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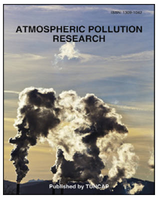

Characteristics and contributions of biogenic secondary organic aerosol tracers to $PM_{2.5}$ in Shanghai, China

Wenfei Zhu [a], Lina Luo [a], Zhen Cheng [a, *], Naiqiang Yan [a], Shengrong Lou [b], Yongpeng Ma [c]

[a] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Shanghai Academy of Environmental Sciences, Shanghai 200233, China
[c] Henan Collaborative Innovation Center of Environmental Pollution Control and Ecological Restoration, School of Material and Chemical Engineering, Zhengzhou University of Light Industry, No. 136, Science Avenue, Zhengzhou 450001, China

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ABSTRACT

To evaluate biogenic secondary organic aerosol (BSOA) tracers from biogenic precursors, fine particles ($PM_{2.5}$) were collected using filter-based high-volume samplers from spring-summer of 2015 in the central part of Shanghai, China. The results showed that the isoprene SOA tracers exhibited the highest levels (17.64 ± 9.75 ng m^{-3}) and were always observed along with higher temperatures, which results in a higher tracer formation rate and isoprene emission strength. However, the isoprene SOA tracers showed a weak correlation with the relative humidity ($p > 0.05$). The isoprene SOA tracers showed remarkable correlations with the $[H^+]$ because of the enhanced formation of isoprene SOA in the acidic aerosols. On the basis of these results, 2-methylglyceric acid was determined to have weak correlations with other isoprene tracers, which indicated that it had different formation pathways from those of other isoprene SOA tracers. *Cis*-pinonic acid had negative correlations with other SOA tracers, indicating that it is the first product in the oxidation process. Furthermore, the isoprene-based tracers ($SOC_{isoprene}$) were calculated to be 0.031–0.299 μg C m^{-3} (with an average of 0.114 ± 0.062 μg C m^{-3}), which accounted for more than half of the biogenic SOA. The SOC estimation with SOA tracers (SOC tracer-based) averaged 0.155 ± 0.066 μg m^{-3}, with a range from 0.049 to 0.309 μg m^{-3} during the sampling period, which amounted to 2.73% OC.

1. Introduction

Biogenic aerosols are ubiquitous in the atmosphere. According to the formation mechanism, biogenic aerosols can be divided into primary biological aerosol (PBAP) and biogenic secondary organic aerosol (BSOA). Primary biological aerosol (PBAP), that is, directly in the form of particulate matter from the biological sources into the atmosphere, such as fungi, bacteria, pollen, viruses, animal and plant debris and insect excrement, etc. Biogenic secondary organic aerosols (BSOA) tracers in the particle phase are produced by homogenous and heterogeneous reactions of biogenic volatile organic compounds (BVOCs), including isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons with ozone O_3, OH and NO_3 radicals and formed through nucleation reactions or condensation onto pre-existing particles (Mielke et al., 2009). Biogenic aerosols have been confirmed as being part of the atmospheric radiation budget, and they play an important role in the formation of cloud droplets and precipitation, serving as cloud condensation and ice nuclei (Pöhlker and Andreae, 2012; Deshmukh et al., 2017; Singh and Gupta, 2017).

Previous studies have shown that biogenic secondary organic aerosols (BSOA) dominate in biogenic aerosols (Pöschl et al., 2010). BVOCs has strong reactivity due to its non-conjugated C–C double bonds. BSOA tracers that derived from specific BVOCs could provide insight into sources, processes and evolutions of SOA. Some BSOA tracers have been identified in ambient samples (Karlsson, 2013). Claeys et al. (2004) first identified 2-methyltetrols in the samples collected in the Amazonian rain forest aerosols as isoprene oxidation products (Claeys et al., 2004). Claeys et al. (2007) further found that the yield of 2-methyltetrols in the oxidation of isoprene under acid catalysis was significantly increased and 2-methylglyceric acid could well indicate the isoprene oxidation SOA (Claeys et al., 2007).

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* Corresponding author.
E-mail address: chengz88@sjtu.edu.cn (Z. Cheng).

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Since then, these compounds have been detected in ambient air samples collected in different regions from Finland (Kourtchev et al., 2005), Hungary (Ion et al., 2005), the United States (Ding et al., 2009), and China (Ding et al., 2012; Liang et al., 2012; Feng et al., 2013). Photo-oxidation products of α-pinene and β-caryophyllene were also characterized in smog chamber experiments and reported in ambient samples (Kourtchev et al., 2005; Surratt et al., 2007a; Szmigielski et al., 2007; Ding et al., 2012).

On the global scale, the emissions of biogenic VOCs (BVOCs) are suggested to be one order of magnitude larger than those of anthropogenic VOCs (Strong et al., 2013). Based on the identified biogenic secondary organic aerosol (BSOA) tracers, published studies mainly focused on contribution and influence process of BVOCs emission from forest and rural ambient aerosols to SOA mass especially in China. (Kourtchev et al., 2005; Cahill et al., 2006; Yan et al., 2009; Ding et al., 2011). Fu et al. (2010) applied the biogenic SOA tracers to ambient aerosols collected at the summit of Mountain Tai, Central East China (CEC) in early summer. They estimated the contribution of biogenic precursors isoprene, α/β-pinene, and β-caryophyllene to SOC formation by using the tracer-based method. The results suggested that isoprene is a more significant precursor for BSOA at high altitudes (Fu et al., 2010). Ding et al. (2011) analyzed the concentration of biogenic SOA tracers at a regional background site in the central Pearl River Delta (PRD) region in south China, and investigated the influence of temperature and aerosol acidity on biogenic SOA tracers (Ding et al., 2011). However, Weber et al. (2007) found that anthropogenic emissions in urban regions could accelerate oxidation of biogenic VOCs (Weber et al., 2007). Carlton et al. (2010) used CMAQ model to evaluate the effect of anthropogenic emissions on the formation of biogenic SOA (Carlton et al., 2010). Their results also indicated that the closure of all controllable anthropogenic emissions could induce significant reductions of biogenic SOA. As large differences may exist in characteristic of BSOA between forest or rural and urban region due to anthropogenic emissions and atmospheric conditions. More field works are needed to characterize biogenic SOA from individual precursor hydrocarbons at urban areas. Studies on the integral BSOA tracers and their contributing sources in real ambient aerosols from urban areas are quite limited up to now. Liang et al. (2012) measured average biogenic SOA tracers (2-methylthreitol and 2-methylerythritol) over four seasons at an urban site in Beijing and investigated the influence of meteorological factors and inorganic components (Liang et al., 2012). Feng et al. (2013) analyzed the seasonal contribution of biogenic SOA tracers in the urban areas of China (Feng et al., 2013). Since emission rates and emission characteristics of the precursor hydrocarbons vary greatly, The BSOA formation process differ for different areas.

