



# HOKKAIDO UNIVERSITY

Title	Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere
Author(s)	Kawamura, Kimitaka; Yasui, Osamu
Citation	Atmospheric Environment, 39(10), 1945-1960 <a href="https://doi.org/10.1016/j.atmosenv.2004.12.014">https://doi.org/10.1016/j.atmosenv.2004.12.014</a>
Issue Date	2005-03
Doc URL	<a href="https://hdl.handle.net/2115/10507">https://hdl.handle.net/2115/10507</a>
Type	journal article
File Information	Kawamura diurnal AE2005.pdf



Submitted to Atmospheric Environment July 9, 2004

Diurnal Changes in the Distribution of Dicarboxylic Acids, Ketocarboxylic Acids and  
Dicarbonyls in the Urban Atmosphere

Kimitaka Kawamura<sup>1,\*</sup> and Osamu Yasui<sup>2,3</sup>

<sup>1</sup>Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, Sapporo 060-0819, Japan

<sup>2</sup>Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-03, Japan

<sup>3</sup>Present address: Mitsui Chemicals, 1-5-2 Higashi-Shinbashi, Minato-ku, Tokyo 105-7117, Japan

\* Corresponding author: Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, Sapporo 060-0819, Japan

Phone: 81-11-706-5457, Fax: 81-11-706-7142, E-mail: kawamura@lowtem.hokudai.ac.jp

Secondary organic aerosol in the urban atmosphere is an important issue from a viewpoint of not only air pollution but also regional and global atmospheric environment. To better understand the production of water-soluble organic aerosols, we analyzed atmospheric particles collected in time-series in Tokyo for dicarboxylic acids ( $C_2$ - $C_{10}$ ), ketocarboxylic acids ( $C_2$ - $C_4$ ) and  $\alpha$ -dicarbonyls ( $C_2$ - $C_3$ ) using a GC and GC/MS. Here, we report, for the first time, diurnal distributions of dicarboxylic acids, ketoacids and dicarbonyls in the urban atmosphere. Oxalic acid was found as the most abundant species, followed by malonic, succinic, pyruvic and glyoxylic acids. Total diacids showed a concentration maximum in daytime (11-14 h) with a dynamic change in their molecular composition especially in summer samples. Relative abundances of unsaturated (maleic, methylmaleic and phthalic) and some saturated (methylsuccinic and adipic) species increased in the morning (8-11 h) whereas those of oxalic acid decreased down to 35 % in 8-11 h but increased up to 58 % toward 17-20 h. The diurnal variations are interpreted by photochemical production of diacids, where unsaturated and some saturated species are preferentially generated early in the morning via photo-oxidation of aromatic hydrocarbons and cyclic olefins and further oxidized to oxalic acid in the afternoon.

## 1. Introduction

Low molecular weight (LMW) dicarboxylic acids with a predominance of oxalic ( $C_2$ ) acid are known as ubiquitous composition of continental aerosols (Grosjean et al., 1978; Norton et al., 1983; Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Rogge et al., 1993; Fraser et al., 2002; Wang et al., 2002) and rainwater and snow (Puxbaum et al., 1988; Talbot et al., 1992; Kawamura et al., 2001). They are also present in the remote marine aerosols from the Pacific (Sempéré and Kawamura, 1994, 2003; Kawamura and Sakaguchi, 1999; Mochida et al., 2003a,b) and Atlantic (Barboukas et al., 2000) and in the polar aerosols from the Arctic (Li and Winchester, 1993; Kawamura et al., 1996a; Kerminen et al., 1999; Hara et al., 2002; Narukawa et al., 2003) and Antarctic (Kawamura et al., 1996b). Because LMW diacids are very water soluble, their existence on the aerosol surface alters the chemical and physical properties of atmospheric aerosols and enhances the capability of aerosols as cloud condensation nuclei (Saxena et al., 1995). The dicarboxylic acids comprise 0.2 % to 2 % of total aerosol carbon with summer time maximum in urban Tokyo (Kawamura and Ikushima, 1993). On the contrary, they account for up to 16 % of the aerosol carbon in the remote marine atmosphere from the equatorial Central Pacific (Kawamura and Sakaguchi, 1999). Previous studies suggested that LMW diacids are produced in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons and fatty acids as well as their oxidation products (Kawamura and Sakaguchi, 1999; Kawamura et al., 1996b). Direct emission from fossil fuel combustion, biomass burning and cooking has also been suggested as a source of diacids (Kawamura and Kaplan, 1987; Legrand and De Angelis, 1996; Narukawa et al., 1999; Schauer et al., 2001, 2002).

Laboratory studies of cyclohexene-ozone reactions reported the production of adipic ( $C_6$ ) acid, whose yield became 5 % in 2 hours and 10 % in 150 hours (Hatakeyama et al., 1987). Cyclohexene is abundantly present in both motor exhausts and urban air (Grosjean and Fung, 1984). However, oxalic, malonic and unsaturated diacids have not been reported as at least major products of the cyclohexene-ozone reaction (Hatakeyama et al., 1987; Kalberer et al., 2000). Based on one-year observation of LMW diacids in the urban aerosols, Kawamura

and Ikushima (Kawamura and Ikushima, 1993) reported an enhanced secondary production of C<sub>2</sub>-C<sub>6</sub> diacids in summer. Photochemical production of LMW diacids has also been supported by a polar sunrise experiment in the Arctic, where concentrations of diacids increased by a factor of 5-20 from the dark winter to light spring (Kawamura et al., 1996a). Although diurnal variations of some diacids have been reported in the suburban atmosphere (Satsumabayashi et al., 1990), previous studies employing methyl ester derivatization failed to detect oxalic acid quantitatively. Methyl ester of oxalic acid is volatile enough to be lost by evaporation during the analytical protocol used. Thus, oxalic acid has often been underestimated in aerosols seriously (Grosjean et al., 1978; Satsumabayashi et al., 1990) and sometimes misinterpreted as being mostly present in gas phase (Satsumabayashi et al., 1990). Recent studies demonstrated that ca. 30 % of oxalic acid is in gas phase, but major portion is in aerosols (Mochida et al., 2003a; Barboukas et al., 2000).

To better understand the photochemical production of small diacids and related compounds in the urban atmosphere, time-series aerosol samples were collected every 3 hours in Tokyo during summer and winter campaigns. In this study, we analyzed the samples for molecular composition of LMW diacids, ketoacids and  $\alpha$ -dicarbonyls employing BF<sub>3</sub>/n-butanol derivatization followed by GC and GC/MS determination. The samples were also analyzed for total carbon and nitrogen and their stable isotopic ratios. Here, we report, for the first time, a case study on the diurnal distributions of bi-functional organic acids (diacids and ketoacids) and dicarbonyls in the urban atmosphere. The results will be discussed in terms of gas phase and heterogeneous production of bi-functional organic acids .

## 2. Experimental

The aerosol samples (n=32) were collected on a pre-combusted quartz filter (Pallflex 2500 QAT-UP) using a high volume air sampler without any particle cut-off on the rooftop of Tokyo Metropolitan University Faculty of Science Building at Setagaya campus (ca. 20 m above the ground). The sampling site was located in the residential area near the central urban Tokyo. The aerosol sampling was conducted on 2-3 June (n=14), 21-22 July (n=10) and 20-

21 November (n=8) in 1989. All the samples were collected with sampling intervals of 02-05, 05-08, 08-11, 11-14, 14-17, 17-20, 20-23, and 23-02 hours. The sampling dates were chosen for hot and/or sunny days with no clouds and no winds. Because of no wind condition during the campaigns, we consider that transport of different air mass does not impact seriously on the observation. Although the highest ambient temperature (31 °C) and radiation (8.6 MJm<sup>-2</sup>) were recorded during July 21-22, oxidants and aerosol mass concentrations did not show a maximum in this period. Highest concentrations of oxidants and aerosol mass were observed during June 2-3.

Filter samples were analyzed for water-soluble dicarboxylic acids, ketoacids and dicarbonyls (Kawamura and Ikushima, 1993; Kawamura, 1993). Briefly, one quarter of the filter was extracted with pure water (10 ml x 3), which was made by oxidizing organic impurities of Milli Q water with potassium permanganate in all glass apparatus followed by distillation. The extracts (water soluble organics) were concentrated to *ca.* 1 ml using a rotary evaporator under a vacuum and then passed through a glass column (Pasteur pipette) packed with a quartz wool to remove particles such as filter debris. They were concentrated by a rotary evaporator and then by nitrogen blow down. The concentrates were reacted with 14 % BF<sub>3</sub>/n-butanol at 100 °C to derive the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals. The diacid butyl esters and acetals were extracted with n-hexane after adding pure water and then determined with GC equipped with a split/splitless injector and fused silica capillary column. Peak identification was performed by a comparison of GC retention times with those of authentic standards. Identification of the esters was confirmed by mass spectral analysis using a GC/MS system.

