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Author(s)	Pavuluri, Chandra Mouli; Kawamura, Kimitaka; Swaminathan, T.
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Water-soluble organic carbon, dicarboxylic acids, ketoacids, and α-dicarbonyls in the tropical Indian aerosols

Chandra Mouli Pavuluri,[1] Kimitaka Kawamura,[1] and T. Swaminathan[2]

[1] Tropical aerosol (PM_{10}) samples ($n = 49$) collected from southeast coast of India were studied for water-soluble dicarboxylic acids (C_2–C_{12}), ketocarboxylic acids (C_2–C_9), and α-dicarbonyls (glyoxal and methylglyoxal), together with analyses of total carbon (TC) and water-soluble organic carbon (WSOC). Their distributions were characterized by a predominance of oxalic acid followed by terephthalic (t-Ph), malonic, and succinic acids. Total concentrations of diacids (227–1030 ng m^{-3}), ketoacids (16–105 ng m^{-3}), and dicarbonyls (4–23 ng m^{-3}) are comparative to those from other Asian megacities such as Tokyo and Hong Kong. t-Ph acid was found as the second most abundant diacid in the Chennai aerosols. This feature has not been reported previously in atmospheric aerosols. t-Ph acid is most likely derived from the field burning of plastics. Water-soluble diacids were found to contribute 0.4%–3% of TC and 4%–11% of WSOC. Based on molecular distributions and backward air mass trajectories, we found that diacids and related compounds in coastal South Indian aerosols are influenced by South Asian and Indian Ocean monsoons. Organic aerosols are also suggested to be significantly transported long distances from North India and the Middle East in early winter and from Southeast Asia in late winter, but some originate from photochemical reactions over the Bay of Bengal. In contrast, the Arabian Sea, Indian Ocean, and South Indian continent are suggested as major source regions in summer. We also found daytime maxima of most diacids, except for C_9 and t-Ph acids, which showed nighttime maxima in summer. Emissions from marine and terrestrial plants, combined with land/sea breezes and in situ photochemical oxidation, are suggested especially in summer as an important factor that controls the composition of water-soluble organic aerosols over the southeast coast of India. Regional emissions from anthropogenic sources are also important in megacity Chennai, but their influence is weakened due to the dispersion caused by dynamic land/sea breeze on the coast.

1. Introduction

[2] South Asia is one of the most important source regions on the globe for atmospheric aerosols and their precursors because of extensive economic development in India, which is similar to modern China. The economy of India had an average annual gross domestic product growth of 6.1% [*World Bank*, 2000] and a high growth rate of energy consumption (21% between 2001 and 2006; http://www.eia.doe.gov/emeu/international/energyconsumption.html). South Asia is predicted to have the highest growth rate of energy consumption in the world by 2010 [*Srivastava and Misra*, 2007] and is likely to become the most important

source region of anthropogenic emissions. Indian Ocean Experiments (INDOEX) indicated a high aerosol loading influenced by growing levels of pollutants in India and Southeast Asia and their significant effect on radiative forcing [*Lelieveld et al.*, 2001; *Mitra*, 2001].

[3] In India, the mode of energy use and combustion technologies is very different from those of North America and Europe. In this country, 85%–90% of cooking energy are from burning of biofuels (wood, agricultural waste, and dung cake), which accounts for 47% of the total energy consumption [*Tata Energy Research Institute*, 1997]. Even in urban area, municipal solid wastes are mostly disposed into open landfills [*Jha et al.*, 2008], which are often ignited to result in field burning without any control. High ambient temperatures and strong solar radiation, as well as high levels of O_3 and NO_x [*Pulikesi et al.*, 2006], further induce photochemical production of aerosols in the atmosphere. Southeast Asian and Indian Ocean monsoons may further influence the chemical and physical properties of tropical Indian aerosols.

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan.
[2]Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India.
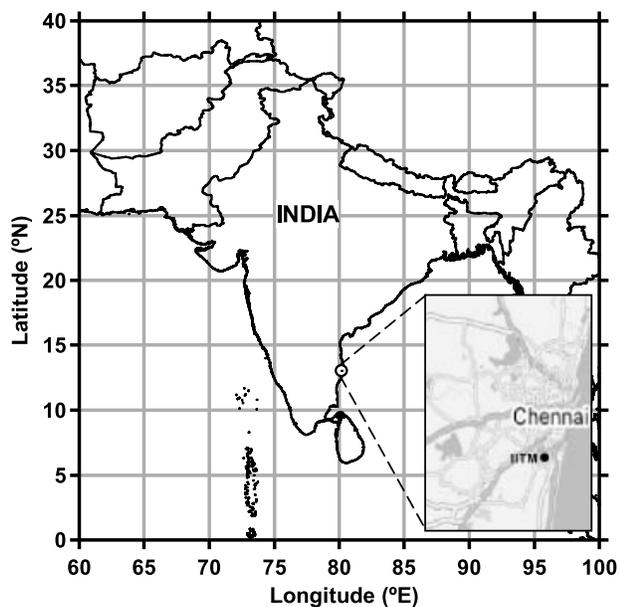
Figure 1. A map of South Asia with sampling site (IITM, solid circle), Chennai (13.04°N; 80.17°E) on the southeast coast of India.

However, tropical Indian aerosols have scarcely been studied for their organic compositions at molecular levels [*Chowdhury et al.*, 2007; *Sharma et al.*, 2003], although inorganic constituents were investigated [e.g., *Negi et al.*, 1987; *Chandra Mouli et al.*, 2006].

[4] Water-soluble organic compounds that are enriched in fine aerosol particles have recently received more attention because of their hygroscopic properties and the capability to act as cloud condensation nuclei [*Novakov and Penner*, 1993]. Dicarboxylic acids and related compounds account for a substantial fraction of the water-soluble organic aerosols [*Saxena and Hildemann*, 1996], which may evolve from a series of chemical reactions occurring in the gas phase, aerosols, and cloud water [*Chebbi and Carlier*, 1996]. Diacids have been studied in aerosols from continental [*Aggarwal and Kawamura*, 2008; *Kawamura and Kaplan*, 1987; *Kawamura and Ikushima*, 1993; *Huang et al.*, 2005; *Ho et al.*, 2006; *Hsieh et al.*, 2008; *Yao et al.*, 2004], coastal marine [*Kawamura et al.*, 2004; *Mochida et al.*, 2003], remote marine [*Kawamura and Sakaguchi*, 1999; *Wang et al.*, 2006], and polar [*Kawamura et al.*, 1996a; *Kawamura et al.*, 1996b] regions. Here we describe the molecular distributions of water-soluble dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls in the tropical Indian aerosols (PM_{10}) from the megacity of Chennai on the southeast coast of the tropical Indian subcontinent. We report seasonal and diurnal changes of these organic compound classes as well as water-soluble organic carbon (WSOC) in the tropical Indian aerosols. Although aerosols over Chennai have been studied for the mass concentrations [*Oanh et al.*, 2006], there is no report on organic compositions at molecular levels.

2. Experimental Procedure

2.1. Site Description

[5] The tropical megacity Chennai is located on the southeast coast of India (13.04°N, 80.17°E), as shown in Figure 1. Its average elevation is 6 m, with a highest point of 60 m. The population of the city was 4.3 million in 2001 (7 million, including suburban area). About 18.6% of the population are living below the standard poverty line (http://en.wikipedia.org/wiki/chennai), using either wood or cow dung as cooking fuel. Chennai and its surroundings are crowded with different kinds of industries like petrochemicals, thermal power plants, etc. [*Jayanthi and Krishnamoorthy*, 2006; *Manju et al.*, 2002], from which significant amounts of organics are released into the atmosphere.

2.2. Aerosol Sampling

[6] A daytime and nighttime aerosol (PM_{10}) sampling was performed during winter (23 January to 6 February, $n = 29$) and summer (22–31 May, $n = 20$) in 2007. An air sampler was placed on the rooftop of the Mechanical Sciences building (~18 m above the ground level) at the Indian Institute of Technology Madras (IITM) campus located in the southern part of Chennai and about 3 km away from the coast. The IITM campus is located in a natural forest area. Sampling was conducted in daytime (roughly ~6:00–18:00, local time (LT)) and nighttime (~18:00–6:00 LT) using a high-volume air sampler (Envirotech APM 460 DX, India) and precombusted (450°C, 4 h) quartz fiber filters (Pallflex 2500QAT-UP, 20 × 25 cm). The sample filter was placed in a preheated glass jar with a Teflon-lined screw cap and stored in darkness at −20°C prior to analysis [*Kawamura and Ikushima*, 1993].

2.3. Chemical Analysis

[7] Samples were analyzed for diacids, ketoacids, and dicarbonyls using a method reported previously [*Kawamura and Ikushima*, 1993; *Kawamura*, 1993]. Briefly, one fifth of the filter was extracted with ultra pure organic-free Milli-Q water (10 mL × 3) under ultrasonication for 10 min. The extracts were concentrated to near dryness using a rotary evaporator under vacuum and then derivatized to dibutyl esters and/or dibutoxy acetals with 14% BF_3/n-butanol at 100°C. Both the esters and acetals were extracted with n-hexane and then analyzed using a capillary gas chromatography (GC; HP 6890). Peak identification was performed by GC retention times and confirmed by mass spectral examination using a GC-mass spectrometry (GC-MS) system.

[8] Recoveries of authentic standards spiked to a precombusted quartz fiber filter were 73% for oxalic acid and more than 84% for malonic, succinic, and adipic acids. Recoveries are higher (e.g., 87% for oxalic acid) when authentic standards were spiked to aerosol filter samples [*Kawamura and Yasui*, 2005]. The analytical errors in duplicate analysis of the filter sample are within 9% for major species. Gas chromatogram of the field and laboratory blanks showed small peaks for oxalic, phthalic, and glyoxylic acids. However, their amounts are less than 2% of the actual samples. Concentrations of all the species reported here are corrected for the field blanks.

[9] Aerosol mass (PM_{10}) in each filter was measured gravimetrically by the mass difference before and after sampling. The filters were conditioned in a desiccator for about 48 h before and after sampling.

