



Molecular Characteristics and Formation Mechanisms of Biogenic Secondary Organic Aerosols in the Summer Atmosphere at Mt. Tai on the North China Plain

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ABSTRACT

To investigate the molecular characteristics and formation mechanisms of biogenic secondary organic aerosol (BSOA), daytime and nighttime PM_{2.5} samples were collected at the summit of Mt. Tai during the summer of 2016. The critical indicators of primary sources, such as elemental carbon (EC) and levoglucosan, displayed similar values during the daytime and nighttime, suggesting that changes in the boundary layer heights (BLHs) produced only inconsequential effects during the observation campaign. The molecular distributions of the BSOA were dominated by isoprene SOA tracers ($68.5 \pm 42.6 \text{ ng m}^{-3}$), followed by monoterpene ($43.5 \pm 24.4 \text{ ng m}^{-3}$) and β -caryophyllene ($16.3 \pm 8.6 \text{ ng m}^{-3}$) SOA tracers. Due to the higher diurnal temperatures and solar radiation, the concentrations of all of the tracers were higher during the day than at night. The ratio of the combined *cis*-pinonic and *cis*-pinic acid to the MBTCA (P/M) was much lower than in Chinese cities and at the Tibetan background site, indicating that the monoterpene SOA was relatively aged in the mountainous atmosphere, in large part because of the stronger solar radiation at the peak of Mt. Tai. The concentrations of the BSOA products exhibited a significantly positive correlation with the level of ozone during the daytime ($R^2 = 0.58\text{--}0.86$) and the temperature over the whole sampling period ($R^2 = 0.37\text{--}0.75$), as higher temperatures can accelerate the emission of biogenic volatile organic compounds and the formation of SOA. By contrast, the BSOA tracers displayed a negative linear correlation with the relative humidity (RH) ($R^2 = 0.43\text{--}0.84$) and the *in situ* particle pH (pH_{is}) ($R^2 = 0.55\text{--}0.70$) because high RH can inhibit the acid-catalyzed formation of BSOA due to the dilution of the aerosol acidity. No correlation between the BSOA tracers and anthropogenic pollutants (e.g., levoglucosan, SO₄²⁻, NO₃⁻ and EC) was observed during the daytime or nighttime, suggesting that BSOA tracers in the atmosphere of Mt. Tai during summer were primarily derived from the local oxidation of BVOCs rather than long-distance-transported anthropogenic emissions from the lowlands.

Keywords: Biogenic secondary organic aerosol (BSOA); Isoprene; Aerosol acidity; Temperature and relative humidity; Anthropogenic pollutants.

INTRODUCTION

Terrestrial vegetation can release plenty of biogenic volatile organic compounds (BVOCs) into the atmosphere, including isoprene, monoterpenes and sesquiterpenes (Kesselmeier and Staudt, 1999). Emissions of BVOCs (1150 Tg y^{-1}) in the global atmosphere are one order of magnitude higher than anthropogenic VOCs (AVOCs), which can significantly increase the concentration levels of secondary organic aerosols (SOA) (Guenther *et al.*, 2006; Li *et al.*, 2013a). SOA are

produced by the oxidation of VOCs with oxidants such as ozone (O₃), hydroxyl radical (OH) and nitrate radical (NO₃), which can affect the atmosphere radiation directly by absorbing and scattering sunlight and indirectly acting as a cloud condensation nuclei (CCN) (Li *et al.*, 2013a; Han *et al.*, 2014; Hu *et al.*, 2018). SOA play an important role in atmospheric visibility, air quality, climate change and human health (Han *et al.*, 2014; Huang *et al.*, 2014; Haque *et al.*, 2016; Zhu *et al.*, 2016; An *et al.*, 2019).

