# Tracer-based estimation of secondary organic carbon in the Pearl River Delta, south China

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[1]   Fine particles ($PM_{2.5}$) were collected using filter-based high-volume samplers during summer-winter 2008 at a rural site in the central Pearl River Delta (PRD), south China, to determine typical secondary organic aerosol (SOA) tracers from significant biogenic (isoprene, monoterpenes, and sesquiterpenes) and anthropogenic (aromatics) precursors. Average isoprene SOA tracers were significantly higher during summer (126 ng m$^{-3}$) than during fall-winter (25.1 ng m$^{-3}$), owing largely to the higher isoprene emission and reaction rates in summer. Average monoterpene SOA tracers during summer (11.6 ng m$^{-3}$) and fall-winter (16.4 ng m$^{-3}$) showed much less difference compared to isoprene SOA tracers, probably resulting from the counteracting effects of temperature on the precursor emission/tracer formation and on gas/particle partitioning. The concentrations of the aromatics' SOA tracer (2,3-dihydroxy-4-oxopentanoic acid) ranged from 1.70 to 52.0 ng m$^{-3}$ with an average of 15.1 ng m$^{-3}$, which was the highest reported in ambient air. The secondary organic carbon (SOC) estimated by the SOA-tracer method averaged 3.07 $\mu$g C m$^{-3}$ in summer and 2.00 $\mu$g C m$^{-3}$ in fall-winter, contributing 38.4% and 8.7% to OC, respectively. During summer, aromatics-SOC and isoprene-SOC reached 2.25 $\pm$ 1.5 $\mu$g C m$^{-3}$ and 0.64 $\pm$ 0.7 $\mu$g C m$^{-3}$ and accounted for 76% and 18% of the estimated SOC, respectively, while during fall-winter, aromatics-SOC (1.64 $\pm$ 1.4 $\mu$g C m$^{-3}$) was dominant with a share of 79% in total estimated SOC. These results indicated that anthropogenic aromatics were dominant SOC precursors in the highly industrialized and urbanized PRD region. During summer, SOC levels estimated by elemental carbon (EC) tracer method were not only consistent with but also correlated well with those by SOA-tracer method. During fall-winter, however, SOC by SOA-tracer method was only about one third of that by EC-tracer method. Their gaps were significantly correlated with the biomass burning tracer levoglucosan, indicating that input from biomass burning emission with very high ratios of OC/EC during fall-winter would result in an overestimate of SOC by EC-tracer method. Therefore cautions should be taken when estimating SOC by EC-tracer method, especially when biomass burning exhibits significant influences.

## 1.  Introduction

[2]   Secondary organic aerosols (SOA) are produced by homogenous [*Claeys et al.*, 2004] and heterogeneous [*Jang et al.*, 2002] reactions of volatile organic compounds (VOCs) as well as aging of primary aerosols [*Jimenez et al.*, 2009] in the air. 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. To fully establish the role of SOA in climate or air quality models, comprehensive knowledge about SOA formation mechanisms is still urgently needed, although great improvement has been achieved in the last decade for the understanding of SOA. As for SOA precursors, global emissions of anthropogenic VOCs (e.g., aromatics) were very minor as compared to those of biogenic VOCs (terpenes) [*Piccot et al.*, 1992; *Guenther et al.*, 1995], about 90% of global SOA were believed to be due to biogenic VOCs [*Kanakidou et al.*, 2005]. However, recent field studies suggested that anthropogenic SOA might be more

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significant than previously thought. On the basis of the observation in Mexico City and extrapolation of the results to the other urban areas, *Volkamer et al.* [2006] estimated the global anthropogenic SOA to be 3–25 Tg $yr^{-1}$, accounting for one third of global SOA. In the United States, urban VOCs were estimated to produce 2.1 Tg $yr^{-1}$ of secondary organic matter (SOM) which dominated over biogenic SOM [*de Gouw et al.*, 2008]. The dominant role of anthropogenic secondary organic carbon (SOC) was also observed in the urban areas in the United States, such as Birmingham [*Ding et al.*, 2008a] and Cleveland, Detroit, and Riverside [*Stone et al.*, 2009]. Moreover, anthropogenic emissions in urban regions might accelerate oxidation of biogenic VOCs [*Weber et al.*, 2007]. *Carlton et al.* [2010] examined the impact of reducing anthropogenic emissions on production of biogenic SOA using CMAQ model. Their modeling results indicated that the closure of all controllable anthropogenic emissions could induce significant reductions of biogenic SOAs by more than 50% or $\sim 1$ $\mu g$ $m^{-3}$. These findings suggest important contributions of anthropogenic sources to SOA particularly in the polluted regions.

[3] To gain insight into ambient SOC, observation-based approaches have been developed to estimate SOC from the bulk to the individual. elemental carbon (EC)-tracer method is a widely applied approach, using EC as the tracer for primary sources and calculating primary OC (POC) in ambient samples with the OC/EC ratios obtained from primary emissions and measured ambient OC and EC levels [*Turpin and Huntzicker*, 1995]. Also there were attempts by receptor models. *Zheng et al.* [2002] used chemical mass balance (CMB) model to apportion POC and attributed the unexplained OC as SOC. *Yuan et al.* [2006] tried direct estimation of SOC with the input of secondary species when applying positive matrix factorization (PMF) model. *Ding et al.* [2008b] approximated ambient SOC in the southeastern United States by subtracting water-soluble organic carbon (WSOC) with OC from wood burning. The newly developed aerosol mass spectrometry (AMS) is an approach with high time resolution. Very recently, *Sun et al.* [2011] concluded that the less oxidized part of oxygenated organic aerosol (OOA) identified by AMS is associated with SOA. In addition to above methods for the estimation of bulk SOC, further knowledge about SOA from different precursors or processes is also of great interest for both scientific and regulatory bodies.

[4] Radiocarbon (^{14}C) analysis is a powerful tool to separate ambient SOC into fossil or contemporary origins. *Schichtel et al.* [2008] combined the EC-tracer method with total carbon ^{14}C data to estimate the relative contributions of contemporary and fossil SOC throughout the United States in summer. *Ding et al.* [2008a] used CMB model in conjunction with carbon isotope results to study the spatial and seasonal variations of fossil and contemporary SOC in the southeastern United States. *Gelencsér et al.* [2007] also estimated the fossil and nonfossil sources of SOC over Europe on the basis of their measurements of radiocarbon, OC, EC, and organic tracers.

[5] More detailed information of SOC precursors can be obtained by a SOA-tracer method developed by *Kleindienst et al.* [2007]. On the basis of the smog chamber experiments, they identified a series of tracer compounds in SOA derived from isoprene, $\alpha$-pinene, $\beta$-caryophyllene and toluene. The ratios of these tracers to SOA or to SOC obtained from the

chamber simulation were used to estimate SOA or SOC from different precursors with measured tracers' levels in ambient samples, given that precursor-tracer-SOA/SOC relationships are the same in the ambient as in the chamber [*Kleindienst et al.*, 2007]. *Lewandowski et al.* [2008] found the measured OC in the midwestern United States could be fully explained by POC from CMB model plus SOC from the SOA-tracer method, suggesting the secondary organic tracer technique could be a valuable method for SOC estimation. *Kleindienst et al.* [2010] further compared the estimated SOC by SOA-tracer method and other four independent methods (multiple regressions, CMB, carbon isotope and EC-tracer) in the southeastern United States and found that these five methods matched reasonably well. The SOC apportionment results were also comparable between SOA-tracer method and PMF model [*Zhang et al.*, 2009; *Hu et al.*, 2010]. As summarized by *Hallquist et al.* [2009], EC-tracer method and SOA-tracer method are two major indirect SOA estimation techniques based on tracers. SOC estimated by the two methods during summer time were consistent with each other at U.S. SEARCH network sites [*Kleindienst et al.*, 2010]. Although SOA-tracer method seemed to be a convincing approach to link SOA and its precursors from previous studies, it is still uncertain whether the precursor-tracer-SOA relationships derived from chamber studies can be successfully applied to the complex ambient situations, particularly in heavily polluted regions.