Shanghai characterized by high population density and well-developed industry, is one of the most important megacities in China. May–June is the spring harvest period, when the gradual recovery of the vegetation is taking place in shanghai. In this study, 23-h $PM_{2.5}$ samples were collected from the central part of Shanghai in May–June, 2015, and biogenic secondary organic aerosol tracers were measured together with the $PM_{2.5}$ and inorganic ions. The purposes of the study are 1) to investigate the concentration levels of biogenic secondary organic aerosol tracers during the special pollution season in Shanghai; 2) to examine the influence of meteorological factors and aerosol acidity on biogenic secondary organic aerosol tracers in the real atmosphere; and 3) to evaluate the contribution of biogenic secondary organic aerosols to OC in $PM_{2.5}$.

2. Material and methods

2.1. Experimental sampling section

Quartz filter samples were collected using high-volume sampler (Ecotech, Hivol 3000) at a flow rate of 1.13 $m^3\ min^{-1}$ from May 22 to June 19, 2015 at an urban site in Shanghai. As shown in Fig. 1, the sampling site (Xu Jia Hui, E121° 25′47″, N31°10′42″) was located in the center of Shanghai, which is representative of a typical urban environment. The sampler was placed on the roof of a 20 m-high building on the Xu Jia Hui (XJH) campus of Shanghai Jiao Tong University. The sampling continued for 23 h periods for each sample. Field blanks were obtained every ten days by setting the filters in the sampler without air flow during the study period. All of the quartz fiber filters (8 × 10 inch) were baked at 550 °C for 5.5 h to remove organic material before being used and then stored at −20 °C after sample collection. A total of 24 samples were obtained, including three field blanks during the study period.

2.2. Chemical analysis

The quartz fiber filters were analyzed for OC and EC by IMPROVE method with a DRI Model 2001A Thermal/Optical Carbon Analyzer. A punch (4.9 cm^2) from each quartz filter was sonicated with 20 mL of ultra-pure deionized water (>18.2 MΩ resistivity) in an ice-water bath for extracting nitrate (NO_3^-), sulfate (SO_4^{2-}) and ammonium (NH_4^+). It is worth noting that the water temperature should be maintained at a temperature of 20–30 °C during the ultrasound. The filtered extract was then analyzed by IC (ion chromatography).

For the analysis of organic aerosols tracers, details of the sample extraction and derivatization have been presented elsewhere (Fu et al., 2009a; Feng et al., 2013). Approximately 20 cm^2 of each filter was extracted three times in 20 mL of dichloromethane/methanol (1:1, v/v) and sonicated for 25 min each time, the combined extracts were evaporated to approximately 1 mL by rotary evaporator, and then they were further concentrated to dryness under a gentle nitrogen stream. As the solution temperature would rise in the ultrasonic process, resulting in solvent evaporation and decomposition of some organic components, an appropriate amount of ice was added into the ultrasonic bath to control the temperature below 30 °C. The samples were then derivatized with 100 mL of N, O-bis-(trimethylsilyl)-tri- fluoroacetamide (BSTFA) and 20 mL of pyridine at 75 °C for 45 min. Each derivatized sample was injected into the GC/MS for identification and quantification. The gas chromatographic conditions were as follows: a constant temperature of 60 °C for 10 min, which was then increased to 300 °C at 10 °C min^{-1}, for 20 min. The flow rate was 1.0 mL min^{-1}, with He serving as the carrier gas. The GC/MS interface temperature was 300 °C. The interface through organic tracers was ionized by electron impact (70 eV), and the scanning ranged from 50 to 500 amu. *cis*-Pinonic acid and pinic acid were quantified by authentic standards. Isoprene SOA tracers were quantified using erythritol (Claeys et al., 2004; Ding et al., 2011); 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; β-caryophyllinic acid was quantified using octadecanoic acid (Ding et al., 2009, 2011). The method detection limits (MDLs) for *cis*-pinonic acid, pinic acid, erythritol and octadecanoic acid were 0.05, 0.08, 0.07 and 0.11 ng m^{-3}, respectively. Limit of quantification of species for *cis*-pinonic acid, pinic acid, erythritol and octadecanoic acid were 0.166, 0.278, 0.234 and 0.399 ng m^{-3}.

2.3. Quality assurance/quality control

Field blanks and laboratory blanks were treated in the same way as the ambient samples for quality assurance. The target compounds were not detected in the blanks. The recoveries of the target compounds were 60–105%. Duplicate analysis showed that the relative standard deviation was generally less than 10%. Recoveries of the target compounds in six spiked samples (authentic standards

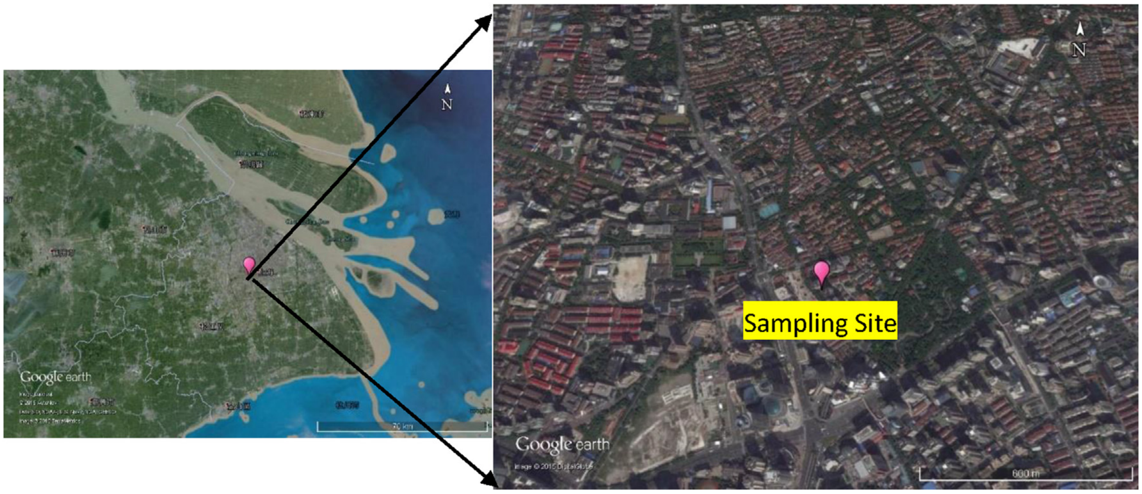

Fig. 1. Map of the Xujiahui (XJH) sampling site, which is in the central part of Shanghai and is surrounded by city clusters.

spiked into solvent with prebaked quartz filter) were 105 ± 5% for *cis*-pinonic acid, 72 ± 14% for pinic acid, 60 ± 12% for erythritoland 79 ± 13% for octadecanoic acid. And the relative standard deviation (RSD) for the quantification of standards were 4.2%, 6.8%, 5.9% and 3.3% for *cis*-pinonic acid, pinic acid, erythritol and octadecanoic acid respectively.