As the oxidation products of BVOCs, biogenic SOA (BSOA) derived from terrestrial ecosystems are polar and hygroscopic (Han *et al.*, 2014; Haque *et al.*, 2016). Claeys *et al.* (2004) discovered that the oxidation production of isoprene, 2-methyltetrols and 2-methylglyceric have a great influence on the formation of BSOA. As the predominant precursors of BSOA, isoprene and monoterpenes account

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for around 50% and 10% of the earth's BVOCs, respectively (Zhu *et al.*, 2016). Investigations on the BSOA tracers of isoprene, monoterpenes and β -caryophyllinic acid have been performed in various environments such as urban (Ren *et al.*, 2018; Zhu *et al.*, 2018a), forested (Ren *et al.*, 2019) and continental background regions (Li *et al.*, 2013b), most of which have been conducted on the ground surface. Compared to the lowland areas, the atmospheric environment of high-altitude regions can provide a unique and ideal situation for the study of SOA due to stronger sunlight, lower temperatures and higher humidity (Li *et al.*, 2013a). Measurement over the high-elevation mountain regions is an alternative research method for high-altitude aerosol characterization, which has such advantage as low cost and long-term sampling compared to aircraft and balloon-based observations (Meng *et al.*, 2014). Mt. Tai is located in the center part of the North China Plain, one of the most heavily polluted areas in the world (Meng *et al.*, 2018). Moreover, the North China Plain is one of the regions with the highest emissions of VOCs in China (Zhu *et al.*, 2018b). In the past decades, a few studies have been performed to investigate the molecular characteristics and the sources of BSOA tracers and evaluate the effect of anthropogenic pollutants from long-range transport on the formation mechanisms of SOA at Mt. Tai (Fu *et al.*, 2010; Zhu *et al.*, 2017). However, most of the studies were conducted during May and June when the effect of anthropogenic activities such as biomass burning (burning of wheat straw) was significant (Fu *et al.*, 2010; Zhu *et al.*, 2017), whereas information on BSOA at the summit of Mt. Tai in the typical summertime season (i.e., July) is very limited when the emission of BVOCs is dominant. Thus, it is essential to elucidate the molecular distributions and formation mechanisms of BSOA in the alpine atmosphere, especially when the biogenic emission is dominant in the summer.

To better investigate the molecular distributions, sources and formation mechanisms of BSOA tracers over the high-elevation remote regions, we collected PM_{2.5} samples at the summit of Mt. Tai and conducted measurements of SOA tracers of isoprene, monoterpenes and β -caryophyllene along with organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC) and inorganic ions. Here, we report the diurnal variations in concentration levels, molecular characteristics and sources of BSOA tracers at Mt. Tai and then investigate the impact of meteorological factors (e.g., O₃, relative humidity and temperature), particle acidity (pH_{is}), liquid water content (LWC) and anthropogenic pollutants (e.g., levoglucosan, SO₄²⁻, NO₃⁻ and EC) on the formation mechanisms of BSOA tracers.

MATERIALS AND METHODS

Aerosol Sampling

Mt. Tai (36°15'N, 117°6'E; 1534 m a.s.l.; Fig. 1) is located in the North China Plain, where almost 80% of the mountainous land is covered by 989 species of vegetation (Fu *et al.*, 2010). The detailed information of sampling site has been reported in our previous study (Meng *et al.*, 2018). In the current work, PM_{2.5} samples were collected from 1 July to 26 July and each sample lasted for 12 h on a day/night basis. PM_{2.5} samples were collected using a medium-volume air sampler (KC-120H; Qingdao Laoshan Company, China) at an airflow rate of 100 L min⁻¹. The daytime samples were collected from 07:00 to 18:50 and the nighttime samples were collected from 19:00 to 6:50 of the next day, respectively. A total of 52 PM_{2.5} samples (26 for daytime and 26 for nighttime) and two blank samples were collected in this study. The blank samples were collected by mounting the blank filter onto the sampler for 10 min without sucking