[10] To measure water-soluble organic carbon (WSOC), three filter discs (2 cm in diameter) were extracted with
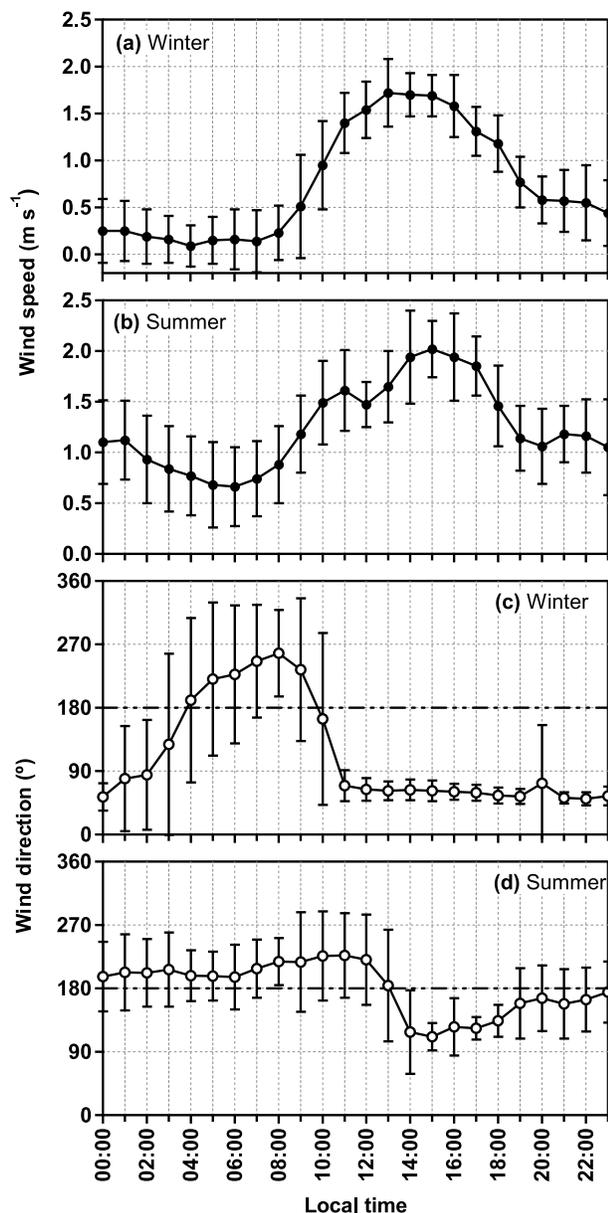
Figure 2. Diurnal variation in (a, b) wind speed and (c, d) wind direction in winter (23 January to 6 February) and summer (22–31 May) 2007 at IITM, Chennai, India. The vertical bars through the points show the standard deviation of the average. The dashed line indicates the coastal boundary.

organic-free Milli-Q water under ultrasonication for 20 min. The water extracts were then passed through a syringe filter (Millex-GV, 0.22 μm, Millipore), and WSOC was measured using TOC analyzer (Shimadzu 5000A) [*Aggarwal and Kawamura*, 2008]. A part of these extracts were used to measure inorganic ions of interest with ion chromatograph (761 Compact IC, Metrohm). Another disc cut was analyzed for aerosol total carbon (TC) content using the elemental analyzer (Carlo Erba NA 1500) [*Kawamura et al.*, 2004]. The analytical errors in duplicate analysis are within 8% and 7% for WSOC and TC, respectively.

2.4. Meteorology

[11] The weather in Chennai is generally hot and humid. According to a meteorological station of IITM (sampling site), the ambient temperature during the campaigns varied from 14.2 to 34.9°C (ave. 23°C; SD 4.3°C) in winter and 28.3–41°C (ave. 32°C; SD 2.9°C) in summer. Relative humidity (RH) ranged from 38% to 89% (ave. 68%; SD 0.1%) in winter and 31%–81% (ave. 60%; SD 0.11%) in summer. No rainfall was observed during the campaigns. The prevailing winds in Chennai are southwesterly in May to September and northeasterly for the rest of the year. Wind speed and wind direction on the near surface showed a clear diurnal oscillation during the campaigns (see Figure 2) due to a strong land/sea thermal gradient. However, such a wind contrast decreases with height and disappears above 1 km [*Srinivas et al.*, 2006].

2.5. Air Mass Trajectories

[12] We computed 10-day backward air mass trajectories arriving in Chennai at an altitude of 500 m for every 6 h, using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the National Oceanic and Atmospheric Administration (http://www.ready.noaa.gov/ready/open/hysplit4.html). The trajectory plots showed three transport pathways and source regions during the campaign (see Figure 3). In winter, the air masses that arrived in Chennai originated mostly from the Middle East and/or the Indian mainland in January and from Southeast Asia in February passing over the Bay of Bengal, except for a few cases. However, in summer the air masses mostly originated from the Arabian Sea and/or the northern Indian Ocean passing over the South Indian subcontinent. Hereafter, we present the results of chemical analyses as three categories of season following the air mass trajectory analysis; early winter (23–28 January), late winter (29 January to 6 February), and summer (22–31 May). However, the trajectories of 31 January (night) and 1 February fall in the category of
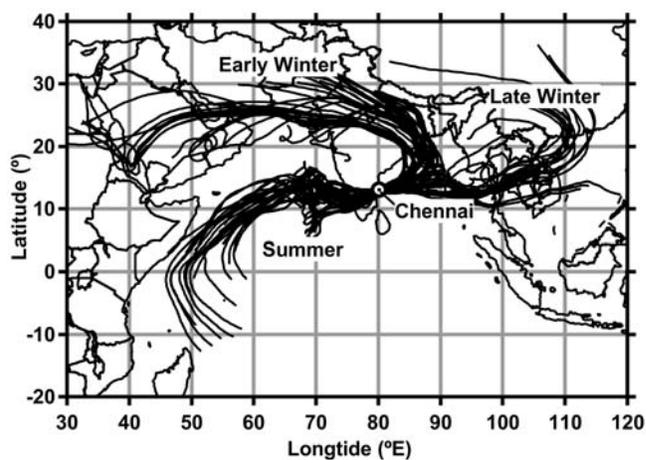

Figure 3. Plots of air mass back trajectories arriving at 500 m above Chennai (13.04°N and 80.17°E) in winter (23 January to 6 February) and summer (22–31 May) 2007, showing three major pathways reflecting early winter, late winter, and summer.

Table 1. Concentrations of Dicarboxylic Acids, Ketocarboxylic Acids, and α-Dicarbonyls, as well as Total Carbon and Water-Soluble Organic Carbon (WSOC), in the Tropical Indian Aerosols (PM_{10}) Collected on Daytime and Nighttime Basis in Early Winter ($n = 15$), Late Winter ($n = 10$), and Summer ($n = 20$) from Megacity Chennai, India, 2007[a]

	Concentrations (ng m^{-3})					
	Early Winter		Late Winter		Summer	
Compounds	Range	Ave. ± SD	Range	Ave. ± SD	Range	Ave. ± SD
Dicarboxylic acids						
Oxalic (C_2)	247.8–696.3	472.4 ± 136.9	229.9–518.9	380.0 ± 89.0	114.4–339.4	241.0 ± 64.2
Malonic (C_3)	30.8–81.4	59.7 ± 15.7	31.2–97.1	57.2 ± 18.0	15.9–70.5	37.2 ± 15.6
Succinic (C_4)	18.8–91.6	39.9 ± 17.4	16.8–92.8	48.4 ± 20.1	14.8–43.9	27.7 ± 8.8
Glutaric (C_5)	3.6–19.5	7.5 ± 3.8	3.1–21.4	11.2 ± 5.1	5.1–21.4	11.4 ± 3.9
Adipic (C_6)	2.2–12.0	4.6 ± 2.2	2.8–11.1	7.1 ± 3.0	4.7–14.7	9.4 ± 2.5
Pimelic (C_7)	0.7–11.3	2.7 ± 2.5	0.9–4.3	2.5 ± 1.2	2.8–25.6	9.0 ± 5.4
Suberic (C_8)	0.0–21.3	2.9 ± 5.3	0.0–7.6	3.7 ± 3.0	5.3–48.3	15.5 ± 10.4
Azelaic (C_9)	4.6–41.9	11.0 ± 9.1	4.4–26.9	14.9 ± 8.0	11.3–60.5	32.4 ± 16.4
Sebacic (C_{10})	0.5–5.0	1.3 ± 1.1	0.9–4.7	2.5 ± 1.2	1.4–9.2	4.6 ± 2.3
Undecanedioic (C_{11})	0.5–4.0	1.5 ± 1.0	0.6–4.0	2.3 ± 1.1	2.0–8.0	4.2 ± 1.5
Dodecanedioic (C_{12})	0.0–0.3	0.1 ± 0.1	0.0–0.4	0.2 ± 0.1	0.2–1.5	0.6 ± 0.4
Methylmalonic (iC_4)	0.5–2.2	1.2 ± 0.4	0.7–2.3	1.3 ± 0.5	0.6–2.9	1.4 ± 0.6
Methylsuccinic (iC_5)	2.3–6.8	3.9 ± 1.4	1.8–8.5	4.6 ± 2.1	1.5–4.7	3.0 ± 0.9
2-Methylglutaric (iC_6)	0.3–1.1	0.6 ± 0.3	0.3–1.6	0.9 ± 0.5	0.7–2.5	1.4 ± 0.5
Maleic (M)	0.7–3.7	1.8 ± 0.8	0.8–3.4	1.9 ± 1.0	1.3–3.9	2.3 ± 0.7
Fumaric (F)	0.3–2.7	1.2 ± 0.8	0.5–2.1	1.2 ± 0.7	0.5–3.1	1.3 ± 0.6
Methylmaleic (mM)	0.6–3.0	1.6 ± 0.8	0.6–3.5	1.8 ± 0.9	1.0–7.0	2.6 ± 1.8
Phthalic (Ph)	4.3–101.4	22.1 ± 23.4	4.9–24.2	15.4 ± 7.5	8.8–60.8	21.5 ± 13.9
Isophthalic (i-Ph)	0.4–2.5	1.1 ± 0.6	0.5–3.8	2.1 ± 1.0	0.8–4.1	1.9 ± 0.9
Terephthalic (t-Ph)	7.6–167.9	38.3 ± 38.8	36.4–92.3	56.5 ± 19.3	24.2–157.6	61.3 ± 41.4
Malic (hC_4)	1.7–8.4	3.8 ± 1.8	1.3–11.9	7.0 ± 3.0	1.9–9.8	4.8 ± 2.0
Oxomalonic (kC_3)	3.0–21.1	11.7 ± 6.3	2.3–21.8	12.1 ± 5.6	1.2–12.3	4.1 ± 2.8
4-Oxopimelic (kC_7)	0.9–10.1	3.4 ± 2.3	1.0–15.0	6.0 ± 3.9	1.5–7.9	4.3 ± 1.7
Subtotal	400.6–1030.4	694.5 ± 176.3	351.4–889.5	640.6 ± 156.6	226.8–652.2	502.9 ± 117.9
Ketocarboxylic acids						
Glyoxalic (ωC_2)	21.7–58.5	39.8 ± 10.7	17.1–70.9	43.2 ± 19.4	7.6–35.2	17.3 ± 6.8
3-Oxopropanoic (ωC_3)	1.5–8.1	4.1 ± 1.7	1.7–8.5	4.8 ± 2.3	1.2–5.4	2.7 ± 1.1
4-Oxobutanoic (ωC_4)	1.4–9.0	5.1 ± 2.0	4.0–10.1	6.7 ± 2.4	3.0–11.3	5.6 ± 1.8
9-Oxononanoic (ωC_9)	0.7–5.5	2.3 ± 1.3	0.4–5.4	2.7 ± 1.3	0.5–2.8	1.3 ± 0.7
Pyruvic (Pyr)	2.7–16.6	8.4 ± 4.0	3.2–13.6	7.4 ± 4.0	1.9–8.1	4.8 ± 1.7
Subtotal	31.9–91.4	59.8 ± 17.1	29.2–104.6	64.8 ± 28.0	15.7–62.2	31.7 ± 11.2
α-Dicarbonyls						
Glyoxal (Gly)	2.2–8.2	4.7 ± 1.8	3.4–12.8	7.4 ± 2.8	1.5–5.8	2.9 ± 1.1
Methylglyoxal (mGly)	3.1–15.8	6.2 ± 3.3	3.4–11.4	6.6 ± 2.8	2.3–5.8	4.2 ± 1.1
Subtotal	5.3–21.1	11.0 ± 4.4	6.8–22.8	14.0 ± 5.4	3.8–11.6	7.1 ± 2.0
PM_{10} (μg m^{-3})						
	74.5–157.5	120.5 ± 29.6	70.4–132.0	89.7 ± 17.8	58.0–100.3	79.6 ± 13.2
TC (μg m^{-3})						
	8.3–29.3	16.8 ± 6.7	12.6–27.7	19.7 ± 4.4	5.3–18.8	11.4 ± 3.4
WSOC (μg m^{-3})						
	1.7–4.6	3.0 ± 0.7	2.7–7.0	4.8 ± 1.3	2.2–6.0	4.1 ± 0.9

