were impregnated with a 2 wt % KOH solution in a 1:1 mixture of methanol:water for collection of organic acids that volatilized from the particles on the first filter during the sampling. The sampler was operated at a flow rate of 16.7 L min^{-1} .

Gaseous-phase samples were extracted in situ from the denuders by adding 5 mL of ultrapure water into the denuder, and then shaking and rotating it for 1 min. The process was repeated three times for each

extraction. The extracted solutions were stored in amber vials at 4 °C until analysis. After sampling, the filters were stored in Petri slides inside aluminum-laminated hermetic bags at – 40 °C until analysis.

2.2 Chemical analysis of organic compounds

Water-soluble diacids, ketocarboxylic acids, and dicarbonyls in denuder and filter samples were analyzed by BF_3/n -butanol derivatization to their esters followed by gas chromatography/mass spectrometry (GC/MS) determination (Kawamura and Yasui, 2005). Each filter was ultrasonically extracted with 8 mL ultrapure water in an ice bath for 15 min, and this process was repeated more twice times. The extracts were passed through a hydrophilic polytetrafluoroethylene filter (Advantec DISMIC-13HP) to remove filter debris. The solutions of both gaseous and particulate samples were concentrated to ca. 0.5 mL in a rotary evaporator under a vacuum at ca. 48 °C. After the extracts were further dried under a nitrogen stream, 14% BF_3/n -butanol (300 μL) was added to derivatize the carboxyl groups to butyl esters, and the aldehyde groups to dibutoxy acetals, at 100 °C for 30 min. After the addition of 300 μL acetonitrile and 10 mL pure water, the derivatives were extracted with 10 mL *n*-hexane, and then washed two times with pure water (10 mL). The *n*-hexane phase was concentrated under a nitrogen stream to ca. 50 μL . After addition of an internal standard compound (tridecane), the derivatives were dissolved in 100 μL *n*-hexane for GC/MS analysis.

Dibutyl esters and other derivatives were determined with a GC/MS (GCMS-QP 5050, Shimadzu Corporation, Kyoto, Japan) equipped with a split/splitless injector and a fused silica capillary column (DB-5; 30.0 m \times I.D. 0.32 mm \times 0.25 μm film thickness). The operating conditions were an injection temperature of 300 °C, a column initial temperature of 50 °C for 2 min, ramped to 120 °C at 30 °C min^{-1} ,

and then to 250 °C at 8 °C min⁻¹ with a 5 min hold; the carrier gas was helium (flow rate, 50 mL min⁻¹; pressure, 80 kPa). The target compounds were five saturated *n*-dicarboxylic acids (C₂: oxalic; C₃: malonic; C₄: succinic; C₅: glutaric; and C₆: adipic acid), two unsaturated diacids (M: maleic and F: fumaric acid), two ketocarboxylic acids (Pyr: pyruvic and WC₂: glyoxylic acid), and two dicarbonyls (Gly: glyoxal and MeGly: methylglyoxal) (Table 1). These target compounds were identified by comparison of GC retention times with mass spectrums of authentic standards containing quantities of 100, 250, 500, 1000, 2500, and 5000 ng of each compound. The calibration curves were evaluated by the ratios of the peak area of each compound in the mass ion chromatogram to the peak of the internal standard. The peak area was calculated from the response to typical ion fragmentations of the corresponding derivatives of the target compounds (Table 1). The concentrations of diacids and other target compounds reported in this paper have been corrected by those of the procedural blanks, but they are not corrected for the collection efficiency of the sampling system and the recoveries of the authentic standards.

2.3 Aerosol mass spectrometer and data analysis

An Aerodyne aerosol mass spectrometer (AMS, Aerodyne Research Inc., Boston, USA) was used to measure the compositions (water content, organics, sulfate, nitrate, chloride, ammonium, etc.) of submicron aerosols (PM₁) during 24–27 July 2007 and 7–13 December 2008. The mass concentrations of hydrocarbon-like organic aerosols (HOA) and oxygenated organic aerosols (OOA) were further separated, using m/z 57 (mostly C₄H₉⁺) and m/z 44 (mostly CO₂⁺) as their tracers (Hagino et al., 2007). In addition, data for atmospheric pollutants and meteorological information (such as concentrations of suspended particulate matter [SPM] and ambient oxidants, temperature, and relative humidity) were provided by the

Atmospheric Environmental Regional Observation System of Japan, at a site located in the Saitama Institute of Public Health, which is about 700 m from the sampling site.