3. Results and discussion

3.1. Concentration of biogenic SOA tracers

This period, sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) were the most important ion components of $PM_{2.5}$. The SO_4^{2-}, NO_3^- and NH_4^+ exhibited similar diurnal variations during the sampling period. The sulfate, nitrate and ammonium ranged from 4.34 to 20.85 $\mu g\ m^{-3}$, 1.49–13.25 $\mu g\ m^{-3}$ and 2.28–8.49 $\mu g\ m^{-3}$, respectively. The average concentrations of sulfate, nitrate and ammonium were 4.34 ± 1.25 $\mu g\ m^{-3}$, 6.67 ± 2.32 $\mu g\ m^{-3}$ and 11.16 ± 3.35 $\mu g\ m^{-3}$ (Table 1, Fig. 2b), respectively.

The SOA tracer quantities are listed in Table 1. Among all of the BSOA tracers (Fig. 3, Table 1), the isoprene SOA tracers ranged from 4.43 to 46.41 ng m^{-3} with an average concentration of 17.64 ± 9.75 ng m^{-3} during our campaign, which were the highest levels, followed by the α-pinene SOA tracers (3.64 ± 1.74 ng m^{-3}) and β-caryophyllinic acid (0.58 ± 0.75 ng m^{-3}). Fig. 3 shows that high levels of isoprene SOA tracers were observed on June 5 along with high temperatures (Fig. 2a). The lowest level of isoprene SOA tracers (4.43 ng m^{-3}) occurred on June. 3, 2015 with the temperature declined to the lowest during the campaign. Meanwhile, the concentration of secondary species (sulfate, nitrate and ammonium) decreased on June 3 and increased on June 5. Although the transformation process of gaseous nitric acid into nitrate particles was strong, the lower temperatures on June 3 were not conducive to the photochemical processed. In addition, low RH was not conducive to aqueous-phase formation processing of SO_2 on June 3. As a result, inorganic secondary species decline on June 3 was a combined result of photochemical production, gas-particle partitioning and aqueous-phase formation.

3.1.1. Isoprene SOA tracers

According to the previous chamber experiments (Claeys et al., 2004; Sato et al., 2011) two 2-methyltetrols, 2-methylglyceric acid and three C5-alkene triols were determined as isoprene tracers. The levels of 2-methyltetrols (sum of 2-methylthreitol and 2-methylerythritol) were the highest among the isoprene SOA tracers (Fig. 4a). During our sampling, NOx level was 25 ± 11 ppbv. Photo-oxidation NO_x in chamber experiments ranged at 70 ppb-1 ppm (Carlton et al., 2009). Obviously, the sampling site in our study belongs to the condition of low-NO_x. This may be beneficial for the formation of 2-methyltetrol. The 2-methyltetrols averaged 6.07 ± 3.86 ng m^{-3}, accounting for up to 50% of the isoprene SOA tracers (Table 1) in this study, which is comparable with that

Table 1
Concentrations of polar organic tracers and other parameters in $PM_{2.5}$ in Shanghai.

	Average	Range		Average	Range
Major components ($\mu g\ m^{-3}$)					
OC	7.17 ± 3.91	3.12–16.28	2-Methylglyceric acid	1.29 ± 0.92	0.31–3.43
EC	2.56 ± 1.38	1.23–5.01	*cis*-2-Methyl-1,3,4-trihydroxy-1-butene	0.95 ± 0.92	0–3.39
SO_4^{2-}	4.34 ± 1.25	4.34–20.85	3-Methyl-2,3,4-trihydroxy-1-butene	1.21 ± 0.92	0.12–3.95
NO_3^-	6.67 ± 2.32	1.49–13.25	*trans*-2-Methyl-1,3,4-trihydoxy-1-butene	2.05 ± 1.84	0.16–6.56
NH_4^+	11.10 ± 3.35	2.28–8.49	2-Methylthreitol	3.04 ± 1.89	0.99–8.32
Organic compounds (ng m^{-3})			2-Methylerythritol	9.1 ± 5.41	1.75–20.7
α-Pinene SOA tracers			Sum of 2-methyltetrols	6.07 ± 3.86	0.78–20.7
cis-Pinonic acid	0.92 ± 0.93	0–3.39	Sum of isoprene SOA tracers	17.6 ± 9.75	4.43–46.1
3-Hydroxyglutaric acid	0.39 ± 0.46	0.16–4.58	β-Caryophyllene SOA tracer		
3-Hydroxy-4,4-dimethylglutaric acid	0.87 ± 0.60	0.1–2.58	β-Caryophyllinic acid	0.58 ± 0.75	0–2.82
3-Methyl-1,2,3-butanetricarboxylicacid	1.45 ± 1.17	0–0.84	Meteorological parameters		
Sum of α-pinene SOA tracers	3.64 ± 1.74	0.91–7.41	RH (%)	78 ± 15	54.4–97.1
			Temperature (°C)	24.4 ± 2.1	22.1–29.9

