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Contributions of isoprene, α/β-pinene and β-caryophyllene to secondary organic aerosol in tropical India

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Polar organic tracers of isoprene, α/β-pinene and β-caryophyllene photooxidation in tropical Indian aerosols (PM_{10}) collected at Chennai were measured using gas chromatography/mass spectrometry. All the biogenic secondary organic aerosol (SOA) tracers showed diurnal variations with higher concentrations at daytime, which is in agreement with the fact that they are photochemical oxidation products of biogenic volatile organic compounds (VOCs). Total concentration ranges of the organic tracers were 18.3-107 ng m^{-3} in summer versus 2.69-66.9 ng m^{-3} in winter. Most of the SOA tracers showed higher concentrations in summer than in winter, while β-caryophyllinic acid, a tracer for β-caryophyllene, showed no seasonal differences. A good correlation ($R^2=0.67$) was found between the concentrations of 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). In addition, both 3-hydroxyglutaric acid and MBTCA were strongly correlated with malic acid, indicating a similar formation pathway of these compounds in the tropical region. This study also suggests that isoprene and α/β-pinene oxidation products contribute almost equally to organic carbon (OC) in tropical India.

1. Introduction

Considerable efforts have been devoted in the last decade to understand secondary organic aerosol (SOA) formation from the photooxidation of both anthropogenic and biogenic volatile organic compounds (VOCs) [*Hoffmann et al*., 1997; *Jang and Kamens*, 1998; *Kavouras et al*., 1999; *Yu et al*., 1999; *Claeys et al*., 2004a; *Zhang et al*., 2004; *Jaoui et al*., 2008], because SOA is an important component in the Earth's atmosphere to influence the atmospheric radiation budget directly by scattering sunlight and indirectly acting as cloud condensation nuclei (CCN) [*Kanakidou et al*., 2005]. On a global scale, the contribution of biogenic VOCs to SOA (18.5-270 Tg/yr) is one order of magnitude greater than that of anthropogenic VOCs (1-30 Tg/yr) [*Andreae and Crutzen*, 1997]. Thus, the biogenic SOA is comparable to the global burden of sulfate aerosol of 180 Tg/yr (±22%) [*Andreae and Rosenfeld*, 2008].

Biogenic VOCs that released from vegetation include isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons such as alcohols, aldehydes and ketones [*Guenther et al*., 2006; *Goldstein and Galbally*, 2007; *Duhl et al*., 2008]. The global emissions of biogenic terpenes and anthropogenic hydrocarbons are both far lower than that of isoprene (500-750 Tg $year^{-1}$) [*Guenther et al*., 2006]. Despite its large flux, isoprene had not been generally considered to be an SOA precursor due to the high volatility of its known reaction products. Claeys et al. [*Claeys et al*., 2004a] first identified two diastereoisomeric 2-methyltetrols as oxidation products of isoprene in the Amazonian rain forest aerosols. Since then, these compounds have been detected in ambient air samples collected in Finland [*Kourtchev et al*., 2005], Hungary

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[*Ion et al*., 2005], the United States [*Edney et al*., 2005; *Xia and Hopke*, 2006; *Clements and Seinfeld*, 2007; *Ding et al*., 2008; *Yan et al*., 2009], China [*Hu et al*., 2008; *Wang et al*., 2008], and the polar region [*Fu et al*., 2009a]. Photooxidation products of α/β-pinene and β-caryophyllene were also characterized in smog chamber experiments and reported in ambient samples [*Jaoui et al*., 2005; *Jaoui et al*., 2007; *Hu et al*., 2008; *Jaoui et al*., 2008; *Kourtchev et al*., 2008b; *Wang et al*., 2008; *Fu et al*., 2009a; *Yan et al*., 2009]. These studies provide insights on sources and processes that influence SOA production and their spatial and seasonal distributions. However to date, little is known about the BVOC oxidation products in tropical regions, especially in South Asia.

Atmospheric brown clouds (ABCs) over Asia, also known as the Indo-Asian haze, are caused by significant biomass burning and fossil fuel combustion [*Lelieveld et al*., 2001; *Gustafsson et al*., 2009]. It can impact on South Asia climate and hydrological cycles [*Ramanathan et al*., 2005]. Recently, Gustafsson et al. [2009] used radiocarbon (^{14}C) as a tracer to quantify biomass and fossil fuel contributions to the ABCs. Chowdhury et al. [2007] reported the organic speciation and source apportionment of fine particles in four Indian cities using a receptor-based method. Furthermore, efforts have been done to understand the changes in the organic aerosol composition due to photochemical oxidation at a molecular level [*Robinson et al*., 2006; *Rudich et al*., 2007]. Tropical region may provide a unique site to study the photochemical aging of organic aerosols because of its high ambient temperature and strong sunlight irradiation. However, knowledge about the organic molecular composition of atmospheric aerosols in tropical India is very limited.