3. Results and discussion

3.1 Collection efficiency of LMW diacids by the AD-FP system

The AD-FP system included two KOH-coated denuders in series; therefore, we evaluated the denuder collection efficiency of each individual diacid in gaseous phase (ε_d) by applying Eq. (1):

$$\varepsilon_d = C_{d1} / (C_{d1} + C_{d2}), \quad (1)$$

where C_{d1} is the concentration in the first denuder and C_{d2} is the concentration in the second denuder. We obtained the collection efficiencies of the first denuder by applying Eq. (1) to data sampled in summer 2007 (Table 2). The average ε_d of total diacids (C_2 – C_6 , F, and M) in the first denuder was 0.86. If the collection efficiencies of the first and second denuders were equal and they were not affected by the concentration, then the collection efficiency of total diacids by the two denuders ($1 - (1 - \varepsilon_d)^2$) was as high as 0.98, suggesting that two KOH-coated denuders in series are efficient to collect gaseous LMW diacids.

Although quartz fiber filters are known to be essentially 100% efficient in removing aerosol particles, semivolatile compounds such as LMW diacids may partly evaporate from the first quartz filter during sampling (Limbeck et al., 2005; Ray and McDow, 2005) and then be adsorbed onto the subsequent KOH-impregnated filters. The collection efficiency of particulate phase diacids by the first quartz filter (ε_f) was evaluated by applying Eq. (2):

$$\varepsilon_f = C_Q / (C_Q + C_{KOH}), \quad (2)$$

where C_Q is the concentration on the first quartz filter, and C_{KOH} is the sum of the concentrations on the second (C_{f2}) and third (C_{f3}) filters. The average ε_f of total diacids on the first filter was 0.80, based on sampling data from summer 2007 (Table 2). Gaseous diacids from the first filter can be collected with certain collection efficiency by KOH-impregnated filters. The low collection efficiency of M was due to its low concentration on the first filter in summer. Oxalic acid (C_2) with its relatively high vapor pressure was the most abundant diacid in gaseous and particulate phases, and its average ε_f on the second, KOH filter ($C_{f2}/(C_{f2} + C_{f3})$) was 0.96 during summer 2007. The other diacids (C_3 – C_6 , F, and M) on the second filter presented low concentrations and they were usually below the detection limit on third filters. Therefore, the three-filter system with two tandem KOH-impregnated filters is an efficient to collect particulate LMW diacids. In particular, the ε_f of malonic acid (C_3) was largest among the detected diacids, possibly owing to its relatively low vapor pressure compared with C_2 and its relatively strong acidity compared with C_4 – C_6 .

3.2 Gaseous and particulate phase concentrations of diacids in summer and winter

Gaseous and particulate phase concentrations of the target compounds in different seasons are shown in Table 3. The concentrations of gaseous and particulate diacids in early-winter were lower than those in summer, but higher than those in late-winter. In summer 2007, the average concentrations of total diacids (C_2 – C_6 , F, and M) in gaseous and particulate phases were 530 and 734 ng m^{-3} , respectively. As the final photochemical reaction product, C_2 was the most abundant species in both gaseous and particulate phases. In addition, glyoxal (Gly) and glyoxylic acid (WC_2) were also observed at higher concentrations, and Gly was mainly in gaseous phase, whereas WC_2 mainly existed in particulate phase in summer. WC_2 , as a simple ketocarboxylic acid, can be produced by photochemical oxidation of Gly in the atmosphere, and can

be further oxidized to C₂ diacid in gaseous and particulate phases.