Recoveries of authentic standards spiked to a pre-combusted quartz fiber filter were 71 % for oxalic acid and better than 80 % for malonic, succinic and adipic acids. Recoveries of glyoxylic acid, pyruvic acid and methylglyoxal were 88 %, 72 % and 47 %, respectively. Spiked experiment of diacid standards to the filter sample (QFF 166) showed higher recoveries of oxalic acid (86 %) and malonic acid (94 %). Duplicate analyses of filter sample showed that analytical errors are within 15% for major species. Procedural blanks showed

small peaks of oxalic and phthalic acids in the GC chromatograms; however, they were less than 0.66 % (oxalic acid) and 5.6 % (phthalic acid) of the aerosol samples. Concentrations of the acids reported here are corrected for the procedural blanks, but are not corrected for the recoveries. The analyses of the filter samples were completed in 1990.

A part of the aerosol filter sample (disc diameter of 2.0 cm) was analyzed for total carbon and nitrogen contents as well as stable carbon and nitrogen isotopic ratios using a Carlo Erba NA 1500 elemental analyzer (EA) and EA/isotope ratio mass spectrometer (Finnigan MAT Delta plus), respectively (Narukawa et al., 1999). Analytical errors in the measurements of TC and TN contents were within 2 %. In order to evaluate a possible contribution of inorganic carbon (such as CaCO<sub>3</sub>) to TC, filter samples were exposed to HCl fume and analyzed for carbon isotopic ratios. The <sup>13</sup>C values (-23.1 ‰ to -26.2 ‰) did not show any serious changes before and after the HCl treatment, indicating a negligible contribution of CaCO<sub>3</sub> (whose <sup>13</sup>C is around 0 ‰) to TC (Kawamura et al., 2004). Here, we used the TC data that were obtained without HCl treatment to normalize organic acid-carbon by TC.

### **3. Results and Discussion**

#### **3.1. TC and TN**

Concentration ranges of TC and TN were 7.7- 63 (av. 24) μgm<sup>-3</sup> and 1.7-20 (av. 5.8) μgm<sup>-3</sup>, respectively. Although both TC and TN varied with time during the campaigns, they showed a daytime maximum around at 08-11 h or 11-13 h in June and July samples (Figure 1), suggesting a secondary production of carbonaceous and nitrogen-containing aerosols. However, a maximum was observed in late afternoon for the November samples, which may be associated with the development of inversion layer where pollutants accumulate. Averaged TC contents (16-40 μgm<sup>-3</sup>) for each campaign are within the range (12-44 μgm<sup>-3</sup>, av. 22 μgm<sup>-3</sup>) reported for Tokyo aerosols collected for 24 hours interval (Kawamura et al., 1995), although they are about an half of those (24-85 μgm<sup>-3</sup>, av. 49 μgm<sup>-3</sup>) reported in Beijing (Sekine et al., 1992). Although adsorption of gaseous organics on quartz filter potentially

occurs during sampling, we feel that a positive artifact should be minimal and not seriously affect the results. Averaged TN contents for each campaign (3.6-7.0  $\mu\text{gm}^{-3}$ ) are also within the range (1-21  $\mu\text{gm}^{-3}$ , av. 5.3  $\mu\text{gm}^{-3}$ ) reported in the 24 hours sampling from Tokyo (Kawamura et al., 1995).

TC comprised 9.2 % to 42 % of aerosol mass with an average of 21 %. These values are similar to those (11-38 %, av. 20 %) reported in the Tokyo aerosol samples with 24 hours sampling interval (Kawamura et al., 1995). Interestingly, the aerosol samples collected for 3 hours interval generally showed higher TC/aerosol mass ratios in daytime (Figure 1), suggesting a gas-to-particle formation of organic aerosols. On the other hand, TN comprised 2.5 to 8.5 % of aerosol mass with an average of 5.1 %. These values are within those (1.9-15 %, av. 5.1 %) reported for the 24 hours sampling (Kawamura et al., 1995), but show a peak in daytime. TN/aerosol ratios also maximized in daytime (the results are not shown here). This suggests that particulate nitrogen is produced via photochemical oxidation of  $\text{NO}_x$  to  $\text{HNO}_3$  followed by the reaction with ammonia ( $\text{NH}_3$ ) to form salt ( $\text{NH}_4\text{NO}_3$ ), which may associate with pre-existing particles. Acidic components such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $(\text{COOH})_2$  either in gas phase or particles may also react with basic nitrogen species such as ammonia and urea to form particulate nitrogen and contribute to aerosol growth.

### **3.2. Molecular compositions of dicarboxylic acids, ketoacids and $\alpha$ -dicarbonyls**

A homologous series of normal saturated , -dicarboxylic acids ( $\text{C}_2$ - $\text{C}_{12}$ ) were detected in the aerosols as well as branched saturated diacids (iso  $\text{C}_4$ - $\text{C}_7$ ). Unsaturated aliphatic (maleic, fumaric and methylmaleic) and aromatic (phthalic) diacids were also detected in the aerosol samples as well as dicarboxylic acids with an additional functional group, i.e., malic (hydroxysuccinic), ketomalonic and 4-ketopimelic acids. Throughout the campaigns, oxalic ( $\text{C}_2$ ) acid was found to be the most abundant diacid, followed by malonic ( $\text{C}_3$ ) or succinic ( $\text{C}_4$ ) acid. The fourth most abundant diacid was malic ( $\text{hC}_4$ ), glutaric ( $\text{C}_5$ ), adipic ( $\text{C}_6$ ), phthalic (Ph), or azelaic ( $\text{C}_9$ ) acids, depending on the sampling time and season.

Further, two types of ketoacids, C<sub>2</sub>-C<sub>4</sub> -oxoacids and C<sub>3</sub> -ketoacid (pyruvic acid), were detected in the aerosols as well as -dicarbonyls (glyoxal and methylglyoxal). Glyoxylic acid (C<sub>2</sub>) is the dominant -oxocarboxylic acid followed by 4-oxobutanoic acid (C<sub>4</sub>). Pyruvic acid was found to be generally more abundant than C<sub>2</sub> during daytime in summer. Citric acid (tricarboxylic acid) was also detected in the samples.

Table 1 gives the concentration ranges of various carboxylic acids and -dicarbonyls for June, July and November samples. Dicarboxylic acids (160-1800 ngm<sup>-3</sup>, av. 540 ngm<sup>-3</sup>) are the most abundant compound class followed by -oxocarboxylic acids (11-150 ngm<sup>-3</sup>, av. 57 ngm<sup>-3</sup>). Concentrations of pyruvic acid and -dicarbonyls are 7-140 (av. 41) ngm<sup>-3</sup> and 8-120 (av. 22) ngm<sup>-3</sup>, respectively. Generally, these compound classes showed the highest concentrations in June when oxidants (mostly ozone) were recorded highest (73 ppb) (Figure1). Throughout 3 hours sampling, concentrations of diacids significantly varied within a day by factor of 3 to 5, showing a maximum at around noontime. Further, we found a dynamic change in the molecular composition of organic acids within a day, a point to be discussed later.

Dicarboxylic acids were found to comprise 0.14-1.2 % (av. 0.48 %) of aerosol masses (54-270 μgm<sup>-3</sup>) whereas ketoacids and -dicarbonyls comprise 0.03-0.21 % (av. 0.09 %) and 0.01-0.07 % (av. 0.03 %), respectively. The relative abundance of diacids are similar to those (0.06-1.1 %, av. 0.46 %) reported for 24 hours sampling in Tokyo (Kawamura and Ikushima, 1993). On the other hand, diacids were found to account for 0.10 to 1.3 % (av. 0.56 %) of aerosol TC (7.7-63 μgm<sup>-3</sup>). The diacid-C/TC ratios are also consistent with those (0.18-1.8 %, av. 0.95 %) reported for the 24 hours sampling (Kawamura and Ikushima, 1993). In contrast, other compound classes account for smaller portion of TC; i.e., 0.06-0.46 % (av. 0.20 %) for ketoacids and 0.02-0.012 % (av. 0.06 %) for -dicarbonyls. Although relative abundances of these components are highly variable, they showed a peak generally in daytime.

### 3.3. Diurnal distributions of dicarboxylic acids

As shown in Figure 2a, total concentrations of diacids increase from the lowest values in nighttime (2-5 h) to the highest values in daytime around at 8-11 h or in the afternoon. Although direct emission of diacids from automobiles obviously contribute to the peak in the morning, its contribution should be less important than the secondary production. Higher concentrations of the diacids were observed on June 2 when higher concentrations of oxidants were obtained. On June 3 the concentrations are similar or even lower than those in July or November at least during the accumulation periods. Oxidant concentrations on July 22 and November 21 are less than half of that of June 3 (Figure 1). In both June and July samples, the diacid concentrations increased early in the morning from 2-5 h to 5-8 h when averaged solar radiation increased from  $0.01 \text{ MJm}^{-2}$  to  $2.0 \text{ MJm}^{-2}$ . However, such an increase starts 3 hours later in winter (November) when the sunrise delays about 2 hours. After the daytime maximum, concentrations of total diacids decrease toward the late afternoon and night, suggesting that *in situ* production of diacids is overwhelmed by a removal via dry deposition or transport out of the sampling area. Alternatively, such a decrease could be caused by the expansion of planetary boundary layer in the afternoon and thus subsequent vertical mixing of the air.

