



# Seasonal cycles of secondary organic aerosol tracers in rural Guangzhou, Southern China: The importance of atmospheric oxidants<sup>☆</sup>

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## ABSTRACT

Thirteen secondary organic aerosol (SOA) tracers of isoprene (SOA<sub>I</sub>), monoterpenes (SOA<sub>M</sub>), sesquiterpenes (SOA<sub>S</sub>) and aromatics (SOA<sub>A</sub>) in fine particulate matter (PM<sub>2.5</sub>) were measured at a Pearl River Delta (PRD) regional site for one year. The characteristics including their seasonal cycles and the factors influencing their formation in this region were studied. The seasonal patterns of SOA<sub>I</sub>, SOA<sub>M</sub> and SOA<sub>S</sub> tracers were characterized over three enhancement periods in summer (I), autumn (II) and winter (III), while the elevations of SOA<sub>A</sub> tracer (i.e., 2,3-dihydroxy-4-oxopentanoic acid, DHOPA) were observed in Periods II and III. We found that SOA formed from different biogenic precursors could be driven by several factors during a one-year seasonal cycle. Isoprene emission controlled SOA<sub>I</sub> formation throughout the year, while monoterpene and sesquiterpene emissions facilitated SOA<sub>M</sub> and SOA<sub>S</sub> formation in summer rather than in other seasons. The influence of atmospheric oxidants (O<sub>x</sub>) was found to be an important factor of the formation of SOA<sub>M</sub> tracers during the enhancement periods in autumn and winter. The formation of SOA<sub>S</sub> tracer was influenced by the precursor emissions in summer, atmospheric oxidation in autumn and probably also by biomass burning in both summer and winter. In this study, we could not see the strong contribution of biomass burning to DHOPA as suggested by previous studies in this region. Instead, good correlations between observed DHOPA and O<sub>x</sub> as well as [NO<sub>2</sub>][O<sub>3</sub>] suggest the involvement of both ozone (O<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>) in the formation of DHOPA. The results showed that regional air pollution may not only increase the emissions of aromatic precursors but also can greatly promote the formation processes.

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## 1. Introduction

Organic aerosol has significant influence on the radiative budget of the earth, the visibility and air quality in regional and global scales (Chen et al., 2016; Hoyle et al., 2009; Pöschl and Shiraiwa, 2015; Sisler and Malm, 1994). Secondary organic aerosol (SOA), which is formed through gas-phase oxidation reactions of biogenic and anthropogenic volatile organic compounds (VOCs) with ozone (O<sub>3</sub>), hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals or heterogeneous

reactions of VOCs with particles, is considered as one of the most important components of organic aerosol (Hallquist et al., 2009; Zhang et al., 2015).

Over the past decades, numerous studies have been conducted to investigate SOA formation (Claeys et al., 2004a, 2007; Kleindienst et al., 2007). However, the formation mechanisms of SOA are complex and still not explicitly understood, especially under a wide range of environmental conditions. Based on current knowledge, air pollutants such as O<sub>3</sub> and nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>), can play important roles in the formation and evolution of SOA, altering the concentration and composition of SOA. The ozonolysis of isoprene and terpenes was reported to form SOA products and their intermediates in chamber studies (Chen

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et al., 2012; Yu et al., 1999). Besides, secondary organic carbon (SOC) was observed increasing along with O<sub>3</sub> enhancement in field measurements (Guo et al., 2012; Hu et al., 2008; Riva et al., 2016). The concentration of NO<sub>x</sub> has been found to be highly influential in the formation pathways and production of SOA for a variety of compounds. Low-NO<sub>x</sub> conditions were reported to favor the aerosol yields of isoprene photooxidation,  $\alpha$ -pinene ozonolysis, toluene and *m*-xylene photooxidation (Deng et al., 2017; Hatakeyama et al., 1991; Kroll et al., 2006; Song et al., 2005). Moreover, different NO<sub>x</sub> levels could change the photooxidation pathway of isoprene, forming different SOA products (Froyd et al., 2010; Surratt et al., 2010). Some pollution events such as biomass burning were also reported to promote the formation and aging of SOA by emitting a large amount of VOCs and forming NO<sub>x</sub> and O<sub>3</sub> (Fu et al., 2014; Gilardoni et al., 2016; Yee et al., 2013). In addition, VOC emissions (Shen et al., 2015), temperature (Ding et al., 2011) and relative humidity (RH) (Fick et al., 2003) have been reported to have pronounced effects on SOA formation. In general, the formation mechanisms were proposed on studies of SOA formed from biogenic VOCs (BVOCs, including isoprene, monoterpenes, sesquiterpenes, etc.), while SOA formed from anthropogenic VOCs (AVOCs, e.g. aromatic hydrocarbons) has not been studied on a large scale but has attracted increasing interest recently (Kleindienst et al., 2004; Offenberg et al., 2007). A study using a global chemical transport model suggested that the contribution of AVOCs-derived SOA can reach as high as 29% of SOA on a global scale (Farina et al., 2010). Currently, 2, 3-dihydroxy-4-oxopentanoic acid (DHOPA) was widely reported to serve as the tracer of aromatic SOA (Kleindienst et al., 2004, 2007).