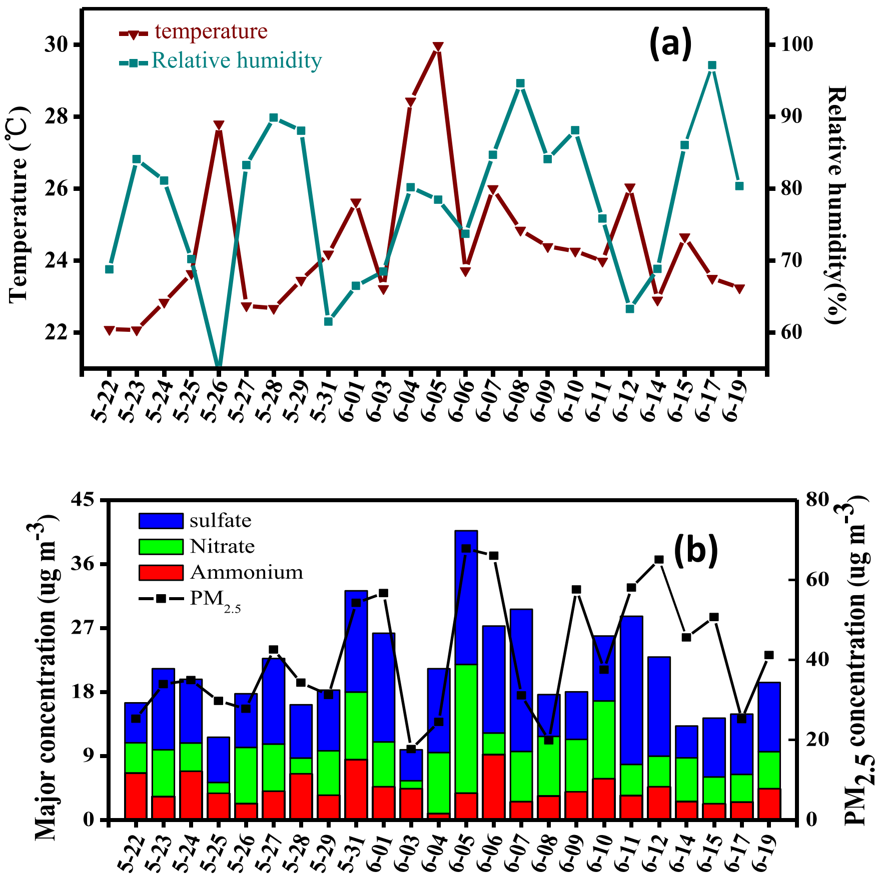

Fig. 2. Daily variations in the temperature and relative humidity (a) and averaged daily variations for chemical species (b).

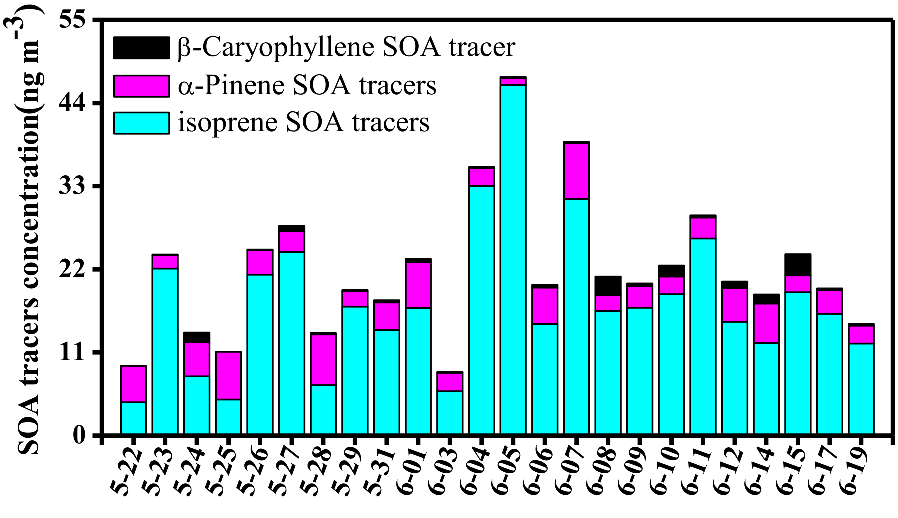

Fig. 3. Averaged daily variations for BSOA tracers.

reported in Guangzhou and Hong Kong during the summer (Hu et al., 2008; Ding et al., 2011), but lower than it was in the US (Xia and Hopke, 2006; Ding et al., 2009; Offenberg et al., 2011). 2-Methyltetrols that reported by Xia and Hopke were about 60 ng m^{-3} in Potsdam, a location just north of the Adirondack State Park. The slope of 2-methylthreitol to 2-methylerythritol in this study was 0.33 ± 0.05, which was equal to those reported in shanghai in 2013 (Feng et al., 2013), which means that the formation rate of these two tracers may be relatively constant (Ding et al., 2011).

Isoprene reactions with ozone (O_3) under low NO_X, including *cis*-2-methyl-1, 3, 4-trihydroxy-1-butane (*cis*-MTHB), 3-methyl-2, 3, 4-trihydroxy-1-butane (MTHB) and *trans*-2-methyl-1, 3, 4-trihydoxy-1-butane (*trans*-MTHB). During our sampling period, C5-alkene

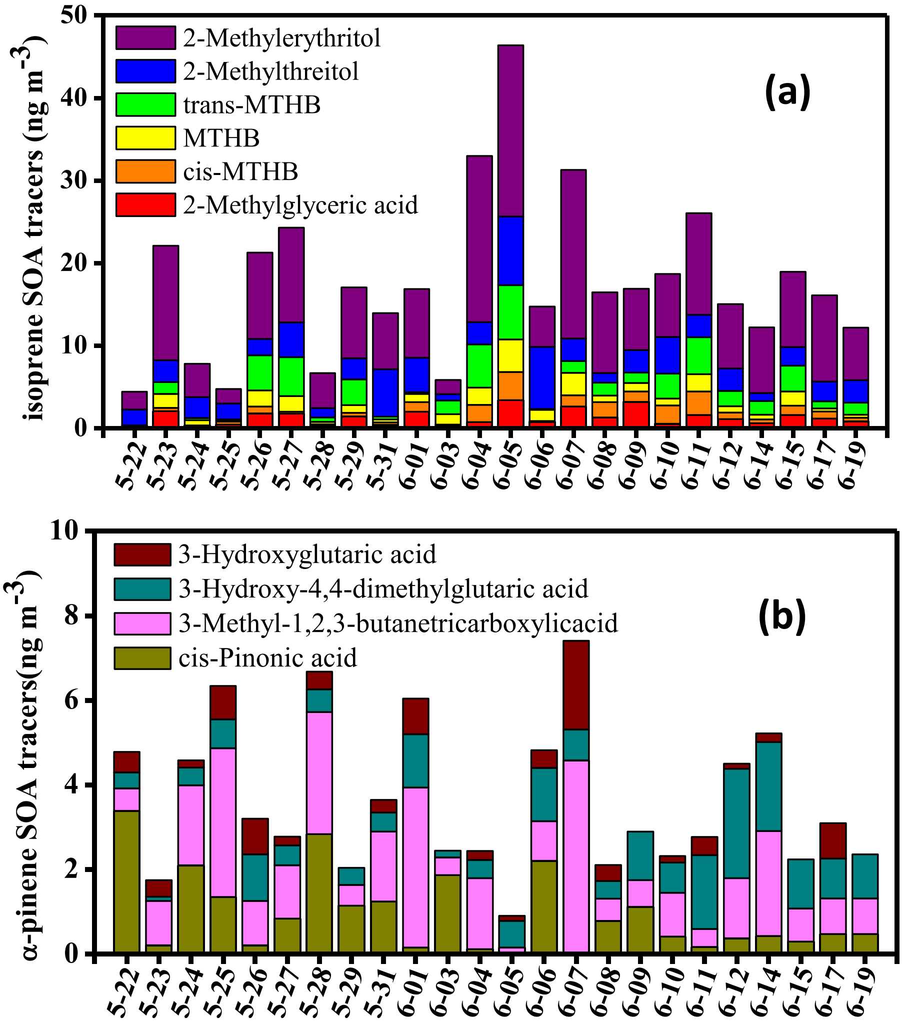

Fig. 4. Averaged daily variations for (a) isoprene and (b) α-pinene SOA tracers.