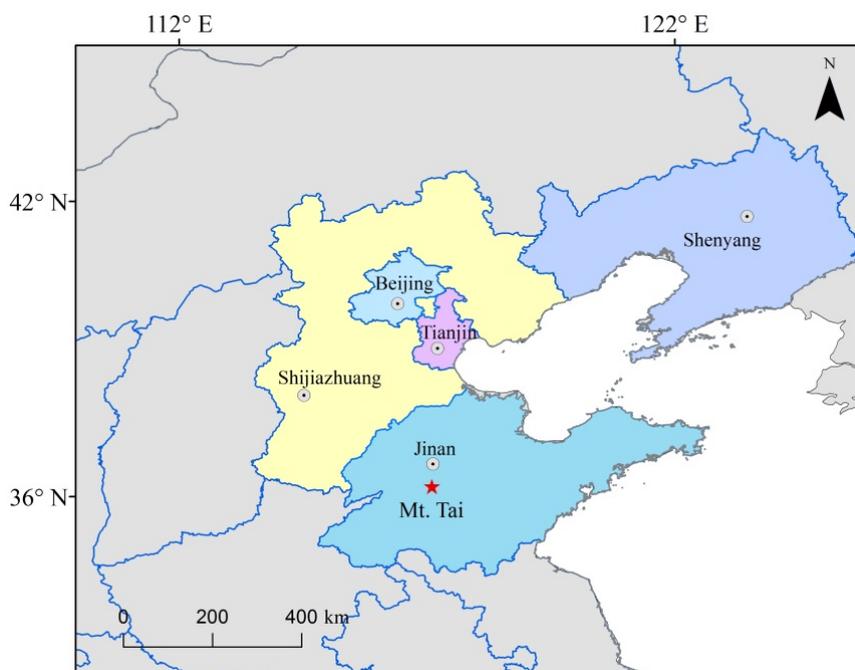


Fig. 1. Map showing the location of the sampling site (Mt. Tai; 36°15'N, 117°6'E; 1534 m a.s.l.).

any air. Before the collection, all samples were placed in pre-baked (450° for 8 h) quartz fiber (Grade 42; Whatman, USA). After the collection, all PM_{2.5} samples were sealed in an aluminum bag and stored at –20°C prior to analysis. In addition, the ozone concentration was synchronously measured *in situ* using a UV absorption analyzer (Model 49C; Thermo Electron Corporation).

Chemical Analysis

Detailed methods for extraction and derivatization were described in previous studies (Wang and Kiawamura, 2006; Wang et al., 2009). Briefly, one fourth of filter was cut into pieces and extracted with a mixture of dichloromethane and methanol (2:1, v/v) under sonication three times each for 15 min. The extracts were concentrated by a rotary evaporator under vacuum and then the filtrate was dried using pure nitrogen stream. After derivatization with a mixture (60 µL) of *N,O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine (5:1, v/v) at 70°C for 3 h, the extracts were diluted with *n*-hexane prior to GC-MS determination. The details of using GC-MS have been described elsewhere (Li et al., 2013a).

All the target compounds were quantified using the peak area of the individual characteristic ion. For the quantification of *cis*-pinic acid and *cis*-pinonic acid (PA), their GC-MS response factors were determined using authentic standards. GC-MS response factors of two 2-methyltetrols (2-methylthreitol and 2-methylerythritol), three C₅-alkene triols (*cis*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and *trans*-2-methyl-1,3,4-trihydroxy-1-butene) were replaced using erythritol. And 2-methylglyceric acid (2-MG), 3-hydroxyglutaric acid (3-HGA), 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) and β-caryophyllinic acid were replaced using the response factors of glyceric acid, tartaric acid, suberic acid and *cis*-pinic acid, respectively (Li et al., 2013a; Ren et al., 2019). Method detection limits (MDLs) for major compounds, that is, *cis*-pinic acid, 2-methylthreitol, 3-methyl-2,3,4-trihydroxy-1-butene, 2-MG, 3-HGA and β-caryophyllinic acid, were 0.04, 0.03, 0.08, 0.12, 0.05 and 0.15 ng m⁻³, respectively. The target compounds in the blank filters were detected to be very low (<3%). The recoveries of all the target compounds ranged from 86% to 110%. Therefore, data published in this study were corrected for both field blanks and recoveries.