Figure 2b presents diurnal variations of total diacid concentrations normalized by aerosol mass. The relative abundance increases from midnight (around 0.2 % at 2-5 h) toward noontime (around 1 % at 11-14 h). A maximum was recorded in June 2 (11-14 h) when the highest concentrations of oxidants were recorded. A rapid increase in the relative abundance in the morning again supports a photochemical production of dicarboxylic acids. Interestingly, the relative abundances are higher in June and July than in November. This is consistent with elevated solar radiation in summer than in winter by ca. 50% for 11-14 h (Figure 1). On the other hand, relative abundance of diacids decreases toward the evening. This may suggest that photochemical production of diacids is canceled out by the atmospheric scavenging either by decomposition or deposition. Alternatively, a possible uptake of water vapor on aerosol particles or quartz filter that increases the aerosol mass may partly contribute to such a decrease if relative humidity increases significantly at night.

### 3.4. Diurnal distributions of $\omega$ -oxocarboxylic acids, pyruvic acid, and $\alpha$ -dicarboxylic acids

Figure 2c illustrates diurnal variations of  $\omega$ -oxocarboxylic ( $C_2$ - $C_4$ ) acids. The total concentrations showed an increase from the early morning (2-5 h) toward the noon, with a maximum either at 8-11 h or 11-14 h. The amplitudes of the peak in summer (June and July) are up to 5 times. The highest concentrations were observed in June 2 when the highest oxidant concentration was recorded (Figure 1), being consistent with the case of dicarboxylic acids. The concentrations of  $\omega$ -oxoacids generally decrease toward the evening. In contrast, the amplitude increase in winter is only twice. This may be caused by the higher concentrations of  $\omega$ -oxoacids in the evening and early morning in winter (Figure 2c), which may be associated with a development of inversion layer. Since  $\omega$ -oxoacids are semi-volatile, they are likely subjected to evaporation from the particles to gas phase when ambient temperature increases. However, this process does not seriously affect the results because their concentrations in aerosols rather increase at daytime (Figure 2c).

Concentrations of  $\omega$ -oxoacids normalized by aerosol mass showed a very sharp increase from 5-8 h to 11-14 h (Figure 2d). Interestingly, they showed a large increase early in the morning from 2-5 h to 5-8 h on July 22 when averaged radiation increased from 0.00 to  $1.37 \text{ MJm}^{-2}$ . In summer samples, the relative abundances generally increase early in the morning, peaked at 11-14 h, and then decrease toward the evening. The amplitude is ca. 5 times for both June 2 and July 22 samples. Similar trend was observed for the November samples (Figures 2d), being in contrast to the case of diacids whose relative abundances in November are much less than June and July samples (Figure 2b). This suggests that  $\omega$ -oxoacids are produced abundantly even under weaker solar radiations in November, but are not effectively converted to other species including diacids. The greater amplitude in the winter samples may suggest a faster production of  $\omega$ -oxoacids than diacids. This is consistent with the results of the Arctic polar sunrise experiment, in which glyoxylic acid ( $C_2$ ) peaked one week earlier than oxalic acid (Kawamura et al., 1996a).  $\omega$ -Oxoacids have been proposed as intermediates to the formation of diacids (Norton et al., 1983; Kawamura et al., 1996a).

Figures 2e and 2f give diurnal variations of concentrations of pyruvic acid as well as its percentages in aerosol mass. Being similar to dicarboxylic acids and  $\alpha$ -ketoacids, this  $\alpha$ -ketoacid also shows a clear diurnal variation with a peak either in 8-11 h or 11-14 h. Its relative abundance also showed a daytime maximum. These results may suggest that the photochemical processes largely control atmospheric concentration of pyruvic acid. Although pyruvic acid production should be significant throughout the day, its removal by degradation and/or deposition may overwhelm the production in the late afternoon. Concentrations of  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal) also showed concentration maximum in 11-14 h or 8-11 h (data are not shown here). Their relative abundance in aerosol mass generally increased in the morning and reached a maximum at 8-11 h or 11-14 h, but July samples showed a peak in 5-8 h, when the solar radiation was already high (av.  $1.37 \text{ MJm}^{-2}$ ).

### **3.5. Relative abundance of dicarboxylic acids, ketoacids and $\alpha$ -dicarbonyls in aerosol TC**

Figure 3a gives diurnal distributions of total dicarboxylic acid-carbon normalized by aerosol TC. Diacid-C/TC ratios generally start to increase in the morning and maximize around noontime, again supporting a photochemical production of diacids by gas-to-particle conversion of hydrocarbons and other precursors as well as the heterogeneous oxidation on the aerosol surfaces. Interestingly, summer samples show a continuous increase of diacid-C/TC ratios even in the afternoon (Figure 3a), mainly due to the production of small diacids ( $\text{C}_2\text{-C}_4$ ) (see Figures 4a,b, and e) via the further oxidation of some intermediate compounds produced by the oxidation of hydrocarbons (Kawamura et al., 1996a). Because oxidants were still high ( $>20$  ppb) in the late evening of June and July (Figure 1), oxidation of organic precursor by ozone likely occurred even in the darkness. Further,  $\text{NO}_3$  radicals that are important oxidant at night (Finlayson-Pitts et al., 2000) may participate in the production of diacids. The secondary production of diacids, especially oxalic, malonic and succinic acids, possibly overwhelms their degradation or deposition in the late afternoon.

Individual compound-C/TC ratios showed a different trend among diacids, although most species peaked at 11-14h (Figure 4). For example, small diacid-C/TC ratios (such as C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>) increased in late evening whereas those of iC<sub>4</sub>, mM, iC<sub>5</sub>, Ph showed a sharp drop in the afternoon and stayed low in the midnight. Such a difference in the diurnal distributions may be caused by a difference in their precursors and/or formation mechanisms. Normal saturated C<sub>2</sub>-C<sub>4</sub> diacids are produced from more common precursors including unsaturated and saturated hydrocarbons, monocarboxylic acids, aldehydes, ketoacids, etc. In contrast, unsaturated and branched-chain diacids have been considered to generate via photochemical oxidation of more specific precursors such as aromatic hydrocarbons (Kawamura et al., 1996a) and methylcycloalkenes (Grosjean and Fung, 1984). Oxidation of aromatic hydrocarbons is mostly involved with OH radicals rather than O<sub>3</sub> (Finlayson-Pitts et al., 2000). Singh et al. (1985) reported diurnal variations of aromatic hydrocarbons such as benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes, and 3- and 4-ethyltoluenes with a concentration minimum around noontime.

As shown in Figure 3b, total  $\alpha$ -oxoacid-carbon normalized by TC generally increase in the morning with a maximum at 11-14 h or 8-11 h, suggesting a photochemical production in gas phase and/or particles. Being similar to small diacids, C<sub>2</sub> and C<sub>4</sub>  $\alpha$ -oxoacids are likely produced at night (see Figures 5a,c), although C<sub>3</sub>  $\alpha$ -oxoacid did not show such an increase (Figure 5b). Figure 3c shows diurnal variations of pyruvic acid-C/TC ratios. The ratios clearly increase early in the morning, maximize at 11-14 h and then decrease toward the evening, suggesting a photochemical production of pyruvic acid in daytime. This acid showed the most pronounced diurnal variation among the water-soluble organics studied due to the decrease at night. Pyruvic acid may be decomposed by attack of NO<sub>3</sub> radicals to result in oxalic acid. The  $\alpha$ -dicarbonyls/TC ratios also increase early in the morning and maximize either at 8-11h or 11-14 h (see Figure 5d for glyoxal). However, their amplitudes are not so significant as  $\alpha$ -oxoacids and pyruvic acid (Figures 3b,c) probably due to their high vapor pressure; dicarbonyls may exist more in gas phase than particles in daytime. Alternatively,

dicarbonyls can be hydrated with H<sub>2</sub>O and oxidized to oxalic acid on aerosols (Warneck, 2003).

### **3.6. *In situ* production of diacids and related compounds: relationship to ambient temperature, solar radiation and oxidants**

Concentrations of diacids generally showed a good correlation with ambient temperature and solar radiation as well as oxidants. Figure 6a plots concentrations of total dicarboxylic acid-carbon normalized by TC against ambient temperature for all the samples. A positive relationship demonstrates that dicarboxylic acids are secondarily produced in the atmosphere by photochemical processes and participate in the formation and growth of organic aerosols. However, at higher temperatures (>20°C), relative abundances of diacid-carbon in TC are fairly variable (Figure 6a). This is consistent with the fact that diacid-C/TC for some species (e.g., C<sub>2</sub>, C<sub>4</sub>) are even higher at night in summer (Figure 4a,e) when ambient temperature drops by ca. 5°C. Deposition of gaseous diacids onto the particles is possible at night in summer. Further, heterogeneous production of diacids is also likely. A positive correlation was also found between diacid-C/TC ratios and solar radiation.