Temporal variations of gaseous and particulate concentrations for the typical diacid (C₂), ketocarboxylic acid (WC₂), and dicarbonyl (Gly) are shown in Fig. 2d, e. In summer 2007, gaseous phase curve of C₂ and WC₂ showed peaks in the daytime, whereas the lowest particulate phase concentrations were reached in the morning. Interestingly, maximum daily gaseous phase concentrations of C₂ and WC₂ occurred in the afternoon (12:00–17:30) during 24–26 July (Fig. 2d), a behavior similar to the variation of oxidants in the atmosphere (Fig. 2a). Further, gaseous phase diacids showed a low correlation with a primary pollutant (NO gas): $r = 0.22$ for C₂; $r = 0.21$ for C₃; $r = 0.16$ for C₄; and $r = 0.19$ for C₅ ($n = 35$, $0.1 < p < 0.5$). But most diacids showed a relatively good correlation with oxidants: $r = 0.56$ for C₂; $r = 0.51$ for C₄; and $r = 0.45$ for C₅ ($n = 35$, $p < 0.05$); the exception was C₃ ($r = 0.28$, $n = 35$, $p < 0.1$). These results suggest that an important source of the diacids in the atmosphere was photochemical generation.

As the typical oxygenated organics, the diacids in particulate phase accounted for about 11.8% (summer) and 8.9% (early-winter) of OOA mass. The concentration line of particulate phase in 2007 summer exhibited a time trend similar to OOA (Fig. 2c); the correlation between the particulate diacid concentrations in summer samples and OOA was good ($r = 0.785$, $n = 13$, $p < 0.01$). In addition, individual organic acid have the better correlation with sulphate than with nitrate.

3.3 Gas/particle partitioning of diacids

Particulate fractions to the total amounts ($F_p = [P]/[G + P]$) of individual diacids, ketocarboxylic acids, and dicarbonyls in summer, late-winter, and early-winter samples are shown in Fig. 3. The variation of F_p among different compounds was larger than that among different seasons. In summer, LMW diacids

(C₂–C₃) and ketocarboxylic acids (WC₂ and Pyr) had higher particulate phase occurrence ($F_P > 56\%$), whereas unsaturated diacids (M and F) had higher gaseous phase occurrence ($F_P < 18\%$). And the F_P values of dicarbonyls (Gly and MeGly) were clear smaller than those of LMW diacids and ketocarboxylic acids.

The difference of vapor pressure is the most direct explanation for the observed difference of F_P values among individual compounds. It is expected that the lower the vapor pressure of a compound is, the higher its particulate phase occurrence will be. However, gaseous phase occurrence of C₄–C₆ acids were relatively higher compared with C₃ in summer (Fig. 3), though vapor pressures of C₄–C₆ are much lower than it of C₃ at room temperature (1.0E-05 mmHg for C₃, 6.9E-07 mmHg for C₄, 4.1E-06 mmHg for C₅, 1.50E-07 mmHg for C₆ at T = 25 °C; Saxena and Hildemann, 1996; Bilde et al., 2003). C₃ has relatively higher acidity and solubility in water than C₄–C₆, and thus is more efficiently scavenged from the gas phase into the particulate phase. Therefore, gas/particle partitioning depends not only on vapor pressure but also on other physical and chemical processes. For example, adsorption onto available particle surfaces or absorption into the liquid phase of an individual compound may allow some gas-to-particle conversion to occur even when the gas phase pressure is below its saturation vapor pressure (Pankow, 1994; Lazaridis, 1999; Limbeck et al., 2005). In addition, aqueous phase reactions by OH radical can be a significant source of diacids in aerosols. The study by Ervens et al. (2004) showed OH oxidation or photolysis of Gly in the gas phase leads to HO₂ and CO or formaldehyde, respectively, but in the aqueous phase photolysis does not occur because Gly is present as the geminal diol due to its high hydration constant. Product studies of the OH reaction in the aqueous phase (Ervens et al., 2003; Carlton et al., 2007) have shown that Gly (the smallest dicarbonyl) can be oxidized to WC₂ (the smallest ketocarboxylic acid) and might be further oxidized to C₂ (the smallest diacid).

