The influence of temperature and aerosol acidity on biogenic secondary organic aerosol tracers: Observations at a rural site in the central Pearl River Delta region, South China

Xiang Ding [a,b], Xin-Ming Wang [a,*], Mei Zheng [c]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Rd, Tianhe, Guangzhou 510640, China
[b] Pearl River Delta Research Center for Environmental Pollution Control, Chinese Academy of Sciences, Guangzhou 510640, China
[c] School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta 30332, USA

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ABSTRACT

At a rural site in the central Pearl River Delta (PRD) region in south China, fine particle ($PM_{2.5}$) samples were collected during fall-winter 2007 to measure biogenic secondary organic aerosol (SOA) tracers, including isoprene SOA tracers (3-methyl-2,3,4-trihydroxy-1-butene, 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol), α-pinene SOA tracers (cis-pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid) and a sesquiterpene SOA tracer (β-caryophyllinic acid). The isoprene-, α-pinene- and sesquiterpene-SOA tracers averaged 30.8 ± 15.9, 6.61 ± 4.39, and 0.54 ± 0.56 ng m^{-3}, respectively; and 2-methyltetrols (sum of 2-methylthreitol and 2-methylerythritol, 27.6 ± 15.1 ng m^{-3}) and cis-pinonic acid (3.60 ± 3.76 ng m^{-3}) were the dominant isoprene- and α-pinene-SOA tracers, respectively. 2-Methyltetrols exhibited significantly positive correlations ($p < 0.05$) with ambient temperature, probably resulting from the enhanced isoprene emission strength and tracer formation rate under higher temperature. The significantly positive correlation ($p < 0.05$) between 2-methyltetrols and the estimated aerosol acidity with a slope of 59.4 ± 13.4 ng m^{-3} per μmol [H$^+$] m^{-3} reflected the enhancement of isoprene SOA formation by aerosol acidity, and acid-catalyzed heterogeneous reaction was probably the major formation pathway for 2-methyltetrols in the PRD region. 2-Methylglyceric acid showed poor correlations with both temperature and aerosol acidity. The α-pinene SOA tracers showed poor correlations with temperature, probably due to the counteraction between temperature effects on the precursor emission/tracer formation and gas/particle partitioning. Among the α-pinene SOA tracers, only cis-pinonic acid and pinic acid exhibited significant correlations with aerosol acidity with slopes of -11.7 ± 3.7 and -2.2 ± 0.8 ng m^{-3} per μmol [H$^+$] m^{-3}, respectively. The negative correlations observed for α-pinene SOA tracers might result from their transfer from particle to gas phase with the increase of aerosol acidity. The ratio of cis-pinonic acid plus pinic acid to 3-methyl-1,2,3-buta-netricarboxylic acid (MBTCA) ranged from 0.28 to 28.9 with a mean of 7.19, indicating the relatively fresh α-pinene SOA tracers during our campaign.

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1. Introduction

Secondary organic aerosols (SOA) are produced by homogenous reactions of biogenic and anthropogenic volatile organic compounds (VOCs) with ozone (O_3), OH and NO_3 radicals, followed by nucleation reactions and condensation onto pre-existing particles, or by direct heterogeneous reactions of VOCs on particle surfaces (Jang et al., 2002). SOA can affect the earth's radiative balance (Hoyle et al., 2009) directly by altering the scattering properties of the atmosphere and indirectly by changing cloud properties. On the global scale, the emissions of biogenic VOCs (BVOCs) dominate over those of anthropogenic VOCs (Piccot et al., 1992; Guenther et al., 1995). The global production of SOA is estimated to reach 6.2 TgC yr^{-1} from isoprene (Henze and Seinfeld, 2006) and 18.5 TgC yr^{-1} from other biogenic precursors (Griffin et al., 1999). However, biogenic contribution to SOA is expected to be relatively lower in urban areas, due to more anthropogenic sources of SOA precursors. Based on the identified SOA tracers, Stone et al. (2009) found that toluene alone had greater contribution to secondary organic carbon (SOC) at the urban sites in United States (US), compared to biogenic precursors including isoprene, α-pinene and β-caryophyllene. With chemical mass balance model

and carbon isotope results, Ding et al. (2008a) estimated that the biogenic contributions were less than 50% in SOC at an urban site in the southeastern US. More complex is that urban emissions can accelerate oxidation of BVOCs (Carlton et al., 2010; Weber et al., 2007; Zhang et al., 2009).

The Pearl River Delta (PRD) region in south China covering ~41700 km^2 is one of the most industrialized and densely populated regions in China with city clusters, e.g. Hong Kong, Guangzhou, Shenzhen, Foshan and Dongguan. The rapid growth in economy has resulted in fast increase in anthropogenic air pollutant emissions in this region (Chan and Yao, 2008). Located in the tropical/subtropical area, the PRD region has annual mean temperature of ~25 °C and higher biogenic emissions are expected here compared to northern parts of China (Zheng et al., 2010). Therefore both anthropogenic and biogenic SOA precursors are comparatively abundant in the PRD region. On the other hand, the elevated atmospheric oxidative capacity in the PRD region was observed, such as the successive increasing trend of O_3 during 1994–2007 in Hong Kong, where is located downwind of the PRD region during fall-winter season and the air quality is deeply impacted by the PRD region (Wang et al., 2009). Additionally, the abundant amounts of sulfate and nitrate in the air make the aerosol very acidic in the PRD region. In Hong Kong, the particles were reported to be highly acidic with the pH values ranging from −0.62 to 2.35 (Pathak et al., 2004). The high aerosol acidity in the PRD region will further favor SOA formation, since acid-catalyzed reactions can significantly enhance SOA yields (Jang et al., 2002; Tanner et al., 2009; Zhang et al., 2007). Either from precursors or from atmospheric oxidative capacity and the acidic aerosols, SOA should be an important component of particles in the PRD region. In fact, the estimated SOC using the ratio of organic carbon (OC) to element carbon (EC) shared about 50% of ambient OC in the PRD region (Cao et al., 2003, 2004; Duan et al., 2007). A study in Hong Kong during summer 2006 observed that SOA levels enhanced about one order of magnitude on days under the PRD regional impact when compared to days under local influence, among which biogenic precursors exhibited dominant contributions to the SOC (Hu et al., 2008). Nevertheless, to understand chemical composition and origins of OC in the heavily polluted PRD region, more field works are needed to characterize biogenic SOA. Up to now in mainland China, however, there is only one report about the biogenic SOA tracers in forest areas during summer time (Wang et al., 2008) and one model study about the spatial distribution of SOC over China (Han et al., 2008).

Previous studies all suggested that air quality during fall-winter season was the worst in a year in the PRD region, based on the monitoring of PM$_{2.5}$, O$_3$, visibility and other criteria pollutants (Wang et al., 2003a; Wu et al., 2005; Xu et al., 2008). As for BVOC emissions in the PRD region, although they are the highest in summer, relatively high emissions are still expected during fall (September to November) in this tropical/subtropical region (Zheng et al., 2010). Indeed, emissions of BVOC are even more significant when compared to those in the northern cities. For example, BVOC emissions (2.55 × 10^9 g C) during fall in Hong Kong contributed 26% of the annual emissions (Leung et al., 2010), while BVOC emissions in Beijing were estimated to be 12.4 × 10^9 g C in summer (June to August) (Wang et al., 2003b). Since the land area of Hong Kong (~1100 km^2) is less than 1/10 of Beijing (~16,800 km^2), the emission strength of BVOCs on unit area in Hong Kong during fall was in fact much higher than that in Beijing during summer. Thus, with relatively high BVOC emissions during fall in the PRD region, it is essential to study the behavior of biogenic SOA in this heavily polluted season, and to investigate the formation mechanism of biogenic SOA under the complex air pollution situation. In the present study, 24-h PM$_{2.5}$ samples were collected consecutively at

a regional background site in the central PRD during October–November, 2007; and biogenic SOA tracers formed from isoprene, α-pinene and sesquiterpene were measured. The purposes are 1) to provide the levels of biogenic SOA tracers in the heavily-polluted season in the PRD region; 2) to check the influence of temperature and aerosol acidity on biogenic SOA tracers in the real atmosphere.