To understand the levels of biogenic SOA and the different content of organic aerosols among different seasons, we carried out a monitoring campaign in tropical India from January to June, 2007. The concentrations of isoprene oxidation products (e.g., 2-methyltetrols), together with α/β-pinene and β-caryophyllene oxidation products (e.g., pinic acid and β-caryophyllinic acid) were measured for the first time in tropical Indian region. We report contributions of each compound class to OC in the samples and discuss the importance of biogenic SOA in the tropical Indian aerosols.

2. Experimental Section

2.1 Aerosol Sampling

Detailed information about the sampling site is presented elsewhere [*Pavuluri et al*., 2010]. Briefly, 49 day- and night-time PM_{10} samples were collected using a high volume air sampler (Envirotech APM 460 DX, India) and pre-combusted (450°C, 4h) quartz fiber filters at the Indian Institute of Technology Madras (IITM) in Chennai (13.04°N, 80.17°E) (Figure 1) during winter and summer 2007. IITM campus is located in a natural forest, covered with vegetations, and is ca. 3 km away from the coast. The sample filter was placed in a clean glass jar with a Teflon-lined screw cap and stored in a dark freezer room at −20°C prior to analysis.

2.2 Extraction and Derivatization

Detailed analytical method has been described elsewhere [*Fu et al*., 2008; 2009a]. Briefly, filter aliquots were extracted with dichloromethane/methanol (2:1; v/v) under ultrasonication. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated by the use of a rotary evaporator, and then blown down to dryness with pure nitrogen gas. The extracts were then reacted with 50 μl of N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 μl of pyridine at 70°C for 3h. After reaction, the derivatives were diluted with 140 μl of *n*-hexane that contains 1.43 ng μl^{-1} of the internal standard (C_{13} *n*-alkane) prior to GC/MS injection.

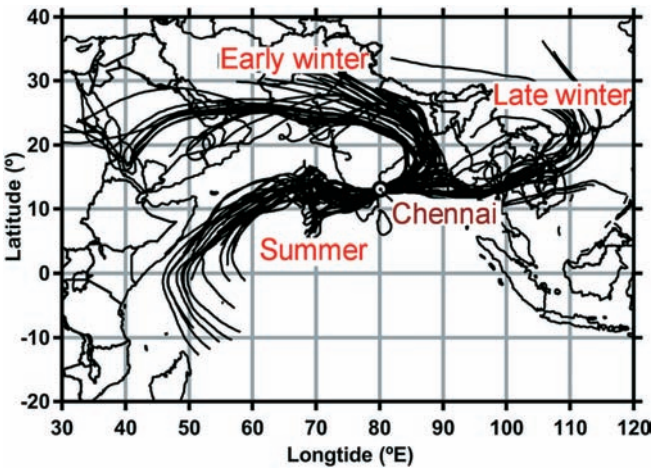

Figure 1：A map showing the location of the Chennai city in South Asia. Plots of 10-day air mass back trajectories arriving at 500 m above Chennai (13.04°N and 80.17°E) in winter (January 23 to February 6) and summer (May 22–31) 2007, showing three major pathways reflecting early winter, late winter and summer [*Pavuluri et al*., 2010].

2.3 GC/MS Analysis

Data were processed with the Chemstation software. Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data [*Claeys et al*., 2004a; *Wang et al*., 2008]. For the quantification of 3-hydroxyglutaric, *cis*-pinonic, and pinic acids, their GC/MS response factors were determined using authentic standards. *cis*-Norpinic acid was quantified using the response factor of *trans*-norpinic acid. β-Caryophyllinic acid was estimated using the response factor of pinic acid. 2-Methylglyceric acid, C_5-alkene triols, 2-methyltetrols and 3-methyl-1,2,3-butanetricarboxylic acid were quantitatively determined by a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m×0.2 mm i. d.×0.5 μm film thickness), and a flame ionization detector (FID). The identification of the organic compounds quantified by GC-FID was confirmed by GC/MS analysis. The standard of *meso*-erythritol, a surrogate compound generally used for the quantification of 2-methyltetrols, was quantitatively determined by both GC/MS and GC-FID. Its relative standard deviation based on these two methods was <5%. Field blank filters were treated as the real samples for quality assurance. Target compounds were not detected in the blanks. Recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz filters and analyzed as same as samples (n=3) were 94±2.6% for *meso*-erythritol, 91±5.5% for 3-hydroxyglutaric acid, 64±5.9% for *cis*-pinonic acid, 93±2.3% for *trans*-norpinic acid, and 79±2.3% for pinic acid. The data reported here were not corrected for the recoveries. Relative standard deviation of the concentrations based on duplicate sample analysis was generally < 10%.