triols exhibited lower average concentrations (4.21 ± 3.32 ng m^{-3}) than 2-methyltetrols (Fig. 4a, Table 1). C5-alkene triols exhibited a concentration trend of *cis*-2-methyl-1, 3, 4-trihydroxy-1-butene (*cis*-MTHB) < 3-methyl-2,3, 4-trihydroxy-1-butene (MTHB) < *trans*-2-methyl-1, 3, 4-trihydoxy-1-butene (*trans*-MTHB), which was consistent with the result from Feng et al. (2013) (Feng et al., 2013). However, 2-methylglyceric acid was the oxidation product of isoprene in high NO_x-level atmospheric environments. The concentration of 2-methylglyceric acid ranged from 0.31 to 3.43 ng m^{-3}, and it averaged 1.29 ± 0.92 ng m^{-3} (Fig. 4a, Table 1), which was comparable with the concentration found in Finland (Ikebe et al., 2008).

3.1.2. α-Pinene SOA tracers

As the largest emissions of monoterpenes found in nature, the measured tracers for SOA from α-pinene in our study included 3-hydroxyglutaric acid (HGA), *cis*-pinonic acid, 3-methyl-1, 2, 3-butane-tricarboxylic acid (MBTCA) and 3-hydroxy-4, 4-dimethylglutaric acid (HDMGA). MBTCA had the highest level (1.45 ± 1.17 ng m^{-3}) during our sampling period (Fig. 4b, Table 1). The reason for this phenomenon should be that it has a promotion effect, resulting in the reduction of intermediate *cis*-pinene and promoting the oxidation of α-pinene to MBTCA during our study period (Szmigielski et al., 2007; Aljawhary et al., 2016). The average concentration of HGA was found to be low (0.39 ng m^{-3}), which was similar to findings in summer samples in Midwestern US cities (Lewandowski et al., 2008).

3.1.3. β-Caryophyllene SOA tracers

Sesquiterpene was rarely reported in volatile organic compounds because of its high and relatively low vapor pressure. β-Caryophyllene was the most frequently released sesquiterpene from plants. β-Caryophyllinic acid was the typical photo-oxidation product of β-caryophyllene, and many studies have confirmed that it could be used as a sesquiterpene secondary organic aerosol tracer (Jaoui et al., 2007; Lewandowski et al., 2007; Fu et al., 2009a). β-Caryophyllinic acid was found at the highest concentration in our study, at 2.44 ng m^{-3}, and most of the samples contained less than 1 ng m^{-3} (Fig. 3), which was much lower than that found in March–May in Cincinnati of US (0.09) (Lewandowski et al., 2007).

3.2. Correlations of SOA tracers with meteorological factors

Meteorological factors can influence the initial release of BVOCs; in addition, they can accelerate the oxidation of BVOCs in the ambient aerosol. The effect of the factor on the SOA tracers can reflect their effect on the precursor-specific, since there is only a conversion coefficient between the SOA tracer concentration and the specific precursor. This study discusses the correlations of isoprene SOA tracers and influence factors. The correlations between the concentrations of isoprene SOA tracers and various meteorological parameters are shown in Figs. 5 and 6. The isoprene SOA tracers exhibited the highest levels (17.64 ± 9.75 ng m^{-3}) and are always found along with higher temperatures, resulting from a higher level of tracer formation rates and isoprene emission strength (Rinne et al., 2002; Ding et al., 2009, 2011). Previous works (Monson et al., 1994) found that the isoprene species emission rate from leaves increased with temperatures rising between 20 °C and 40 °C, but when temperatures exceeded 40 °C, the emission rate started to decrease, due to the inactivity of isoprene enzyme system at high temperature (Kuzma et al., 1995).

Unlike the correlation with the temperature, the concentrations of the isoprene SOA tracers exhibited no evident relations with the relative humidity during our campaign (Fig. 5a). However, Kamens et al. (2011) argued that the formation rate of aromatic SOA was 2–5 times lower under dry conditions than the formation rates under humid conditions (Kamens et al., 2011). Therefore, the statistical analysis of the isoprene SOA tracers in relation to the relative humidity was further divided into three patterns (RH 50–70%, RH 70–85% and RH 85–100%) in this study. Fig. 6b shows that the concentrations of isoprene SOA tracers (except 2-methylglyceric acid) in this study increased with RH levels below 85%, and the concentrations decreased again, at RH > 85%. It could not be simply assumed that humidity has no effect on isoprene SOA formation because the effect of atmospheric relative humidity on isoprene SOA generation may be indirect. The factors that directly affect SOA formation may be the amount of water in the particulate matter. The relative humidity is only an indirect representation of the moisture content in the gas phase. The relative humidity is only one of the factors that affect the water content of the particles, the chemical composition of the particles determines the moisture absorption of particulate matter, which is an important factor affecting the water content. To give a sound explanation to the field results, further studies are needed about the influence of RH on 2-methyltetrols formation, particularly of high RH as occurring in the YRD region. The 2-methylglyceric acid concentrations were decreased with increasing humidity, which was consistent with the published work (Zhang et al., 2011). Zhang et al. (2011) showed that 2-methylglyceric acid formation was related to the air relative humidity, and lower relative humidity was more conducive to the formation of 2-methylglyceric acid.

3.3. *Correlations of SOA tracers with aerosol acidity*

Three conditions are assumed for the neutralization status of ammonium: NH_4NO_3+H_2SO_4, NH_4NO_3+NH_4HSO_4, NH_4NO_3+$(NH_4)_2SO_4$. The status depends on the fresh emission, transport, and aging processes, and abundances of corresponding gaseous species. As the sites are located in the city center, most of the ammonium should be in the form of the third type. The relationship between simulated NH_4^+ and measured NH_4^+ were observed. It was found that particles of SO_4^{2-} and NO_3^- mainly were in the form of ammonium salts in our site. Then using a charge balance formula of SO_4^{2-}, NO_3^- and NH_4^+ aerosol acidity ($[H^+]$, mmol m^{-3}) was calculated in this study as follows (Ding et al., 2011):

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

The calculated $[H^+]$ in this study ranged from −0.18–0.47 mmol m^{-3}.