[a]Ave., average concentration; SD, standard deviation; TC, total carbon; WSOC, water-soluble organic carbon.

early winter. Meanwhile, the results of 29 January (day), 30 January (night), 31 January (day), and 2 February (day) were not included in either categories and handled as such, because their air masses originated from the mixed regions.

3. Results and Discussion

3.1. Molecular Characteristics of Dicarboxylic Acids and Related Compounds

[13] Homologous series of normal (C_2–C_{12}) and branched chain (iso C_4–C_6) saturated α, ω-diacids were detected in the tropical Indian aerosols (PM_{10}). We also found unsaturated aliphatic (maleic, fumaric, and methylmaleic) and aromatic (phthalic, isophthalic, and terephthalic) diacids. Diacids with an additional functional group, i.e., malic (hydroxysuccinic), ketomalonic, and 4-ketopimelic acids, were detected as well, together with ω-ketoacids (C_2–C_4

and C_9), α-ketoacid (pyruvic), and α-dicarbonyls (glyoxal and methylglyoxal). Table 1 summarizes the concentrations of these compounds in the aerosols over Chennai ($n = 49$) as well as TC and WSOC for early winter, late winter, and summer. Histograms of diacids and related compounds are shown in Figure 4 for day and night samples in three seasons.

[14] Concentrations of total diacids (C_2–C_{12}) ranged from 227 ng m^{-3} to 1030 ng m^{-3} (ave. 612 ng m^{-3}, $n = 49$). In all the samples, oxalic (C_2) acid was found as the most abundant diacid species. Relative abundances of C_2 in total diacids in the Chennai aerosols ranged from 35% to 79% (ave. 58%), followed by terephthalic (t-Ph; 1%–28%, ave. 9%), malonic (C_3; 4%–13%, ave. 8%), and succinic (C_4) acids (3%–10%, ave. 7%). Concentrations of normal diacids generally decreased with an increase in carbon chain length, except for C_8 and C_9 acids (Table 1). Azelaic (C_9) acid is the fifth
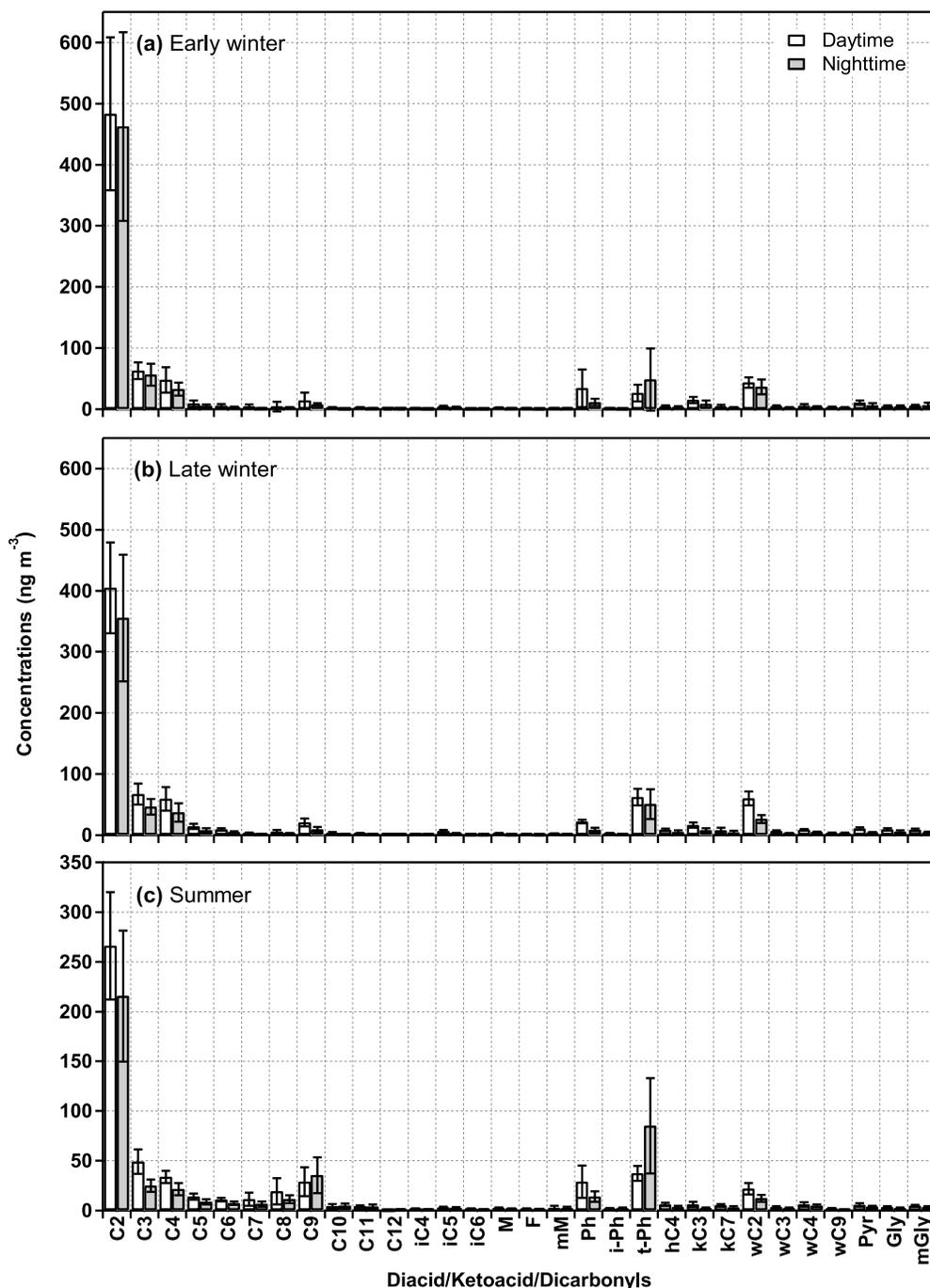
Figure 4. Averaged molecular distributions of diacids, ketoacids, and dicarbonyls in the tropical aerosols (PM$_{10}$) collected on day and night basis in (a) early winter, (b) late winter, and (c) summer 2007 from Chennai, India. Bars show the standard deviation of the average of 5–10 samples.

most abundant diacid species (0.8%–11%, ave. 4%). The branched C$_4$ (methylmalonic), C$_5$ (methylsuccinic), and C$_6$ (2-methylglutaric) diacids are less abundant than the corresponding normal structures (Table 1). Concentration ranges of total ketoacids and dicarbonyls were 16–105 ng m^{-3} and 4–23 ng m^{-3}, respectively. Glyoxylic (ωC$_2$) acid was the most abundant ketoacid species, comprising 45%–74% (ave. 62%) of total ketoacids, followed by pyruvic acid (ave. 14%). Methylglyoxal was generally more abundant than glyoxal (Table 1).