3. Results and Discussion

3.1 Meteorology and air mass back trajectories

Detailed weather information has been mentioned elsewhere [*Pavuluri et al*., 2010]. In brief, the weather in Chennai is generally hot and humid. The ambient temperatures during the campaigns varied from 14.2–34.9°C (average 23°C) in winter and 28.3–41°C (32°C) in summer. No rain was recorded during the campaigns. A clear diurnal oscillation in wind speed and wind direction was found in Chennai due to a strong land-sea thermal gradient. During sampling period in the present study, 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, local time) during both winter and summer, and accelerates subsequently as a result of the onset of sea breeze. The onset of sea breeze at daytime that introduce cool marine air passing over a warmer land surface results in a thermal internal boundary layer (TIBL) below the planetary boundary layer (PBL). In contrast, the onset of land breeze at nighttime may remove the TIBL and the PBL moves down.

Air mass trajectory analysis (Figure 1) showed that most of the air masses were transported long distances from North India and the Middle East in early winter (Jan. 23–28) and from Southeast Asia over the Bay of Bengal in late winter (Jan. 29–Feb. 6). In contrast, the Arabian Sea, Indian Ocean and South Indian continent are suggested as major source regions in summer (May 22–31) [*Pavuluri et al*., 2010]. Back trajectory analysis also showed that the air masses originated from mixed regions (North India and Southeast Asia) between January 30 and February 2. Thus, we present the seasonal differences of some compound classes and their discussions as three categories following the air mass trajectory analysis.

3.2 Isoprene Oxidation Products

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is highly reactive because of the presence of C=C bonds, which makes it susceptible to react with oxidants (e.g., OH, O_3, and NO_3) [*Atkinson and Arey*, 1998]. Isoprene oxidation products can partition in the particle phase and lead to SOA formation [*Claeys et al*., 2004a; *Kroll et al*., 2006; *Sato*, 2008; *Carlton et al*., 2009; *Hallquist et al*., 2009]. In this study, six compounds were identified as isoprene SOA tracers in the aerosols, including 2-methylglyceric acid, three C_5-alkene triols, and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol) (Figure 2). Their concentrations were higher in summer than in winter. The concentration ranges of 2-methyltetrols were 0.57–10.5 ng m^{-3} (average 3.06 ng m^{-3}) at daytime and 0.17–10.6 ng m^{-3} (2.42 ng m^{-3}) at nighttime in winter. In summer, their concentration ranges were 4.89–43.2 ng m^{-3} (16.6 ng m^{-3}) at daytime versus 3.54–18.9 ng m^{-3} (11.1 ng m^{-3}) at nighttime. The concentrations 2-methylerythritol were about 2.5-fold more abundant

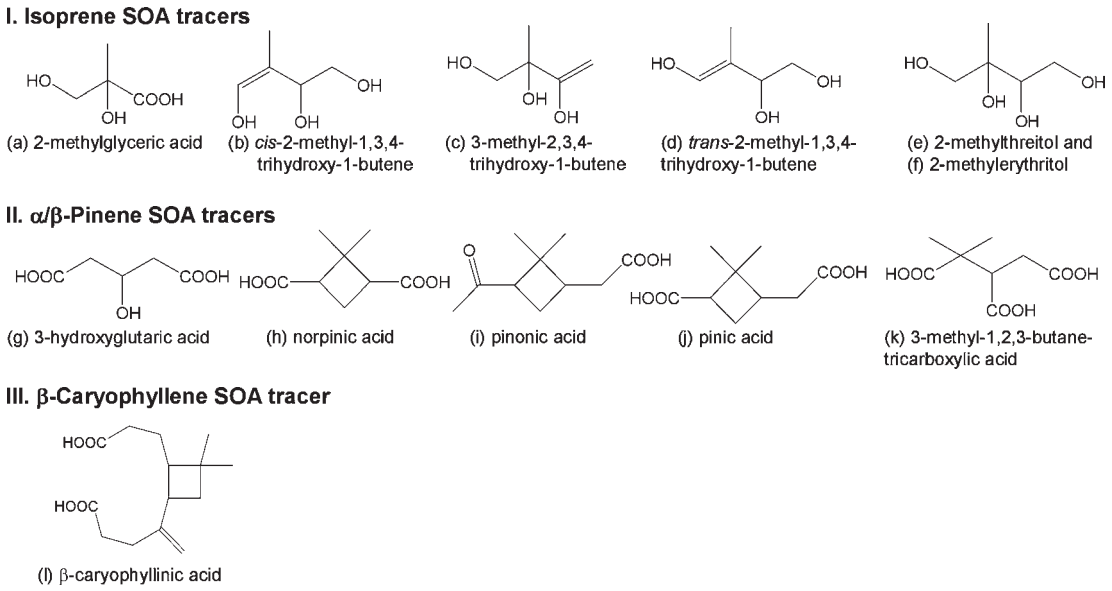

Figure 2 : Chemical structures of the polar organic compounds detected in PM_{10} aerosols collected at Chennai, tropical India.