As shown in Figure 6b, diacid-C/TC ratios increase with an increase in the concentrations of oxidants. This positive correlation ( $r=0.76$ ) again suggests that diacids are *in situ* produced in the atmosphere by the oxidation of gaseous precursors such as aromatic hydrocarbons as well as the heterogeneous reactions on the aerosol surface. Similarly, pyruvic acid- and -oxoacid-C normalized by TC also showed positive correlations with oxidants, but correlation coefficients were much lower ( $r = 0.34$  and  $0.40$ , respectively). The weaker relationship may be involved with a partitioning of these semi-volatile compounds between gas phase and particles; they are present more in gas phase when ambient temperature increases. Because the production of oxidants is associated with solar radiation, these results suggest that origins of diacids and ketoacids are largely involved with secondary photochemical processes in the atmosphere rather than primary emissions from automobiles although automobiles are major sources for the precursors of bi-functional organic acids.

### 3.7. Preferential production of unsaturated diacids early in the morning and late production of oxalic acid: implication for the oxidation of unsaturated precursors

Although oxalic acid is the dominant diacid throughout the campaigns, a significant variation was found in their molecular composition within a day. Figure 7 presents diurnal variations in the relative abundance of oxalic ( $C_2$ ), methylmaleic (mM), and adipic ( $C_6$ ) acids in the total diacids. Oxalic acid shows a decrease early in the morning with a minimum at 8-11 h or 11-14 h and then an increase in the afternoon toward the midnight. In contrast, mM and  $C_6$  show an increase early in the morning (Figures 7b,c). These results indicate that a preferential production of mM and  $C_6$  over  $C_2$  occurs early in the morning. Other unsaturated species such as maleic and phthalic acids, as well as methylsuccinic ( $iC_5$ ) acid, also showed a trend similar to mM. Unsaturated diacids can be produced by photochemical oxidation of aromatic hydrocarbons such as benzene, toluene and naphthalene (Kawamura and Ikushima, 1993). Some saturated diacids such as  $C_6$  and  $iC_5$  may be generated from cyclic olefins via  $O_3$  and OH reactions in gas phase (Grosjean et al., 1978, 1980; Hatakeyama et al., 1987). Cyclohexene and other cyclic olefins, as well as aromatic hydrocarbons, are present in the urban atmosphere (Grosjean and Fung, 1984; Singh et al., 1985). In contrast, other major diacids such as  $C_3$ ,  $C_4$  and  $C_5$  did not show any diurnal trend in their relative abundances.

Concentrations of some diacids and ketoacids were found to correlate inversely with relative abundance of  $C_2$  (%) in total diacids, which has been proposed as a proxy for photochemical aging of organic aerosols (Kawamura and Sakaguchi, 1999). Relatively strong anti-correlations were obtained between  $C_2$  (%) and some diacid species; e.g.,  $iC_4$  ( $r=0.96$ ),  $C_6$  (0.80), M (0.81), mM (0.94) and Ph (0.96) during June 2-3 campaign (except 05-08, 08-11 and 11-14 h), suggesting that these unsaturated and saturated diacids are formed in an early stage of photochemical processes. Similar relationships were also observed for  $\alpha$ -oxocarboxylic acids ( $C_2$ - $C_4$ ) and pyruvic acid (e.g.,  $r=0.96$  for  $C_2$  and 0.93 for Pyr), and, to a lesser extent, for  $\alpha$ -dicarbonyls. Figure 8 plots organic acid-C normalized by TC for  $iC_4$ ,  $iC_5$ , mM,  $C_6$ , Ph, and Pyr as a function of  $C_2$  (%). Similar anti-correlations were also found for

other organic acids such as M, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>. These results demonstrate that unsaturated and some saturated diacids and ketoacids are produced in the early stages of photochemical oxidation of aromatic hydrocarbons and cyclic olefins and are further oxidized to oxalic acid by the subsequent reactions.

### **Acknowledgements**

We thank the Pollution Monitoring Section, Environmental Assessment Division, Tokyo Metropolitan Government for the supply of oxidant and meteorological data. N. Tsubonuma and T. Watanabe are acknowledged for the help in the measurements of total carbon and nitrogen content. Experimental work has partly been done at Department of Chemistry, Tokyo Metropolitan University, where K. K. stayed as a faculty member. This study was in part supported by the Ministry of Education, Science and Culture through Grant-in-Aid No. 63740321 and 01470041.

## References

- Barboukas, E. D., Kanakidou, M., Mihalopoulos, N., 2000. Carboxylic acids in gas and particulate phase above the Atlantic Ocean. *J. Geophys. Res.* 105, 14,459-14,471,.
- Finlayson-Pitts, B. J., Pitts, J. N. Jr., 2000. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*. Academic Press pp.969.
- Fraser, M. P., Yue, Z. W., Tropp, R. J. Kohl, S. D., Chow, J. C., 2002. Molecular composition of organic fine particulate matter in Houston, TX. *Atmos. Environ.* 36, 5751-5758.
- Grosjean, D., Van Cauwenberghe, K., Schmid, J. P., Kelley, P. E., Pitts, J. N. Jr., 1978. Identification of C<sub>3</sub>-C<sub>10</sub> aliphatic dicarboxylic acids in airborne particulate matter. *Environ. Sci. Technol.* 12, 313-317.
- Grosjean, D., Fung, K., 1984. Hydrocarbons and carbonyls in Los Angeles air. *JAPCA* 34, 537-543.
- Grosjean, D., Friedlander, S. K., 1980. Formation of organic aerosols from cyclic olefins and diolefins, *Adv. Environ. Sci and Technol.* 9, 435-473.
- Hatakeyama, S., Ohno, M., Weng, J., Takagi, H., Akimoto, H. 1987. Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air. *Environ. Sci. Technol.* 21, 52-57.
- Hara, K., Osada, K., Matsunaga, K., Sakai, T., Iwasaka, Y., Furuya, K. 2002. Concentration trends and mixing states of particulate oxalate in Arctic boundary layer in winter/spring. *J. Geophys. Res.* 107, 4399, doi: 10.1029/2001JD001584.
- Kalberer, M., Yu, J., Cocker, D. R., Flagan, R. C., Seinfeld, J. H., 2000. Aerosol formation in the cyclohexene-ozone system. *Environ. Sci. Technol.* 34, 4896-4901.
- Kawamura, K., 1993. Identification of C<sub>2</sub>-C<sub>10</sub> -oxocarboxylic acids, pyruvic acid and C<sub>2</sub>-C<sub>3</sub> -dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS. *Anal. Chem.* 65, 3505-3511.
- Kawamura, K., Kosaka, M., Sempéré, R., 1995. Distributions and seasonal changes of hydrocarbons in urban aerosols and rainwaters. *Chikyukagaku (Geochemistry)* 29, 1-15.
- 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, 3501-3509.
- 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., Ikushima, K., 1993. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. *Environ. Sci. Technol.* 27, 2227-2235.
- 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., Sempéré, R., Imai, Y., Hayashi, M., Fujii, Y., 1996b. Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols. *J. Geophys. Res.* 101, No. D13, 18,721-18,728.
- Kawamura, K., Steinberg, S., Ng, L., Kaplan, I. R., 2001. Wet deposition of low molecular weight mono- and di-carboxylic acids, aldehydes and inorganic species in Los Angeles. *Atmospheric Environment* 35, 3917-3926.
- Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanaba, T., and Lee, M., 2004. Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition. In: *Geochemical Investigation in Earth and Space Science (eds. R. J. Hill et al.)*, The Geochemical Society, Publication No. 6 (in press).
- Kerminen, V. -M., Teinilä, K., Hillamo, R., Mäkelä, T., 1999. Size-segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere. *Atmospheric Environment* 33, 2089-2100.
- Legrand, M., De Angelis, M., 1996. Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone. *J. Geophys. Res.* 101, 4219-4145.
- Li, S. M., Winchester, J. W., 1993. Water soluble organic constituents in arctic aerosols and