2. Experimental section

2.1. Field sampling

24-Hour PM$_{2.5}$ samples were collected using a high volume sampler (Tisch Environmental Inc.) at a rate of 1.1 m^3 min^{-1} from October 23 to November 24, 2007 at a rural site, Wangqingsha (WQS, 22°42′N, 113°32′E) in the PRD region. As showed in Fig. 1, the sampling site is located in the central PRD, with the Pearl River estuary in the south and surrounding city clusters approximately 60 km away. The sampler was put on the rooftop, about 30 m above ground, of a seven-floor building in a high school. Since the surrounding terrain is flat with large farmland nearby and rare traffic, this site can serve as an ideal location to monitor the regional background level of air pollution in the PRD region. Pre-fired 8 × 10 inch quartz filters were covered with aluminum foil and stored in a zipped bag containing silica gel at 4 °C before and −20 °C after collection. A total of 32 air samples were collected with two field blanks.

2.2. Chemical analysis

A punch (1.5 × 1.0 cm) of each filter was taken for the measurements of OC and EC using the thermo-optical transmittance (TOT) method (NIOSH, 1999) by an OC/EC Analyzer (Sunset Laboratory Inc.). An additional punch was taken from each filter and extracted in 20 mL of 18-MOhm milliQ water and sonicated for 30 min in an ice-water bath. After filtered, the extract was analyzed for sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$) and ammonium (NH$_4^+$) with an ion chromatography (Metrohm 761, Switzerland). All the data were corrected using field blank. Atmospheric visibility was recorded during the sampling by a visibility sensor (Belfort Model 6000).

For the analysis of biogenic SOA tracers, 1/8 of each filter was extracted three times by sonication with 40 mL of dichloride methane (DCM)/methanol (1:1, v/v) for each time. Prior to solvent extraction, hexadecanoic acid-D$_{31}$, phthalic acid-D$_4$, and levoglucosan-^{13}C$_6$ were spiked into the samples as internal standards. The extracts of each sample were combined, filtered and concentrated to ~2 mL. Then each sample was separated in two parts. One was blown to dryness under a gentle stream of nitrogen, and kept at room temperature for one hour to derivatize acids to methyl esters after adding 200 μL of DCM, 10 μL of methanol and 300 μL of fresh prepared diazomethane. The methylated extract was blown to 200 μL and analyzed for α-pinene SOA tracers (cis-pinonic acid, pinic acid and 3-methyl-1,2,3-butanetricarboxylic acid). The other part was blown to dryness for silylation with 100 μL of pyridine and 200 μL of N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) in an oven at 70 °C for one hour. The silylated extract was analyzed for α-pinene SOA tracers (3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid), isoprene SOA tracers (3-methyl-2,3,4-trihydroxy-1-butene, 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol) and sesquiterpene SOA tracer (β-caryophyllinic acid). The typical total ion chromatograms for silylated and methylated samples are presented in Figs. 2 and 3.

Samples were analyzed by an Agilent 5973N gas chromatography/mass spectrometer detector (GC/MSD) in the scan mode with

Fig. 1. Sampling site in PRD. Green pentacle is regional background site, Wangqingsha (WQS) which is in the central of PRD and surrounded by city clusters.

a 30 m HP-5 MS capillary column (i.d.0.25 mm, 0.25 μm film thickness). Splitless injection of a 1 μL sample was performed. The GC temperature was initiated at 80 °C (held for 2 min) and increased to 290 °C at 5 °C min^{-1} then held for 20 min. *cis*-Pinonic acid and pinic acid were quantified by authentic standards. Due to lack of standards, isoprene SOA tracers were quantified using erythritol (Ding et al., 2008b); α-pinene SOA tracers (3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid) were quantified using pinic acid. For β-caryophyllinic acid, octadecanoic acid was used for quantification due to their adjacent retention times (Fig. 2). These

SOA tracers were identified by the comparison of mass spectra with literature data (Claeys et al., 2004, 2007; Jaoui et al., 2007; Kleindienst et al., 2007; Szmigielski et al., 2007; Wang et al., 2005) and their retention times relative to other known compounds in the GC chromatograms. The method detection limits (MDLs) for *cis*-pinonic acid, pinic acid, erythritol and octadecanoic acid were 0.04, 0.07, 0.09 and 0.02 ng m^{-3}, respectively under the average volume of 1575 m^3. It should be noted that 2-methyltetrols can form sulfate and nitrate esters (Surratt et al., 2007a, 2008), which will be measured as free 2-methyltetrols with the derivatization GC-MS method (Wang et al., 2008). Table 1 summarizes the
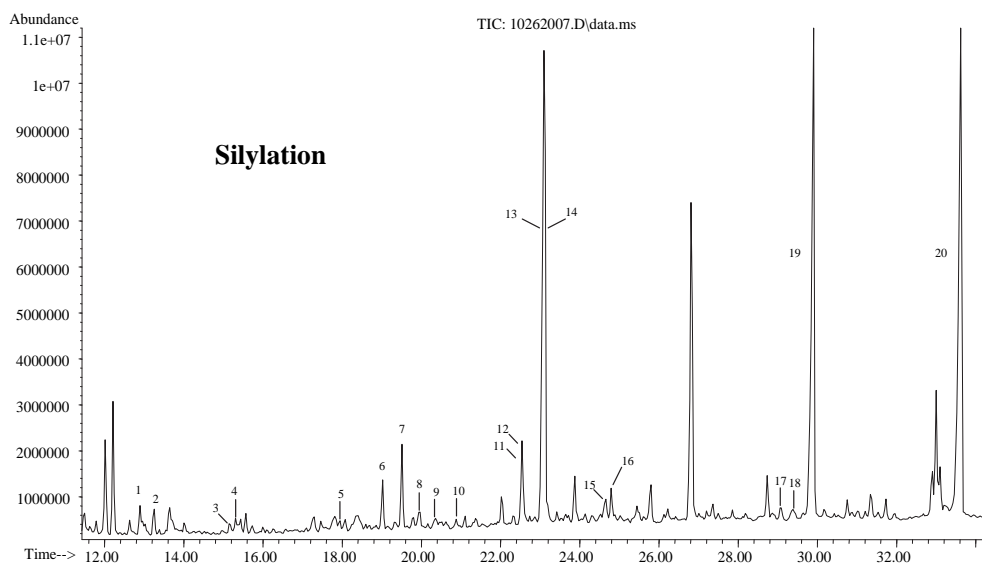