than 2-methylthreitol (Table 1). This ratio is similar to those observed in other studies [*Claeys et al*., 2004a; *Ion et al*., 2005; *Cahill et al*., 2006]. The levels of 2-methyltetrols are lower than those reported in mountain aerosols such as Mt. Changbai, Northeast China (22–282ng m^{-3}) [*Wang et al*., 2008], and forested sites such as Amazon [*Claeys et al*., 2004a], Hungary [*Ion et al*., 2005], Finland [*Kourtchev et al*., 2008a], Germany [*Kourtchev et al*., 2008b].

C_5-Alkene triols, which are recently reported as photooxidation products of isoprene [*Wang et al*., 2005], were detected in all samples with average concentrations similar to those of 2-methyltetrols. However, they are lower than those (~50 ng m^{-3}) reported in subtropical Hong Kong [*Hu et al*., 2008], but are comparable to those reported in other studies from midlatitudes, e.g., a Californian pine forest, USA (3.47 ng m^{-3}) [*Cahill et al*., 2006], and Jülich, Germany (1.6–4.9 ng m^{-3}) [*Kourtchev et al*., 2008b], and about 2 orders of magnitude higher than those reported in the Arctic [*Fu et al*., 2009a]. The concentration ranges of 2-methylglyceric acid, which is possibly formed by further oxidation of methacrolein and methacrylic acid from isoprene [*Claeys et al*., 2004b; *Surratt et al*., 2006], were 0.24–1.66 ng m^{-3} (average 0.69 ng m^{-3}) at daytime and 0.16–1.90 ng m^{-3} (0.64 ng m^{-3}) at nighttime in winter. In summer, their concentration ranges were 1.30–8.23 ng m^{-3} (4.35 ng m^{-3}) at daytime versus 1.06–3.20 ng m^{-3} (2.09 ng m^{-3}) at nighttime.

The concentrations of isoprene SOA tracers were found to be higher in summer than in winter and at daytime than at nighttime (Figure 3a), which is in agreement with their photooxidation nature. This pattern is different from those of biomass burning tracers (e.g., levoglucosan) and other anthropogenic organics such as hopanes and PAHs [*Fu et al*., 2009b]. The nighttime maxima of these organic compounds may be associated with the land/sea breeze circulation in Chennai [*Pavuluri et al*., 2010].

3.3 α/β-Pinene Oxidation Products

Pinonic, norpinic, and pinic acids were detected as α/β-pinene oxidation products. These acids are produced by photooxidation of α/β-pinene via reac-

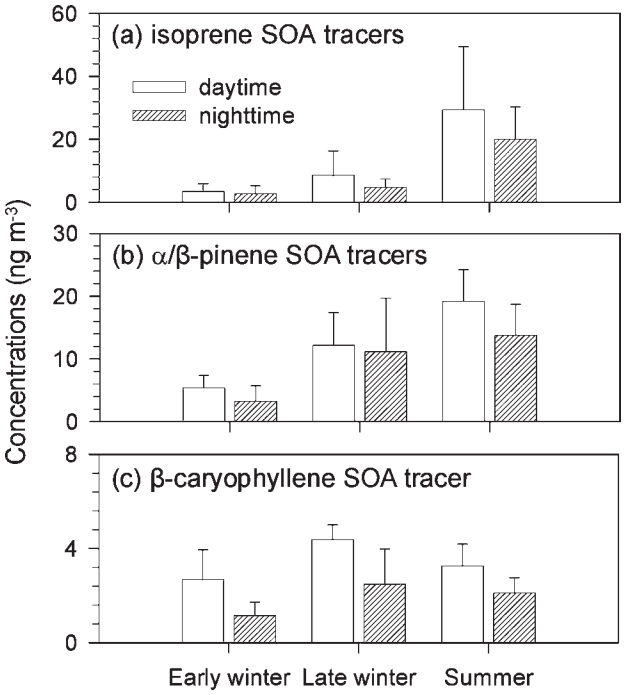

Figure 3 : Winter/summer and day/night differences of the total concentrations of SOA tracers detected in atmospheric aerosols from Chennai, tropical India.