- snow pack. *Geophys. Res. Lett.* 20, 45-48.
- Mochida, M., Kawabata A., Kawamura, K., Hatsushika, H., Yamazaki, K., 2003a. The seasonal variations and the origins of dicarboxylic acids in the atmosphere over the western North Pacific. *J. Geophys. Res.* 108(D6) 4193, doi:10.1029/2002JD002355.
- Mochida, M., Kawamura, K., Umemoto, N., Kobayashi, M., Matsunaga, S., Lim, H., Turpin, B. J., Bates, T. S., Simoneit B. R. T., 2003b. Spatial distribution of oxygenated organic compounds (dicarboxylic acids, fatty acids and levoglucosan) in marine aerosols over the western Pacific and off coasts of East Asia: Asian outflow of organic aerosols during the ACE-Asia campaign. *J. Geophys. Res.*, 108, No. D23, 8639, doi:10.1029/2002JD003256.
- 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.
- Narukawa, M., Kawamura, K., Anlauf, K. G., Barrie, L. A., 2003. Fine and coarse modes of dicarboxylic acids in the arctic aerosols collected during the Polar Sunrise Experiment 1997. *Journal of Geophysical Research* 108, NO. D18, 4575, doi:10.1029/2003JD00364.
- Norton, R. B., Roberts, J. M., Huebert, B. J., 1983. Tropospheric oxalate. *Geophys. Res. Lett.* 10, 517-520.
- Puxbaum, H., Rosenberg, C., Gregori, M., Lanzerstorfer, C., Ober, E., Winiwarter, W., 1988. Atmospheric Concentrations of Formic and Acetic Acid and Related Compounds in Eastern and Northern Austria. *Atmos. Environ.* 22, 2841-2850.
- Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., Simoneit, B. R. T., 1993. Quantification of urban organic aerosols on a molecular level: Identification, abundance and seasonal variation, *Proc. Fourth Int. Conf. on Carbonaceous Particles in the Atmosphere. Atmos. Environ.* 27A, 1309-1330.
- Satsumabayashi, H., Kurita, H., Yokouchi, Y., Ueda, H., 1990. Photochemical formation of particulate dicarboxylic acids under long-range transport in central Japan. *Atmos. Environ.* 24A, 1443-1450.
- 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. T., 2001. Measurement of emissions from air pollution sources. 3. C<sub>1</sub>-C<sub>29</sub> organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* 35(9), 1716-1728.
- Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T., 2002. Measurement of emission from air pollution sources. 4. C<sub>1</sub>-C<sub>27</sub> organic compounds from cooking with seed oils. *Environ. Sci. Technol.* 36(4), 567-575.
- Sekine, Y., Hashimoto, Y., Nakamura, T., Chen, Z., Mitsuzawa, S., 1992. Characterization of atmospheric aerosols components at Beijing, China. *J. Japan Soc. Air Pollut.* 27, 237-245.
- Sempéré, R., Kawamura, K., 1994. Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere. *Atmos. Environ.* 28, 449-459.
- Sempéré, R., Kawamura, K., 2003. Trans-hemispheric contribution of C<sub>2</sub>-C<sub>10</sub> dicarboxylic acids and related polar compounds to water soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions. *Global Biogeochemical Cycles* 17, No.2, 1069, doi: 10.1029/2002GB001980.
- Singh, H. B., Salas, L. J., Cantrell, B. K., Redmond, R. M., 1985. Distribution of aromatic hydrocarbons in the ambient air. *Atmos. Environ.* 11, 1911-1919.
- Talbot, R. W., Vijgen, A. S., Harriss, R. C., 1992. Soluble species in the arctic summer troposphere: acidic gases, aerosols, and precipitation. *J. Geophys. Res.*, 97, 16,531-16,543.
- Wang, G. S., Liu, N. C., Wang, L., 2002. Identification of dicarboxylic acids and aldehydes of PM<sub>10</sub> and PM<sub>2.5</sub> aerosols in Nanjing, China. *Atmos. Environ.* 36, 1941-1950.
- Warneck, P., 2003. In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.* 37, 2423-2427.

Table 1. Concentrations ( $\text{ngm}^{-3}$ ) of dicarboxylic acids, ketocarboxylic acids and  $\alpha$ -dicarbonyls in the aerosol samples from Tokyo.

Water-soluble components	June 2-3 (n=14)				July 21-22 (n=10)				November 20-21 (n=8)			
	min.	max.	av.	med.	min.	max.	av.	med.	min.	max.	av.	med.
<b>Dicarboxylic acids</b>												
Oxalic, C <sub>2</sub>	164	815	357	274	89.4	260	157	142	93.4	401	186	144
Malonic, C <sub>3</sub>	30.1	163	71.4	63.4	16.2	101	44.0	32.0	18.4	88.1	40.5	29.1
Succinic, C <sub>4</sub>	25.4	168	73.4	64.2	13.1	84.5	40.5	32.4	22.5	79.0	47.4	47.3
Glutaric, C <sub>5</sub>	8.5	49.6	23.1	19.9	3.8	23.4	10.9	9.0	8.7	26.5	18.2	17.2
Adipic, C <sub>6</sub>	4.1	88.8	25.8	21.0	4.1	30.9	13.4	13.3	7.9	23.0	14.2	13.8
Pimelic, C <sub>7</sub>	1.3	32.2	9.9	8.0	1.3	9.9	4.6	3.7	2.3	14.5	8.2	8.5
Sebacic, C <sub>8</sub>	2.2	33.1	11.0	6.9	0.0	5.9	2.4	1.9	3.0	17.4	9.1	8.7
Azelaic, C <sub>9</sub>	4.8	40.5	15.1	11.5	5.9	20.1	11.1	9.3	11.5	36.1	20.6	19.6
Decanedioic, C <sub>10</sub>	0.0	16.2	4.9	3.2	0.0	3.3	1.1	0.0	3.3	11.4	7.3	6.9
Methylmalonic, iC <sub>4</sub>	1.2	19.9	7.2	5.1	1.1	10.1	4.0	2.2	0.4	11.8	5.1	4.2
Methylsuccinic, iC <sub>5</sub>	3.9	25.2	12.9	12.7	2.8	12.6	7.4	7.0	4.4	17.5	10.9	11.4
2-Methylglutaric, iC <sub>6</sub>	0.0	22.4	7.3	5.4	0.0	15.1	3.5	2.4	0.0	5.6	2.2	2.0
2-Methyladipic, iC <sub>7</sub>	0.0	11.3	3.5	2.4	0.0	8.5	1.8	0.0	0.0	5.4	1.3	0.0
Maleic, M	2.5	30.8	11.7	10.6	2.6	11.3	5.7	4.3	5.3	14.0	8.4	7.1
Fumaric, F	1.9	9.6	4.5	3.7	1.0	5.4	2.9	2.8	4.9	10.6	7.3	7.2
Methylmaleic, mM	2.1	73.6	17.5	9.5	1.6	11.0	5.7	3.9	4.7	21.1	10.9	8.2
Phthalic, Ph	5.0	110	32.6	24.4	8.2	76.6	29.0	26.6	13.1	36.1	24.0	23.6
Malic, hC <sub>4</sub>	2.9	99.1	27.3	12.4	0.0	5.9	3.8	4.3	3.3	14.7	8.8	7.1
Ketomalonic, kC <sub>3</sub>	0.9	8.0	3.5	3.3	1.1	4.9	2.4	2.1	1.8	6.8	3.7	3.3
4-Ketopimelic, kC <sub>7</sub>	2.5	20.5	6.6	4.6	1.3	11.8	4.3	2.6	1.5	8.9	5.3	5.3
total Diacids	300	1804	726	636	164	682	355	291	234	825	438	400
<b>Tricarboxylic acid</b>												
Citric, Cit	0.0	29.9	9.0	5.7	1.8	7.5	3.6	3.3	2.1	15.3	7.1	5.6
<b>Ketocarboxylic acids</b>												
Pyruvic	9.0	138	49.7	38.0	6.6	46.8	24.8	23.1	18.8	67.6	44.8	44.7
Glyoxylic, C <sub>2</sub>	16.3	105	44.3	33.1	5.3	49.3	21.0	17.7	18.0	85.3	41.5	35.4
3-Oxopropanoic, C <sub>3</sub>	2.3	15.2	6.8	5.8	1.2	15.8	6.0	4.2	4.2	10.7	7.2	6.6
4-Oxobutanoic, C <sub>4</sub>	7.3	26.9	15.9	14.8	5.0	22.4	10.2	8.1	10.8	24.2	17.2	17.2
total ketoacids	35	285	117	95	22	123	62	52	62	177	111	99
<b><math>\alpha</math>-Dicarbonyls</b>												
Methylglyoxal, mGly	15.2	42.9	26.2	26.3	4.7	28.1	14.3	16.0	7.4	51.5	24.1	22.5
Glyoxal, Gly	6.1	72.9	19.9	13.0	2.1	22.1	7.8	5.3	10.1	39.3	21.5	18.6
total dicarbonyls	21	116	46	39	8	44	22	19	21	91	46	42

## Figure captions

Figure 1. Variations of total carbon (TC), total nitrogen (TN), TC/aerosol mass, oxidants (mostly O<sub>3</sub>) and solar radiation during three campaigns (June 2-3, July 21-22, and November 20-21) in 1989. Oxidant and radiation data were supplied by the Pollution Monitoring Section, Tokyo Metropolitan Government and averaged for the sampling intervals (3 hours). Time 20 means 20-23pm.

Figure 2. Diurnal variations of (a) concentrations of total dicarboxylic acids (C<sub>2</sub>-C<sub>10</sub>), (b) their abundances relative to aerosol mass, (c) concentrations of total  $\alpha$ -oxocarboxylic acids (C<sub>2</sub>-C<sub>4</sub>) and (d) their abundances relative to aerosol mass, (e) concentrations of pyruvic acid and (f) its abundances relative to aerosol mass.

Figure 3. Diurnal variations of organic acid-C/TC ratios (%) for (a) total diacids, (b) total  $\alpha$ -oxoacids and (c) pyruvic acid.

Figure 4. Diurnal variations of diacid-C/TC ratios (%) for selected dicarboxylic acid species.