[6] The Pearl River Delta (PRD) in south China is one of the most industrialized and densely populated regions in China. The rapid growth in economy has resulted in fast increase in anthropogenic emissions of air pollutants in this region [*Chan and Yao*, 2008]. Aromatic hydrocarbons as important anthropogenic SOA precursors showed elevated levels in ambient air [*Lee et al.*, 2002; *Wang et al.*, 2002; *Zhao et al.*, 2004; *Chan et al.*, 2006; *Barletta et al.*, 2008; *Liu et al.*, 2008]. On the other hand, biogenic emissions in the region are expected to be significant [*Zheng et al.*, 2010] since the PRD is located in the subtropical area with the annual temperature of $\sim 25°C$ and more evergreen vegetation. Considering the high precursor emissions, the high atmospheric oxidative capacity [*Chan and Yao*, 2008], and the high aerosols acidity [*Ding et al.*, 2011], SOA should be an important component of particles in the PRD. In fact, previous studies, mostly based on EC-tracer method, found that the estimated SOC shared about 50% of ambient OC in the PRD even during winter [*Cao et al.*, 2003, 2004]. In the current study, 24 h $PM_{2.5}$ samples were collected consecutively at a regional background site in the central PRD during summer and fall-winter, respectively; and the SOA tracers from isoprene, monoterpenes, $\beta$-caryophyllene and aromatics were measured. The purposes are (1) to acquire the seasonal variations of biogenic and anthropogenic SOA tracers, (2) to assess the role of anthropogenic precursors in SOA formation in the highly industrialized and urbanized PRD region, and (3) to compare SOC estimated by SOA-tracer method with that by EC-tracer method.

## 2. Experimental Section

### 2.1. Field Sampling

[7] $PM_{2.5}$ samples were collected using a high-volume sampler (Tisch Environmental, Inc.) at a rate of 1.1 $m^3$

**Figure 1.** Sampling site Wangqingsha (WQS).

min$^{-1}$ at a rural site, Wangqingsha (WQS, 22°42′N, 113°32′E) in the PRD. As Figure 1 shows, the sampling site is located in the central PRD and surrounded by city clusters (e.g., Hong Kong, Guangzhou, Shenzhen, Foshan, and Dongguan) about 60 km away and adjacent to the Pearl River estuary. The sampler was placed on the rooftop, about 30 m above ground, of a seven-floor building on the campus of 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 of air pollution in the PRD [*Guo et al.*, 2009]. Field campaigns were carried out in summer (28 August to 21 September 2008) and fall-winter (10 November to 9 December 2008). Twenty-four hour sampling (19:00–19:00 LT) was taken during both campaigns. Prefired 8 × 10 inch quartz filters were covered with aluminum foil and stored in a bag containing silica gel at 4°C before sample collection and at −20°C after collection. A total of 52 field samples (22 in summer and 30 in fall-winter) and four field blanks were collected.

## 2.2. Chemical Analysis

[8] 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 [*National Institute of Occupational Safety and Health*, 1999] by an OC/EC Analyzer (Sunset Laboratory Inc.).

[9] For the analysis of SOA tracers, the detailed description is elsewhere [*Ding et al.*, 2011]. Briefly, filters were extracted three times by sonication with 40 mL of dichloride methane (DCM)/methanol (1:1, v/v) 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 of the concentrated extracts was separated into two parts. One was blown to dryness under a gentle stream of nitrogen, and kept at room temperature for 1 h to derivatize acids to methyl esters after adding 200 $\mu$L of DCM, 10 $\mu$L of methanol and 300 $\mu$L of fresh prepared diazomethane. The methylated extract was blown to 200 $\mu$L

and analyzed for $\alpha$-pinene SOA tracers (*cis*-pinonic acid, pinic acid and 3-methyl-1,2,3-butanetricarboxylic acid) by a gas chromatography–mass selective detector (GC-MSD). The second part was blown to dryness for derivatization with 100 $\mu$L of pyridine and 200 $\mu$L of *N*,*O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) in an oven at 70°C for 1 h. The silylated extract was analyzed for $\alpha$-pinene SOA tracers (3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid), isoprene SOA tracers (C$_5$-alkentrols, 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol), $\beta$-caryophyllene SOA tracer ($\beta$-caryophyllinic acid), toluene SOA tracer (2,3-dihydroxy-4-oxopentanoic acid) and levoglucosan. The typical total ion chromatograms for methylated and silylated compounds are presented elsewhere [*Ding et al.*, 2011]. As suggested by *Kleindienst et al.* [2007], $\alpha$-pinene SOA tracers were also detected in laboratory-generated $\beta$-pinene and *d*-limonene SOA [*Jaoui et al.*, 2005]. The toluene SOA tracer, 2,3-dihydroxy-4-oxopentanoic acid, was also formed during photooxidation of other aromatic compounds, such as xylenes [*Kleindienst et al.*, 2007]. Thus, it is reasonable to attribute tracers of $\alpha$-pinene to monoterpenes, and the tracer of toluene to aromatics. In the following text, we use monoterpenes instead of $\alpha$-pinene and aromatics instead of toluene when discussing the precursors.

[10] Samples were analyzed by an Agilent 5975 GC-MSD in the scan mode with a 30 m HP-5 MS capillary column. Splitless injection of a 1 $\mu$L sample was performed. The GC temperature was initiated at 65°C (held for 2 min) and increased to 290°C at a rate of 5°C min$^{-1}$ then held for 20 min. *cis*-Pinonic acid, pinic acid and levoglucosan were quantified by authentic standards. Owing to a lack of standards, isoprene SOA tracers were quantified using erythritol [*Claeys et al.*, 2004; *Ding et al.*, 2008b]; monoterpene SOA tracers (3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid) were quantified using pinic acid; $\beta$-caryophyllinic acid and 2,3-dihydroxy-4-oxopentanoic acid were quantified using octadecanoic acid and azelaic acid, respectively,

**Table 1.** Summary of SOA Tracers (ng m$^{-3}$)

| | Summer | | | | Fall-Winter | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | Median | Minimum | Maximum | Mean | Median | Minimum | Maximum | S/F[a] |
| Temperature (°C) | 29.0 | 29.2 | 25.8 | 31.3 | 22.6 | 22.1 | 17.6 | 27.6 | |
| RH (%) | 66 | 65 | 54 | 81 | 47 | 47 | 23 | 73 | |
| PM$_{2.5}$ ($\mu$g m$^{-3}$) | 80.2 | 74.8 | 25.5 | 148 | 103 | 104 | 46.7 | 157 | 0.78 |
| Sulfate ($\mu$g C m$^{-3}$) | 23.0 | 21.7 | 8.41 | 46.8 | 15.9 | 15.1 | 7.97 | 29.8 | 1.45 |
| OC ($\mu$g C m$^{-3}$) | 7.78 | 7.43 | 1.92 | 13.7 | 22.5 | 22.6 | 10.1 | 43.7 | 0.35 |
| EC ($\mu$g C m$^{-3}$) | 2.38 | 2.25 | 0.69 | 5.07 | 4.29 | 4.23 | 2.47 | 7.05 | 0.55 |
| OC/EC | 3.41 | 3.31 | 1.99 | 5.45 | 5.29 | 5.03 | 3.74 | 9.57 | 0.64 |
| *Isoprene SOA Tracers (ng m$^{-3}$)* | | | | | | | | | |
| cis-2-Methyl-1,3,4-trihydroxy-1-butene | 7.71 | 2.00 | 0.08 | 34.14 | 1.00 | 0.65 | 0.06 | 4.20 | 7.73 |
| 3-Methyl-2,3,4-trihydroxy-1-butene | 4.96 | 1.67 | 0.14 | 21.8 | 0.76 | 0.44 | 0.09 | 2.62 | 6.49 |
| trans-2-Methyl-1,3,4-trihydoxy-1-butene | 14.2 | 4.50 | 0.26 | 56.7 | 2.53 | 1.67 | 0.18 | 8.64 | 5.62 |
| 2-Methylglyceric acid | 7.71 | 6.45 | 0.86 | 25.9 | 4.75 | 4.03 | 1.40 | 14.7 | 1.62 |
| 2-Methylthreitol | 25.6 | 12.7 | 1.36 | 98.2 | 5.14 | 3.34 | 0.68 | 18.3 | 4.99 |
| 2-Methylerythritol | 65.9 | 35.2 | 3.61 | 221 | 10.9 | 7.08 | 1.66 | 40.0 | 6.05 |
| C$_5$-alkenetriols[b] | 26.9 | 8.13 | 0.48 | 113 | 4.29 | 3.08 | 0.40 | 15.1 | 6.27 |
| 2-Methyltetrols[c] | 91.5 | 49.2 | 4.97 | 319 | 16.0 | 10.3 | 2.34 | 58.3 | 5.71 |
| Sum of isoprene SOA tracers | 126 | 64.8 | 8.58 | 451 | 25.1 | 19.6 | 4.14 | 85.2 | 5.03 |
| *Monoterpenes SOA Tracers (ng m$^{-3}$)* | | | | | | | | | |
| cis-Pinonic acid | 1.69 | 0.53 | nd[d] | 10.7 | 6.73 | 5.76 | 0.64 | 39.3 | 0.25 |
| Pinic acid | 0.70 | 0.34 | nd[d] | 3.14 | 0.99 | 0.79 | 0.24 | 2.52 | 0.71 |
| 3-Methyl-1,2,3-butanetricarboxylic acid | 4.95 | 3.20 | 0.09 | 22.4 | 3.56 | 1.51 | 0.07 | 13.9 | 1.39 |
| 3-Hydroxyglutaric acid | 2.62 | 1.82 | 0.27 | 15.2 | 3.57 | 2.43 | 0.38 | 14.7 | 0.74 |
| 3-Hydroxy-4,4-dimethylglutaric acid | 1.61 | 0.66 | nd[d] | 11.8 | 1.59 | 0.61 | nd[d] | 7.15 | 1.02 |
| Sum of monoterpene tracers | 11.6 | 8.49 | 0.49 | 50.3 | 16.4 | 13.9 | 4.72 | 42.7 | 0.70 |
| *$\beta$-Caryophyllene SOA Tracer (ng m$^{-3}$)* | | | | | | | | | |
| $\beta$-Caryophyllenic acid | 2.87 | 2.53 | 0.50 | 11.8 | 3.25 | 2.74 | 0.53 | 13.4 | 0.88 |
| *Aromatics SOA Tracer (ng m$^{-3}$)* | | | | | | | | | |
| 2,3-Dihydroxy-4-oxopentanoic acid | 17.8 | 16.5 | 2.84 | 52.0 | 13.1 | 9.53 | 1.70 | 48.9 | 1.36 |
| *Biomass Burning Tracer (ng m$^{-3}$)* | | | | | | | | | |
| Levoglucosan | 81.0 | 70.8 | 27.1 | 168 | 310 | 270 | 80.5 | 1156 | 0.26 |
| *SOC ($\mu$g C m$^{-3}$)* | | | | | | | | | |
| Isoprene | 0.64 | 0.37 | 0.05 | 2.19 | 0.13 | 0.11 | 0.02 | 0.47 | 4.78 |
| Monoterpenes | 0.05 | 0.04 | 0.00 | 0.22 | 0.07 | 0.06 | 0.02 | 0.18 | 0.70 |
| $\beta$-Caryophyllene | 0.12 | 0.11 | 0.02 | 0.51 | 0.14 | 0.12 | 0.02 | 0.58 | 0.88 |
| Aromatics | 2.25 | 2.08 | 0.36 | 6.58 | 1.65 | 1.21 | 0.22 | 6.19 | 1.36 |
| SOC by SOA-tracer method | 3.07 | 2.83 | 0.45 | 8.24 | 2.00 | 1.49 | 0.30 | 7.41 | 1.54 |
| SOC by EC-tracer method | 3.19 | 3.40 | 0.39 | 8.54 | 6.72 | 5.00 | 0.52 | 26.7 | 0.48 |