Fig. 2. Total ion chromatogram for silylated sample. 1. succinic acid; 2. 2-methylglyceric acid; 3. 3-methyl-2,3,4-trihydroxy-1-butene; 4. glutaric acid; 5. adipic acid; 6. 2-methylthreitol; 7. 2-methylerythritol; 8. 3-hydroxyglutaric acid; 9. pimelic acid; 10. 3-hydroxy-4,4-dimethylglutaric acid; 11. phthalic acid-D$_4$ (IS); 12. phthalic acid; 13. levoglucosan; 14. levoglucosan-^{13}C$_6$ (IS); 15. terephthalic acid; 16. azelaic acid; 17. β-caryophyllinic acid; 18. hexadecanoic acid-D$_{31}$ (IS); 19. hexadecanoic acid; 20. octadecanoic acid. Besides SOA tracers, other polar compounds were also quantified but not involved in the current paper.
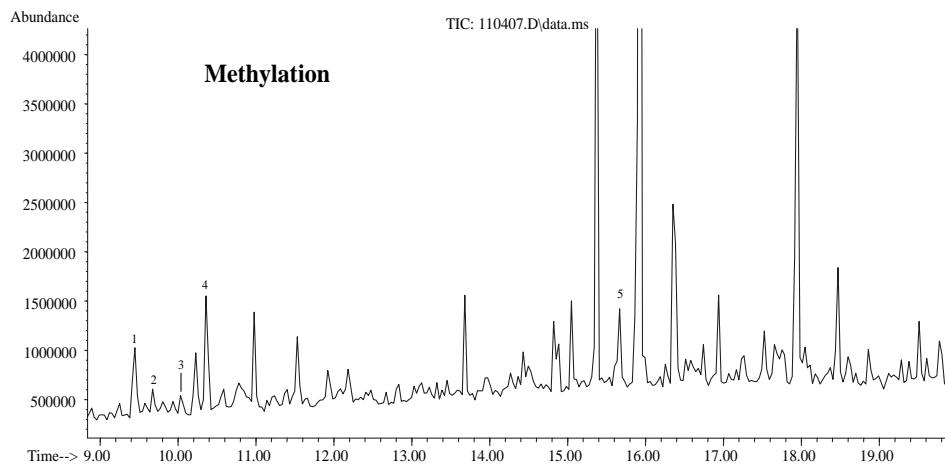
Fig. 3. Total ion chromatogram for methylated sample. 1. *cis*-pinonic acid; 2. pinic acid; 3. 3-methyl-1,2,3-butanetricarboxylic acid; 4. phthalic acid-D_4 (IS); 5. hexadecanoic acid-D_{31} (IS).

average and range of all measured chemical species during this campaign.

2.3. Quality assurance/quality control (QA/QC)

The field and laboratory blanks were extracted and analyzed in the same way as the field samples. The target compounds were not detected in the field and laboratory blanks. Recoveries of the target compounds in six spiked samples (authentic standards spiked into solvent with pre-baked quartz filter) were $104 \pm 2\%$ for *cis*-pinonic acid, $68 \pm 13\%$ for pinic acid, $62 \pm 14\%$ for erythritol, and $78 \pm 10\%$ for octadecanoic acid. The relative differences for the target compounds in duplicate samples ($n = 6$) were all <15%.

3. Results and discussion

3.1. Ambient concentrations of biogenic SOA tracers

During our campaign, relative humidity (RH) and temperature were in the range of 40–83 % and 17.6–26.6 °C (Table 1), respectively. $PM_{2.5}$ averaged 113 ± 23.6 µg m^{-3}, which was about 3 times higher than USEPA 24-hour standard of 35 µg m^{-3} (USEPA, 2006). The highest level of $PM_{2.5}$ reached 171 µg m^{-3} and the worst visibility dropped to 5.5 km during the sampling period. Sulfate, OC and nitrate were the dominant components in $PM_{2.5}$ (Table 1). As Fig. 4a

showed, $PM_{2.5}$, sulfate, nitrate and ammonium exhibited similar daily variation during this period. Among the SOA tracers (Fig. 4b), the isoprene SOA tracers exhibited the highest levels, 30.8 ± 15.9 ng m^{-3}, followed by the α-pinene SOA tracers (6.61 ± 4.39 ng m^{-3}), and β-caryophyllinic acid (0.54 ± 0.56 ng m^{-3}).

Among the four isoprene SOA tracers, 2-methylerythritol had the highest levels (Fig. 5a). 2-Methyltetrols (sum of 2-methyl-threitol and 2-methylerythritol) averaged 27.6 ± 15.1 (5.00 to 64.4) ng m^{-3}, which is comparable to the results reported during the same season in US (Ding et al., 2008b; Xia and Hopke, 2006) and during summer in China (Hu et al., 2008; Wang et al., 2008). 3-Methyl-2,3,4-trihydroxy-1-butene (MTHB) and 2-methylglyceric acid were 1.16 ± 0.83 and 2.04 ± 1.90 ng m^{-3}, respectively. The summed isoprene SOA tracers ranged from 5.77 to 68.3 ng m^{-3}. The lowest occurred on Nov. 1, 2007 (Fig. 5a) when a cold air mass from North China intruded (Fig. 6) with the ambient air temperature dropped to the lowest (17.7 °C) during the campaign. Another low value observed on Nov. 19 also coincided with cold air mass transport (Fig. 6). The levels of isoprene SOA tracers were expected to be lower when the cold front intruding, due to the dilution of strong winds. As showed in Fig. 4a, the levels of primary (EC) and secondary species (sulfate, nitrate and ammonium), as well as those of $PM_{2.5}$ and OC, all decreased on Nov. 1 and Nov. 19. The highest level of isoprene SOA tracers occurred around Oct. 27, 2007 with the mean air temperature of 25.1 °C and air mass from the eastern

Table 1
Summary of SOA tracers (ng m^{-3}) and other parameters.

|	Average	Range		Average	Range
Major components (µg m^{-3})			*Meteorological parameters*		
$PM_{2.5}$	113 ± 23.6	63.6–171	RH (%)	56 ± 11	40–83
OC	19.3 ± 4.81	10.2–31.3	Temperature (°C)	22.3 ± 2.20	17.6–26.6
EC	3.55 ± 1.09	1.76–5.65	Visibility (km)	11.4 ± 3.2	5.5–16.2
SO_4^{2-}	24.2 ± 6.37	15.3–43.4			
NO_3^-	9.54 ± 5.31	2.16–22.5	*Isoprene SOA tracers*		
NH_4^+	5.90 ± 1.22	3.87–9.66	3-Methyl-2,3,4-trihydroxy-1-butene	1.16 ± 0.83	0.18–3.45
			2-Methylglyceric acid	2.04 ± 1.90	0.21–8.48
α-Pinene SOA tracers			2-Methylthreitol	9.60 ± 5.32	2.04–24.4
cis-Pinonic acid	3.60 ± 3.76	0.34–15.3	2-Methylerythritol	18.0 ± 9.89	2.96–42.0
Pinic acid	1.25 ± 0.79	0.23–3.96	Sum of 2-methyltetrols	27.6 ± 15.1	5.00–64.4
3-Methyl-1,2,3-butanetricarboxylic acid	1.16 ± 0.99	0.17–4.51	Sum of isoprene SOA tracers	30.8 ± 15.9	5.77–68.3
3-Hydroxyglutaric acid	0.43 ± 0.59	nd ^{a}–2.76			
3-Hydroxy-4,4-dimethylglutaric acid	0.17 ± 0.13	nd–0.53	*β-Caryophyllene SOA tracer*		
Sum of α-pinene SOA tracers	6.61 ± 4.39	0.91–18.3	β-Caryophyllinic acid	0.54 ± 0.56	0.03–1.97