3.2. Comparison of Molecular Composition of Diacids in Chennai With Previous Studies in East Asia: Unique Features of Tropical Aerosols

[15] Table 2 presents the ranges and mean concentrations of diacids, ketoacids, and dicarbonyls in Chennai ($n = 49$) together with those reported for different sites in East Asia. Concentration range of total diacids (C$_2$–C$_{12}$; 227–1030 ng m^{-3}, ave. 612 ng m^{-3}) in Chennai is comparable to those reported in Tokyo (90–1360 ng m^{-3}), Hong Kong (224–1381 ng m^{-3}),

Table 2. Concentrations of Diacids, Ketoacids, and α-Dicarbonyls in Chennai, India and Different Sites in East Asia[a]

	Concentrations (ng m^{-3})									
	Chennai		Sapporo[b]		Tokyo[c]		Hong Kong[d]		Jeju Island[e]	
Compounds	Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.
Diacids										
Oxalic (C$_2$)	114–696	360	44–391	192	36–730	270	63.8–767	373	98–1550	473
Malonic (C$_3$)	16–103	52	16–148	77	6.4–190	55	10.5–145	68.4	10–175	67
Succinic (C$_4$)	15–93	39	17–139	58	11–140	37	13.1–121	52.5	8.3–153	52
Glutaric (C$_5$)	3.1–21	10	4.8–24	13	3.2–36	11	2.82–28.1	13.5	0.8–34	11
Adipic (C$_6$)	2.2–15	7.2	1.8–9.6	5.1	2.6–55	16	3.78–32.1	11.7	0.6–43	8.4
Pimelic (C$_7$)	0.74–26	5.2	0.28–5.8	2.6	0.5–23	5.3	0.74–9.69	2.3	0.2–9.3	2.6
Suberic (C$_8$)	0.00–48	8.2	0.03–3.3	1.1	2.1–30	8.4	0.00–6.67	2.25	0.0–9.6	2.6
Azelaic (C$_9$)	4.4–60	21	2.3–12	6.5	6.5–73	23	6.01–28.1	12.9	1.2–14	4.7
Sebacic (C$_{10}$)	0.48–9.2	2.9	BDL–4.4	1.3	0.7–19	4.8	0.00–3.97	1.49	0.0–4.7	1.1
Undecanedioic (C$_{11}$)	0.50–8.0	2.8	0.25–2.9	1			0.94–4.61	2.6	0.0–3.9	1.3
Dodecanedioic (C$_{12}$)	0.00–1.5	0.32	BDL–0.44	0.12			0.00–3.97	0.26	0.0–3.2	0.1
Methylmalonic (iC$_4$)	0.53–2.9	1.4	0.19–3.7	1.6	0.4–7.5	2.5	1.24–7.91	3.2	0.0–4.2	1.1
Methylsuccinic (iC$_5$)	1.5–8.5	3.8	1.8–9.2	3.9	0.0–16	5.1	1.98–15.3	7.17		
2-Methylglutaric (iC$_6$)	0.26–2.5	1	0.41–3.6	1.7			0.62–3.00	1.43	0.0–4.0	1.0
Maleic (M)	0.73–3.9	2.1	2.2–9.5	4.1	0.0–17	5.6	2.21–37.2	16.2	0.4–15	4.9
Fumaric (F)	0.32–3.1	1.3	0.31–4.7	2.1	0.7–15	3.7	0.29–8.66	3.26	0.5–14	5.2
Methylmaleic (mM)	0.61–7.0	2.1	1.0–8.6	2.8	0.0–14	3.8	1.15–14.3	6.46	0.4–21	5.3
Phthalic (Ph)	4.3–101	21	8.2–31	17			40.1–105	83.9	0.5–40	9.8
Isophthalic (i-Ph)	0.41–4.1	1.7	BDL–1.7	0.7			2.00–63.0	14.1		
Terephthalic (t-Ph)	7.6–168	52	0.01–5.6	2.6						
Malic (hC$_4$)	1.3–12	5.1	0.23–16	2.5	3.2–100	23	1.15–10.1	4.53	0.0–9.7	3.0
Oxomalonic (kC$_3$)	1.2–26	9.2	1.8–6.1	3.8			0.00–15.7	6.66	0.0–9.6	1.9
4-Oxopimelic (kC$_7$)	0.86–15	4.6	1.1–15	6.3			0.00–14.0	4.08	0.0–13	4.5
Subtotal	227–1030	612	106–787	406	90–1360	480	224–1381	692	130–2070	660
Ketoacids[f]										
Glyoxalic (ωC$_2$)	7.6–71	32	7.5–42	22	7.2–154	39	2.49–74.4	30.9	4.3–133	36
3-Oxopropanoic (ωC$_3$)	1.2–8.5	3.8	BDL–1.2	0.46	1.0–5.4	3.0	0.28–1.19	0.66	0.0–5.9	1.7
4-Oxobutanoic (ωC$_4$)	1.4–11	5.7	0.44–2.4	0.97	0.4–11	3.6	0.00–7.49	3.01	0.0–9.5	2.5
9-Oxononanoic (ωC$_9$)	0.40–6.4	2.1	BDL–6.7	2.1	0.8–6.7	2.3	0.00–6.15	2.59	0.0–4.0	1.4
Pyruvic (Pyr)	1.9–17	6.8	2.1–31	9.6	0.7–26	6.7	0.00–8.2	2.36	0.6–54	13
Subtotal	16–105	51	13–81	35	12–197	55	9.85–89.2	39.5	2.1–172	53
α-Dicarbonyls										
Glyoxal (Gly)	1.5–13	4.6	1.9–11	4.6	1.1–67	12	0.00–7.61	2.73	0.0–3.9	0.5
Methylglyoxal (mGly)	2.3–16	5.5	0.34–21	5.1	1.9–102	21	0.00–16.6	8.22	0.7–83	11
Subtotal	3.8–23	10	2.6–28	9.7	3.1–169	33	0.00–21.0	10.9	0.08–84	12

[a]Ave., Average.
[b]TSP samples collected in spring and summer [*Aggarwal and Kawamura*, 2008].
[c]TSP samples collected for one year period [*Kawamura and Ikushima*, 1993].
[d]PM$_{2.5}$ samples collected in winter and summer [*Ho et al.*, 2006].
[e]TSP samples collected for one year period [*Kawamura et al.*, 2004].
[f]Ketoacids and dicarbonyls data for Tokyo in 1988–1989 (K. Kawamura, unpublished data, 1990).

and Gosan site, Jeju Island (130–2070 ng m^{-3}) but higher than those reported in Sapporo (106–787 ng m^{-3}; Table 2). The predominance of oxalic (C$_2$) acid found in Chennai aerosols is consistent with previous studies from urban [*Kawamura and Kaplan*, 1987; *Kawamura and Ikushima*, 1993; *Ho et al.*, 2006; *Hsieh et al.*, 2008; *Huang et al.*, 2005; *Yao et al.*, 2004], coastal marine [*Kawamura et al.*, 2004; *Mochida et al.*, 2003], and remote marine aerosols [*Kawamura and Sakaguchi*, 1999; *Wang et al.*, 2006], because C$_2$ acid is the final product of the photooxidation of aromatic hydrocarbons, isoprene, ethylene, and acetylene [*Ervens et al.*, 2004; *Kawamura et al.*, 1996a; *Lim et al.*, 2005; *Sorooshian et al.*, 2006; *Warneck*, 2003] and may also be emitted from fossil fuel combustion [*Kawamura and Kaplan*, 1987] and biomass burning [*Narukawa et al.*, 1999] but not significantly [*Huang and Yu*, 2007].

[16] The predominance of maleic acid over fumaric acid (Table 1) suggests that the Chennai aerosols contain relatively fresh oxidation products of aromatic hydrocarbons emitted from local pollution sources [*Kawamura and Ikushima*, 1993]. Concentration levels of ketoacids (ave. 51 ng m^{-3}) are comparable to those of Tokyo (ave. 55 ng m^{-3}) and Jeju Island (ave. 53 ng m^{-3}; Table 2). However, concentration levels of dicarbonyls (ave. 10 ng m^{-3}) are rather similar to those reported in Sapporo (ave. 9.7 ng m^{-3}) and Hong Kong (ave. 10.9 ng m^{-3}; Table 2).

[17] Although we found that t-Ph acid is the second most abundant diacid (ave. 52 ng m^{-3}), it has never been reported before in aerosols studied in midlatitudinal regions, except in Sapporo, where concentrations are very low (ave. 2.6 ng m^{-3}) [*Aggarwal and Kawamura*, 2008]. This aromatic diacid is used as major raw material for polyester (polyethylene terephthalate) fiber and plastic bottles [*Ding and Li*, 2003] and is produced by the burning of plastics [*Simoneit et al.*, 2005]. Concentrations of Ph acid (ave. 21 ng m^{-3}), which is a good tracer for anthropogenic emission [*Kawamura and Ikushima*, 1993], are 4 times lower than those from Hong Kong (ave. 83.9 ng m^{-3}), where it was attributed to the emission

from fossil fuel combustion followed by photochemical oxidation [*Ho et al.*, 2006]. However, its concentrations are comparable to those (ave. 17 ng m^{-3}) from Sapporo, in which aerosols were interpreted as photochemically aged [*Aggarwal and Kawamura*, 2008]. Similarly, concentrations of C_6 diacid (ave. 7.2 ng $^{-3}$), which is another tracer for anthropogenic emission [*Kawamura and Ikushima*, 1993], are also comparable to those reported in Sapporo (ave. 5.1 ng m^{-3}) and Jeju Island (ave. 8.4 ng m^{-3}) but lower than in Tokyo (ave. 16 ng m^{-3}) and Hong Kong (ave. 11.7 ng m^{-3}; Table 2).

[18] Another characteristic of Chennai aerosols is the predominance of C_3 over C_4 even in winter, suggesting that the tropical aerosols were photochemically aged during long-range transport before arrival at the sampling site [*Aggarwal and Kawamura*, 2008]. This feature is different from the molecular compositions of diacids in winter aerosols from the temperate zone including Tokyo [*Kawamura and Ikushima*, 1993] and Jeju Island [*Kawamura et al.*, 2004], where C_4 is more abundant than C_3 in winter but vice versa in summer. However, it is consistent with the molecular composition (C_3 = 3.4% and C_4 = 2.2%) of free tropospheric aerosols collected over Gulf of Mexico, in which oxidative decay of higher carbon number diacids was attributed to the production of next lower homologous diacids [*Sorooshian et al.*, 2007]. These results and comparisons suggest that the tropical aerosols from Chennai are photochemically more aged than the aerosols from midlatitudes.

[19] Although ketoacids in the aerosols over Chennai showed a predominance of ωC_2, their distribution is different from that of urban Tokyo [*Kawamura and Yasui*, 2005], in which pyruvic acid was dominant. However, it is more similar to the aerosols from Jeju Island [*Kawamura et al.*, 2004], suggesting that the aerosols from Chennai are photochemically more aged than those from Tokyo.