[a]S/F means the ratio of summer to fall-winter.
[b]The C5-alkenetriols are the sum of cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, and trans-2-methyl-1,3,4-trihydoxy-1-butene.
[c]The 2-methyltetrols are the sum of 2-methylthreitol and 2-methylerythritol.
[d]The nd means not detected.

owing to their approximate retention times [*Ding et al.*, 2011]. These SOA tracers were identified by comparison of mass spectra with literature data [*Claeys et al.*, 2004, 2007; *Wang et al.*, 2005; *Jaoui et al.*, 2007; *Kleindienst et al.*, 2007; *Szmigielski et al.*, 2007; *Hu et al.*, 2008] and their retention times relative to other known compounds in the GC chromatograms. These tracers were identified first by CI mode and then quantified by EI mode. The method detection limits (MDLs) for *cis*-pinonic acid, pinic acid, levoglucosan, erythritol, octadecanoic acid, and azelaic acid were 0.05, 0.07, 0.15, 0.06, 0.09, and 0.11 ng m$^{-3}$, respectively. Table 1 summarizes the average values and ranges of the measured SOA tracers. It should be noted that ketopinic acid was used as surrogate for the quantification of all SOA tracers by *Kleindienst et al.* [2007], while different surrogates were used to quantify different SOA

tracers in this study and in Hong Kong by *Hu et al.* [2008]. As estimated by *Hu et al.* [2008], the quantification uncertainty caused by using surrogate calibration and different surrogates other than ketopinic acid should be within a factor of 3.

### 2.3. Quality Assurance/Quality Control

[11] Field blank samples and laboratory blank samples were extracted and analyzed in the same way as field samples. 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 prebaked quartz filter) were 104 ± 2% for *cis*-pinonic acid, 68 ± 13% for pinic acid, 87 ± 4% for levoglucosan, 62 ± 14% for erythritol, 78 ± 10% for octadecanoic acid and 81 ± 9% for azelic acid. And the relative standard deviation
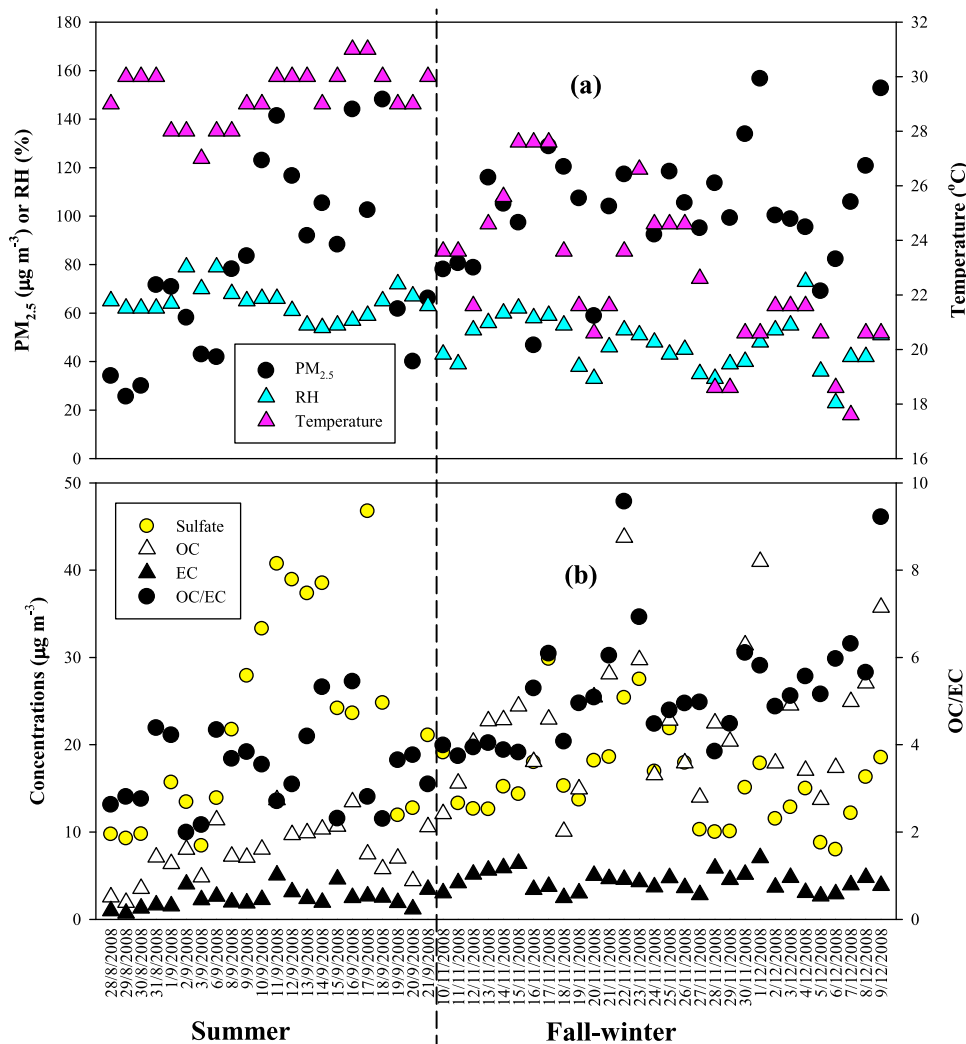
**Figure 2.** Day-to-day variations of major components in $PM_{2.5}$ and meteorological parameters in summer and fall-winter.

(RSD) for the quantification of authentic standards were 4.2%, 5.8%, 12.5%, 5.0%, 7.5% and 9.1% for *cis*-pinonic acid, pinic acid, levoglucosan, erythritol, octadecanoic acid, and azelaic acid, respectively. The relative differences for all target compounds in paired duplicate samples (n = 6) were all <15%.