Detailed methods for the analysis of elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC) and inorganic ions in PM_{2.5} samples were described elsewhere (Meng et al., 2018). Briefly, EC and OC in aerosols were detected by the DRI Model 2001 Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2004). WSOC and inorganic ions were determined using a Total Carbon Analyzer (TOC-L CPH; Shimadzu, Japan) and an ion chromatography (Dionex 600; Dionex, USA), respectively. In this study, aerosol liquid water content (LWC) and particle *in situ* pH (pH_{is}) were calculated by the Aerosol Inorganic Model (AIM) using a SO₄²⁻-NO₃⁻-NH₄⁺-H⁺ system (AIM-II; <http://www.aim.env.uea.ac.uk/aim/aim.php>) (Li et al., 2013a).

RESULTS AND DISCUSSION

Diurnal Variations of Major Chemical Components of PM_{2.5}

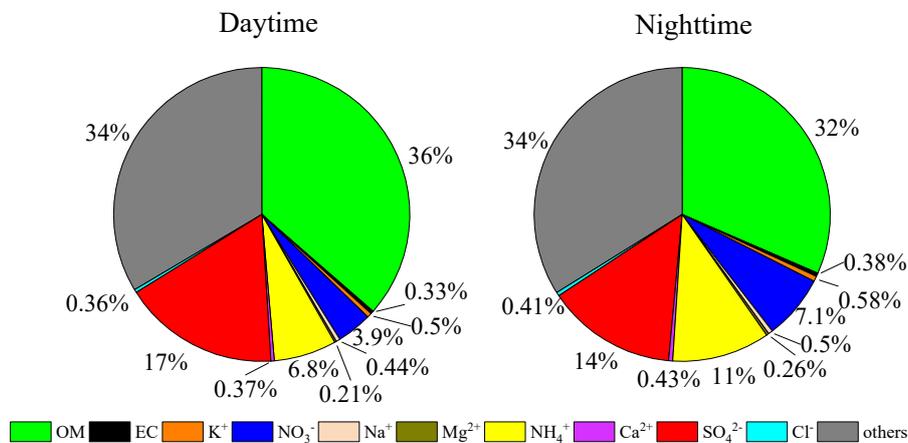
The diurnal variations of main chemical components including OC, EC, WSOC and water-soluble inorganic ions in the atmosphere of Mt. Tai were summarized in Table 1 and Fig. 2 along with meteorological parameters. As a key marker of primary combustion source (Verma et al., 2017), the EC concentration was pretty small (0.40 ± 0.15 µg m⁻³) and presented similar value during the daytime and nighttime (*p* > 0.05) (Table 1), suggesting that the effect of both the changes in the boundary layer heights (BLHs) and the anthropogenic pollutants from long-range transport was minor. The daytime concentrations of OC and WSOC were higher than those in the nighttime, and the daytime ratios of OC/EC and WSOC/OC were also about 1.5 times higher than at night (Table 1). These comparisons suggested that the photochemical oxidation was much stronger in the daytime because of the stronger solar irradiation and higher temperature (Hegde and Kawamura, 2012; Meng et al., 2018). As a significant tracer for biomass burning (Liu et al., 2019), levoglucosan concentration was 22.0 ± 18.0 ng m⁻³, which was 20 times lower than that in the biomass-burning period of 2006 (May–June: 425 ng m⁻³ (Fu et al., 2008); early June: 403 ng m⁻³ (Fu et al., 2012)) at Mt. Tai. Moreover, EC, OC and WSOC did not exhibit any correlation with levoglucosan at Mt. Tai, suggesting the insignificant impact of biomass burning on the mountainous aerosol during the sampling period.