3.3. Temporal Variations of Diacids, Ketoacids, and α-Dicarbonyls: Role of Emissions and Meteorological Factors

[20] Figure 5 presents temporal variations in the concentrations of total diacids and selected diacid species (C_2–C_4, C_9, Ph, and t-Ph). Concentrations of total diacids maximized in winter and decreased toward summer, showing a diurnal variation with daytime maxima in particular in summer (Figure 5a and Table 1). Concentrations of C_2, which is the dominant diacid, showed a decline from early winter to summer. C_3 and C_4 diacids also showed a similar trend with much clearer daytime maxima (Figures 5c and 5d). Conversely, longer-chain (C_6–C_{12}) diacids appear to increase from winter to summer (Table 1), with daytime maxima in winter but nighttime maxima in most of the summer samples (see Figure 5e for C_9). Ph concentrations stay rather constant with daytime maximum (Figure 5f). In contrast, concentrations of t-Ph, which is the isomer of Ph, are low in early winter (ave. 38 ng m^{-3}) but increased in late winter (ave. 56 ng m^{-3}) and summer (ave. 61 ng m^{-3}; Table 1) with nighttime maxima (Figure 5g).

[21] Total ketoacids and dicarbonyls showed a temporal variation similar to total diacids, except for few samples (data are not shown in Figure 5). On average, total ketoacids as well as dicarbonyls are comparable in early (60 ng m^{-3} and 11 ng m^{-3}, respectively) and late winter (65 ng m^{-3} and

14 ng m^{-3}) but less abundant in summer (32 ng m^{-3} and 7 ng m^{-3}; Table 1).

[22] Analysis of variance based on Tukey's test revealed that the variations were significant ($p < 0.05$) between summer and winter (both early and late-winter) seasons only but not in between early and late winter. No significant differences were found between Ph and t-Ph acids from season to season. Further, daytime and nighttime variations were significant ($p < 0.05$) for C_6 and C_{12} acids in early winter, C_5–C_{12} (except C_8) and Ph acids in late winter, and C_3–C_7, Ph, and t-Ph acids in summer. These results suggest that sources and source regions of individual organic acids and their precursors in Chennai are different from one season to another. Further, anthropogenic local emissions and meteorological factors may have an influence on molecular composition of diacids.

[23] As Chennai is dense with high population and many industries like petrochemicals, thermal power plants, etc. [*Jayanthi and Krishnamoorthy*, 2006; *Manju et al.*, 2002], local emissions of diacids and their precursors may be significant. In fact, we detected t-Ph acid as the second most abundant species as stated above. However, meteorological factors including height of atmospheric boundary layer (ABL) and wind patterns are dynamic in the east coast of the Indian subcontinent including Chennai [*Vittal Murthy et al.*, 1980]. These meteorological situations may dilute the local pollutants by long-range transported air masses. The highest mixing heights in Chennai region (Manali, 20 km away from Chennai) were reported to be 1260 and 1540 m in winter and summer, respectively. On the other hand, the lowest mixing heights were less than only 100 m in all seasons. These meteorological situations can cause a clear diurnal variation with the highest ABL at 13 h (LT) [*Manju et al.*, 2002].

[24] In this study, Ph acid, which is a tracer for anthropogenic emissions (vehicle exhaust) [*Kawamura and Ikushima*, 1993], did not show any seasonal trend but showed a diurnal trend (except in early winter, $p = 0.059$). Further, it did not correlate with NO_3^- that is expected to be contributed from vehicle exhausts. On the other hand, t-Ph acid that may be derived from industrial emissions [*Dai et al.*, 2005] and solid waste (plastic) burning [*Simoneit et al.*, 2005] showed neither seasonal ($p \geq 0.05$) nor diurnal variation (except in summer, $p = 0.006$) although it showed an increasing trend from early winter to summer (Figure 5g). In addition, t-Ph acid did not correlate with $nssSO_4^{2-}$ that is supposed to be emitted from industrial activities. Interestingly, *Pulikesi et al.* [2006] reported that concentrations of surface ozone (O_3) did not show any seasonal trend in Chennai for the period March to October 2005, but they became higher when the wind flow was onshore. The monthly mean O_3 concentrations during daytime (18–38 ppb) were reported to be 2–3 times higher than in nighttime (5–16 ppb) [*Pulikesi et al.*, 2006].

[25] Chennai is located on the coast where a diurnal pattern of the wind is caused by land/sea breeze in all seasons [*Srinivas et al.*, 2006, 2007; *Venkatesan et al.*, 2009]. The wind is southwesterly (land breeze) during early hours of the day. However, it turns northeasterly and southeasterly at noon hours (12:00–13:00 LT) during winter and summer, respectively, and accelerates subsequently (Figure 2) as a result of the onset of sea breeze. The breeze may continue
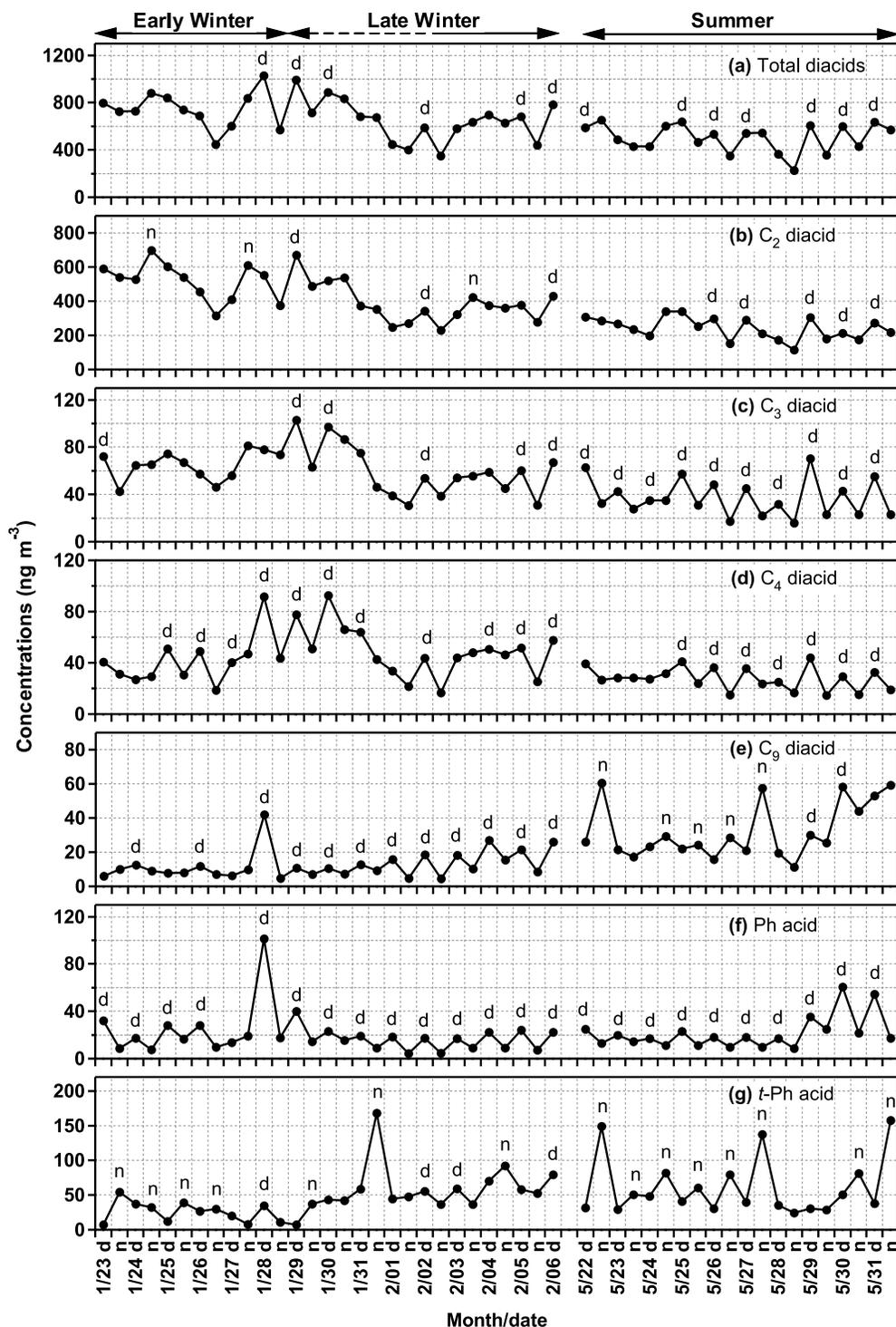
Figure 5. Temporal variations (ng m^{-3}) of (a) total diacids, (b) C_2, (c) C_3, (d) C_4, (e) C_9, (f) Ph, and (g) t-Ph acids in the tropical aerosol samples (PM$_{10}$) collected in Chennai, India on day (d) and night (n) basis in 2007. Data points of transition periods are given with dashed line in late winter on the top x axis.

until late night [*Venkatesan et al.*, 2009], but its strength vary with the changes in wind speed. Interestingly, the changes in trends of winds observed at the sampling site during sampling period (Figure 2) are comparable to that of simulated atmospheric circulation over Chennai region for winter and summer in 2003 [*Srinivas et al.*, 2006].

However, further analyses of meteorological conditions are beyond the scope of the present study.