## 3. Results and Discussion

### 3.1. Seasonal Variations of SOA Tracers

[12] As Figure 2 shows, the meteorological conditions and chemical characteristics were quite different between summer and fall-winter. Both temperature and relative humidity (RH) were higher in summer (averagely 29.0°C and 66%) than fall-winter (averagely 22.6°C and 47%). $PM_{2.5}$ levels were averagely 80.2 and 103 $\mu g\ m^{-3}$ in summer and fall-winter, respectively, which were much higher than U.S. EPA 24 h standard of 35 $\mu g\ m^{-3}$ (U.S. Environmental Protection Agency, National Ambient Air Quality Standards (NAAQS), available at http://www.epa.gov/air/criteria.html, 2006). Typically air quality during fall-winter seasons was the worst in a year in the PRD region [*Wang et al.*, 2003]. From our

study the concentrations of $PM_{2.5}$, OC, and EC were indeed higher than those during summer (Figure 2, p < 0.05); sulfate, however, exhibited higher levels during summer (Figure 2b, p = 0.017), especially in the middle of September.

[13] The sum of isoprene SOA tracers ranged 8.58–451 ng $m^{-3}$ with an average of 126 ng $m^{-3}$ in summer and 4.14–85.2 ng $m^{-3}$ with an average of 25.1 ng $m^{-3}$ in fall-winter. Among these isoprene SOA tracers, 2-methyltetrols (sum of 2-methylthreitol and 2-methylerythritol) were dominant in both seasons with the mean concentrations of 91.5 (4.97–319) ng $m^{-3}$ in summer and 16.0 (2.34–58.3) ng $m^{-3}$ in fall-winter. Table 2 lists the concentration ranges of SOA tracers from different studies. The levels of 2-methyltetrols during summer and fall-winter at WQS were comparable with those around the world during the same seasons (Table 2). $C_5$-alkenetriols (sum of *cis*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and *trans*-2-methyl-1,3,4-trihydoxy-1-butene) averaged 26.9 in summer and 4.29 ng $m^{-3}$ in fall-winter, respectively. 2-Methylglyceric acid averaged 7.71 ng $m^{-3}$ in summer and 4.75 ng $m^{-3}$ in fall-winter. As shown in Figure 3a, the isoprene SOA tracers exhibited obviously seasonal difference

**Table 2.** Comparison of Concentrations of SOA Tracers (ng m$^{-3}$) in Different Studies[a]

| Location | Season | Reference | 2-Methyltetrols | Isoprene Tracers[b] | Monoterpene Tracers[a] | β-Caryophyllenic Acid | 2,3-Dihydroxy-4-Oxopentanoic Acid |
|---|---|---|---|---|---|---|---|
| WQS, south China | Summer | This study | 4.97–319 | 8.58–451 | 0.49–50.3 | 0.50–11.8 | 2.84–52.0 |
| WQS, south China | Fall-winter | This study | 2.34–58.3 | 4.14–85.2 | 4.72–42.7 | 0.53–13.4 | 1.70–48.9 |
| Potsdam, northern U.S. | Summer-winter | Xia and Hopke [2006] | 0.09–131 | | | | |
| Five sites, midwestern U.S. | Summer | Lewandowski et al. [2008] | 2.2–304 | 4.1–335 | 19.6–170 | 0.8–10.0 | nd-3.2 |
| Five sites, midwestern U.S. | Fall-winter | Lewandowski et al. [2008] | nd-183 | 0.6–212 | 14.3–63.9 | 2.0–10.3 | 0.4–2.1 |
| Four sites, southeastern U.S. | Summer | Ding et al. [2008b] | 0.74–784 | | nd-20.8 | | |
| Four sites, southeastern U.S. | Fall-winter | Ding et al. [2008b] | nd-99.3 | | nd-34.9 | | |
| Three cities, North America | Summer | Stone et al. [2009] | 6–68.5 | 52.7–336 | 30.4–60.6 | 0.6–2 | 5.1–16.1 |
| North Carolina, southeastern U.S. | Summer | Kleindienst et al. [2007] | 43.1–273 | 2.7–136 | 78.9–290 | nd-27.7 | 0.8–6.9 |
| North Carolina, southeastern U.S. | Fall-winter | Kleindienst et al. [2007] | 1.8–123 | 19.2–305 | 31.5–64.0 | nd-4.7 | nd-1.2 |
| Four sites, southeastern U.S. | Summer | Kleindienst et al. [2010] | 15.3–296 | | nd-194 | nd-2.98 | nd-13.3 |
| K-puszta, Europe | Summer | Ion et al. [2005] | 1.82–119 | 4.02–137 | | | |
| Hyytiälä, Europe | Summer | Kourtchev et al. [2005] | 15.1–33.3 | 24.2–64.3 | | | |
| Hyytiälä, Europe | Fall | Kourtchev et al. [2005] | 0.46–0.49 | 0.46–0.49 | | | |
| Mediterranean, Europe | Summer | El Haddad et al. [2011] | 0.02–13 | 0.05–18.9 | 3.01–78 | 0.01–1.1 | |
| Amazonian rain forest | Summer | Claeys et al. [2004] | 49.2–64.7 | | | | |
| Hong Kong, China | Summer | Hu et al. [2008] | 0.74–119 | 1.32–954 | 8.07–1114 | 1.15–80.3 | 0.33–6.45 |
| WQS, south China | Fall-winter | Ding et al. [2011] | 5.0–64.4 | 5.77–68.3 | 0.91–18.3 | 0.03–1.97 | |
| Forests, eastern China | Summer | Wang et al. [2008] | 4.4–49 | 4.8–53 | nd-31 | | |

[a]Abbreviation: nd means not detected.
[b]Composition of tracers is different in different studies.

($p < 0.01$). All the isoprene SOA tracers were higher in summer than fall-winter (Table 1). The seasonal variation of SOA tracers could be influenced by several major factors, including emission and reaction rates and meteorological conditions (temperature, intensity of solar radiation, RH and the height of mixing layer). The emission rates of isoprene are positively influenced by light and temperature [*Rinne et al.*, 2002]. Thus, the high emissions of isoprene are expected during summer when light is intense and temperature is high. The seasonal variation of isoprene emissions in the PRD was reported as reaching the highest during summer and gradually dropping during fall to winter [*Zheng et al.*, 2010]. Intense light and high temperature during summer also favor isoprene reactions in the air. For the influence of mixing layer, the higher mixing layer could favor the diffusion of SOA and result in the lower concentrations observed; while the lower mixing layer could favor the accumulation of SOA and lead to the higher concentrations observed [*Strader et al.*, 1999]. Although the height of mixing layer should be generally higher in summer than fall-winter, the high levels of isoprene SOA tracers observed during summer suggested that the height of mixing layer might have minor influence on the seasonal trend of the isoprene SOA tracers. The seasonal trend of the isoprene SOA tracers at WQS was similar to that in the United States [*Xia and Hopke*, 2006; *Kleindienst et al.*, 2007; *Ding et al.*, 2008b; *Lewandowski et al.*, 2008]. It is interesting to note that the isoprene SOA tracers were relatively lower in the period from late August to early September but dramatically increased in the middle of September (Figure 3a). Since temperature and RH did not show great variations during summer, it might be factors other than meteorological parameters significantly influencing the formation of isoprene SOA tracers. Considering the notable increase of sulfate in the middle of September (Figure 2b) as well as the significant correlations between total isoprene SOA tracers and sulfate ($r = 0.696$, $p = 0.001$) during summer, the dramatic increase of isoprene SOA tracers might be related to sulfate. On the basis of the chamber simulation [*Surratt et al.*, 2007] and ambient observation [*Ding et al.*, 2011], aerosol acidity has been proven to have positive influence on isoprene SOA tracers' formation. Since sulfate is the key compound determining aerosol acidity, the increase of aerosol acidity might be the reason for the significant increase of the isoprene SOA tracers in this period. The S/F ratio of 2-methylglyceric acid was considerably lower than those of other isoprene SOA tracers. Unlike other isoprene SOA tracers, 2-methylglyceric acid tends to be affected not by acidic aerosol [*Surratt et al.*, 2007] but more significantly by RH [*Zhang et al.*, 2011]. Since lower RH favors 2-methylglyceric acid formation, in fall-winter with lower RH (47%) 2-methylglyceric acid was formed more easily than in summer with higher RH (66%), resulting in lower S/F ratio of 2-methylglyceric acid relative to other isoprene SOA tracers.