Figure 5. Diurnal variations of compound-C/TC ratios (%) for (a) glyoxylic acid (C<sub>2</sub>), (b) 3-oxopropanoic acid (C<sub>3</sub>), (c) 4-oxobutanoic acid (C<sub>4</sub>), and (d) glyoxal.

Figure 6. Relationship of total diacid-carbon/TC ratios (%) with (a) ambient temperature and (b) oxidants. The data from all the aerosol samples are plotted here.

Figure 7. Diurnal variations of relative abundance of (a) oxalic acid, (b) methylmaleic acid, and (c) adipic acid in total diacids.

Figure 8. Changes in organic acid-C/TC ratios (%) as a function of relative abundance of oxalic acid in total diacids (%). (a) methylmalonic, (b) methylsuccinic, (c) methylmaleic, (d) adipic, (e) phthalic, (f) pyruvic acids. Three samples (05-08, 08-11 and 11-14 h) are not included in the figure.

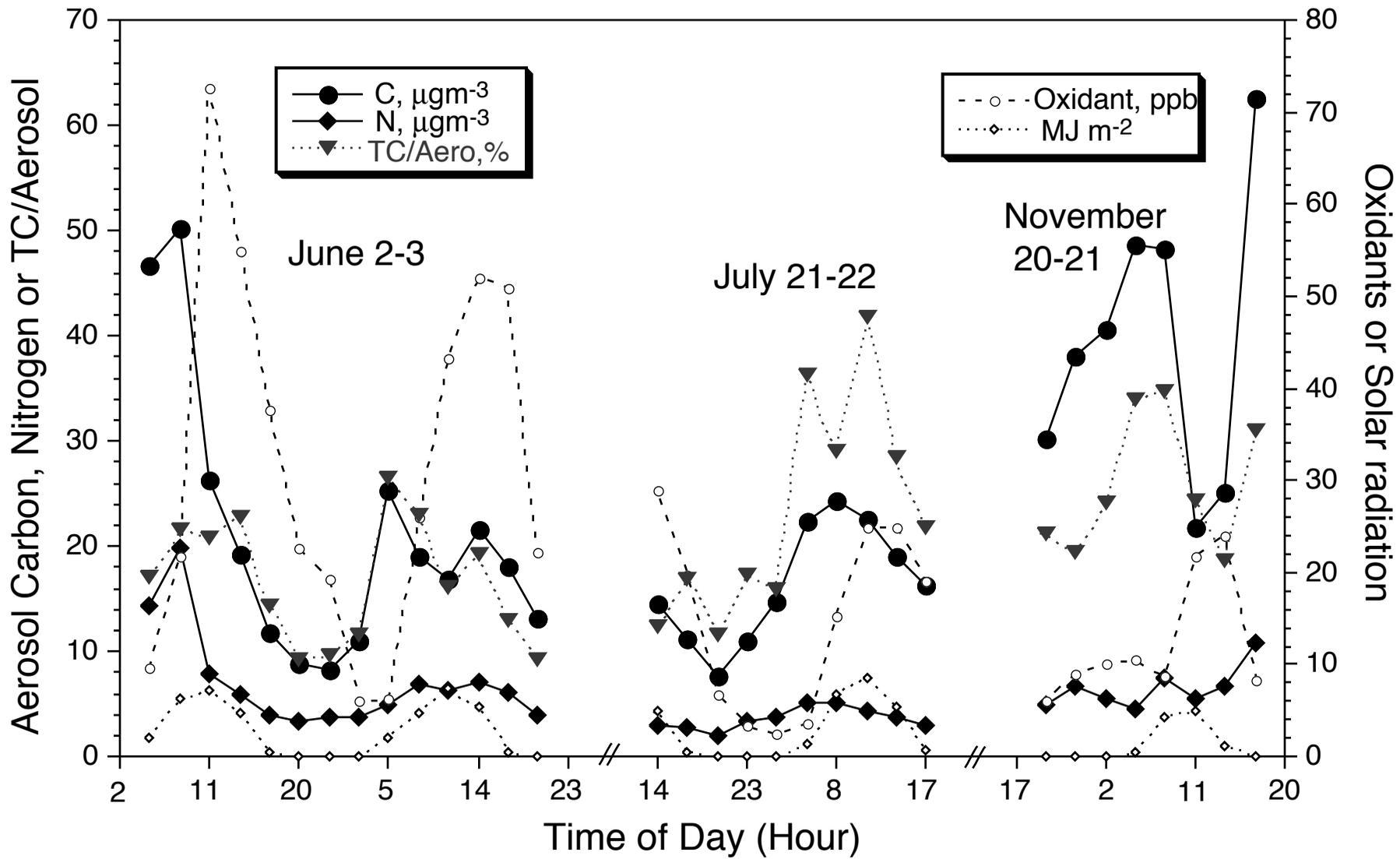


Fig. 1 (Kawamura)

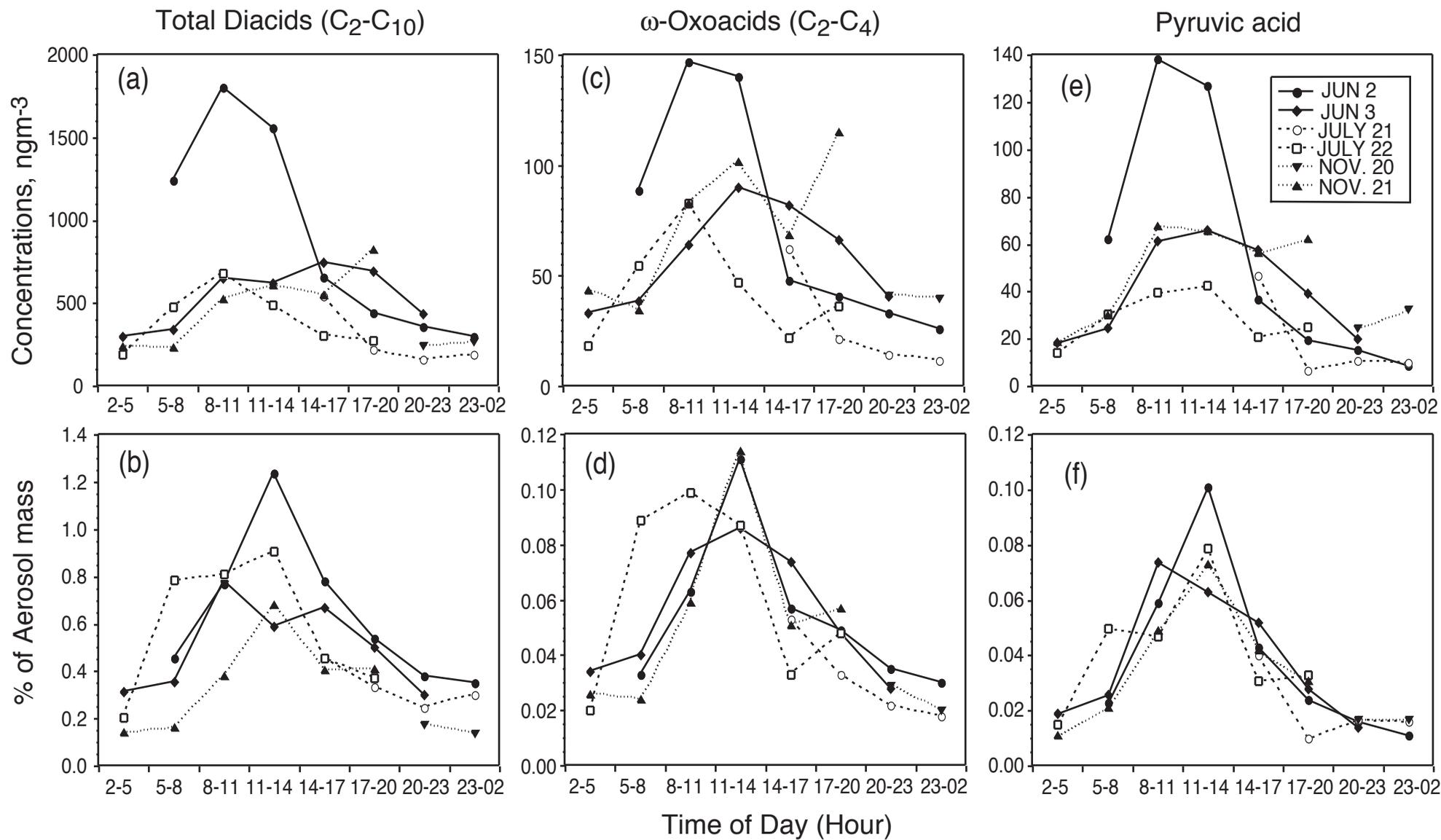


Fig. 2 (Kawamura)

Fig. 3 (Kawamura)