As shown in Fig. 3, the average F_p value of individual diacid was larger in winter than in summer, possibly because of seasonal environmental differences (temperature, sunlight, relative humidity, etc.). Further, the F_p value of individual diacid was regularly larger at night than in the daytime. The F_p diurnal variation of C_2 , WC_2 , and Gly is shown in Fig. 4. In summer, the particulate phase occurrence of C_2 and WC_2 increased from their lowest values in the morning (06:00–11:30) to their highest values at night (18:00–21:30 or 00:00–05:30). Specially, the F_p diurnal variation of WC_2 is much smaller in winter than in summer. The F_p diurnal variation of the diacids and ketocarboxylic acids exhibited a similar trend to the diurnal variation of relative humidity in the atmosphere, which is low in the daytime and becomes high at night (Fig. 2a). One interpretation of these results is that water-soluble acids in the gaseous phase dissolved in water contained in the particles. This formation mechanism may be the main gas-to-particle conversion pathway in winter, explaining the higher winter particulate phase occurrence of these acids.

3.4 Gas-to-particle sorption

To discuss gas-to-particle sorption on the basis of physical interactions, the gas/particle partition coefficient K_p is used (Pankow, 1994). The distribution of mass between gaseous and particulate phases at equilibrium can be described by K_p as follows:

$$K_p = [P]/([TSP]*[G]) , \quad (3)$$

where K_p is the gas/particle partition coefficient for the target compound ($m^3 \mu g^{-1}$), $[TSP]$ is the concentration of total suspended particles ($m^3 \mu g^{-1}$), $[G]$ is the gaseous phase concentration of the target compound ($ng m^{-3}$), and $[P]$ is the particulate phase concentration ($ng m^{-3}$). During the sampling period, diurnal TSP concentrations were not available; thus, we used the mass concentration of SPM (particle

diameter < 10 μm , a good approximation to TSP in Saitama city) instead of TSP concentration in Eq. (3). The K_p values of individual compounds in different seasons are showed in Table 4. The K_p values of diacids in late-winter (the average temperature 4.2 $^{\circ}\text{C}$) were clear larger than those in summer (the average temperature 26.2 $^{\circ}\text{C}$). The log K_p values of individual compounds showed a good negative correlation with the ambient temperature: $r = -0.74$ for C_2 (Fig. 5), $r = -0.75$ for C_3 , $r = -0.78$ for C_4 , $r = -0.62$ for C_5 , $r = -0.53$ for C_6 , $r = -0.78$ for WC_2 , $r = -0.72$ for Gly; $n = 35$, $p < 0.01$. These results indicated the temperature dependence of gas-particle partitioning in the atmosphere, which is consistent with the observed seasonal variation of gas/particle partitioning in Fig. 3.

When we take the logarithm of the Eq. (3) and put the log K_p for y-axis and log [TSP] for x-axis, the curve is linear with a slope of -1 :

$$\log K_p = -\log [\text{TSP}] + \log ([P]/[G]) \quad (4)$$

To investigate the effect of the aerosol composition on gas-to-particle conversion, the relationship of K_p and sorption medium is expressed as Eq.5:

$$\log K_p = m \log [\text{sorption medium}] + b \quad (5)$$

Under equilibrium conditions, the expected slope (m) of Eq. 5 is a constant. However, sampling condition, sampling artifacts and /or nonequilibrium conditions may lead to variation of m values. Interpretation of the intercept term (b) depends on the assumed mechanism of particle-gas interaction. We used the concentrations of water content, sulfate, nitrate, ammonium, and organics in PM_{10} (measured by AMS) instead of TSP as the sorption medium in Eq. (5).