As shown in Table 1 and Fig. 2, SO₄²⁻ was observed to be the most abundant inorganic ion, followed by NO₃⁻ and NH₄⁺ throughout the whole sampling period. The daytime concentration and relative abundance of SO₄²⁻ were larger than at night (Table 1 and Fig. 2), largely because the higher temperature and humidity in the daytime can promote the formation of SO₄²⁻ from the oxidation of SO₂ in the aqueous phase (Fang et al., 2017; Jiang et al., 2017; Wu et al., 2017). In contrast, the smaller concentrations and relative abundances of NO₃⁻ and NH₄⁺ were observed during the daytime than during the nighttime (Table 1 and Fig. 2), mainly being attributed to the enhanced volatility of NH₄NO₃ at the higher temperature in daytime (Meng et al., 2016; Li et al., 2018b; Priyadharshini et al., 2019). The remaining five kinds of inorganic ions including K⁺, Na⁺, Ca²⁺, Mg²⁺ and Cl⁻ accounted for relatively small fraction (5.7%) of PM_{2.5} mass. As the important indicators of primary sources, K⁺, Na⁺, Ca²⁺, Mg²⁺ and Cl⁻ did not present significant diurnal variations (*p* > 0.05) (Table 1), again suggesting that the impact of BLHs was inessential on the aerosols of Mt. Tai.

In this study, pH_{is} and LWC were calculated by the AIM-II model. Previous studies have demonstrated that LWC is determined by anthropogenic inorganic salts and RH (Meng et al., 2018; Ren et al., 2018). The total concentration of SO₄²⁻, NO₃⁻ and NH₄⁺ in daytime (32.8 ± 17.8 µg m⁻³) was nearly equal to that in nighttime (33.2 ± 14.4 µg m⁻³), but the daytime RH (77.5 ± 4.7%) was much lower than that during nighttime (89.2 ± 4.4%). Thus, the daytime LWC

Table 1. Meteorological factors and concentrations of inorganic ions, ozone, carbonaceous compounds, *in situ* pH (pH_{is}) and liquid water content (LWC) in PM_{2.5} samples in Mt. Tai during the sampling time.

	Daytime (n = 26)	Nighttime (n = 26)	Total (n = 52)	p-value (t-test)
Inorganic ions (μg m⁻³)				
SO ₄ ²⁻	20.2 ± 10.4	14.7 ± 5.8	17.5 ± 8.8	0.003
NO ₃ ⁻	4.6 ± 3.2	7.3 ± 4.0	6.0 ± 3.8	0.038
NH ₄ ⁺	8.1 ± 4.2	11.1 ± 4.3	9.6 ± 4.5	0.001
Na ⁺	0.5 ± 0.2	0.5 ± 0.3	0.5 ± 0.3	0.742
K ⁺	0.6 ± 0.2	0.6 ± 0.3	0.6 ± 0.2	0.257
Ca ²⁺	0.4 ± 0.2	0.4 ± 0.3	0.4 ± 0.2	0.314
Mg ²⁺	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.138
Cl ⁻	0.4 ± 0.2	0.4 ± 0.1	0.4 ± 0.1	0.132
Meteorological parameters and ozone				
T (°C)	21.4 ± 2.5	12.2 ± 2.3	16.8 ± 5.2	0.035
RH (%)	77.5 ± 4.7	89.2 ± 4.4	83.3 ± 7.4	0.002
O ₃ (ppb)	28.5 ± 16.9	17.2 ± 9.5	22.9 ± 14.7	0.118
Other species (μg m⁻³)				
OC	3.6 ± 1.3	2.1 ± 0.3	2.8 ± 1.2	0.132
EC	0.40 ± 0.16	0.40 ± 0.14	0.40 ± 0.15	0.534
WSOC	2.3 ± 0.9	0.9 ± 0.3	1.6 ± 1.0	0.019
WSOC/OC	0.6 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.500
OC/EC	9.3 ± 2.7	5.9 ± 1.9	7.6 ± 2.9	0.901
pH _{is}	-0.1 ± 0.3	1.6 ± 0.5	0.7 ± 1.0	0.017
LWC	17.0 ± 10.2	24.9 ± 14.3	20.9 ± 12.9	0.039
Levogluconan (ng m ⁻³)	21.9 ± 18.2	22 ± 18.1	22.0 ± 18.0	0.822
PM _{2.5}	45.8 ± 19.2	43.8 ± 14.2	44.8 ± 16.7	0.003

**Fig. 2.** Chemical composition of PM_{2.5} during daytime and nighttime in Mt. Tai.

(17.0 ± 10.2 μg m⁻³) was lower than that at night (24.9 ± 14.3 μg m⁻³) (Table 1). However, pH_{is} exhibited an opposite diurnal variation pattern to the concentration of LWC (Table 1), suggesting that the aerosols were more acidic on the top of Mt. Tai in daytime.