[26] Sea breeze alofts the marine air masses onshore [*Lu and Turco*, 1994; *Miller et al.*, 2003] and develops the thermal internal boundary layer (TIBL) extending up to 50–100 m above ground level under atmospheric boundary
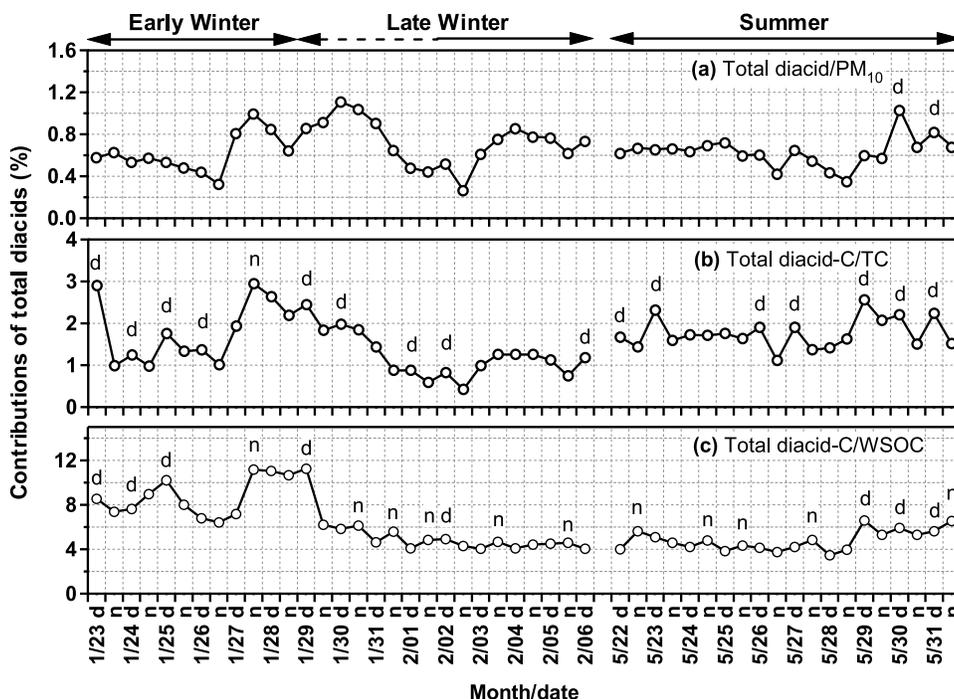
Figure 6. Temporal variations in the contributions (%) of total diacids to (a) aerosol mass (PM_{10}), (b) total carbon (TC), and (c) water-soluble organic carbon (WSOC) in the tropical aerosols (PM_{10}) collected in Chennai, India on day (d) and night (n) basis during early winter, late winter, and summer 2007. Data points of transition periods are given with dashed line in late winter on the top x axis.

layer (ABL) at the coast in Chennai region [*Srinivas et al.*, 2007]. Hence the horizontal dispersion is significantly developed in Chennai, which further promotes the dilution of local pollutants in the coastal region in all seasons although local emissions are significant in this region [*Manju et al.*, 2002]. Due to the photochemical production of water-soluble organic compounds such as oxalic acid, their concentrations would elevate in summer, but the strong dispersion conditions would lead to their levels even lower in summer than in winter.

[27] The sum of short-chain (C_2–C_4) diacids showed a positive correlation with $nssSO_4^{2-}$ in early winter ($r = 0.52$) and summer ($r = 0.68$) and with Ph acid ($r = 0.65$) in late winter, indicating that they originated from anthropogenic emissions and become higher in early and late winter when the air masses arrived from North India and Southeast Asia (Figure 3). On the other hand, long-chain (C_6–C_{12}) diacids showed a significant correlation with Ph acid in early winter ($r = 0.94$), late winter ($r = 0.77$), and summer ($r = 0.72$) and with t-Ph acid ($r = 0.67$) and levoglucosan [*Fu et al.*, 2010] ($r = 0.83$) in late winter. A good correlation between Ph acid and sum of long-chain (C_6–C_{12}) diacids indicates a significant contribution of marine emissions [*Carlson*, 1982; *Kawamura and Sakaguchi*, 1999]. Alternatively, a good correlation with levoglucosan in late winter indicates a contribution from biomass burning when the air masses arrived from Southeast Asia where the forest fires occur frequently. Further, a positive correlation with t-Ph acid in late winter suggests that open burning of solid waste may also be an important source for diacid precursors. Long-chain diacids increased from winter to summer (Figure 5e). This suggests that their photochemical production would be

promoted in summer, but also the emission of their precursors, i.e., unsaturated fatty acids, would also increase due to enhanced productivity of vegetation on land and in the ocean under strong radiation and higher temperature conditions.

3.4. Seasonal Changes in Mass Fractions of Diacids, Ketoacids, and α-Dicarbonyls to PM_{10}, TC, and WSOC

[28] Total diacids comprised 0.2%–1.1% of PM_{10} aerosol mass. Total diacids/PM_{10} ratios did not show a distinct trend among three seasonal categories (Figure 6a). Total diacid-C/TC ratios ranged from about 0.4% to 3% with an average of 1.58%. The averaged ratio is higher in summer (ave. 1.8%) than late winter (ave. 1.2%; Figure 6b). They also showed a weak daytime maximum, suggesting a daytime production of diacids in Chennai and its vicinity. The average contribution of total diacids to TC (1.58%) in the aerosols over Chennai is higher than that (0.95%) from urban Tokyo [*Kawamura and Ikushima*, 1993] and comparable to that (1.8%) from Sapporo [*Aggarwal and Kawamura*, 2008]. This signifies an intensive photochemical production of diacids via gas-to-particle conversion of precursor organics as well as heterogeneous reactions on aerosols under strong solar radiation and high humidity conditions (RH: up to 89%). However, the average value (1.58%) is lower than that (8.8%) reported in the remote marine aerosols from the Pacific including tropics [*Kawamura and Sakaguchi*, 1999].

[29] On the other hand, total diacid-C/WSOC ratios ranged from about 4% to 11% with an average of 7.9% in early winter, 4.7% in late winter, and 4.8% in summer (Figure 6c). The average total diacid-C/WSOC ratio (5.9%)

Table 3. Results of Principal Component Analysis of the Selected Dicarboxylic Acids and Related Compounds in the Tropical Aerosols (PM_{10}) Collected in Chennai, India During Early Winter, Late Winter, and Summer 2007

Compounds	Early Winter			Late Winter		Summer		
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 1	Component 2	Component 3
Oxalic (C_2)	0.03	0.87	−0.24	−0.08	0.89	0.89	−0.04	0.11
Malonic (C_3)	0.30	0.58	−0.61	0.02	0.99	0.80	0.35	−0.25
Succinic (C_4)	0.89	0.27	−0.10	0.09	0.97	0.92	0.12	−0.20
Glutaric (C_5)	0.93	0.23	0.03	0.27	0.93	0.96	0.03	−0.09
Adipic (C_6)	0.96	0.20	−0.02	0.76	0.64	0.74	0.54	0.21
Pimelic (C_7)	0.92	0.32	−0.10	0.89	0.39	0.23	0.95	0.16
Suberic (C_8)	0.94	0.04	−0.02	0.96	−0.08	0.14	0.97	0.17
Azelaic (C_9)	0.94	0.16	0.10	0.96	0.19	−0.08	0.47	0.86
Sebacic (C_{10})	0.97	0.06	0.11	0.90	0.22	−0.13	0.57	0.81
Maleic (M)	0.55	0.68	0.29	0.71	0.66	0.81	0.14	−0.30
Phthalic (Ph)	0.94	0.24	−0.17	0.57	0.76	0.20	0.96	−0.07
Terephthalic (t-Ph)	0.04	−0.31	0.82	0.76	−0.11	−0.16	−0.22	0.95
Glyoxylic (ωC_2)	0.38	0.87	0.02	0.49	0.80	0.92	0.26	−0.17
Glyoxal (Gly)	0.02	0.21	0.94	0.87	0.30	0.94	0.11	0.04
Variance (%)	54	20	15	47	43	45	28	19

in Chennai samples is higher than that (about 3%) of Tokyo (range: 0.3%–6.2%, Kawamura et al., unpublished data, 2005) and that (3.8%) of the Arctic aerosols (range 1.5%–9.1%, Kawamura et al., in preparation, 2010) and even that (range: 2.8%–8.1%, ave. 4.8%) of Sapporo [*Aggarwal and Kawamura*, 2008]. The higher values obtained in this study indicate that the tropical aerosol samples collected from southeast coast of the Indian subcontinent contain more dicarboxylic acids that are probably produced by photochemical oxidations of organic precursors, suggesting that the tropical organic aerosols are photochemically more aged. Interestingly, diurnal variations with daytime maximum were not clearly observed in diacid-C/WSOC ratios.

[30] The concentrations of ketoacids and dicarbonyls normalized by PM_{10}, TC, and WSOC also showed temporal variations similar to total diacids (data are not shown here). This suggests that ketoacids and dicarbonyls are also produced in daytime by photochemical processes in the atmosphere. Averaged contributions of ketoacids and dicarbonyls to TC are 0.15% and 0.032% in early winter, 0.13% and 0.033% in late winter, and 0.11% and 0.030% in summer, respectively. In contrast, those of ketoacids and dicarbonyls to WSOC are 0.77% and 0.17% in early winter, 0.49% and 0.13% in late winter, and 0.29% and 0.08% in summer, respectively.

3.5. Principal Component Analysis for Selected Species

[31] Previous studies reported that C_2–C_4 diacids, ketoacids, and dicarbonyls are likely produced either by photo-oxidation of volatile hydrocarbons and/or direct emissions from fossil fuel combustion [*Kawamura and Kaplan*, 1987; *Kawamura and Ikushima*, 1993; *Kawamura et al.*, 1996a]. In addition, C_2 acid is formed by oxidation of ωC_2 acid that is produced by the photooxidation of glyoxal, pyruvic acid, or other precursors [*Ervens et al.*, 2004; *Kawamura et al.*, 1996a; *Lim et al.*, 2005; *Warneck*, 2003]. C_5–C_6 diacids have been proposed as oxidation products of cyclic olefins [*Hatakeyama et al.*, 1987]. Maleic acid may be produced by ring opening of aromatic hydrocarbons such as toluene and benzene [*Kawamura and Sakaguchi*, 1999; *Kawamura et al.*, 1996a] whereas Ph acid can be produced by photooxidation of naphthalene and other polynuclear aromatic hydrocarbons [*Kawamura and Sakaguchi*, 1999; *Kawamura et*

al., 1996b; *Ho et al.*, 2006], which are derived from incomplete combustion of fossil fuels [*Graedel et al.*, 1986]. In contrast, longer-chain ($\geq C_4$) diacids have been proposed as oxidation products of unsaturated fatty acids [*Kawamura et al.*, 1996b; *Kawamura and Gagosian*, 1987; *Stephanou and Stratigakis*, 1993].

[32] To better discuss the sources and/or formation processes of diacids and related compounds in the tropical aerosols, principal component analysis (PCA) was applied for the data sets of selected water-soluble species ($n = 14$) [*Hsieh et al.*, 2008; *Kawamura and Sakaguchi*, 1999]. Table 3 gives the results of PCA with two to three components detected in three types of aerosols. In early winter samples, C_4–C_{10} diacids showed a good correlation with component 1 (Table 3), which should be associated with photochemical oxidation of unsaturated fatty acids derived from terrestrial and/or marine plants. In contrast, C_2, C_3, maleic, and ωC_2 acids were found to correlate with component 2, indicating that their precursors are associated with anthropogenic activities including fossil fuel and biomass/fuel combustion. t-Ph and glyoxal showed a correlation with component 3, suggesting an important emission from field burning of municipal wastes because t-Ph is produced via burning processes of municipal solid wastes and/or plastic polymers [*Simoneit et al.*, 2005] and glyoxal is produced by the photooxidation of p-xylene [*Volkamer et al.*, 2001], which is a raw material for terephthalic acid dimethyl ester.