Based on the sampling data in 2007 summer and 2008 early-winter, regression statistics of $\log K_p$ against \log [sorption medium] are carried out (Table 5). Sulfate and water content showed a strong bias to Eq. (5) for most target organic compounds. SO_4^{2-} are secondary formation in fine particles, and can enhance the surface area and polarity of the existing particles, causing gas phase organic acids to be easily adsorbed and absorbed. Further, $\log K_p$ showed a particularly strong correlation with \log [water content] for C_2 - C_5 diacids (Table 5), especially for C_3 ($r = -0.89$, $n = 27$, $p < 0.01$; Fig. 6). The amounts of polar organic compounds would be clearly increased as relative humidity rises above $\sim 50\%$ (Seinfeld et al., 2001; Erdakos and Pankow, 2004). The higher humidity may cause formation of droplets in which the gaseous phase organic acids can dissolve, thus promoting gas-to-particle conversion. A weak correlation between $\log [K_p]$ and \log [nitrate] was observed for all target compounds (Table 5), suggesting that the nitrate component in aerosols are not a good sorption medium for water-soluble organic acids. These results suggest that gas/particle partitioning of diacids depends not only on physical and chemical characteristics of the individual organic acid (vapor pressure, water solubility, acidity constant, etc.) but also on the compositions of the aerosols, such as its water content (affecting aerosol's sorption properties), sulfate (affecting secondary particle formation), and ammonium (affecting aerosol acidity and ammonium salt formation).

4. Conclusions

An annular denuder-filter pack system using KOH as the sorbent can efficiently collect gaseous and particulate dicarboxylic acids in the atmosphere. Concentrations of LMW diacids determined by GC/MS were higher in summer than in winter, and exhibited higher particulate phase occurrence than gaseous

phase occurrence. Gaseous diacid concentrations tended to be higher in daytime and showed a good correlation with oxidants, whereas particulate diacid concentrations were lowest in the morning and their occurrence showed a similar trend to the diurnal variation of relative humidity in the atmosphere. These findings suggest that photochemical generation is an important source of gaseous diacids, but that gas-to-particle partitioning of diacids depends not only on the concentration level of gaseous phase by photochemical oxidation but also on the atmosphere state (such as temperature, sunlight, and relative humidity) and aerosol characteristics (such as particle mass, aerosol acidity, particle surface, and water content, etc.).

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ACCEPTED MANUSCRIPT

339 **Table Headings**

340 Table 1 Retention times, slopes, and regression coefficients (r^2) for calibration curves of the target
341 compounds

342 Table 2 Collection efficiencies of the first denuder for gaseous phase compounds and of the quartz filter for
343 particulate phase compounds

344 Table 3 Concentrations (ng m^{-3}) of diacids, ketocarboxylic acids, and dicarbonyls in gaseous and particulate
345 phases in different seasons

346 Table 4 Gas/particle partition coefficient K_p of diacids, ketocarboxylic acids, and dicarbonyls in different
347 seasons

348 Table 5 Regression statistics of $\log K_p$ against \log [sorption medium] for the diacids, ketocarboxylic acids,
349 and dicarbonyls in summer and early-winter samples ($n = 27$)

350

351 **Figure Captions**

352 Fig. 1. Schematic diagram of the annular denuder–filter pack (AD-FP) system.

353 Fig. 2. Temporal variations of (a) ambient oxidant concentration and relative humidity, (b) sulfate, nitrate,
 354 and ammonium, (c) HOA and OOA, (d) gaseous concentrations and (e) particulate concentrations of main
 355 organic compounds (D1, 6:00–11:30; D2, 12:00–17:30; N1, 18:00–23:30; N2, 00:00–05:30; D,
 356 7:00–18:30; N, 19:00–06:30).

357 Fig. 3. Particulate fraction (F_p) of the individual diacids, ketocarboxylic acids, and dicarbonyls in different
 358 seasons.

359 Fig. 4. Diurnal variation of particulate fraction (F_p) of C_2 , WC_2 , and Gly in different seasons (D1,
 360 6:00–11:30; D2, 12:00–17:30; N1, 18:00–23:30; N2, 00:00–05:30; D, 7:00–18:30; N, 19:00–06:30).