The Pearl River Delta (PRD) region in southern China is characterized by a subtropical monsoonal climate, with relatively high temperature and humidity and sufficient solar radiation. The conditions are suitable for plant growth, leading to a total estimated annual emission of BVOCs as high as 296 kt (Zheng et al., 2010). Meanwhile, the PRD region has been experiencing severe air pollution problems, with considerable levels of particulate matter, NO<sub>x</sub>, and especially, increasing O<sub>3</sub> level (Song et al., 2017; Wang et al., 2009; Zhong et al., 2013). Thus, it is ideal to study SOA formation in this region using molecular tracers to understand the contributions of SOA from biogenic and anthropogenic sources, and to explore the influence of anthropogenic induced air pollution on SOA formation. To our best knowledge, few studies have focused on the seasonal cycles of SOA formation from different precursors and under different influences in the PRD region (Ding et al., 2012; Hu et al., 2008; Hu and Yu, 2013; Lyu et al., 2017; Wang et al., 2017). Here we present a one-year observation of SOA tracers in fine particulate matter (PM<sub>2.5</sub>) at Tianhu, a regional site in Guangzhou, from March 2012 to February 2013.

## 2. Experimental section

### 2.1. Field sampling

PM<sub>2.5</sub> samples were collected on the roof of a building at Tianhu (23.65°N, 113.63°E), a regional site at a distance of ~60 km north-east of the city center of Guangzhou. The site is located in rural area with no direct stationary source nearby, and the major roads are more than 2 km away from the site (Lai et al., 2016). Evergreen coniferous and broadleaved mixed woods are the dominant coenotypes around this site (Zheng et al., 2010).

PM<sub>2.5</sub> sampling was conducted from 18 March 2012 to 23 February 2013 using a medium volume sampler (300 L/min, Mingye, China) and a mini volume sampler (5 L/min, Airmetrics, US). Filter samples were collected every 6 days with a duration of 24 h. A

quartz filter (25 × 20 cm, Pall, US) and a PTFE filter ( $\phi = 47$  mm, Pall, US) were loaded into a medium and a mini volume sampler, respectively. A total of 51 quartz and 52 PTFE filter samples as well as field blank samples were collected in the whole campaign. Before sampling, the quartz filters were pre-combusted at 550 °C for 10 h to remove organic contaminants. After sampling, all quartz and PTFE filters were stored in the freezer at –20 °C prior to analysis.

### 2.2. Chemical analysis

#### 2.2.1. SOA tracers

In this study, SOA tracers were detected in 49 out of 51 quartz filter samples. Detailed information of SOA tracer analysis has been described elsewhere (Ding et al., 2011). Briefly, filter aliquots were extracted three times by sonication with 40 mL of dichloromethane (DCM)/methanol (1:1, v/v) each time and hexadecanoic acid-D<sub>31</sub> and phthalic acid-D<sub>4</sub> were used as internal standards. The combined and filtered sample extracts were concentrated, separated into two parts and then blown to dryness with pure nitrogen gas. One was blown to dryness with pure nitrogen gas, then kept at room temperature for 1 h to derivatize acids after adding 200  $\mu$ L of DCM, 10  $\mu$ L of methanol and 300  $\mu$ L of fresh prepared diazomethane. After the reaction, the derivative was blown to 200  $\mu$ L and analyzed for monoterpene SOA (SOA<sub>M</sub>) tracers, i.e. *cis*-pinonic acid (PNA), pinic acid (PA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). The other part was blown to dryness, and then derived 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 isoprene SOA (SOA<sub>I</sub>) tracers, i.e., three C<sub>5</sub>-alkene triols (*cis*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene), 2-methylglyceric acid (MGA), two methyltetrols (MTLs), i.e. 2-methylthreitol (MT) and 2-methylerythritol (ME), SOA<sub>M</sub> tracers, i.e., 3-hydroxyglutaric acid (HGA) and 3-hydroxy-4,4-dimethylglutaric acid (HDGA), sesquiterpene SOA (SOA<sub>S</sub>) tracer ( $\beta$ -caryophyllinic acid, CPA) and aromatic SOA (SOA<sub>A</sub>) tracer (DHOPA). The derivatized samples were analyzed by gas chromatography coupled to a mass spectrometric detector (Agilent 5975N, GC/MSD) in the scan mode with a 30 m HP-5 MS capillary column (i.d. 0.25 mm, 0.25  $\mu$ m film thickness). Splitless injection of a 1  $\mu$ L sample was performed. The GC temperature was initiated at 80 °C (held for 2 min) and increased to 290 °C at a rate of 5 °C min<sup>-1</sup> then held for 20 min. The analytes were qualified by comparison of mass spectra with literature data and their retention times relative to other known compounds in the GC chromatograms (Claeys et al., 2004a; Hu et al., 2008; Jaoui et al., 2007; Szmigielski et al., 2007), and quantified by authentic standards and corresponding surrogates (Ding et al., 2008, 2011). The details of the method including quantification standards, method detection limits (MDLs), recoveries and relative standard deviation (RSD) are shown in Table S1.

#### 2.2.2. Analysis of PM<sub>2.5</sub> mass and carbonaceous fractions

Mass concentration of PM<sub>2.5</sub> was measured by an electronic microbalance with a sensitivity of  $\pm 0.001$  mg (Satorius MC5, Germany) using PTFE filters. A punch (1.0 cm<sup>2</sup>) of each quartz filter was taken to measure organic carbon (OC) and elemental carbon (EC) using the thermo-optical transmittance (TOT) method (NIOSH protocol) by an OC/EC analyzer (Sunset Laboratory Inc., US). The analytical procedure of carbonaceous fractions is described elsewhere (Lai et al., 2016).

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