[33] In late winter, C_2–C_5 and C_7–C_{10} diacids showed a strong correlation with components 2 and 1, respectively. Component 1 may be associated with photooxidation of unsaturated fatty acids whereas component 2 may be involved with anthropogenic sources. On the other hand, C_6, maleic, and Ph acids that are mainly derived by photooxidation of anthropogenic hydrocarbons correlate with both components 1 and 2. These results suggest that a mixing of air masses originated from anthropogenic and marine biogenic sources is significant in the coastal Chennai atmosphere in late winter, followed by photochemical aging during long-range transport in the continental and marine atmosphere.

[34] During summer season, C_2–C_6 diacids, M, ωC_2, and Gly strongly correlate with component 1, which should be associated with anthropogenic emissions followed by pho-
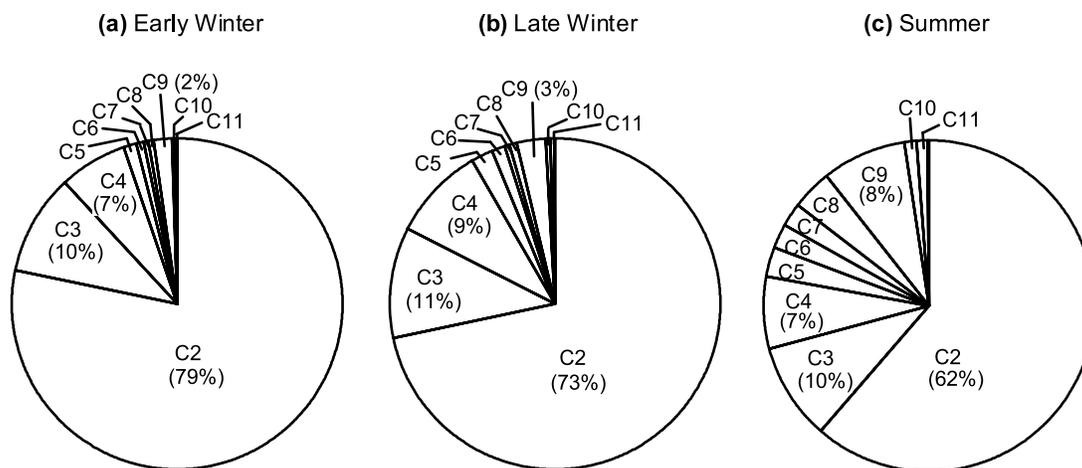
Figure 7. Pie diagrams of relative abundances (%) of individual diacids in total straight-chain diacids (C_2–C_{12}) in the tropical aerosols (PM_{10}) collected in Chennai, India during (a) early winter, (b) late winter, and (c) summer 2007.

tochemical production. In contrast, longer-chain C_7–C_8 and C_9–C_{10} diacids showed a strong correlation with components 2 and 3, respectively (see Table 3). This result suggests that their precursors (unsaturated fatty acids) may have dual origins, i.e., one derived from marine algae and the other from terrestrial higher plants. Ph acid showed a strong correlation with component 2. This aromatic diacid may be derived from phenolic compounds [*Kawamura and Sakaguchi*, 1999; *Kawamura et al.*, 1996b], which are present in sea surface slicks [*Carlson*, 1982], although it can also be produced by photooxidation of naphthalene and other aromatic hydrocarbons as stated above. Interestingly, t-Ph acid showed a strong correlation with component 3, again suggesting the presence of anthropogenic emissions from burning of municipal solid wastes and/or plastic polymers. However, Gly correlated well with component 1 instead of 3, because its production might be more intensive by the photooxidation of acetylene and ethylene and isoprene contributed from anthropogenic and/or marine emissions [*Warneck*, 2000; 2003] and terrestrial plant emissions [*Guenther et al.*, 2006], respectively.

3.6. Long-Range Atmospheric Transport and Photochemical Production of Diacids

[35] Figure 7 presents pie diagrams (%) of individual diacid species in total straight-chain diacids (C_2–C_{12}) for early winter, late winter, and summer samples. Three small diacids (C_2–C_4) account for 96% in early winter and 93% in late winter. However, the values decreased down to 79% in summer. In particular, the relative abundance of C_2 decreased from 79% in early winter to 62% in summer (see Figure 7). Accordingly, those of longer-chain diacids (C_5–C_{12}) increased from early winter to summer by a factor of 2–5. For example, the relative abundance of C_9 diacid increases from 2% in early winter to 8% in summer (Figure 7), suggesting the presence of specific source(s) of C_9 in summer, a topic to be discussed later.

[36] When higher relative abundances of C_2–C_4 diacids were obtained in early winter (Figure 7), air masses were

delivered from South Asia (Figure 3). A similar feature was obtained in late winter, when air masses arrived from Southeast Asia. The predominance of shorter-chain diacids can be interpreted by enhanced emission of aromatic hydrocarbons derived from fossil/biofuel combustion or biomass burning process, followed by subsequent photochemical oxidation in the atmosphere during long-range transport over the Bay of Bengal. In contrast, higher abundances of C_9 and other longer-chain diacids in summer aerosols are associated with the air masses originated from the Arabian Sea and the Indian Ocean and traveled across the South Indian subcontinent. Both oceanic and continental air should contain abundant unsaturated fatty acids, which are produced by marine algae and terrestrial higher plants. After their emission to the atmosphere, unsaturated fatty acids are oxidized at a double bond to result in C_9 and other diacids ($\geq C_4$) [*Kawamura and Gagosian*, 1987; *Kawamura et al.*, 1996b; *Stephanou and Stratigakis*, 1993].

[37] *Kawamura and Ikushima* [1993] proposed that C_3 is produced by photochemical oxidation of C_4 in the atmosphere, and hence C_3/C_4 ratio has been used as an indicator of enhanced photochemical production of diacids [*Aggarwal and Kawamura*, 2008; *Huang et al.*, 2005; *Kawamura et al.*, 1996a; *Sorooshian et al.*, 2006; *Yao et al.*, 2004]. The C_3/C_4 ratios (0.85–2.46 with an average of 1.4; n = 49) found in Chennai aerosols are much higher than that (ave. 0.35) reported in automobile exhausts [*Kawamura and Kaplan*, 1987], indicating a serious photochemical modification of the aerosols over Chennai. The average ratio in Chennai aerosols is comparable with those reported for Sapporo aerosols (ave. 1.4) [*Aggarwal and Kawamura*, 2008] and summer aerosols from Tokyo (ave. 1.6) [*Kawamura and Ikushima*, 1993] and Hong Kong (ave. 1.5 at Kwun Tong and 2.5 at Hong Kong Polytechnic University) [*Yao et al.*, 2004] and also the aerosols collected at higher altitudes (500–4000 m) over Gulf of Mexico (>1) [*Sorooshian et al.*, 2007], in which photochemical production and transformations are significant. However, the average C_3/C_4 ratio in
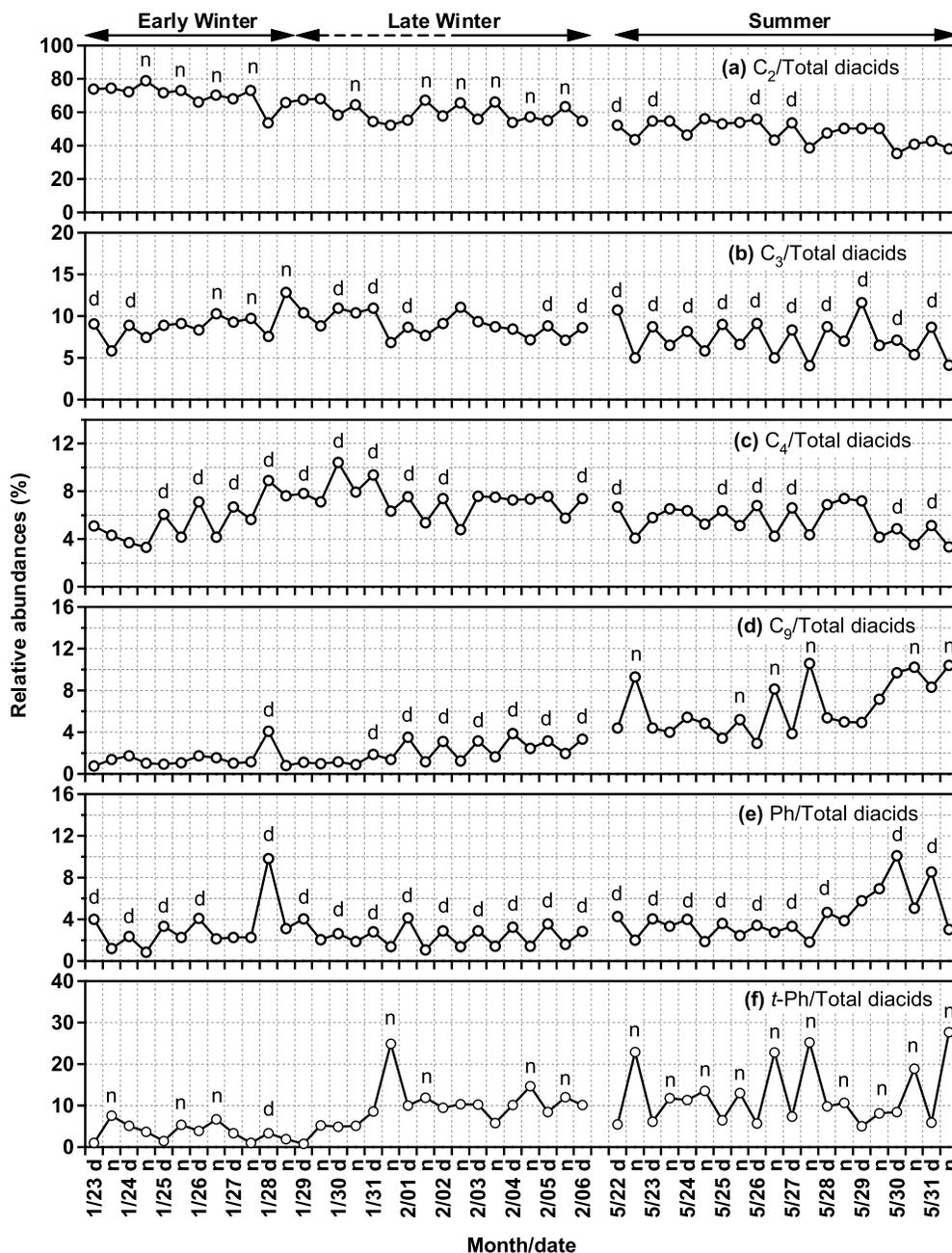
Figure 8. Temporal variations in the relative abundances (%) of selected diacids in total diacids in the tropical aerosols (PM_{10}) collected in Chennai, India on day (d) and night (n) basis during early winter, late winter, and summer 2007. (a) Oxalic (C_2), (b) malonic (C_3), (c) succinic (C_4), (d) azelaic (C_9), (e) phthalic (Ph), and (f) terephthalic (t-Ph) acids. Data points of transition periods are given with dashed line in late winter on the top x axis.