The slope of 2-methyltetrols vs. acidity was 29.01 ng m^{-3} per mmol $[H^+]$ m^{-3} (2-Methylerythritol) and 9.22 ng m^{-3} per mmol $[H^+]$ m^{-3} (2-Methylthreitol) respectively. The isoprene SOA tracers showed remarkable correlations with the $[H^+]$, r values of all tracers were above 0.7 because of the enhanced formation of isoprene SOA in the acidic aerosols in Shanghai (Fig. 7), which also confirmed the findings from previous studies (Surratt et al., 2007a; Ding et al., 2011). Isoprene oxidation products can be substantially enhanced in the presence of an acidic catalyst such as sulfuric acid and nitric acid and their precursors, as confirmed by studies in a smog chamber (Myoseon et al., 2003; Surratt et al., 2007b). Myoseon et al. (2003) indicated that atmospheric organic carbonyls can contribute significantly to the formation of secondary organic aerosol through acid-catalyzed heterogeneous reactions.

3.4. *Formation pathways of the SOA tracers*

Correlations between the SOA tracers are listed in Table 2. Correlations were used to estimate whether these chemical compositions formed in similar pathway or not. Among isoprene SOA tracers, remarkable correlations were observed between isoprene tracers except for 2-methylglyceric acid. Surratt et al. (2010) suggested that 2-methyltetrols have previously been postulated to form from further acid-catalyzed heterogeneous reaction processing of gas isoprene, such as epoxy diene (IEPOX) of isoprene under low NO_x conditions (Surratt and Finlayson-Pitts, 2010). The 2-

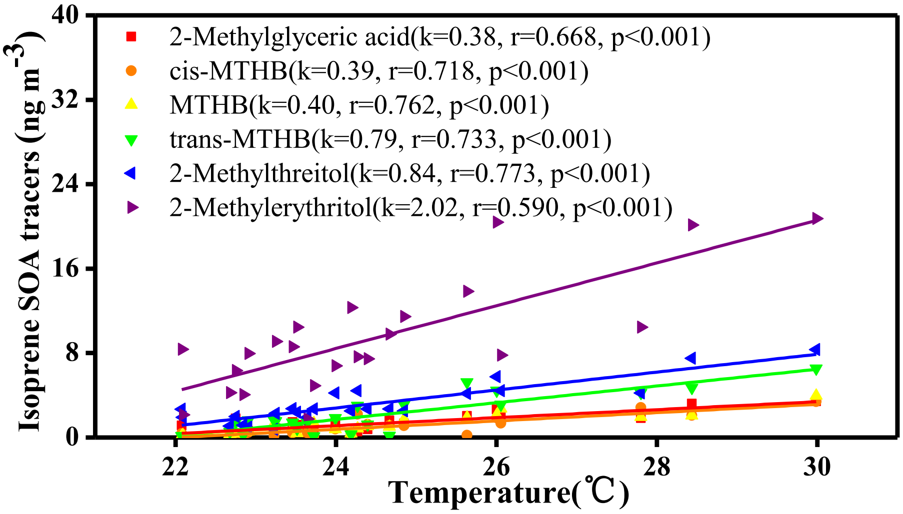

Fig. 5. Correlations between isoprene SOA tracers and temperatures. K is the slope of correlation.

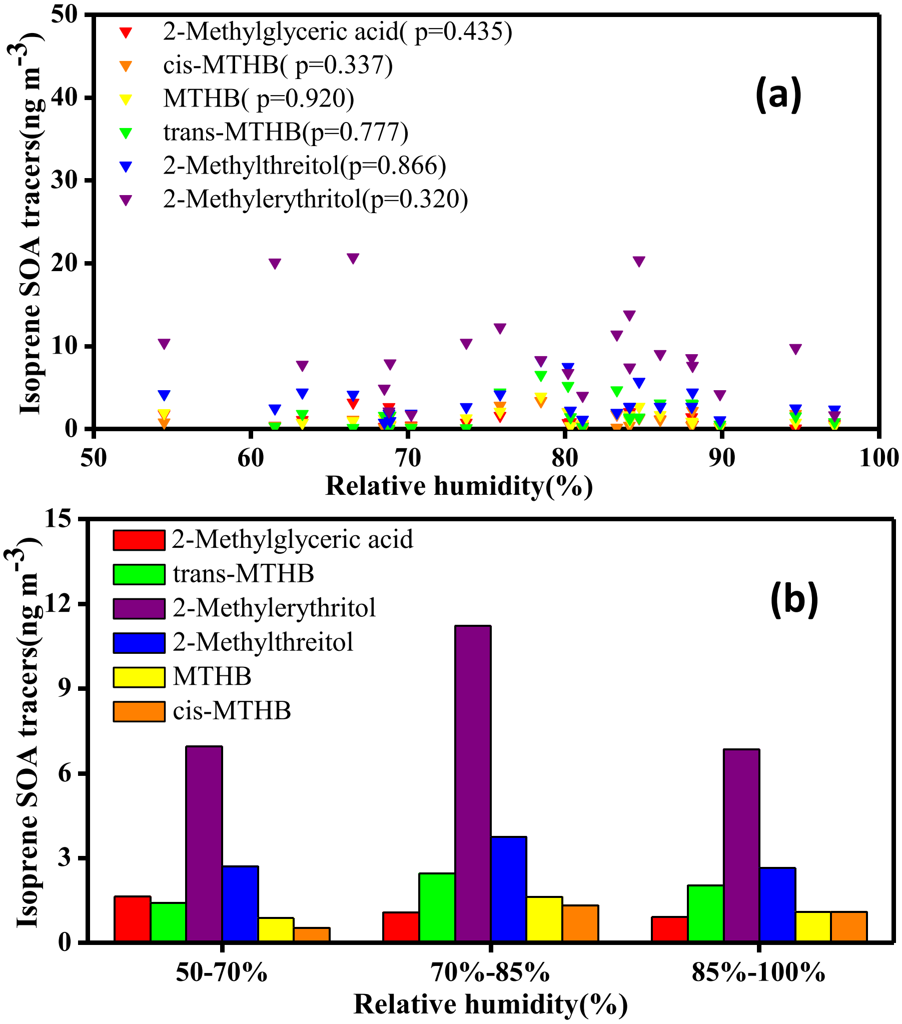

Fig. 6. Correlations between isoprene SOA tracers and RH.