^{a} "nd" means "not detected".
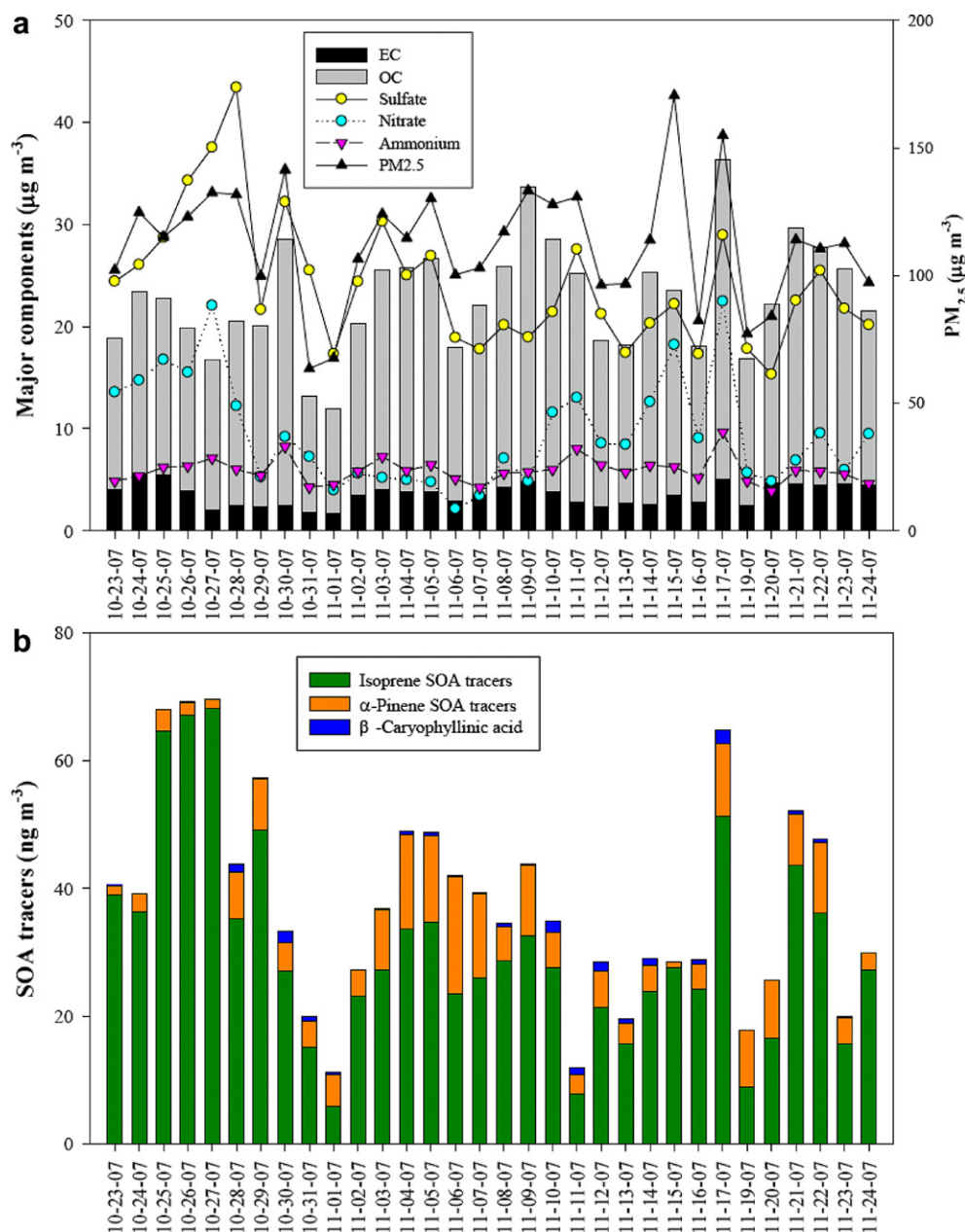
Fig. 4. Daily variations of major components (a) and SOA tracers (b).

seashore (Fig. 6). Ambient temperature appeared to be an important factor influencing the levels of isoprene SOA tracers. As Fig. 7 showed, the higher levels of isoprene SOA tracers always tracked higher temperature (except 2-methylglyceric acid) during our campaign, probably resulting from the enhanced isoprene emission strength and tracer formation rate under higher temperature (Rinne et al., 2002; Ion et al., 2005; Ding et al., 2008b).

The carbon contribution of 2-methyltetrols to OC was $0.07 \pm 0.04\%$ with the maximum of 0.19% during our campaign. The OC fraction of 2-methyltetrols was reported as 0.21–0.85% in southeastern US (Ding et al., 2008b), 0.74–2% in the Amazonian rain forest (Claeys et al., 2004), and 0.02–0.75% in the forest of Eastern China (Wang et al., 2008). Cao et al. (2003) reported average OC level of 14.7 $\mu g\,m^{-3}$ in the PRD mega-cities during winter 2001. Andreae et al. (2008) reported OC of 22.4 $\mu g\,m^{-3}$ during fall 2004 in urban Guangzhou. In the present study, OC

averaged as high as 19.3 $\mu g\,m^{-3}$. Consequently, although 2-methyltetrols in the present study exhibited comparable levels to those reported in the forest (Claeys et al., 2004; Ding et al., 2008b; Wang et al., 2008), their shares in aerosol OC were much lower due to much higher OC in the PRD region than those in forest areas.

The sum of five α-pinene SOA tracers ranged from 0.91 to 18.3 $ng\,m^{-3}$ with an average of $6.61 \pm 4.39\,ng\,m^{-3}$ (Table 1, Fig. 5b). Among the α-pinene SOA tracers, cis-pinonic acid had the highest level ($3.60 \pm 3.76\,ng\,m^{-3}$), while the concentrations of pinic acid ($1.25 \pm 0.79\,ng\,m^{-3}$) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA, $1.16 \pm 0.99\,ng\,m^{-3}$) were about one third of that of cis-pinonic acid. Only trace amounts of 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid (HDMGA) were detected. The levels of these tracers during our campaign were also comparable to those in the same season in US (Ding et al., 2008b; Lewandowski et al., 2008; Sheesley et al., 2004). Unlike the isoprene SOA tracers,
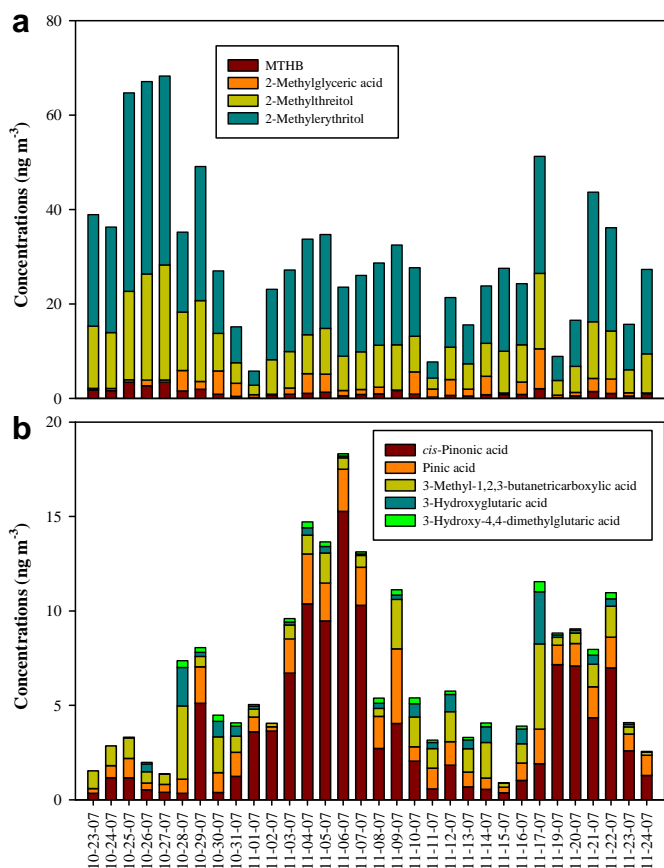
Fig. 5. Daily variation of isoprene (a) and α-pinene (b) SOA tracers.

Fig. 7. Correlations between isoprene SOA tracers and temperature. k is the slope of correlation.

α-pinene SOA tracers and temperature might be the result of counteraction of temperature effects on the precursor emission/tracer formation and gas/particle partitioning. Similarly, the sesquiterpene SOA tracer, β-caryophyllinic acid, also showed poor correlation with temperature ($p > 0.05$).