[14] The sum of monoterpene SOA tracers averaged 11.6 (0.49–50.3) ng m$^{-3}$ in summer and 16.4 (4.72–42.7) ng m$^{-3}$ in fall-winter, which were comparable with those reported in China mainland and Europe, but lower than those observed in the United States and Hong Kong (Table 2). Total monoterpene SOA tracers exhibited no significantly seasonal difference ($p > 0.05$, Figure 3b). The emission and reaction rates of monoterpenes are expected to be high
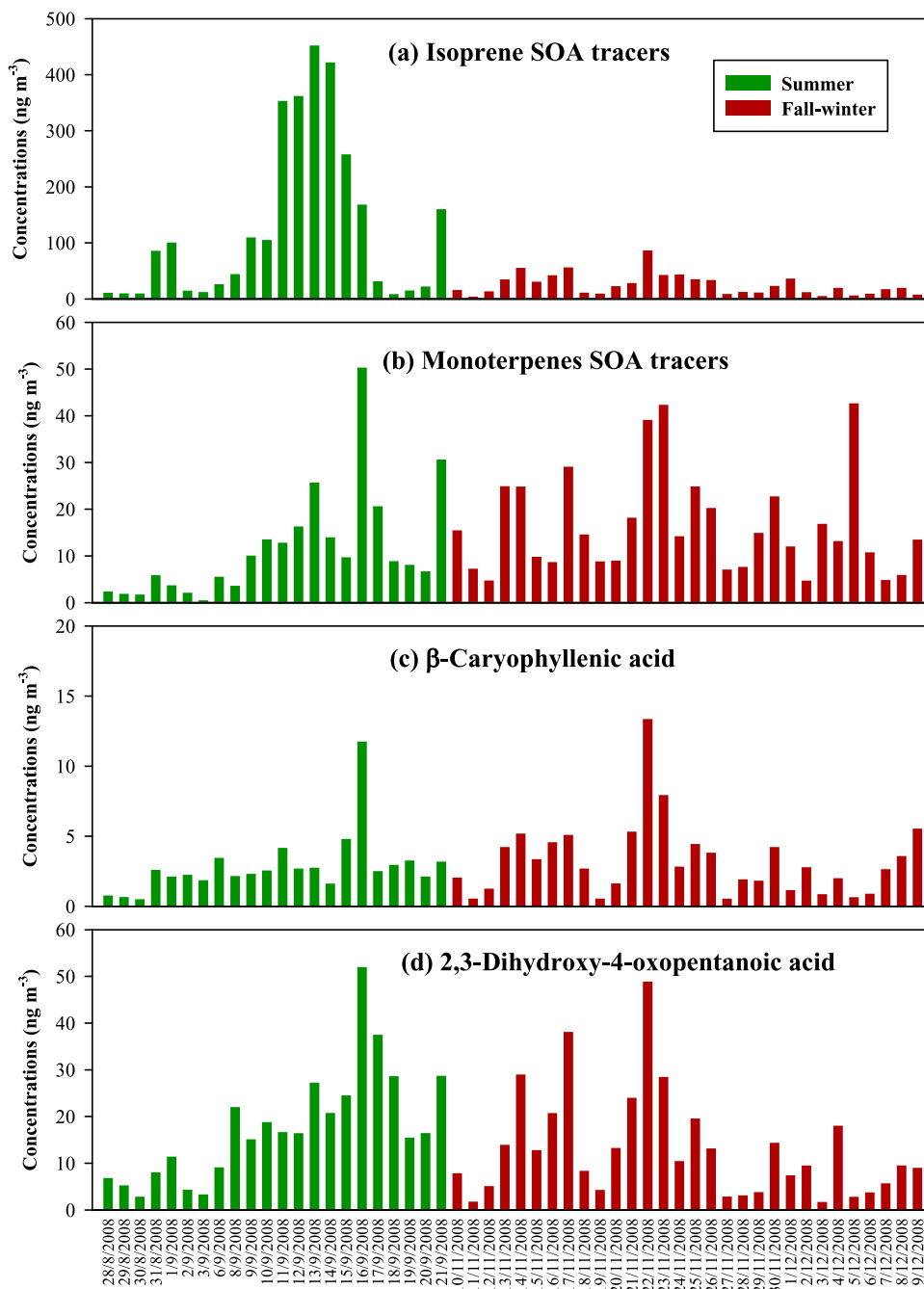
**Figure 3.** Day-to-day variations of SOA tracers in summer and fall-winter.

during summer owing to high temperature and intense solar radiation [*Zheng et al.*, 2010]. Although lower temperature during fall-winter would reduce monoterpene emissions and SOA-tracer formation, it would favor SOA tracers condensing to the particulate phase [*Saathoff et al.*, 2009]. By model simulation, a 10°C decrease in temperature was estimated to increase SOA yields 20−150% [*Sheehan and Bowman*, 2001]. Since the difference of the average temperature between summer and fall-winter reached 6.4°C (29.0°C versus 22.6°C), the effect of temperature on gas/particle partitioning could result in the increase of tracer levels in the particle phase. Thus, the counteracting effects of temperature on the precursor emissions/tracer formation and

on gas/particle partitioning smoothed seasonal variation of monoterpene SOA tracers at WQS. Moreover, the lower mixing layer during fall-winter could also favor the accumulation of SOA. Our observed seasonal trend of monoterpene SOA tracers at WQS was not like that in the southeastern [*Kleindienst et al.*, 2007] and midwestern United States [*Lewandowski et al.*, 2008] where significantly lower levels occurred in fall-winter. The low temperature and defoliation of deciduous trees during fall-winter could lead to the sharp drop of monoterpene emissions in these temperate regions. The PRD, however, is located in the subtropic with the average temperature higher than 22°C in fall-winter season and more evergreen vegetation. Thus, the

drop of monoterpene emissions during fall-winter in the PRD is not as sharp as that in the southeastern and midwestern United States [*Zheng et al.*, 2010]. During summer, 3-methyl-1,2,3-butanetricaric acid was the dominant compound ($4.95 \pm 5.8$ ng m$^{-3}$), followed by 3-hydroxyglutaric acid ($2.62 \pm 3.2$ ng m$^{-3}$). These two tracers were also observed as the dominant monoterpene SOA tracers during summer in the U.S [*Lewandowski et al.*, 2008; *Kleindienst et al.*, 2010]. However, their concentrations during summer at WQS were about 1 order of magnitude lower than those in the U.S ($\sim$40 ng m$^{-3}$) [*Lewandowski et al.*, 2008; *Kleindienst et al.*, 2010]. The 3-methyl-1,2,3-butanetricaric acid and 3-hydroxyglutaric acid exhibited no significant seasonal difference (p > 0.05), while *cis*-pinonic acid became the dominated monoterpene SOA tracer in fall-winter with significantly higher levels than in summer (p < 0.01). Such a difference in tracer compositions could be explained by photodegradation and/or gas/particle partitioning. Previous studies proposed that *cis*-pinonic acid and pinic acid could further photodegrade to 3-methyl-1,2,3-butanetricaric acid [*Claeys et al.*, 2007; *Szmigielski et al.*, 2007]. Thus, the ratio of *cis*-pinonic acid plus pinic acid to 3-methyl-1,2,3-butanetricaric acid (P/M) should be lower when more *cis*-pinonic acid and pinic acid photodegrade to 3-methyl-1,2,3-butanetricaric acid. In the current study, mean P/M during summer was 0.48, much lower than that of 2.17 during fall-winter, consistent with more intense photodegradation during summer. Temperature effect is another reason for higher P/M during fall-winter. Since *cis*-pinonic acid is the most volatile among the monoterpene SOA tracers, lower temperature during fall-winter could result in more *cis*-pinonic acid partitioning in the particle phase, as reflected by the increased average ratio of *cis*-pinonic acid to pinic acid from summer (2.09) to fall-winter (6.90). This relatively enrichment of *cis*-pinonic acid in particle phase during fall-winter would also lead to the increase of the P/M ratio. The sesquiterpene SOA tracer, $\beta$-caryophyllenic acid, also exhibited no significant difference (p = 0.577) between summer and fall-winter (Figure 3c). The average level was about 3 ng m$^{-3}$ in both seasons (Table 1), which were consistent with the data from other places (Table 2).