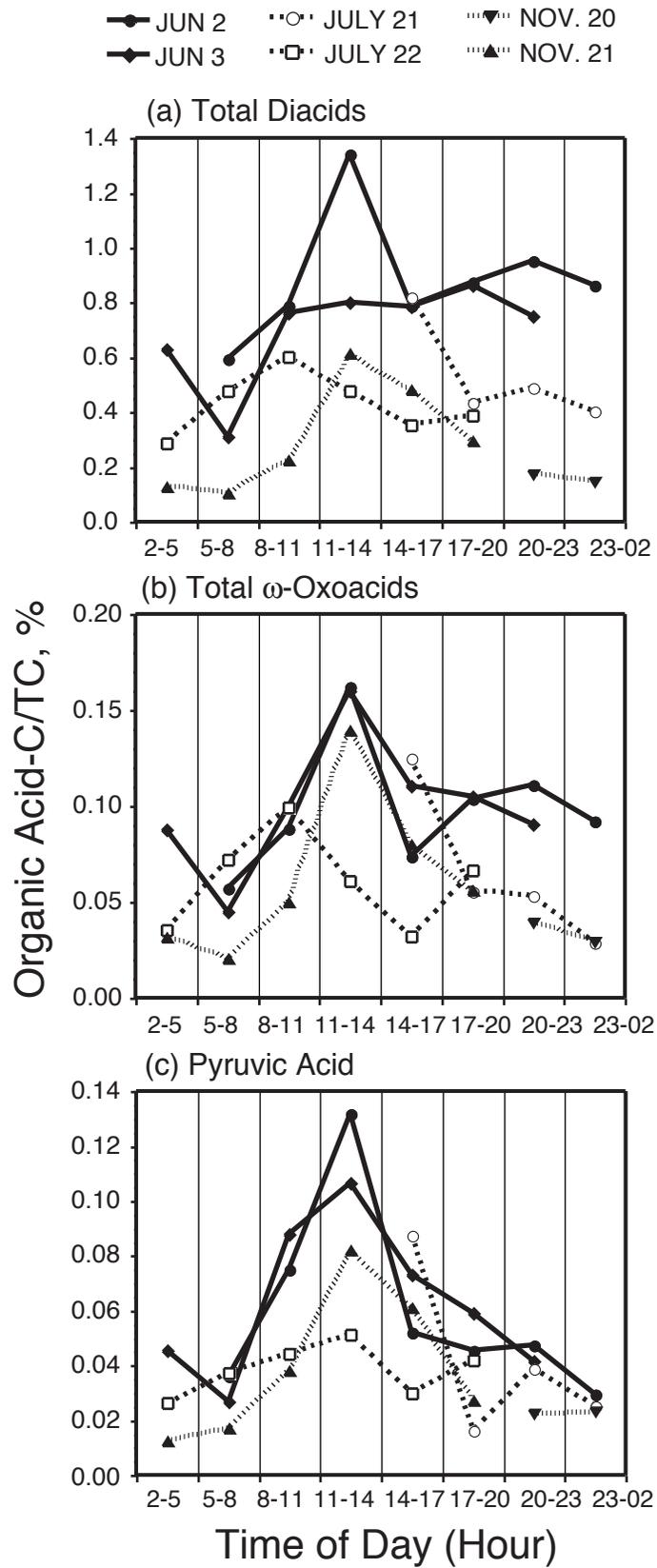


Figure 4

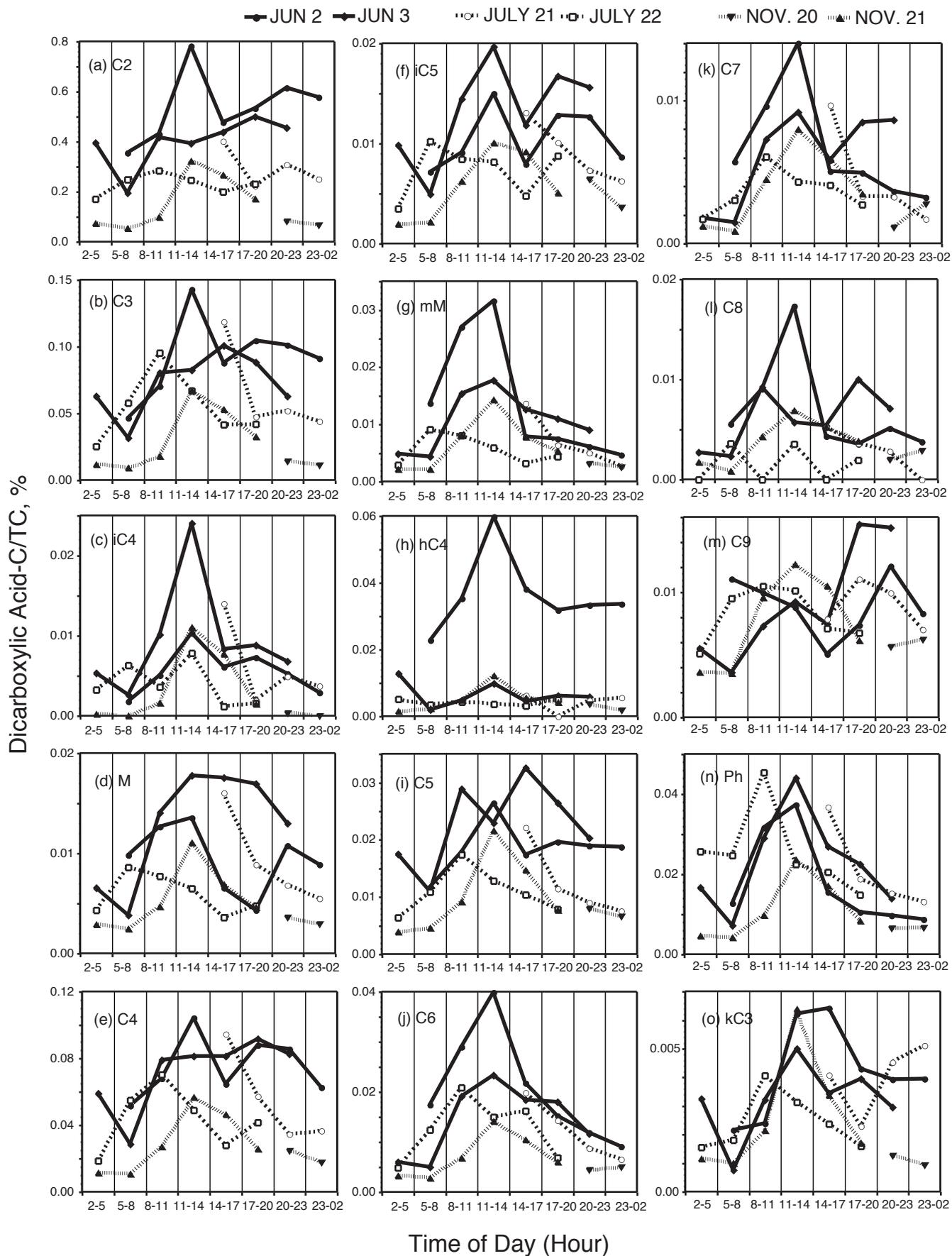


Fig. 5 (Kawamura)