361 Fig. 5. Log K_p against T for C_2 .362 Fig. 6. Log K_p against log [water content] for C_3 .

Table 1 Retention times, slopes, and regression coefficients (r^2) of the calibration curves for the target compounds

Retention time (min)	Target compound (abbr.)	Type	m/z ^a	Slope	r^2 value
5.88	Methylglyoxal (MeGly)	Dicarbonyl	41, 57, 103	1.72	0.971
6.67	Oxalic acid (C ₂)	Saturated <i>n</i> -dicarboxylic acid	41, 57	2.81	0.991
7.51	Malonic acid (C ₃)	Saturated <i>n</i> -dicarboxylic acid	41, 57, 87, 105, 143	2.62	0.982
8.68	Maleic acid (M)	Unsaturated dicarboxylic acid	41, 57, 99, 117	2.34	0.985
8.95	Succinic acid (C ₄)	Saturated <i>n</i> -dicarboxylic acid	41, 57, 101, 157	2.23	0.995
9.23	Fumaric acid (F)	Unsaturated dicarboxylic acid	41, 56, 117, 155	1.98	0.992
9.41	Pyruvic acid (Pyr)	Ketocarboxylic acid	41, 61, 89	1.75	0.976
9.55	Glyoxylic acid (WC ₂)	Ketocarboxylic acid	41, 57, 103	3.17	0.969
10.23	Glutaric acid (C ₅)	Saturated <i>n</i> -dicarboxylic acid	41, 55, 87, 115, 171	2.08	0.995
11.60	Adipic acid (C ₆)	Saturated <i>n</i> -dicarboxylic acid	41, 87, 111, 129,	1.86	0.993
11.85	Glyoxal (Gly)	Dicarbonyl	41, 55, 159	3.76	0.988

^a Typical ion fragmentations of corresponding derivatives.

366 Table 2 Collection efficiencies of the first denuder for gaseous phase compounds and of the quartz filter for
 367 particulate phase compounds

Compound	Denuder			Filter		
	ε_d	S.D. ^a	n^b	ε_f	S.D. ^a	n^b
Oxalic (C ₂)	0.80	0.16	12	0.77	0.18	12
Malonic (C ₃)	0.90	0.08	12	0.90	0.14	12
Succinic (C ₄)	0.90	0.09	12	0.70	0.15	12
Glutaric (C ₅)	0.83	0.10	12	0.82	0.15	12
Adipic acid (C ₆)	0.85	0.17	12	0.81	0.12	12
Maleic (M)	0.93	0.03	8	0.52	0.24	10
Fumaric (F)	0.82	0.23	8	0.83	0.14	10
Glyoxylic (WC ₂)	0.90	0.06	12	0.93	0.04	12
Methylglyoxal (MeGly)	0.94	0.07	12	0.86	0.22	12
Total diacids	0.86	0.12	12	0.80	0.10	12

Table 3 Concentrations (ng m^{-3}) of diacids, ketocarboxylic acids, and dicarbonyls in gaseous and particulate phases in different seasons

Compound	2007 summer ($n = 13$)				2008 late-winter ($n = 8$)				2008 early-winter ($n = 14$)			
	Gaseous		Particulate		Gaseous		Particulate		Gaseous		Particulate	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Diacids												
C ₂	302	158	473	255	92	99	154	63	148	52	304	146
C ₃	26.8	28.3	122	98.9	3.7	3.6	32.7	23.7	4.8	4.0	51.3	18.6
C ₄	54.7	36.4	70.6	39.3	3.4	2.2	26.1	22.0	7.7	16.8	62.1	23.0
C ₅	20.3	14.4	27.9	35.3	12.5	10.0	16.9	17.4	5.5	3.8	9.8	4.2
C ₆	38.4	16.2	28.8	16.8	6.1	5.5	16.1	22.0	31.6	17.2	18.0	10.9
M	42.6	41.5	5.0	3.2	1.3	0.8	2.4	2.8	34.6	28.7	6.1	3.5
F	45.4	20.3	6.4	3.2	6.6	5.5	2.0	3.6	15.7	17.7	10.2	5.9
Total diacids	530	273	734	406	125	105	250	138	248	97	462	193
Other target compounds												
WC ₂	29.4	17.9	56.5	44.7	6.2	4.8	45.8	27.4	29.0	14.4	102	32.1
Pyr	37.9	17.5	61.1	51.2	8.7	4.0	10.6	5.5	41.9	39.8	85.3	29.7
Gly	88.0	83.9	26.7	15.9	24.4	13.1	21.7	18.2	50.3	27.6	60.9	25.8
MeGly	31.5	26.6	19.8	13.4	37.5	60.7	18.0	16.3	65.2	47.9	39.3	14.3