[15] The concentrations of aromatics SOA tracer, 2,3-dihydroxy-4-oxopentanoic acid, ranged from 1.70 to 52.0 ng m$^{-3}$ with an average of 15.1 ng m$^{-3}$. Its levels varied from 2.84 to 52.0 ng m$^{-3}$ in summer and 1.70 to 48.9 ng m$^{-3}$ in fall-winter. Our observations in the heavily polluted PRD stood to have the highest maximums and averages of aromatics SOA tracer among those reported (Table 2). Aromatics, for example, toluene and xylenes, are typically the most abundant VOCs in ambient air of PRD [*Chan et al.*, 2006; *Barletta et al.*, 2008], and their levels in the PRD are almost the highest as compared to the other places of China [*Tang et al.*, 2008] or of the world [*von Schneidemesser et al.*, 2010]. During our second campaign, VOCs were also measured every 2 h from 25 November to 2 December 2008, and the sum of toluene, xylenes, and ethylbenzene averaged 6.1 ppbv with a maximum of 60.6 ppbv (Y. Zhang et al., Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Perl River Delta region, south China, submitted to *Journal of Geophysical Research*, 2012). Aromatics SOA tracer exhibited no statistically seasonal difference (p = 0.158, Figure 3d). Previous

studies revealed that the major sources of aromatics in the PRD were industry solvent evaporation and vehicle exhaust [*Chan et al.*, 2006; *Zheng et al.*, 2009]. These anthropogenic emissions are expected to be relatively constant during the whole year. Although higher temperature and intense solar radiation in summer would favor SOA formation, the increasing levels of the aromatics SOA tracer could be compromised by factors like higher mixing layer in summer.

### 3.2. Source Apportionment of SOC by SOA-Tracer Method

[16] The SOA-tracer method was first proposed by *Kleindienst et al.* [2007] to estimate SOA from different precursors. On the basis of chamber simulations, the mass fraction of the tracers in SOA ($f_{\mathrm{soa}}$) for an individual precursor is defined as

$$f_{soa} = \frac{\sum_i [\mathrm{tr}i]}{[SOA]}, \tag{1}$$

where $\sum_i [\mathrm{tr}_i]$ is the sum of all tracers' concentrations for a certain precursor $i$ and [SOA] is the mass concentration of SOA. The carbon mass fraction ($f_{\mathrm{soc}}$) of the tracers in SOC were reported as $0.231 \pm 0.11$ $\mu$g $\mu$g C$^{-1}$, $0.155 \pm 0.039$ $\mu$g $\mu$g C$^{-1}$, $0.023 \pm 0.0046$ $\mu$g $\mu$g C$^{-1}$ and $0.00797 \pm 0.0026$ $\mu$g $\mu$g C$^{-1}$ for $\alpha$-pinene, isoprene, $\beta$-caryophyllene, and toluene, respectively [*Kleindienst et al.*, 2007]. With these $f_{\mathrm{soa}}$ or $f_{\mathrm{soc}}$ factors from the chamber studies, SOA or SOC from different precursors in the ambient can be estimated by $\sum_i [\mathrm{tr}_i]$ in the ambient dividing $f_{\mathrm{soa}}$ or $f_{\mathrm{soc}}$ factors [*Kleindienst et al.*, 2007; *Hu et al.*, 2008; *Lewandowski et al.*, 2008; *Stone et al.*, 2009; *Kleindienst et al.*, 2010]. In the current study, the same set of SOA tracers as reported by *Kleindienst et al.* [2007] were used for SOC estimation, including 2-methylglyceric acid and 2-methyltetrols for isoprene-derived SOC (SOC$_I$), $\beta$-caryophyllenic acid for $\beta$-caryophyllene-derived SOC (SOC$_C$) and 2,3-dihydroxy-4-oxopentanoic acid for aromatics-derived SOC (SOC$_A$). For monoterpene-derived SOC (SOC$_M$), there were nine tracers involved in the source profile [*Kleindienst et al.*, 2007]. However, only five of the nine monoterpene SOA tracers were detected in the current study and the rest four tracers were not found in our samples. Similarly, six and five of the nine tracers were detected in Hong Kong [*Hu et al.*, 2008] and in the United States [*Stone et al.*, 2009], respectively, and SOC$_M$ estimation based on these tracers both gave reasonable results. In the present study we also used the detected five monoterpene SOA tracers to estimate SOC$_M$. The calculation of uncertainties of SOC estimation is based on the uncertainties of quantification of organic tracers and determination of tracer/SOC factors. Therefore, the uncertainty of final result reflects all of these uncertainties through error propagation. The RSD of SOC estimation in this study was 48% for monoterpenes, 25% for isoprene, 21% for $\beta$-caryophyllene and 34% for toluene. The results of estimated SOC from different precursors are listed in Table 1.

[17] Figure 4 presents the daily variations of estimated SOC based on SOA-tracer method. On average, estimated SOC in summer (3.07 $\mu$g C m$^{-3}$) was significantly higher (p < 0.05) than in fall-winter (2.00 $\mu$g C m$^{-3}$), and their contributions to measured OC were also highly different
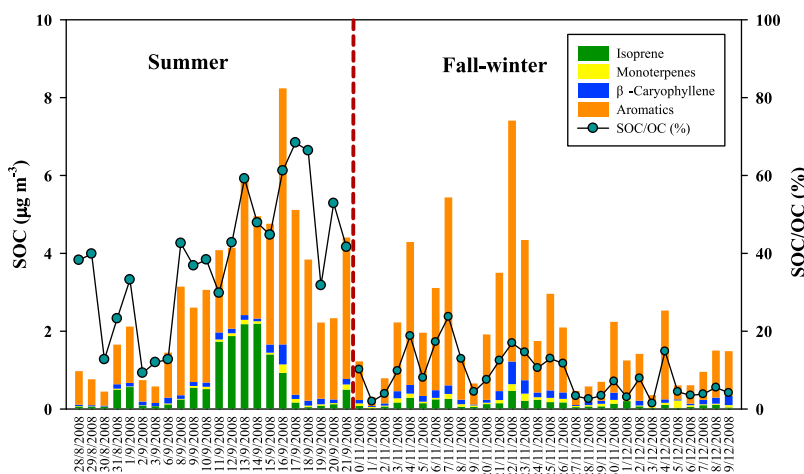
**Figure 4.** Estimated SOC between summer and fall-winter.

(38.4% versus 8.8%, p < 0.001). Anthropogenic aromatics were the dominant precursors against biogenic ones including isoprene and terpenes. Estimated SOC from aromatics accounted for 76% and 79% of total estimated SOC in summer and fall-winter, respectively (Figure 5). This anthropogenic aromatics dominance as SOA precursors could largely be explained by substantial anthropogenic emissions in the highly industrialized and urbanized PRD region. The emission inventories of VOCs in the PRD revealed that the anthropogenic sources (880 kT yr$^{-1}$) were dominant over biogenic ones (296 kT yr$^{-1}$) [*Zheng et al.*, 2009]. The sum of the five aromatics alone (toluene, xylenes and ethylbenzene) reached 204 kT yr$^{-1}$ which was about 1.6 times higher than the sum of isoprene and monoterpenes, and contributed 17.8% of the total VOCs emissions [*Zheng et al.*, 2009]. This SOC$_A$ dominant pattern in the central PRD was also observed in the three U.S. urban locations during summer [*Stone et al.*, 2009]. In a modeling study, ambient SOC in San Joaquin Valley (California) could reach 15–20 $\mu$g C m$^{-3}$ and aromatic hydrocarbons contributed 75% of the ambient SOC in some cases [*Strader et al.*, 1999]. During summer in Hong Kong in the southeast corner of PRD, a biogenic dominant pattern was observed [*Hu et al.*, 2008], partly because during summer, Hong Kong is least influenced by the heavily polluted inner PRD region owing to monsoon conditions and there are few local industry emissions.

[18] SOC$_A$ was 2.25 ± 1.5 $\mu$g C m$^{-3}$ in summer and 1.64 ± 1.4 $\mu$g C m$^{-3}$ in fall-winter. Our estimated SOC$_A$ levels in summer were about twice of that observed in the three urban locations (1.06 ± 0.4 $\mu$g C m$^{-3}$) during summer in the United States [*Stone et al.*, 2009] and about 4 times higher than that (0.47 $\mu$g C m$^{-3}$) in Hong Kong when it was under the PRD regional influence in summer [*Hu et al.*, 2008]. SOC$_A$ levels observed in other locations in the United States were even lower [*Kleindienst et al.*, 2007; *Lewandowski et al.*, 2008; *Kleindienst et al.*, 2010] owing to much less emission of aromatics. SOC$_I$ in the PRD were 0.64 ± 0.7 $\mu$g C m$^{-3}$ in summer and 0.13 ± 0.1 $\mu$g C m$^{-3}$ in fall-winter. SOC$_I$ contributed 18% of estimated SOC during summer (Figure 5a), but its contribution was minor (8%) during fall-winter (Figure 5b). During summer in China,

estimated SOC$_I$ ranged from 0.03 to 0.32 $\mu$g C m$^{-3}$ in the eastern forests [*Wang et al.*, 2008] and 0.01 to 0.81 $\mu$g C m$^{-3}$ in Hong Kong [*Hu et al.*, 2008]. On the basis of the same set of isoprene tracers, SOC$_I$ during summer was estimated in the range of undetectable level to 2.65 $\mu$g C m$^{-3}$ in the United States [*Kleindienst et al.*, 2007; *Ding et al.*, 2008a; *Lewandowski et al.*, 2008; *Stone et al.*, 2009; *Kleindienst et al.*, 2010] and Europe [*Kourtchev et al.*, 2009]. Our estimate of SOC$_I$ (0.05 to 2.19 $\mu$g C m$^{-3}$) during summer was comparable to those previous studies. For SOC$_C$ and SOC$_M$, they had minor contributions to SOC in both seasons (Figure 5 and Table 1).