3.2. Correlations between SOA tracers and aerosol acidity

Previous chamber studies have revealed that acid-catalyzed heterogeneous reactions can significantly enhance SOA yields (Jang et al., 2002; Surratt et al., 2010). In this study, aerosol acidity ([H^+], μmol m^{-3}) was estimated using a charge balance of SO_4^{2-}, NO_3^- and NH_4^+ and calculated as below (Pathak et al., 2009):

$$\left[H^+\right] = 2 \times \left[SO_4^{2-}\right] + \left[NO_3^-\right] - \left[NH_4^+\right]$$

where [X] represents the molar concentration of the ion X. In this study, the estimated [H^+] in the particulate ranged from 0.15 to 0.77 μmol m^{-3}, which was in the same range in the major cities of China (Pathak et al., 2004, 2009).

Significant correlations were observed between the estimated [H^+] and the isoprene SOA tracers (Fig. 8a), reflecting the enhancement of isoprene SOA formation in the acidic aerosols in the PRD. The slopes for MTHB, 2-methylthreitol and 2-methylery-thritol were 3.6 ± 0.7, 22.9 ± 4.4 and 36.5 ± 9.2 ng m^{-3} per μmol [H^+] m^{-3}, respectively (Fig. 8a). Similar to chamber simulation (Surratt et al., 2007b), 2-methylglyceric acid had poor correlation with aerosol acidity in our ambient study (Fig. 8a). The slope of 2-methyltetrols vs. acidity was 59.4 ± 13.4 ng m^{-3} per μmol [H^+] m^{-3} or 26.2 ± 6.9 ngC m^{-3} per μmol [H^+] m^{-3}, which was more than 2 orders of magnitude lower than that (0.00925 μg C m^{-3} per nmol [H^+] m^{-3} or 9.25×10^3 ng C m^{-3} per μmol [H^+] m^{-3}) obtained in chamber studies (Surratt et al., 2007b; Offenberg et al., 2009).

There might be several reasons for the huge gap observed between chamber simulation and our ambient measurement in 2-methyltetrols' level responding to aerosol acidity. In consideration of the analytical aspects, the calibration standard used to determine 2-methyltetrols was erythritol in this study instead of cis-ketopinic acid (KPA) in the chamber studies (Surratt et al., 2007b; Offenberg et al., 2009). However, as reported by Hu et al. (2008), the uncertainty caused by using compounds other than KPA was estimated to be within a factor of 3, which is minor

the α-pinene SOA tracers showed poor correlations with temperature ($p > 0.05$, all tracers). Although high temperature could enhance both α-pinene emission (Guenther et al., 1995) and tracer formation, increasing temperature would favor the evaporation of these tracers from the particle phase into the gas phase (Saathoff et al., 2009). Therefore, the poor correlations observed between
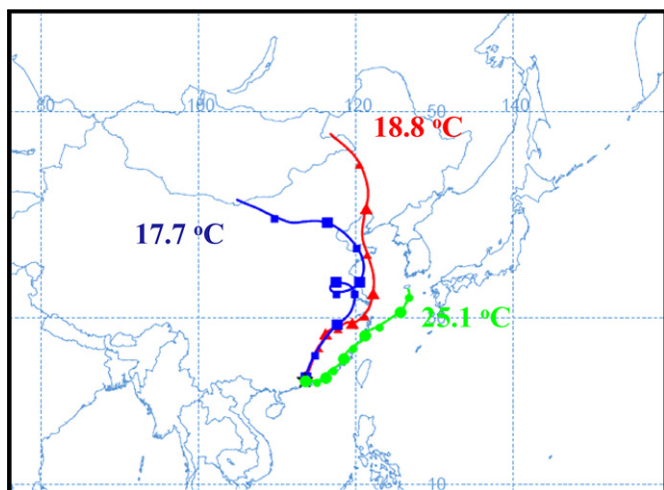

Fig. 6. Five-day back trajectories of air mass 100 m above ground on day Oct. 27 (green), Nov. 1 (blue) and Nov. 19 (red) using HYSPLIT 4.9 software from the Air Resources Laboratory (ARL) in NOAA (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).
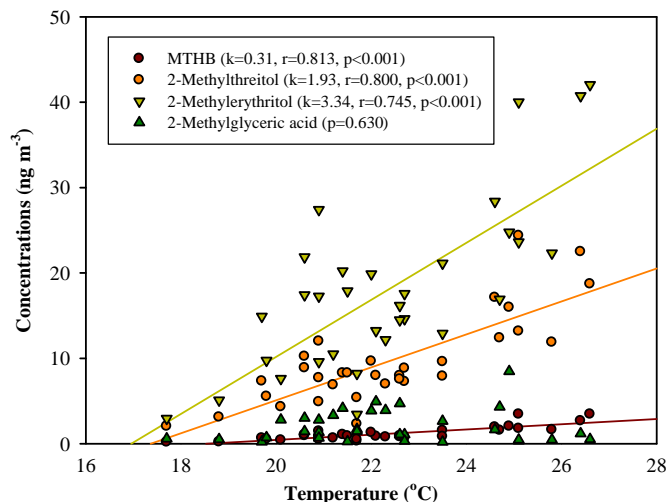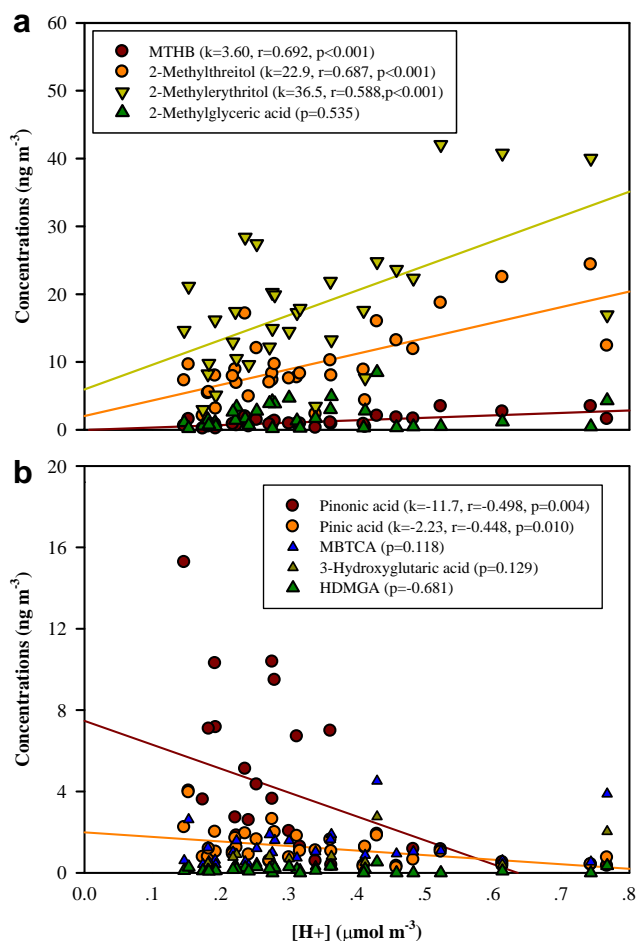
Fig. 8. Correlations of aerosol acidity with isoprene (a) and α-pinene (b) SOA tracers. *k* is the slope of correlation.

compared to 2 orders of magnitude for the observed difference in slopes. Also it is worth noting that the charge balance method was used to estimate aerosol acidity in the present study, while aerosol acidity was determined by measuring pH in the chamber studies (Surratt et al., 2007b; Offenberg et al., 2009). It should be stressed that the charge balance method may have uncertainties, since that only three water soluble ions were considered to estimate aerosol acidity, and that fine particles were not homogeneously mixed, i.e., some particles were not acidic while others were much more acidic. Thus, the two methods would result in difference in measured [H+] values, but such a difference was unlikely as huge as 2 orders of magnitude. Therefore, despite of the difference in above analytical methods, the major reason for the observed difference in slopes of 2-methyltetrols to [H+] should be that the ambient conditions were much more complicated than those in chamber simulation.