methyltetrols showed remarkable correlations with aerosol acidity in this study (Fig. 7). That means the acid catalyzed reaction of IEPOX plays an important role in the formation of 2-methyletetrols in shanghai, which was consistent with that in the PRD region,

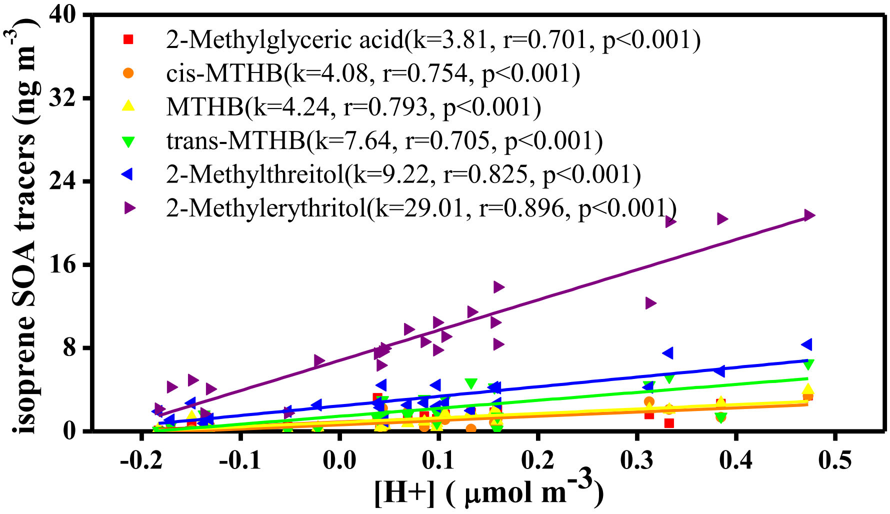

Fig. 7. Correlations between isoprene SOA tracers and aerosol acidity. K is the slope of correlation.

Table 2
Correlations between the SOA tracers in $PM_{2.5}$ in Shanghai.[a]

Isoprene[b]							α-Pinene[c]				
	I-1	I-2	I-3	I-4	I-5	I-6		A-1	A-2	A-3	A-4
I-1	1	*0.53*	*0.58*	*0.45*	*0.66*	*0.50*	A-1	1	*−0.16*	*−0.33*	*−0.06*
I-2		1	**0.74**	**0.77**	**0.78**	*0.68*	A-2		1	**0.73**	*0.43*
I-3			1	**0.75**	**0.81**	**0.72**	A-3			1	**0.78**
I-4				1	**0.77**	**0.79**	A-4				1
I-5					1	**0.88**					
I-6						1					

[a] Numbers in bold and italics are indicative of $p < 0.01$ and $p < 0.05$, respectively.
[b] I-1 to I-6 are indicative of 2-methylglyceric acid, *cis*-3-methyl-1,3,4-trihydroxy-1-butene, 3-Methyl-2,3,4-trihydroxy-1-butene, *trans*-3-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol, and 2-methylerythritol, respectively.
[c] A-1 to A-4 are indicative of *cis*-pinonic acid, 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, and MBTCA, respectively.

Table 3
Average concentrations of Biogenic secondary organic carbon (BSOC) at XJH estimated with the tracer based method (unit: μg C m^{-3}).

	Average	Range
$SOC_{isoprene}$	0.114 ± 0.062	0.031–0.299
SOC $_{\alpha\text{-pinene}}$	0.0158 ± 0.007	0.0039–0.0288
$SOC_{\beta\text{-caryophyllene}}$	0.025 ± 0.032	0–0.123
Total BSOC	0.155 ± 0.066	0.049–0.309
$BSOC_{total}$/OC	2.73%	0.57%–10.25%

China (Ding et al., 2011). C5-alkene triols (I2/I3/I4) had remarkable correlations with 2-methyltetrols (I5/I6). MTHB in turn is believed to be formed under low NO_x conditions as 2-methyltetrols (Mcneill, 2015). Significant correlations between 2-methyltetrols and MTHB (I3) were also observed in this study (Table 2), indicating that they had similar formation mechanisms. However, the 2-methylglyceric acid (I1) had a very different pathway from that of the other isoprene tracers, resulting in weak correlations among them (Table 2), which was shown by Surratt (Surratt and Finlayson-Pitts, 2010). Surratt suggested that 2-methylglyceric acid was mainly formed by the decomposition of C4-hydroxy nitrate-PAN under high NO_x conditions. It shares different pathways from other isoprene SOA tracers at low NO_x in the aerosol phase.

Correlations between α-pinene SOA tracers exhibited distinct patterns. *cis*-Pinonic acid is the primary degradation product of α-pinene, which has been reported in smog chamber experiments (Moglioni et al., 2000). MBTCA and HDMGA had remarkable correlations with each other (Table 2), suggesting their similar formation pathways. Previous studies have shown that *cis*-pinonic acid can be further degraded to MBTCA (Claeys et al., 2007; Szmigielski et al., 2007). It is quite interesting that *cis*-pinonic acid (A1) and the other SOA tracers displayed negative correlations. Ding et al. (2011) proposed that the ratio of *cis*-pinonic acid to MBTCA (P/M) can be used to indicate the aging degree of α-pinene SOA. They thought higher P/M ratio (28.9) suggested that alpha-pinene-based SOA was relatively fresh, that is, *cis*-pinonic acid was less transformed to MBTCA, and the lower P/M ratio (0.28) was the opposite (Ding et al., 2011). The average P/M ratio observed during our campaign was 0.63, implying that alpha-pinene-based SOA was relatively aged. This indicated that more *cis*-pinonic acid was transformed to MBTCA, which may explain the different pathway of *cis*-pinonic acid and the relatively low or undetectable levels of *cis*-pinonic acid in the ambient aerosol of this study.

3.5. *SOC estimation from SOA tracers*

The SOC tracer mass fractions (fsoc) were 0.155 ± 0.039 μg μgC^{-1}, 0.231 ± 0.0046 μg μgC^{-1} and 0.0230 ± 0.11 μg μgC^{-1} for isoprene, α-pinene and β-caryophyllene, respectively, as obtained in the laboratory and measured by (Kleindienst et al., 2007), which has been used in many studies (Fu et al., 2009b; El Haddad et al., 2010). The formula was as follows:

$$[SOC_x] = [SOA_x]/fsoc_i$$

where the [x] refers to isoprene, α-pinene and β-caryophyllene, respectively, in this study.