[19] It should be noted that the application of SOA-tracer method is limited by the number of identified SOA tracers and chamber parameters which could not represent all ambient situations and thus lead to significant uncertainty [*Kleindienst et al.*, 2007]. The choice of SOA tracers might also introduce great uncertainty in SOC estimation [*El Haddad et al.*, 2011]. The $f_{soc}$ factors reported by *Kleindienst et al.* [2007] were successfully used in the United States [*Kleindienst et al.*, 2007; *Lewandowski et al.*, 2008; *Stone et al.*, 2009; *Kleindienst et al.*, 2010] and in Hong Kong [*Hu et al.*, 2008, 2010]; nevertheless, it is not clear about the uncertainty when these $f_{soc}$ factors from chamber simulations are applied to the heavily polluted ambient air in the PRD. Moreover, only four types of SOA precursors were considered in the current SOA-tracer method. The "nontraditional" SOA, such as SOA from aqueous-phase production and/or aging of primary aerosol, was excluded from SOC by SOA-tracer method and would be included in the residual nonsecondary OC fraction. Since EC-tracer method is a widely applied approach to estimate the bulk SOC, it can include the "nontraditional" SOA and offer an independent test of SOA-tracer method. In the following text, detailed comparisons are made between the estimated SOC by SOA-tracer method and EC-tracer method.

### 3.3. Comparison of SOC Estimated by EC-Tracer Method and SOA-Tracer Method

[20] Total SOC can be estimated by EC-tracer method using primary OC/EC ratio (OC/EC$_p$) and taking EC as the primary tracer [*Turpin and Huntzicker*, 1995]. POC is first

**(a) Summer**

18%

1%

5%

76%

■ Isoprene ■ Monoterpenes ■ β-caryophyllene ■ Aromatics

**(b) Fall-winter**

8%

5%

8%

79%

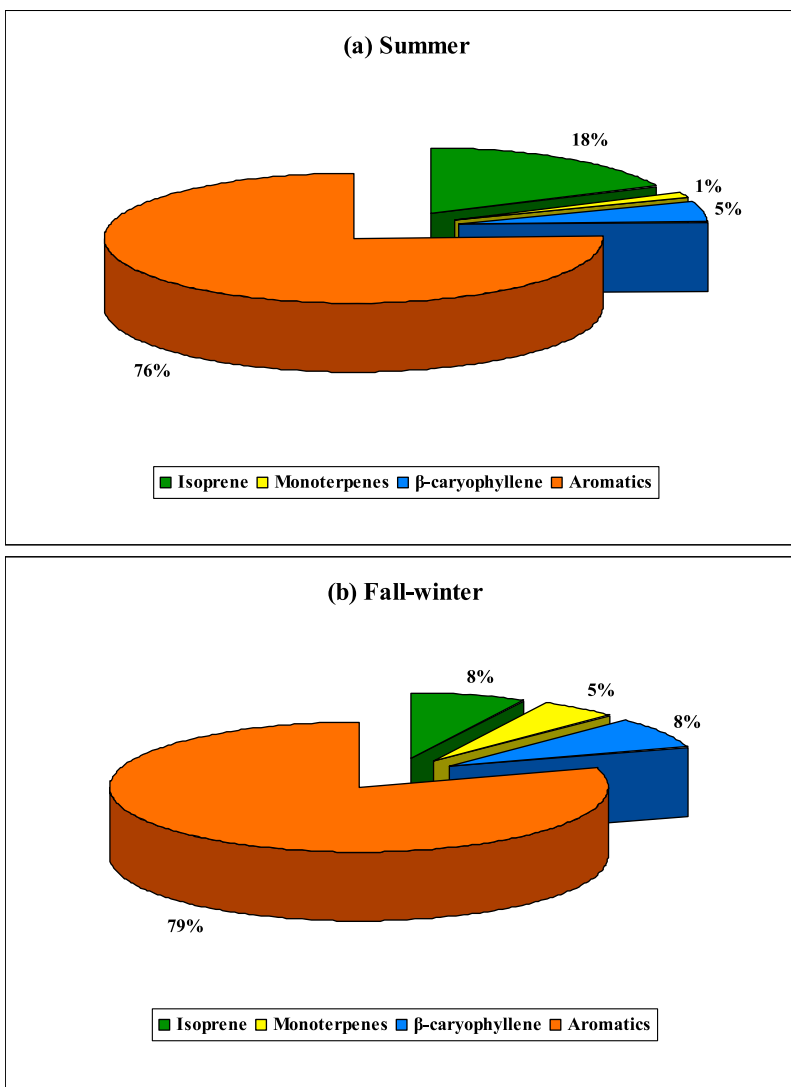■ Isoprene ■ Monoterpenes ■ β-caryophyllene ■ Aromatics

**Figure 5.** Compositions of SOC during (a) summer and (b) fall-winter.

estimated, and then SOC is calculated by subtracting POC from OC:

$$POC = (OC/EC)_p \times EC, \qquad (2)$$

$$SOC = OC - POC. \qquad (3)$$

[21] Similar to the previous studies in the PRD [*Cao et al.*, 2004; *Duan et al.*, 2007], the minimum ratio of OC/EC was assigned for $OC/EC_p$ for each season to estimate SOC in the current study (1.99 for summer and 3.74 for fall-winter). These ratios we used were comparable to the typical values of 2.26 and 4.22 in Guangzhou for SOC estimation during summer and winter, respectively [*Duan et al.*, 2007]. With calculated SOC by EC-tracer method ($SOC_{EC\text{-}tracer}$), we can compare them with estimated SOC by SOA-tracer method ($SOC_{SOA\text{-}tracer}$). During summer $SOC_{SOA\text{-}tracer}$ and $SOC_{EC\text{-}tracer}$ were similar (3.07 $\mu$g C m$^{-3}$ versus 3.19 $\mu$g C m$^{-3}$ in average, Table 1), and correlated well (p < 0.01) with each other with a slope of 0.913 (Figure 6). As discussed

above, the "nontraditional" SOA are not included in SOA-tracer method but in EC-tracer method. The agreement between these two methods suggests that such "nontraditional" SOA were possibly not as significant in the PRD during summer. However, the correlation was not strong (r = 0.568), implying that there might have particular processes and/or SOA sources that are captured better by one approach or the other, especially for these disagreement samples. During fall-winter, however, $SOC_{SOA\text{-}tracer}$ was only one third of $SOC_{EC\text{-}tracer}$ (2.00 $\mu$g C m$^{-3}$ versus 6.72 $\mu$g C m$^{-3}$ in average), and there was no significant correlation between them (p > 0.05, Figure 6). The biggest gap between these two methods was observed on 22 November 2008 when $SOC_{EC\text{-}tracer}$ was estimated as 26.7 $\mu$g C m$^{-3}$ but $SOC_{SOA\text{-}tracer}$ was only 7.41 $\mu$g C m$^{-3}$.