Firstly, up to now the effects of acidity on the formation of 2-methyltetrols in chamber studies (Surratt et al., 2007b; Offenberg et al., 2009) are limited to low RH (30%). During our field campaign, however, the RH values were much higher (40–83%). Higher RH was more likely to induce a relatively lower acidity in the aerosol droplets due to more water uptake; the enhancement of 2-methyltetrols formation by acidity was thus reduced. In this aspect, to give a sound explanation to the field results, further chamber studies are needed about the influence of RH on 2-methyltetrols formation, particularly of high RH as occurring in the PRD region. Secondly, ambient isoprene levels were quite different from those

in chambers. In the chamber studies (Surratt et al., 2007b; Offenberg et al., 2009), an excess of isoprene was maintained to decouple the influence of isoprene level on the simulation result; while in the ambient, mixing ratios of isoprene were often less than 1 ppbv and its emission from plants varied greatly during a day, typically reaching maximum at noon but nearly zero at night. Thirdly, the compositions of airborne species in both gas and particulate phases were much more complicated with even more complicated interactions than those in chambers. It may be true in the highly manipulated chamber studies that the acidity of the aerosol solely causes the increase of isoprene SOA tracers, but not so in the ambient. In the real atmosphere, isoprene SOA formation depends on not only aerosol acidity but also other factors, such as emission strength, reaction rate, and oxidant levels. Although it is not easy to figure out an explanation for the difference at present, the huge gap observed for the dependence of 2-methyltetrols on aerosol acidity between chamber simulation and our ambient measurement suggested that further chamber studies are needed especially under the situations as occurring in the PRD region to narrow the gap between chamber simulation and the real atmosphere.

Two α-pinene SOA tracers, *cis*-pinonic acid and pinic acid, exhibited negative correlations with the estimated [H+] with the slopes of -11.7 ± 3.7 and -2.23 ± 0.81 ng m^{-3} per μmol [H+] m^{-3}, respectively (Fig. 8b). Other three α-pinene SOA tracers did not show significant correlations with aerosol acidity ($p > 0.05$, Fig. 8b). The possible explanation for the negative correlation is the influence of aerosol acidity on the gas/particle partitioning. High acidity could result in more *cis*-pinonic acid and pinic acid in the molecular form in the aqueous solutions of the particle phase. These two acids were semi-volatile and typically dominant in gas phase (Yu et al., 1999). More *cis*-pinonic acid and pinic acid in the molecular form in particles under more acidic environment would favor their release from the particle phase into the gas phase, therefore the decreasing trend of these tracers in the particle phase would be expected with increasing aerosol acidity. The sesquiterpene-SOA tracer, β-caryophyllinic acid did not show significant correlation with aerosol acidity ($p > 0.05$).

Since *cis*-pinonic acid and pinic acid were the dominant compounds among the five α-pinene SOA tracers, the sum of α-pinene SOA tracers also exhibited the acidity dependence ($r = -0.41$, $p = 0.02$, $n = 32$) with a slope of -11.3 ± 4.6 ng m^{-3} per μmol [H+] m^{-3} or -7.8 ± 2.8 ng C m^{-3} per μmol [H+] m^{-3}. In the chamber study, the summed concentration of nine α-pinene tracers decreased linearly by 0.00380 μg C m^{-3} per nmol [H+] m^{-3} or 3.8×10^3 ng C m^{-3} per μmol [H+] m^{-3} (Offenberg et al., 2009). Since the remaining four tracers were not detected during our campaign (Fig. 2), the slope (-7.8 ± 2.8 ng C m^{-3} per μmol [H+] m^{-3}) observed in the current study could represent that of the whole nine tracers. This slope was also more than 2 orders of magnitude lower than that from above chamber study (Offenberg et al., 2009). Again, a huge gap was observed for the acidic dependence of α-pinene SOA tracers between chamber simulation and our ambient measurement, suggesting that further chamber studies are needed especially under the situations as occurring in the PRD region to narrow the gap between chamber simulation and the real atmosphere.

3.3. Implication of formation pathway for SOA tracers

As showed in Table 2a, significant correlations were observed between isoprene tracers except for 2-methylglyceric acid. As Surratt et al. (2010) proposed, 2-methyltetrols can be formed by further acid-catalyzed heterogeneous reactions of gaseous isoprene oxidation products, such as epoxydiols of isoprene (IEPOX) under

Table 2
Pearson coefficients for SOA tracers.[a]

	I-1	I-2	I-3	I-4		P-1	P-2	P-3	P-4	P-5
	(a) isoprene[b]					**(b) pinene[c]**				
I-1	1	0.007	**0.960**	**0.951**	P-1	1	**0.601**	−0.181	−0.302	−0.156
I-2		1	0.043	−0.043	P-2		1	0.26	−0.047	0.304
I-3			1	**0.956**	P-3			1	**0.888**	**0.776**
I-4				1	P-4				1	**0.706**
					P-5					1

[a] Numbers in bold and italics are indicative of $p < 0.01$ and $p < 0.05$, respectively.
[b] I-1 to I-4 are indicative of 3-methyl-2,3,4-trihydroxy-1-butene, 2-methyl-glyceric acid, 2-methylthreitol, and 2-methylerythritol, respectively.
[c] P-1 to P-5 are indicative of cis-pinonic acid, pinic acid, MBTCA, 3-hydroxyglutaric acid, and 3-hydroxy-4,4-dimethylglutaric acid, respectively.

low-NOₓ conditions. The particle-phase ring-opening reaction of IEPOX played an important role in the enhancement of 2-methyl-etetrols from 0.1 to 5.1 $\mu g\,m^{-3}$ when aerosol acidity increased from the neutral to the highly acidic (Surratt et al., 2010). During our sampling, NOₓ level was 31 ± 2 ppbv (Guo et al., 2009). Obviously, the rural site is a low-NOₓ case. Moreover, 2-methyletetrols exhibited significantly positive correlations with aerosol acidity in this study (Fig. 8a); and there was one order of magnitude enhancement of 2-methyltetrols (5.59 to 64.83 $ng\,m^{-3}$) with aerosol acidity increasing from 0.17 to 0.74 $\mu mol\,[H^+]\,m^{-3}$. Furthermore, since the C₅-alkene triol, MTHB also shares the same low-NOₓ formation pathway as 2-methyltetrols (Surratt et al., 2010), the good correlations between MTHB and 2-methyltetrols are expected, which were observed in the current study (Table 2a). All these indicated that acid-catalyzed heterogeneous reaction was the major formation pathway for 2-methyltetrols in the PRD region. The slope of 2-methylthreitol to 2-methylerythritol was 0.52 ± 0.03, quite near those reported in US (Ding et al., 2008b; Xia and Hopke, 2006; Yan et al., 2009), implying the ratio of the production rates for these two tracers might be relatively constant from place to place. On the other hand, 2-methylglyceric acid was not correlated with other tracers (Table 2a), indicating it had different formation mechanism from other isoprene SOA tracers. In fact, Surratt et al. (2010) proposed that 2-methylgriteric acid was produced by decomposition of C₄-hydroxynitrate-PAN in the aerosol phase under high-NOₓ conditions, which is quite different from the pathway of 2-methyltetrols under low-NOₓ conditions. It worth noting that 2-methylglyceric acid is an acid while other three isoprene SOA tracers are polyhydric alcohols. 2-Methylglyceric acid would, as discussed above, probably be more influenced by aerosol acidity in its gas/particle partitioning.