Chennai aerosols is lower than those reported for marine aerosols from Chichi-jima (ave. 2.0) [*Mochida et al.*, 2003] and from remote Pacific (ave. 3.9) [*Kawamura and Sakaguchi*, 1999].

[38] These comparisons again suggest that the aerosols over Chennai are significantly aged due to photochemical processes. Further, C_3/C_4 ratios showed a very weak correlation ($r^2 \leq 0.14$) with local ambient temperature, being in contrast from urban aerosols from Tokyo [*Kawamura and Ikushima*, 1993], in which a strong correlation was found.

This suggests that the local photochemical production of diacids and the subsequent evolution at Chennai are not significant. Rather, secondary photochemical production of diacids and subsequent transformation should be more important along with the mixing of polluted air mass with relatively clean air masses in the remote marine atmosphere during long-range transport over the Indian Ocean and Bay of Bengal.

[39] Although C_2 and SO_4^{2-} are not directly linked chemically, the correlation between C_2 and SO_4^{2-} has been

used to investigate the production processes of C_2 [*Huang et al.*, 2005; *Sorooshian et al.*, 2006; *Yao et al.*, 2004; *Yu et al.*, 2005] based on the fact that both reaction mechanisms require the aqueous medium. *Sorooshian et al.* [2006] observed a strong correlation between SO_4^{2-} and oxalate ($r^2 = 0.80$) in aerosols collected by aircraft sampling at downwind of a coal-fired power plant in the vicinity of Ohio, in which local emissions and subsequent in situ photochemical production might be significant. In contrast, a weak correlation ($r^2 = 0.33$) was found between SO_4^{2-} and oxalate in cloud droplet residual particle collected over Gulf of Mexico, and the SO_4^{2-} was typically decreased from below to above cloud while the C_2 exhibited an opposite behavior [*Sorooshian et al.*, 2007] that can be attributed to photochemical aging. Interestingly, we found a weak correlation between SO_4^{2-} and C_2 in Chennai aerosols in early ($r^2 = 0.32$) and late ($r^2 = 0.35$) winter and summer ($r^2 = 0.53$). These results clearly indicate that the Chennai aerosols are significantly aged due to photochemical processes that occurred during long-range atmospheric transport before their arrival at Chennai.

3.7. Diurnal Variation of Diacids: Sea Breeze Effect

[40] The concentrations of C_2 diacid did not show a clear diurnal trend, except for certain periods (e.g., 29–31 May; Figure 5b). This is in contrast to the results from Tokyo, where a strong diurnal variation was found with the concentration maxima in daytime [*Kawamura and Yasui*, 2005]. However, we found that relative abundances of C_2 in total diacids are higher in nighttime than daytime for most of the winter samples (Figure 8a). In contrast, C_3 and C_4 concentrations often showed clear daytime maxima throughout the campaigns (see Figures 5c and 5d). Their relative abundances also showed daytime maxima (Figures 8b and 8c). Concentrations of C_5–C_8 and Ph diacids, as well as their relative abundances, also increased in daytime (for Ph see Figures 5f and 8e). Similarly, concentrations of longer-chain diacids (C_9–C_{12}) and their relative abundances in winter generally increased in daytime but showed an opposite trend in summer (see Figures 5e and 8d for C_9 diacid). On the other hand, t-Ph and its relative abundance showed diurnal patterns similar to C_9 in particular during summer (Figures 5g and 8f). Interestingly, distinct nighttime maxima were found in the concentration ratios of t-Ph/Ph throughout the campaigns (data not shown here).

[41] As discussed earlier (section 3.3), the land/sea breeze circulation [*Srinivas et al.*, 2006] may have significant influence on organic aerosol compositions in Chennai. The onset of sea breeze in daytime may depress the stable structure of the planetary boundary layer (PBL) by introducing cool marine air that passes over a warmer land surface, resulting in a thermal internal boundary layer (TIBL) below the PBL [*Srinivas et al.*, 2006, 2007]. In contrast, the TIBL may disappear and the PBL moves down after the onset of the land breeze in nighttime. In addition, the oxidant concentration may stay high under nighttime smog condition at surface level [*Miller et al.*, 2003]. Hence land/sea breeze circulation may significantly affect the dispersion of pollutants in the atmosphere of coastal regions [*Lu and Turco*, 1994; *Miller et al.*, 2003].

[42] The sea breeze causes onshore flow of marine air masses in daytime [*Miller et al.*, 2003], which are enriched

with relatively fresh marine aerosols containing unsaturated fatty acids. They should produce diacids ($\geq C_4$) by photochemical oxidation [*Kawamura and Gagosian*, 1987; *Kawamura et al.*, 1996b; *Stephanou and Stratigakis*, 1993]. In addition, the developed TIBL may suppress the vertical dispersion of aerosol species by acting as a lid during daytime. In contrast, the precursors of smaller diacid (C_2–C_4) of inland origin (e.g., aromatic hydrocarbons) may effectively stay within the PBL above the TIBL [*Miller et al.*, 2003]. Hence C_2–C_4 diacid concentrations would not increase significantly in daytime. However, the production of C_4 from marine precursors and its photochemical breakdown into C_3 may be significant in daytime [*Kawamura and Sakaguchi*, 1999; *Kawamura et al.*, 1996b]. We found the increased concentrations of C_5–C_{12} and Ph in daytime on 28 January and 30–31 May (see Figures 5e and 5f, for C_9 and Ph), again supporting an inflow of marine air over coastal Chennai in daytime [*Miller et al.*, 2003].

3.8. Preferential Production of C_9–C_{12} Diacids: Enhanced Higher Plant Emissions in Summer

[43] Although C_9–C_{12} diacids are more abundant in daytime than nighttime during early and late winter, an opposite trend was generally found during summer (see Figure 5e for C_9 diacid). The nighttime maxima in summer may arise from a peculiar feature of the tropical Indian monsoon, which is superimposed by the enhanced higher plant emissions in summer. *Padhy and Varshney* [2005] reported an increased emission of volatile organic compounds (such as isoprene and α-pinene) from tropical plants in India during summer. Similarly, emissions of unsaturated fatty acids from tropical plants should be enhanced to result in the increased production of azelaic acid (C_9) in summer. Hence the nighttime increase of C_9–C_{12} diacids during summer can be interpreted by an enhanced plant activity in daytime and the onset of land breeze in nighttime [*Miller et al.*, 2003]; the latter initiates the transport of inland air enriched with C_9 over the sampling site on the coast at night.

[44] This situation at the southeast coast of the Indian subcontinent may produce a unique feature of the source and source strength of organic aerosols in tropical urban Chennai, which is different from other regions in midlatitudes. It is of interest to note an abrupt increase in the concentrations of C_9 in nighttime on 22 and 27 May (see Figure 5e). This feature may be caused by the appearance of a land breeze front [*Miller et al.*, 2003] that can significantly transport the inland air masses offshore. The occurrence of a land breeze front in nighttime on 22 and 27 May can be supported by a sharp change in wind direction (SW-W-SE-SW and S-SW-SE-S) and by sudden increases in wind speed by 0.5–1 m s^{-1}. Moreover, nighttime reactions might be intensified by the accumulated oxidants (nighttime smog) at surface level [*Miller et al.*, 2003]. The present study demonstrates that enhanced terrestrial higher plant emissions of unsaturated fatty acids followed by the production of long-chain (C_9–C_{12}) diacids is an important factor that alters the organic aerosol composition in the coastal tropical Indian atmosphere.

4. Summary and Conclusion

[45] Molecular characteristics of water-soluble diacids and their related compounds have been studied in the tropical

aerosols (PM_{10}) collected at Chennai on the southeast coast of the Indian subcontinent during winter (23 January to 6 February) and summer (22–31 May) campaigns in 2007. Oxalic (C_2) acid was found as the most abundant diacid species (35%–79% of total diacids) followed by terephthalic (t-Ph), malonic (C_3), and succinic (C_4) acids. Total concentrations of diacids (227–1030 ng m^{-3}), ketoacids (16–105 ng m^{-3}), and dicarbonyls (4–23 ng m^{-3}) were higher in winter than summer. However, some species including normal C_5–C_{12}, branched iC_4 and iC_6, unsaturated (maleic), and aromatic diacids showed an opposite trend. Water-soluble diacids were found to account for up to 3% of TC and 11% of WSOC in the tropical Indian aerosols, suggesting that the aerosols over Chennai are photochemically aged.

[46] Molecular distributions and backward air mass trajectories demonstrated that diacids and/or their precursor compounds are likely transported long distances from North India and the Middle East in early winter and from Southeast Asia in late winter, but some originate from photochemical reactions in the atmosphere over the ocean. Following the change in the Indian Ocean Monsoon, the aerosols in Chennai are transported from the Arabian Sea and Indian Ocean across the South Indian continent in summertime. Although local emissions are important in controlling the diacid compositions of Chennai aerosols, their source strength seems to be weakened due to the dilution caused by a strong land/sea breeze developed on the coast of peninsular South India. The analyses of day/night samples demonstrated an important role of diurnal land/sea breezes that occur at Chennai to deliver precursors such as unsaturated fatty acids emitted from marine and terrestrial plants and control the organic chemical composition of the tropical Indian aerosols.

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K. Kawamura and C. M. Pavuluri, Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, Sapporo 060-0819, Japan. (kawamura@lowtem.hokudai.ac.jp)

T. Swaminathan, Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600 036, India.