tions with O_3 and OH radicals [*Hoffmann et al*., 1997; *Yu et al*., 1999; *Glasius et al*., 2000; *Iinuma et al*., 2004]. They have been observed in smog chamber experiments [*Jang and Kamens*, 1998; *Yu et al*., 1999; *Glasius et al*., 2000] and reported in the ambient aerosols [*Ding et al*., 2008; *Kourtchev et al*., 2008b; *Fu et al*., 2009a; 2009c]. Concentrations of pinic acid and pinonic acid were similar during winter, whereas in summer the concentrations of pinonic acid were higher than those of pinic acid (Table 1), although the vapor pressure of pinonic acid is about 2 orders of magnitude higher than pinic acid. This pattern is consistent with those found in tropospheric aerosols over Mt. Tai in Central East China, in which the concentrations of pinonic acid were twice more abundant than pinic acid. Similar patterns have been reported in other studies [*Kavouras et al*., 1999; *Kavouras and Stephanou*, 2002; *Cahill et al*., 2006; *Bhat and Fraser*, 2007; *Yan et al*., 2008]. However, higher concentrations of pinic acid than pinonic acid have been reported in the aerosols from a coniferous forest in Germany [*Plewka et al*., 2006] and Research Triangle Park (RTP), USA [*Kleindienst et al*., 2007].

Two novel compounds were recently identified in aerosols as 3-hydroxyglutaric acid (3-HG) [*Claeys et al*., 2007] and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) [*Szmigielski et al*., 2007]. Both 3-HG and MBTCA are generated in smog chamber experiments of α-pinene with an irradiation of UV in the presence of NO_x [*Claeys et al*., 2007; *Szmigielski et al*., 2007]. The concentrations of 3-HG were higher than those of other α/β-pinene oxidation products.

3.4 β-Caryophyllene Oxidation Product

Regarding their high reactivity and relatively low vapor pressure, sesquiterpenes have been the least studied BVOCs. Among sesquiterpenes emitted from the plants, β-caryophyllene is one of the most abundant species and most frequently reported [*Duhl et al*., 2008]. β-Caryophyllinic acid, an ozonolysis or photo-oxidation product of β-caryophyllene [*Jaoui et al*., 2007], was identified in both winter and summer samples without any significant differences (Table 1). However, relatively higher levels of β-caryophyllinic acid were observed during late winter (Figure 3c) when the air masses originated from Southeast Asia [*Pavuluri et al*., 2010], indicating that Southeast Asia is a strong "emitter" of β-caryophyllene.

3.5 Temporal Variations

Figure 4 presents the overall seasonal and diurnal variations of the polar organic tracers. We found that most of the biogenic SOA tracers gave diurnal trends with higher concentrations at daytime, suggesting a photochemical production of these compounds. The isoprene oxidation tracers showed very similar temporal trends each other (Figure 4a-c), except for the diurnal patterns in summer (Figure 4c). In winter, one concentration peak was observed during January 30-February 1 (Figure 4a-c). Such a peak can also be found for other SOA tracers (Figure 4e-i). In summer, the temporal patterns of isoprene SOA