[22] Fall-winter is the harvest season of crop; and the cereal straw combustion can emit large amount of fine particles into the air during this period in China [*Wang et al.*, 2007]. As shown in Figure 7, biomass burning (BB) tracer levoglucosan [*Simoneit et al.*, 1999] was significant increased during fall-winter, and its level was on average
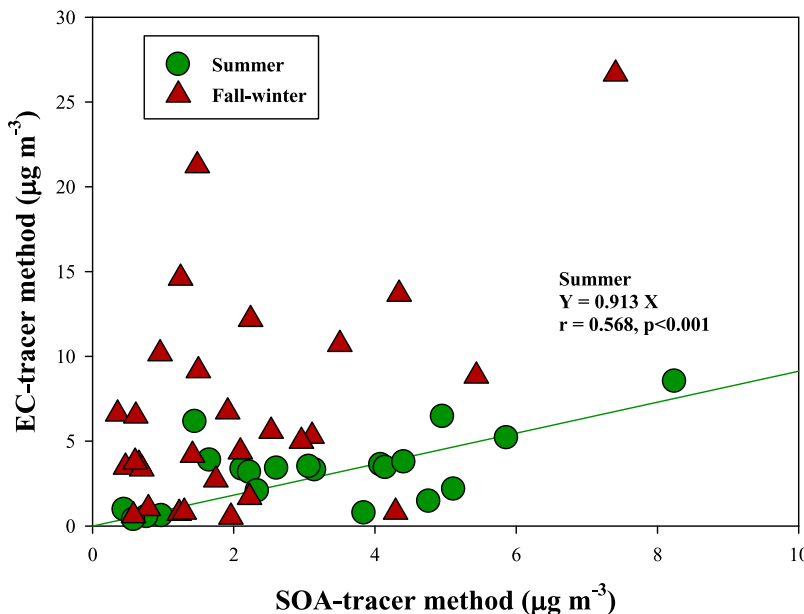
**Figure 6.** Comparison of estimated SOC by SOA-tracer method and EC-tracer method in different seasons.

$81.0 \pm 44$ ng m$^{-3}$ in summer but about 4 times higher in fall-winter ($310 \pm 210$ ng m$^{-3}$), indicating the great enhancement of BB in the PRD in fall-winter. During our campaigns, the highest level of levoglucosan reached 1156 ng m$^{-3}$ on 22 November 2008 when the OC mass and OC/EC ratio reached $43.7 \mu$g C m$^{-3}$ and 9.57, respectively. Since BB aerosols have primary OC/EC ratio more than 7 or even higher [*Fine et al.*, 2001, 2002; *Schauer et al.*, 2001; *Zhang et al.*, 2007], the enhanced OC/EC ratio observed in fall-winter (Table 1) cannot be fully explained by SOA formation but partly by BB emission. Since we applied the minimum ratio as OC/EC$_p$ to estimate SOC, the high OC/EC ratio due to BB input could lead to taking parts of primary BB OC as SOC and overestimating SOC by EC-tracer method. To check our conclusion, the difference between SOC$_{EC\text{-tracer}}$ and SOC$_{SOA\text{-tracer}}$, $\Delta$SOC, is calculated as

$$\Delta\text{SOC} = \text{SOC}_{EC-tracer} - \text{SOC}_{SOA-tracer}. \qquad (4)$$

[23] As shown in Figure 8, $\Delta$SOC exhibited a significantly positive correlation with levoglucosan during fall-winter ($r = 0.666$, $p < 0.001$), indicating the significant impacts of BB on the gap between SOC$_{EC\text{-tracer}}$ and SOC$_{SOA\text{-tracer}}$. When the influence of BB was slight during summer, the BB-induced overestimate of SOC$_{EC\text{-trace}}$ was not significant, and no significant correlation was observed between $\Delta$SOC and levoglucosan ($p = 0.488$, Figure 8) while the estimated SOC by these two methods matched very well (Figure 6).

[24] The EC-tracer method has been widely used to estimate SOC. However, the main disadvantage of this method is the difficulty of estimating a representative value for (OC/EC)$_p$. The thermal-optical OC/EC analysis can be corrupted by multiple factors, including mineral oxides, organic charring, heavy refractory organics, and also change of source contributions. (OC/EC)$_p$ varies from source to source, from 1–2 for most primary sources [*Chow et al.*, 2007] to >7 for BB [*Fine et al.*, 2001, 2002; *Schauer et al.*, 2001; *Zhang et al.*, 2007]. Therefore, changes in source contributions, particularly when BB plays an important role as fall-winter time in this study, would make it difficult to find a proper (OC/EC)$_p$ for all samples when calculating SOC on the basis
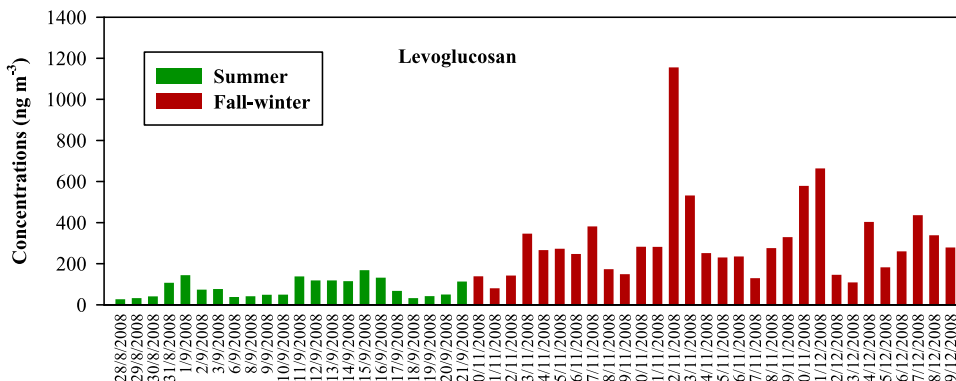


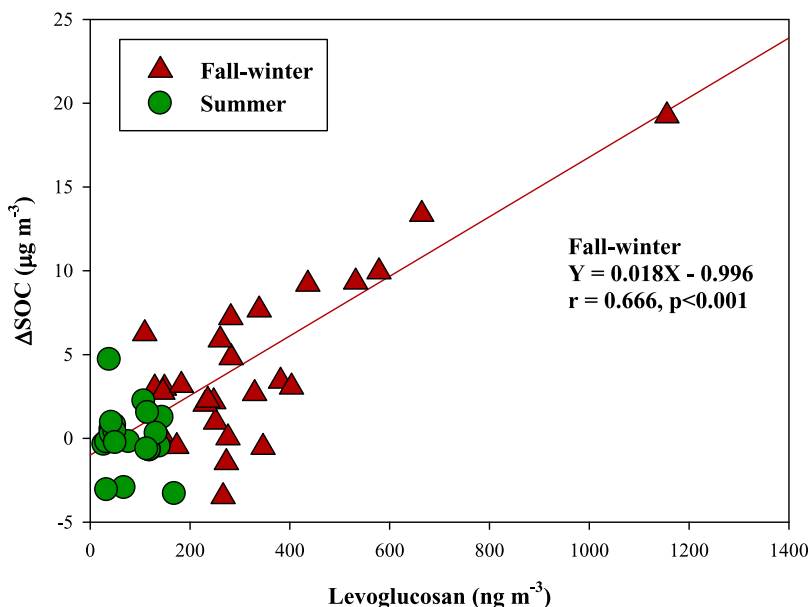**Figure 7.** Day-to-day variations of levoglucosan in summer and fall-winter.

**Figure 8.** Correlations of levoglucosan with ΔSOC.

of the EC-tracer method. In the present study, the results of SOC by the two methods are consistent during summer but great discrepancy exhibited during fall-winter, suggesting that the minimum OC/EC ratio could not be representative of $(OC/EC)_p$ in BB season.

## 4. Conclusions

[25] In this study, SOA tracers from significant biogenic (isoprene, monoterpenes, sesquiterpenes) and anthropogenic (aromatics) precursors were measured in the highly industrialized Pearl River Delta (PRD) region in south China. SOA tracers from isoprene in the region showed much more distinct seasonal variation, and SOA tracer from aromatics in average was the highest reported in ambient air. On the basis of these tracers, estimated SOC from different precursors revealed that over 75% of the estimated SOC were from aromatic precursors in both summer and fall-winter, suggesting the dominant role of anthropogenic precursors in the production of SOA in the highly industrialized and urbanized PRD region. A comparison was made between SOC estimated by SOA-tracer method and EC-tracer method. For summertime, the results from the two methods agreed remarkably well. For samples taken during fall-winter, however, there was a broad gap between the results from the two methods. This gap correlated well with levoglucosan, a BB marker, indicating that EC-tracer method would overestimate SOC when there had input from BB to carbonaceous aerosols. BB is the largest source of primary fine carbonaceous particles in the global atmosphere [*Bond et al.*, 2004]. The savanna fire in tropical region is the dominant contributor in global BB categories [*Andreae and Merlet*, 2001; *Akagi et al.*, 2011]. In the United States, about one third of the primary fine particles come from BB (e.g., wildfires, prescribed burning, and wood combustion) (U.S. Environmental Protection Agency, 2008 National Emissions Inventory Data, http://www.epa.gov/ttn/chief/net/2008inventory.html). In Europe, BB is the major source of OC during winter

and spring [*Gelencsér et al.*, 2007]. Since BB can emit particles with high OC/EC ratio, cautions should be taken when estimating SOC by EC-tracer method, especially when BB exhibits significant influences.

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