371 Table 4 Gas/particle partition coefficient K_P of diacids, ketocarboxylic acids, and dicarbonyls in different
 372 seasons

Compound	K_P ($\text{m}^3 \mu\text{g}^{-1}$)		
	Summer ($n = 13$)	Late-winter ($n = 8$)	Early-winter ($n = 14$)
C ₂	0.014	0.034	0.025
C ₃	0.018	0.044	0.034
C ₄	0.015	0.040	0.033
C ₅	0.011	0.030	0.024
C ₆	0.010	0.029	0.014
M	0.008	0.024	0.010
F	0.003	0.010	0.020
WC ₂	0.013	0.043	0.031
Pyr	0.010	0.026	0.026
Gly	0.008	0.021	0.020
MeGly	0.010	0.025	0.017

Table 5 Regression statistics of $\log K_P$ against \log [sorption medium] for the diacids, ketocarboxylic acids, and dicarbonyls in summer and early-winter samples ($n = 27$)

Compound	Water content ^a			Sulfate			Nitrate			Ammonium			Organics		
	r^b	m	b	r	m	b	r	Slope	Inter	r	Slope	Inter	r	Slope	Inter
C ₂	-0.76	-0.40	-1.41	-0.75	-0.48	-1.65	-0.24	-0.17	-1.71	-0.41	-0.36	-1.61	-0.62	-0.84	-1.01
C ₃	-0.89	-0.48	-1.20	-0.86	-0.57	-1.49	-0.29	-0.22	-1.56	-0.52	-0.48	-1.43	-0.68	-0.97	-0.77
C ₄	-0.82	-0.56	-1.21	-0.80	-0.67	-1.54	-0.06	-0.06	-1.70	-0.34	-0.39	-1.55	-0.49	-0.88	-0.93
C ₅	-0.69	-0.41	-1.46	-0.61	-0.45	-1.72	-0.04	-0.03	-1.83	-0.14	-0.15	-1.78	-0.42	-0.66	-1.24
C ₆	-0.44	-0.29	-1.76	-0.53	-0.43	-1.91	-0.26	-0.24	-1.94	-0.37	-0.42	-1.83	-0.29	-0.51	-1.57
M	-0.44	-0.54	-1.92	-0.51	-0.76	-2.20	0.05	0.09	-2.45	-0.24	-0.51	-2.18	-0.23	-0.74	-1.74
F	-0.69	-0.78	-1.49	-0.63	-0.87	-1.96	0.27	0.42	-2.37	0.00	0.00	-2.21	-0.20	-0.60	-1.66
WC ₂	-0.78	-0.51	-1.29	-0.73	-0.58	-1.59	-0.16	-0.14	-1.70	-0.31	-0.34	-1.60	-0.56	-0.96	-0.89
Pyr	-0.60	-0.45	-1.43	-0.49	-0.45	-1.72	-0.05	-0.05	-1.83	-0.06	-0.07	-1.81	-0.39	-0.76	-1.15
Gly	-0.77	-0.69	-1.37	-0.64	-0.70	-1.81	0.01	0.02	-2.01	-0.15	-0.23	-1.90	-0.37	-0.89	-1.20
MeGly	-0.54	-0.38	-1.64	-0.60	-0.52	-1.84	-0.30	-0.28	-1.88	-0.35	-0.42	-1.79	-0.46	-0.85	-1.21

^a The concentrations of water content, sulfate, nitrate, ammonium, and organics in PM₁ are from AMS data;

^b The correlation coefficient (r), slope (m), and intercept (b) of Eq. 5.