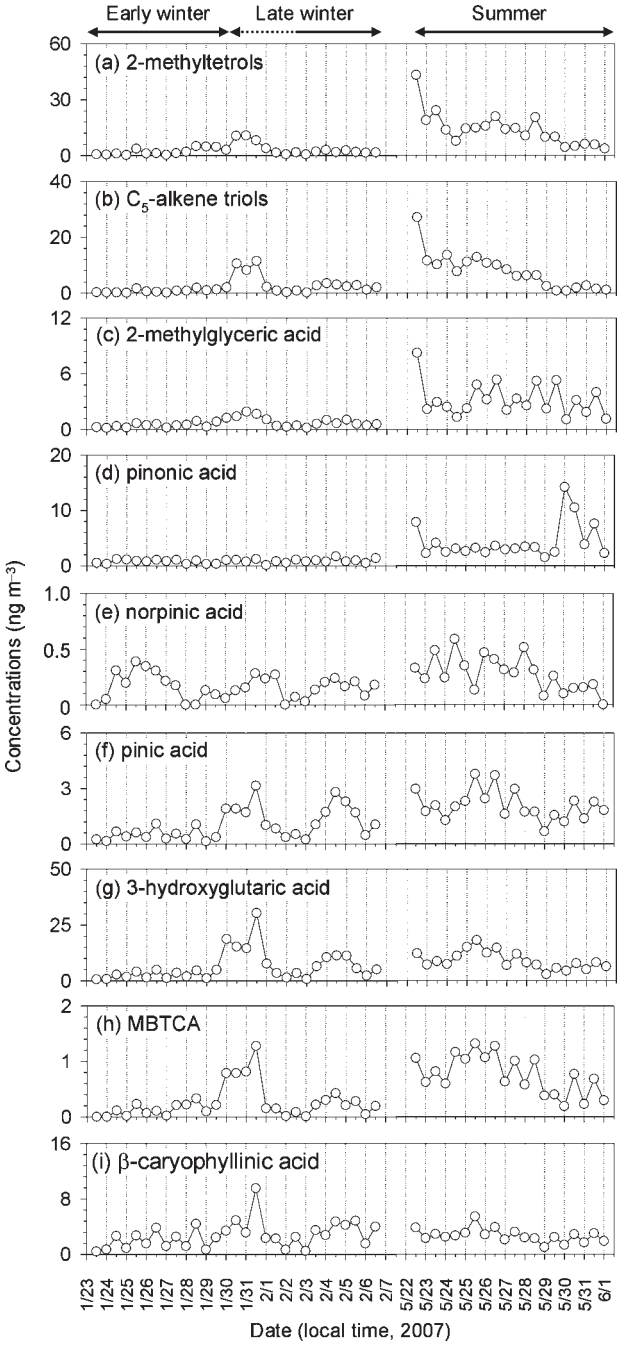

Figure 4 : Temporal variations of individual biogenic SOA tracers in PM_{10} aerosols collected at Chennai, tropical India.

tracers and other biogenic oxidation products were different.

A good correlation was found between the concentrations of 2-methyltetrols and C_5-alkene triols (R^2=0.80, n=49) in the Chennai samples because they are both derived from the oxidation of isoprene. However, their formation processes are different. Wang et al. (2005) reported that 2-methyltetrols are formed through diepoxy derivatives of isoprene, which can be converted into 2-methyltetrols through acid-catalyzed hydrolysis. Alternatively, the formation of C_5-alkene triols was explained through rearrangement reactions of hydroxyperoxy radicals that are formed in the initial photooxidation of isoprene [*Surratt et al*., 2006]. The temporal pattern of 2-methylglyceric acid (Figure 4c) was similar to those of 2-methyltetrols and C_5-alkene triols (Figure 4a-b). In addition, a clear diurnal variation can be found for 2-methylglyceric acid during summertime with higher concentrations at daytime.

The temporal variations of α/β-pinene oxidation tracers (Figure 4d-h) were different from those of isoprene oxidation tracers (Figure 4a-c). A poor correlation between α/β-pinene oxidation products and 2-methyltetrols in mountain aerosols was reported by Cahill et al. (2006). Furthermore, the temporal patterns of pinonic acid and norpinic acid were different from those of pinic acid, 3-HG and MBTCA. MBTCA and 3-HG are higher-generation photooxidation products of α/β-pinene compared to pinonic and pinic acids [*Kourtchev et al*., 2009]. A good correlation (R^2=0.67, n=49) was found between the concentrations of 3-hydroxyglutaric acid and MBTCA in the Chennai aerosols. In addition, both 3-hydroxyglutaric acid and MBTCA were strongly correlated with malic acid (Figure 5), indicating a similar formation pathway in the tropical region. Malic acid can be produced by the photochemical oxidation of succinic acid [*Kawamura and Ikushima*, 1993], which is one of the oxidation products of biogenic unsaturated fatty acids in the atmosphere [*Matsunaga et al*., 1999].

Temporal variations of β-caryophyllinic acid (Figure 4i) showed one major peak during January 30-February 1. This pattern was different from those of isoprene or α/β-pinene oxidation tracers (Figure 4a-h). A positive correlation between β-caryophyllinic acid and levoglucosan, a specific biomass burning tracer, was found in Mt. Tai aerosols during MTX2006 campaign when the field burning activities

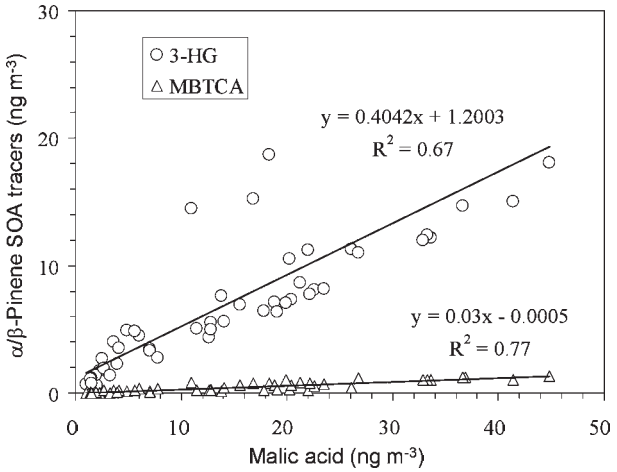

Figure 5：Relations between malic acid and two α/β-pinene SOA tracers: 3-hydroxyglutaric acid (3-HG) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA).

of wheat straws were very active in Central East China [*Fu et al*., 2009c]. In this study, the correlation coefficients (R^2) between levoglucosan and β-caryophyllinic acid were 0.25 in winter versus 0.06 in summer. This difference indicates that the formation of β-caryophyllinic acid in the urban atmosphere over Chennai may be partly influenced by biomass burning during wintertime when the ambient temperatures are relatively low.