For α-pinene SOA tracers, interestingly, their correlations exhibited distinct patterns (Table 2b). cis-Pinonic acid and pinic acid were correlated well, while MBTCA, 3-hydroxyglutaric acid and HDMGA were significantly correlated with each other. However, the former two tracers showed poor correlations with the latter three. Although MBTCA has other precursors apart from α-pinene (Jaoui et al., 2005; Szmigielski et al., 2007), the significant correlations among MBTCA, 3-hydroxyglutaric acid and HDMGA suggested α-pinene was probably its major precursor. Previous studies proposed that cis-pinonic acid and pinic acid could further photo-degrade to MBTCA (Claeys et al., 2007; Szmigielski et al., 2007), which partly explained the relatively low or undetectable levels of cis-pinonic acid and pinic acid in the air (Hu et al., 2008; Wang et al., 2008). If such a photo-degradation process does exist in the real atmosphere, the ratio of cis-pinonic acid plus pinic acid to MBTCA (P/M) can be employed to check the aging of α-pinene SOA. Higher P/M ratio indicates less transformation of cis-pinonic acid and pinic acid to MBTCA and thus α-pinene SOA is relatively fresh; while lower P/M ratio points to relatively aged α-pinene SOA.
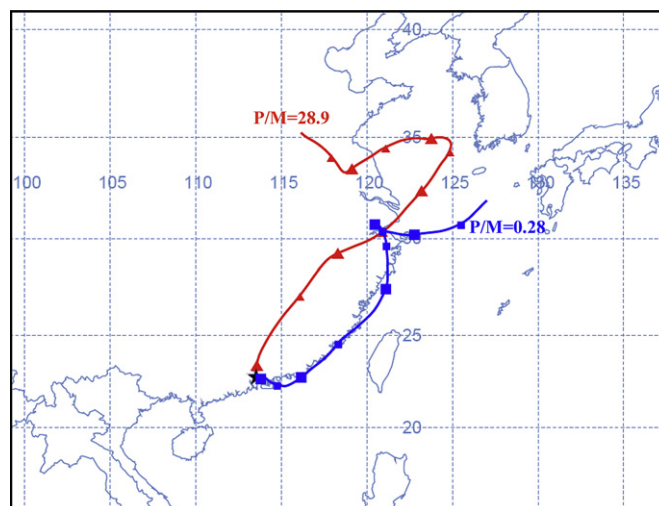

Fig. 9. Five-day back trajectory of air mass on the day when P/M ratio was the highest (Nov. 06) and the lowest (Oct. 28), respectively.

In the current study, the lowest P/M ratio (0.28) was observed when the air mass came from the eastern seashore; while the highest P/M (28.9) coupled with the air mass from the continent (Fig. 9). Since there should have fresh input of α-pinene in the land but not so over the sea, α-pinene SOA from the eastern seashore would be more aged compared to that from the continent. The P/M ratios averaged 7.19 ± 7.48, indicating that overall the α-pinene SOA tracers were relatively fresh during our campaign.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2010.11.057.

References

Andreae, M.O., Schmid, O., Yang, H., Chand, D., Zhen Yu, J., Zeng, L.M., Zhang, Y.H., 2008. Optical properties and chemical composition of the atmospheric aerosol in urban Guangzhou, China. Atmospheric Environment 42, 6335–6350.

Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K., Chow, J.C., Watson, J.G., 2003. Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period. Atmospheric Environment 37, 1451–1460.

Cao, J.J., Lee, S.C., Ho, K.F., Zou, S.C., Fung, K., Li, Y., Watson, J.G., Chow, J.C., 2004. Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China. Atmospheric Environment 38, 4447–4456.

Carlton, A.G., Pinder, R.W., Bhave, P.V., Pouliot, G.A., 2010. To what extent can biogenic SOA be controlled? Environmental Science & Technology 44, 3376–3380.

Chan, C.K., Yao, X., 2008. Air pollution in mega cities in China. Atmospheric Environment 42, 1–42.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., Maenhaut, W., 2004. Formation of secondary organic aerosols through photooxidation of isoprene. Science 303, 1173–1176.

Claeys, M., Szmigielski, R., Kourtchev, I., VanderVeken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., Edney, E.O., 2007. Hydroxydicarboxylic acids: markers for secondary organic aerosol from the photooxidation of α-pinene. Environmental Science & Technology 41, 1628–1634.

Ding, X., Zheng, M., Edgerton, E.S., Jansen, J.J., Wang, X., 2008a. Contemporary or fossil origin: split of estimated secondary organic carbon in the southeastern United States. Environmental Science & Technology 42, 9122–9128.

Ding, X., Zheng, M., Yu, L., Zhang, X., Weber, R.J., Yan, B., Russell, A.G., Edgerton, E.S., Wang, X., 2008b. Spatial and seasonal trends in biogenic secondary organic aerosol tracers and water-soluble organic carbon in the southeastern United States. Environmental Science & Technology 42, 5171–5176.

Duan, J., Tan, J., Cheng, D., Bi, X., Deng, W., Sheng, G., Fu, J., Wong, M.H., 2007. Sources and characteristics of carbonaceous aerosol in two largest cities in Pearl River Delta Region, China. Atmospheric Environment 41, 2895–2903.

Griffin, R.J., Cocker III, D.R., Seinfeld, J.H., Dabdub, D., 1999. Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons. Geophysical Research Letters 26, 2721–2724.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100, 8873–8892.

Guo, H., Jiang, F., Cheng, H.R., Simpson, I.J., Wang, X.M., Ding, A.J., Wang, T.J., Saunders, S.M., Wang, T., Lam, S.H.M., Blake, D.R., Zhang, Y.L., Xie, M., 2009. Concurrent observations of air pollutants at two sites in the Pearl River Delta and the implication of regional transport. Atmospheric Chemistry and Physics 9, 7343–7360.

Han, Z.W., Zhang, R.J., Wang, Q.G., Wang, W., Cao, J.J., Xu, J., 2008. Regional modeling of organic aerosols over China in summertime. Journal of Geophysical Research 113. doi:10.1029/2007JD009436.

Henze, D.K., Seinfeld, J.H., 2006. Global secondary organic aerosol from isoprene oxidation. Geophysical Research Letters 33, L09812. doi:10.1029/2006GL025976.

Hoyle, C.R., Myhre, G., Berntsen, T.K., Isaksen, I.S.A., 2009. Anthropogenic influence on SOA and the resulting radiative forcing. Atmospheric Chemistry and Physics 9, 2715–2728.

Hu, D., Bian, Q., Li, T.W.Y., Lau, A.K.H., Yu, J.Z., 2008. Contributions of isoprene, monoterpenes, β -caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006. Journal of Geophysical Research 113, D22206. doi:10.1029/2008JD010437.

Ion, A.C., Vermeylen, R., Kourtchev, I., Cafmeyer, J., Chi, X., Gelencsér, A., Maenhaut, W., Claeys, M., 2005. Polar organic compounds in rural PM2.5 aerosols from K-puszta, Hungary, during a 2003 summer field campaign: sources and diurnal variations. Atmospheric Chemistry and Physics 5, 1805–1814.

Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814–817.

Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., Edney, E.O., 2005. Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups. 2. organic tracer compounds from monoterpenes. Environmental Science & Technology 39, 5661–5673.

Jaoui, M., Lewandowski, M., Kleindienst, T.E., Offenberg, J.H., Edney, E.O., 2007. β-Caryophyllinic acid: an atmospheric tracer for β-caryophyllene secondary organic aerosol. Geophysical Research Letters 34, L05816. doi:10.1029/2006GL028827.

Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Lewis, C.W., Bhave, P.V., Edney, E.O., 2007. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. Atmospheric Environment 41, 8288–8300.

Leung, D.Y.C., Wong, P., Cheung, B.K.H., Guenther, A., 2010. Improved land cover and emission factors for modeling biogenic volatile organic compounds emissions from Hong Kong. Atmospheric Environment 44, 1456–1468.

Lewandowski, M., Jaoui, M., Offenberg, J.H., Kleindienst, T.E., Edney, E.O., Sheesley, R.J., Schauer, J.J., 2008. Primary and secondary contributions to ambient PM2.5 in the midwestern United States. Environmental Science & Technology 42, 3303–3309.