The estimated results are listed in Table 3. The BSOC estimation with BSOA tracers (SOC tracer-based) averaged 0.155 ± 0.066 μg m^{-3} at XJH during the sampling period, which amounted to 2.73% OC. Compared with contribution of BSOC estimation with BSOA tracers to OC in other sites, the concentration in our study lower than that of observed in Mount Tai, central east China in the same period in 2010 (9.9%) (Fu et al., 2010) and in Wangqingsha, rural site in PRD region (10.4%) (Ding et al., 2011), which was consistent with those of 2.23% in Centreville in US (Ding et al., 2008), but higher than those of 0.67% in summer in North Birmingham in US (Ding et al., 2008) and other cities in China, such as shanghai in April–May (1.05%) (Feng et al., 2013). Slight contribution of SOC based on α-pinene and β-

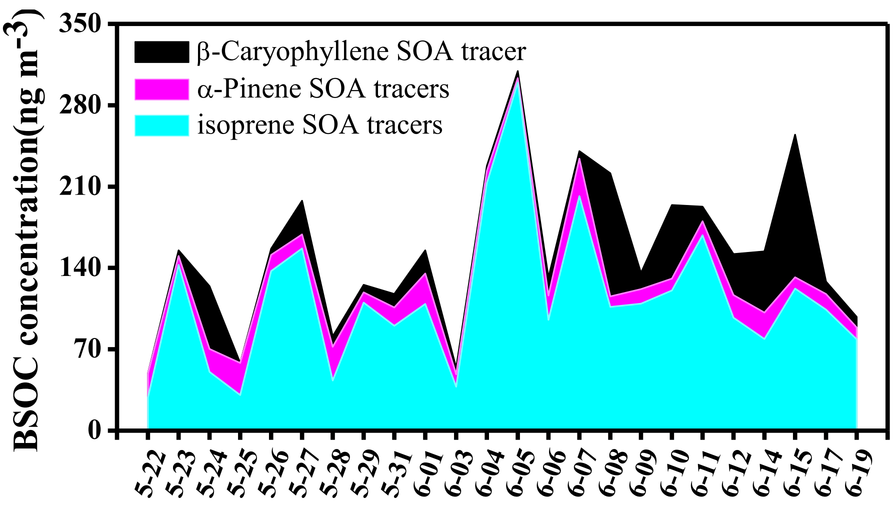

Fig. 8. Compositions of the BSOC during our sampling period.

Table 4
BSOC measured in Shanghai compared to those reported in other studies (unit: µg C m^{-3}).

Location	Season	Site	SOC_I	SOC_α	SOC_β	Reference
Shanghai,China	May–Jun	urban	0.11	0.02	0.03	This study
K-puszta, Hungary	Summer	forest	0.28	/	/	(Ivan et al., 2009)
Mt.Tai, China	June	forest	1.01	0.1	0.52	(Fu et al., 2010)
Changbai, China	July	forest	0.32	/	/	(Wang et al., 2008)
Hainan, China	November	forest	0.27	/	/	(Wang et al., 2008)
Chongming, China	June	forest	0.03	/	/	(Wang et al., 2008)
Dinghu, China	August	forest	0.16	/	/	(Wang et al., 2008)
Wangqingsha, China	Aug–Sep	rural	0.64	/	0.12	(Ding et al., 2012)
Wangqingsha, China	Nov–Dec	rural	0.13	/	0.14	(Ding et al., 2012)
Bondville, USA	Jan–Dec	rural	0.32	0.21	0.12	(Michael et al., 2008)
Tung Chung, Hong Kong	Jul–Aug	rural	0.47	/	1.58	(Hu et al., 2008)
Alert, Canada	Feb–Jun	rural	0.00173	/	0.00522	(Fu et al., 2009a)
Northbrook, USA	Jan–Dec	urban	0.22	0.17	0.18	(Michael et al., 2008)
Cincinnati, USA	Jan–Dec	urban	0.56	0.18	0.14	(Michael et al., 2008)
Detroit, USA	Jan–Dec	urban	0.25	0.25	0.3	(Michael et al., 2008)
East St. Louis, USA	Jan–Dec	urban	0.9	0.18	0.09	(Michael et al., 2008)
Yuen Long, Hong Kong	Jul–Aug	urban	0.44	/	1.53	(Hu et al., 2008)
Tsuen Wan, Hong Kong	Jul–Aug	urban	0.47	/	2.01	(Hu et al., 2008)

SOC_I, SOC_α and SOC_β are indicative of $SOC_{isoprene}$, SOC $_{\alpha\text{-pinene}}$ and $SOC_{\beta\text{-caryophyllene}}$, respectively.

caryophyllene to total BSOC are observed during our campaign. The concentration of $SOC_{\alpha\text{-pinene}}$ ranged from 0.0039 to 0.0289 µg C m^{-3} with an average concentration of 0.0158 ± 0.007 µg C m^{-3} during our campaign (Table 3). For β-caryophyllene-based tracer ($SOC_{\beta\text{-caryophyllene}}$), the average concentration was 0.025 ± 0.032 µg C m^{-3}.

Furthermore, the isoprene-based tracers ($SOC_{isoprene}$ in Table 3) were the most important contributors of biogenic SOA, and they accounted for over 50% of the SOC tracer-based portion (Fig. 8), with an average level of 0.114 ± 0.062 µg C m^{-3}. The results compared to other previous studies were list in Table 4. The values of the isoprene-based tracers in our current study were compared quite well with the data that were reported for Dinghu, China, during the summer of 2006 (Wang et al., 2008). However, the values were lower than those reported for East St. Louis, USA (Lewandowski et al., 2008), but they were approximately 1–2 orders of magnitude higher than those found in Canada (Fu et al., 2009a) (Table 4), which resulted from different factors such as the plant species and the meteorological conditions (Liang et al., 2012).

4. Conclusions

Biogenic SOA tracers from isoprene, a-pinene and β-caryophyllene were measured in $PM_{2.5}$ in the central part of Shanghai, China. These tracers averaged 17.64 ± 9.75 ng m^{-3}, 3.64 ± 1.74 ng m^{-3} and 0.58 ± 0.75 ng m^{-3}, respectively. Meteorological factors, such as the temperature, influenced the release rate of the BVOC precursors (i.e., isoprene) and the formation of secondary aerosol traces. The isoprene SOA tracers displayed remarkable correlations with the calculated $[H^+]$ because of the enhanced formation of isoprene SOA in the acidic aerosols. Correlations between SOA tracers exhibited distinct patterns. Furthermore, isoprene plays an important role in the formation of BSOA, even in urban areas, as shown in this study for Shanghai, China.

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