The temporal variation of total concentrations of BVOC oxidation products detected in this study is shown in Figure 6a. The total concentration ranges of biogenic SOA tracers detected in tropical Indian aerosols are 18.3–107 ng m^{-3} in summer and 2.85–66.9 ng m^{-3} in winter (Table 1). These values are relatively low when compared with those reported in forested sites at midlatitudes [*Ion et al*., 2005; *Kourtchev et al*., 2008a; *Kourtchev et al*., 2008b; *Wang et al*., 2008; *Fu et al*., 2009c], or even in a subtropical urban site in Hong Kong [*Hu et al*., 2008], especially for 2-methyltetreols. This suggests that in tropical India, biogenic SOA tracers such as 2-methyltetrols and MBTCA may be further oxidized to lower molecular compounds such as oxalic acid under strong sunlight radiation, a point warrants future study.

3.6 Contributions of BVOC Oxidation Products to OC

To better understand the chemical composition of SOA in tropical India, the contributions of isoprene, α/β-pinene and β-caryophyllene oxidation products to OC were examined. Mean contributions of total SOA tracers to OC in summer (0.30±0.12% at daytime versus 0.19±0.09% at nighttime) were about 3 times

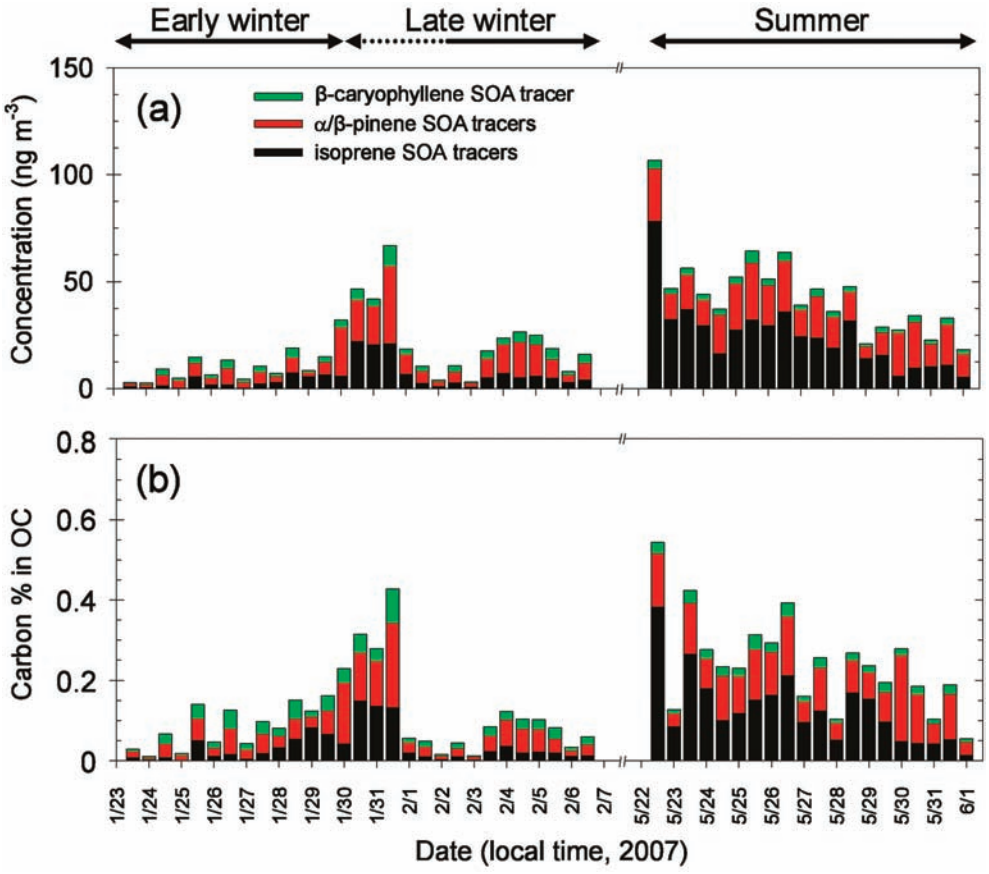

Figure 6：Temporal variations of (a) total concentrations of isoprene, α/β-pinene and β-caryophyllene SOA tracers, and (b) the carbon percentage of biogenic SOA tracers in organic carbon (OC) in the tropical Indian aerosols.