NIOSH, 1999. Method 5040 Issue 3 (Interim): elemental carbon (diesel exhaust). In: NIOSH Manual of Analytical Methods. National Institute of Occupational Safety and Health, Cincinnati, OH.

Offenberg, J.H., Lewandowski, M., Edney, E.O., Kleindienst, T.E., Jaoui, M., 2009. Influence of aerosol acidity on the formation of secondary organic aerosol from biogenic precursor hydrocarbons. Environmental Science & Technology 43, 7742–7747.

Pathak, R.K., Louie, P.K.K., Chan, C.K., 2004. Characteristics of aerosol acidity in Hong Kong. Atmospheric Environment 38, 2965–2974.

Pathak, R.K., Wu, W.S., Wang, T., 2009. Summertime PM$_{2.5}$ ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. Atmospheric Chemistry and Physics 9, 1711–1722.

Piccot, S., Watson, J., Jones, J., 1992. A global inventory of volatile organic compound emissions from anthropogenic sources. Journal of Geophysical Research 97 (D9), 9897–9912.

Rinne, H.J.I., Guenther, A.B., Greenberg, J.P., Harley, P.C., 2002. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. Atmospheric Environment 36, 2421–2426.

Saathoff, H., Naumann, K.H., Möhler, O., JonssonÅ, M., Hallquist, M., Kiendler-Scharr, A., Mentel, T.F., Tillmann, R., Schurath, U., 2009. Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α-pinene and limonene. Atmospheric Chemistry and Physics 9, 1551–1577.

Sheesley, R.J., Schauer, J.J., Bean, E., Kenski, D., 2004. Trends in secondary organic aerosol at a remote site in Michigan's Upper Peninsula. Environmental Science & Technology 38, 6491–6500.

Stone, E.A., Zhou, J., Snyder, D.C., Rutter, A.P., Mieritz, M., Schauer, J.J., 2009. A comparison of summertime secondary organic aerosol source contributions at contrasting urban locations. Environmental Science & Technology 43, 3448–3454.

Surratt, J.D., Kroll, J.H., Kleindienst, T.E., Edney, E.O., Claeys, M., Sorooshian, A., Ng, N.L., Offenberg, J.H., Lewandowski, M., Jaoui, M., Flagan, R.C., Seinfeld, J.H., 2007a. Evidence for organosulfates in secondary organic aerosol. Environmental Science & Technology 41, 517–527.

Surratt, J.D., Lewandowski, M., Offenberg, J.H., Jaoui, M., Kleindienst, T.E., Edney, E.O., Seinfeld, J.H., 2007b. Effect of acidity on secondary organic aerosol formation from isoprene. Environmental Science & Technology 41, 5363–5369.

Surratt, J.D., Gmez-Gonzalez, Y., Chan, A.W.H., Vermeylen, R., Shahgholi, M., Kleindienst, T.E., Edney, E.O., Offenberg, J.H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R.C., Seinfeld, J.H., 2008. Organosulfate formation in biogenic secondary organic aerosol. The Journal of Physical Chemistry A 112, 8345–8378.

Surratt, J.D., Chan, A.W.H., Eddingsaas, N.C., Chan, M., Loza, C.L., Kwan, A.J., Hersey, S.P., Flagan, R.C., Wennberg, P.O., Seinfeld, J.H., 2010. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. Proceedings of the National Academy of Sciences of the United States of America 107, 6640–6645.

Szmigielski, R., Surratt, J.D., Gómez-González, Y., Veken, P.V.D., Kourtchev, I., Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., Edney, E.O., Seinfeld, J.H., Maenhaut, W., Claeys, M., 2007. 3-Methyl-1,2,3-butanetricarboxylic acid: an atmospheric tracer for terpene secondary organic aerosol. Geophysical Research Letters 34, L24811. doi:10.1029/2007GL031338.

Tanner, R.L., Olszyna, K.J., Edgerton, E.S., Knipping, E., Shaw, S.L., 2009. Searching for evidence of acid-catalyzed enhancement of secondary organic aerosol formation using ambient aerosol data. Atmospheric Environment 43, 3440–3444.

USEPA, 2006. National Ambient Air Quality Standards (NAAQS). Available from: http://www.epa.gov/air/criteria.html.

Wang, T., Poon, C.N., Kwok, Y.H., Li, Y.S., 2003a. Characterizing the temporal variability and emission patterns of pollution plumes in the Pearl River Delta of China. Atmospheric Environment 37, 3539–3550.

Wang, T., Wei, X.L., Ding, A.J., Poon, C.N., Lam, K.S., Li, Y.S., Chan, L.Y., Anson, M., 2009. Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007. Atmospheric Chemistry and Physics 9, 6217–6227.

Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, i., Claeys, M., 2005. Characterization of oxygenated derivatives of isoprene related to 2-methyletrols in Amazonian aerosols using trimethylsilylation and gas chromatography/ ion trap mass spectrometry. Rapid Communications in Mass Spectrometry 19, 1343–1351.

Wang, W., Wu, M.H., Li, L., Zhang, T., Li, H.J., Wang, Y.J., Liu, X.D., Sheng, G.Y., Claeys, M., Fu, J.M., 2008. Polar organic tracers in PM2.5 aerosols from forests in eastern China. Atmospheric Chemistry and Physics 8, 7507–7518.

Wang, Z., Bai, Y., Zhang, S., 2003b. A biogenic volatile organic compounds emission inventory for Beijing. Atmospheric Environment 37, 3771–3782.

Weber, R.J., Sullivan, A.P., Peltier, R.E., Russell, A., Yan, B., Zheng, M., de Gouw, J.A., Warneke, C., Brock, C., Holloway, J.S., Atlas, E.L., Edgerton, E., 2007. A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. Journal of Geophysical Research 112, D13302. doi:10.1029/2007JD008408.

Wu, D., Tie, X., Li, C., Ying, Z., Kai-Hon Lau, A., Huang, J., Deng, X., Bi, X., 2005. An extremely low visibility event over the Guangzhou region: a case study. Atmospheric Environment 39, 6568–6577.

Xia, X., Hopke, P.K., 2006. Seasonal variation of 2-methyltetrols in ambient air samples. Environmental Science & Technology 40, 6934–6937.

Xu, H., Wang, X., Pöesch, U., Feng, S., Wu, D., Yang, L., Li, S., Song, W., Sheng, G., Fu, J., 2008. Genotoxicity of total and fractionated extractable organic matter in fine air particulate matter from urban Guangzhou: comparison between haze and nonhaze episodes. Environmental Toxicology & Chemistry 27, 206–212.

Yan, B., Zheng, M., Hu, Y., Ding, X., Sullivan, A.P., Weber, R.J., Baek, J., Edgerton, E.S., Russell, A.G., 2009. Roadside, urban, and rural comparison of primary and secondary organic molecular markers in ambient PM$_{2.5}$. Environmental Science & Technology 43, 4287–4293.

Yu, J., Griffin, R.J., Cocker III, D.R., Flagan, R.C., Seinfeld, J.H., Blanchard, P., 1999. Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. Geophysical Research Letters 26, 1145–1148.

Zhang, Q., Jimenez, J.L., Worsnop, D.R., Canagaratna, M., 2007. A case study of urban particle acidity and its influence on secondary organic aerosol. Environmental Science & Technology 41, 3213–3219.

Zhang, R., Wang, L., Khalizov, A.F., Zhao, J., Zheng, J., McGraw, R.L., Molina, L.T., 2009. Formation of nanoparticles of blue haze enhanced by anthropogenic pollution. Proceedings of the National Academy of Sciences of the United States of America 106, 17650–17654.

Zheng, J., Zheng, Z., Yu, H., Zhong, L., 2010. Temporal, spatial characteristics and uncertainty of biogenic VOC emissions in the Pearl River Delta region, China. Atmospheric Environment 44, 1960–1969.