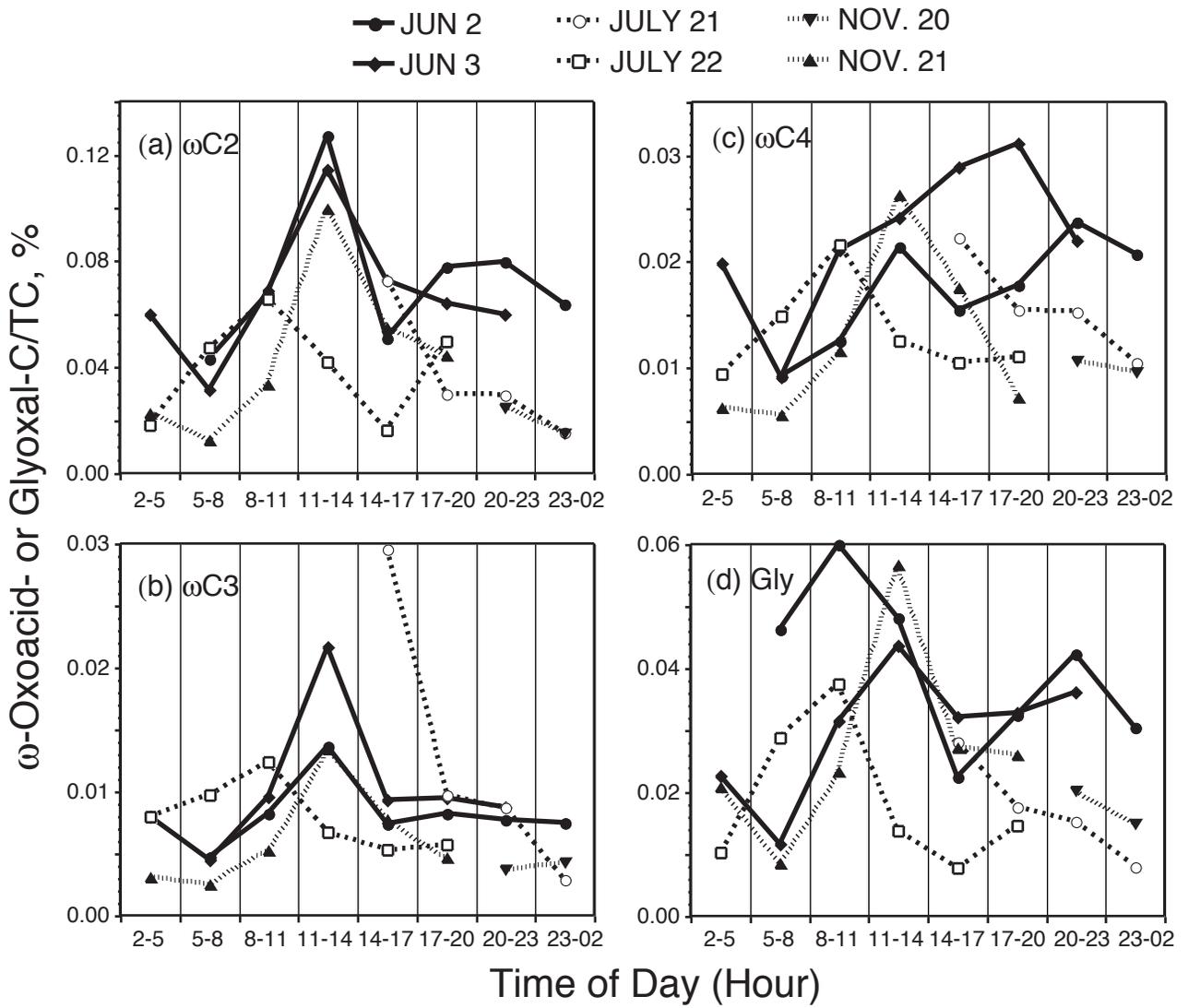


Fig. 6 (Kawamura)

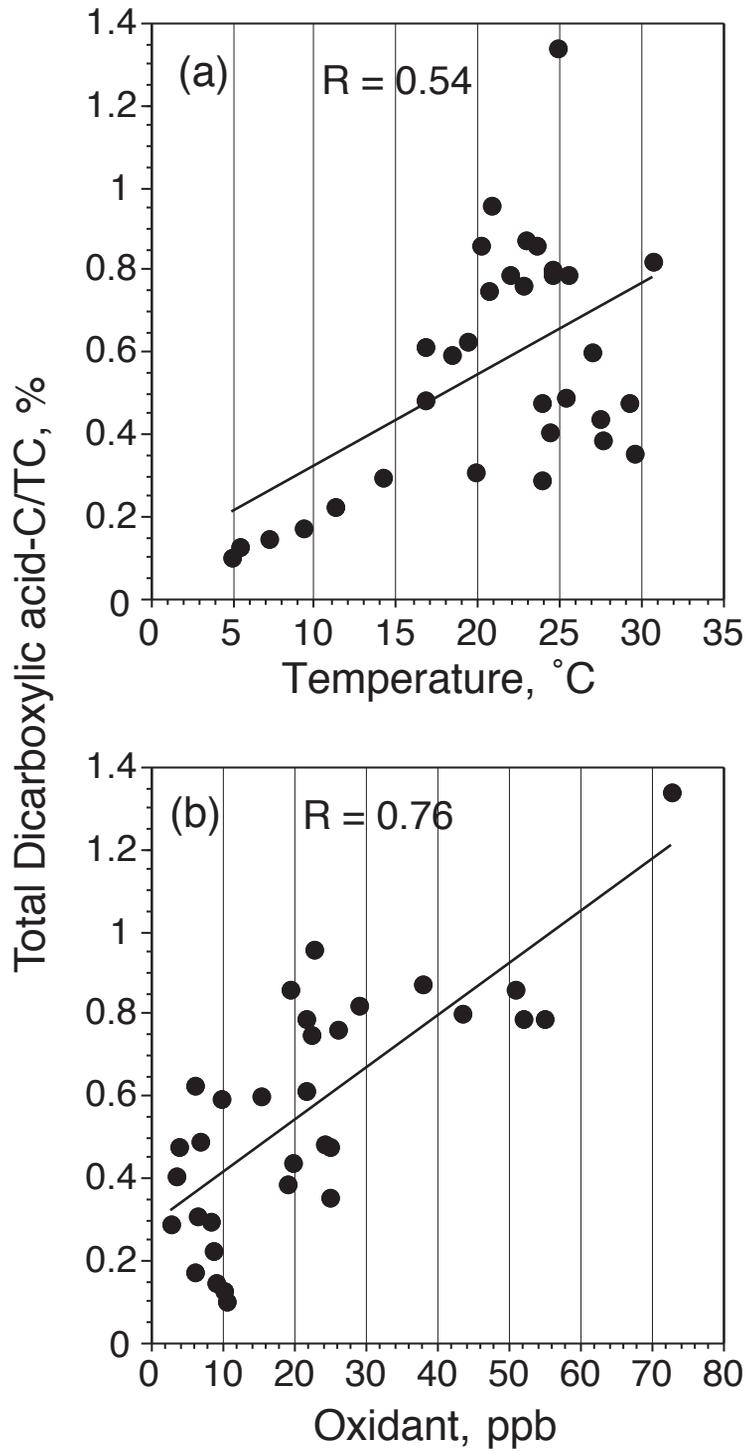
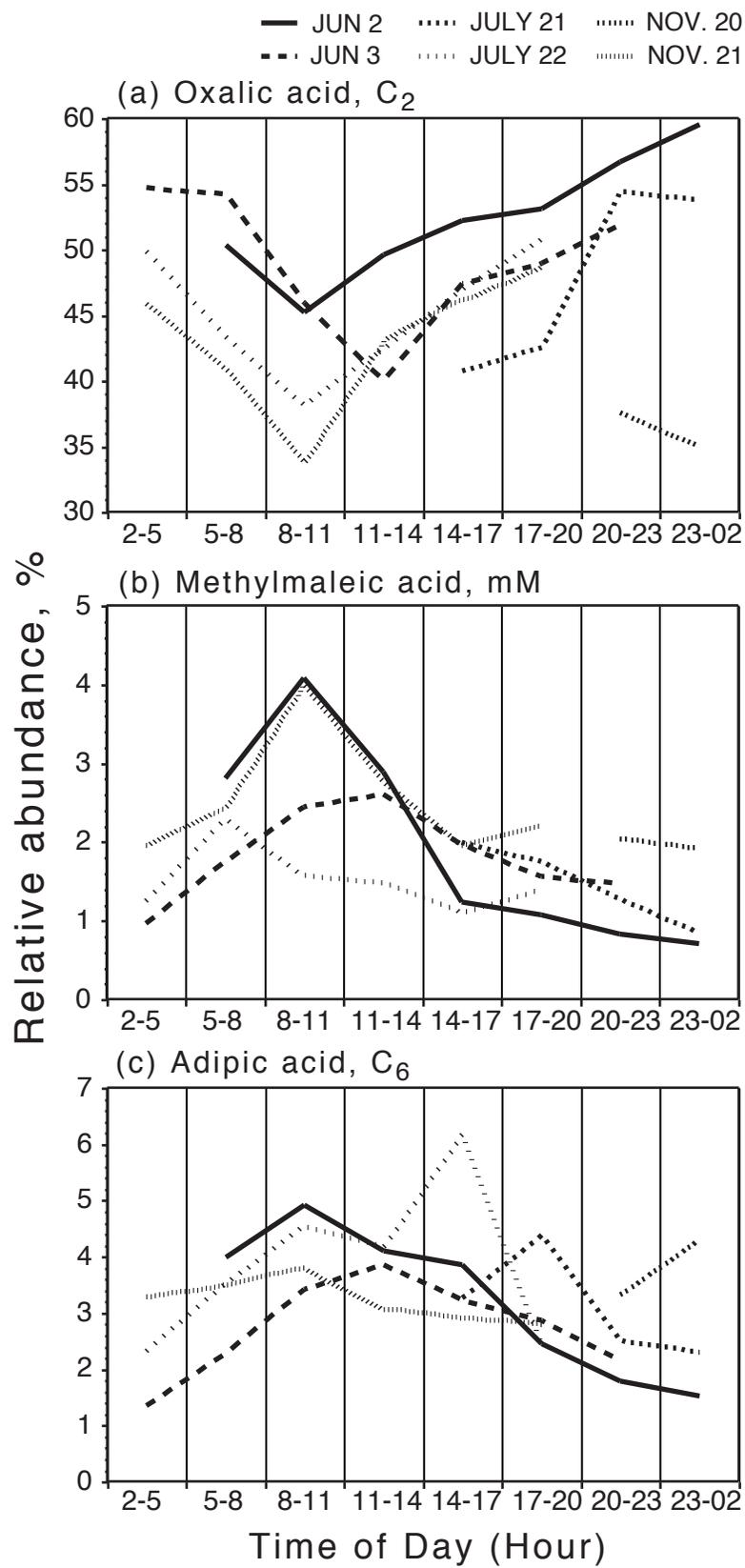


Fig. 7 (Kawamura)



June 2-3