Table 1：Concentrations of polar organic tracers in PM_{10} samples from Chennai, tropical India, ng m^{-3}

Compound	Winter						Summer					
	daytime (n=15)			nighttime (n=14)			daytime (n=10)			nighttime (n=10)		
	range	average	SD[a]	range	average	SD	range	average	SD	range	average	SD
tracer for isoprene SOA												
2-methylglyceric acid	0.24–1.66	0.69	0.39	0.16–1.90	0.64	0.53	1.30–8.23	4.35	1.88	1.06–3.20	2.09	0.64
ΣC_5-alkene triols[b]	0.20–11.5	2.72	3.49	0.08–8.21	1.61	2.16	0.77–27.1	8.42	7.72	0.71–13.5	6.84	4.86
2-methylthreitol	0.15–3.06	0.86	0.83	0.04–3.30	0.71	0.86	1.11–11.6	4.72	3.12	0.87–5.44	3.25	1.55
2-methylerythritol	0.42–7.41	2.20	2.03	0.13–7.35	1.71	1.90	3.79–31.6	11.9	8.36	2.68–13.4	7.84	3.60
subtotal	1.08–22.4	6.47	6.53	0.45–20.8	4.67	5.30	9.84–78.6	29.4	20.1	5.74–32.6	20.0	10.2
tracer for monoterpene SOA												
3-hydroxyglutaric acid	0.59–30.3	7.05	7.35	0.73–18.7	5.36	6.02	5.64–18.1	10.5	3.84	2.80–15.1	7.55	3.68
cis-pinonic acid	0.34–1.69	1.00	0.32	0.10–1.10	0.62	0.29	2.44–10.5	4.86	2.74	1.49–14.2	3.76	3.72
cis-norpinic acid	n.d.–0.39	0.18	0.12	n.d.–0.34	0.13	0.10	0.13–0.59	0.31	0.15	n.d.–0.52	0.25	0.17
pinic acid	0.24–3.14	1.17	0.86	0.14–2.29	0.81	0.76	1.55–3.78	2.54	0.78	0.67–2.45	1.62	0.53
MBTCA[c]	n.d.–1.27	0.31	0.32	n.d.–0.81	0.20	0.34	0.40–1.32	0.95	0.29	0.19–1.07	0.56	0.31
subtotal	1.36–36.2	9.72	8.58	1.24–22.4	7.12	7.06	10.3–26.5	19.2	5.04	5.42–21.4	13.7	4.95
tracer for β-caryophyllene SOA												
β-caryophyllinic acid	0.41–9.52	3.68	2.03	0.48–4.24	1.77	1.20	2.28–5.44	3.26	0.93	1.01–3.07	2.11	0.65
Total tracers	2.85–66.9	19.9	16.4	2.69–41.8	13.6	12.5	28.7–107	51.8	23.1	18.3–52.2	35.9	12.8
Total tracers in OC (%)	0.03–0.32	0.11	0.07	0.01–0.23	0.07	0.06	0.19–0.54	0.30	0.12	0.05–0.29	0.19	0.09

[a]SD: standard deviation; [b]C_5-alkene triols: *cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene; [c]MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

higher than those in winter (0.11±0.07% at daytime versus 0.07±0.06% at nighttime) (Table 1). Figure 6b shows the temporal contributions of isoprene, α/β-pinene and β-caryophyllene oxidation products to OC with higher values in summer when photochemical activity is high. Isoprene and α/β-pinene SOA tracers contribute almost equally to OC. The mean carbon % of β-caryophyllene SOA tracer is much lower than that of isoprene and α/β-pinene SOA tracers. However, the relative abundances of β-

caryophyllinic acid in OC are higher in winter than in summer (Figure 6b). This finding suggests that there is no significant seasonal difference for the emissions of β-caryophyllene or the SOA formation from β-caryophyllene oxidation in tropical India.

4. Conclusions

Secondary oxidation products from biogenic VOCs including isoprene, α/β-pinene and β-caryophyllene were identified and quantified in the atmospheric aerosols collected at Chennai in tropical India. The ambient concentrations of biogenic SOA tracers were used to estimate the contributions to OC. Mean contributions of total SOA tracers to OC in summer ($0.30\pm0.12\%$ at daytime versus $0.19\pm0.09\%$ at nighttime) were higher than those in winter ($0.11\pm0.07\%$ at daytime versus $0.07\pm0.06\%$ at nighttime). Isoprene and α/β-pinene oxidation products were found to contribute almost equally to OC. However, the concentrations of isoprene and α/β-pinene SOA tracers detected in this study were lower than those reported in other forested or urban sites [*Claeys et al*., 2004a; *Ion et al*., 2005; *Kourtchev et al*., 2005; *Hu et al*., 2008; *Kourtchev et al*., 2008a; *Kourtchev et al*., 2008b; *Fu et al*., 2009c]. This may indicate that under the conditions of high ambient temperatures and strong sunlight irradiation, the organic molecular composition of atmospheric aerosols in tropical regions should be different from those in mid- or high latitudinal regions, although it is poorly understood up to date. Further study on organic aerosols in the tropical regions is needed.

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