Diurnal Characteristics of BSOA Tracers

Isoprene SOA Tracers

Six kinds of isoprene SOA tracers quantified in the PM_{2.5} samples of Mt. Tai were summarized in Table 2 during the summertime. The total concentrations of isoprene SOA tracers during daytime (71.6 ± 46.2 ng m⁻³) were higher than those during nighttime (65.4 ± 39.4 ng m⁻³), largely because the stronger solar radiation and higher temperature conditions

in daytime can accelerate the emission of biogenic VOCs and the production of SOA (Yuan *et al.*, 2018).

As shown in Table 2 and Fig. 4, 2-methyltetrols (25.2 ± 16.4 ng m⁻³) were the most abundant isoprene SOA tracers in the aerosols of Mt. Tai and accounted for 19.6% of the total BSOA tracers, followed by C₅-alkene triols (18.8%) and 2-methylglyceric acid (15.0%). As shown in Fig. 4, 2-methylthreitol correlated strongly with 2-methylerythritol during the daytime ($R^2 = 0.98$) and nighttime ($R^2 = 0.80$), respectively. Such a phenomenon was also observed in Chinese cities and the background site of Qinghai Lake (Ren *et al.*, 2018), indicating that 2-methylthreitol and 2-methylerythritol experienced the similar formation pathways. Surratt *et al.* (2006) have pointed out that both C₅-alkene

Table 2. Diurnal concentrations (ng m⁻³) of biogenic secondary organic aerosols in PM_{2.5} during summer in Mt. Tai.

Compounds	Daytime (<i>n</i> = 28)	Nighttime (<i>n</i> = 29)	Total (<i>n</i> = 57)	<i>p</i> -value (<i>t</i> -test)
Isoprene SOA tracers				
2-methylglyceric acid	20.4 ± 10.2	18 ± 9.1	19.2 ± 9.6	0.266
C ₅ -alkene triols ^a	25.3 ± 21.3	23 ± 17.8	24.1 ± 19.5	0.000
2-methyltetrols ^b	25.9 ± 17.3	24.5 ± 15.7	25.2 ± 16.4	0.026
Subtotal	71.6 ± 46.2	65.4 ± 39.4	68.5 ± 42.6	0.005
Monoterpene SOA tracers				
<i>cis</i> -pinonic acid	7.7 ± 4.7	5.1 ± 2.6	6.4 ± 4.0	0.878
<i>cis</i> -pinic acid	2.5 ± 1.7	2.1 ± 1.3	2.3 ± 1.5	0.968
3-hydroxyglutaric acid	29.4 ± 17.8	25.5 ± 16.4	27.5 ± 17.1	0.185
MBTCA ^c	7.5 ± 4.0	7.2 ± 4.7	7.4 ± 4.3	0.279
Subtotal	47.1 ± 26.1	40.0 ± 22.6	43.5 ± 24.4	0.280
β-caryophyllene SOA tracers				
β-caryophyllinic acid	20.8 ± 8.2	11.7 ± 6.3	16.3 ± 8.6	0.048
Total tracers	139.5 ± 76.4	117.1 ± 64.4	128.3 ± 70.9	0.041

^a C₅-alkene triols: 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-trihydroxy-1-butene.

^b 2-methyltetrols: the sum of 2-methylthreitol and 2-methylerythritol.

^c MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

triols and 2-methyltetrols are derived from chemical reactions of isoprene with OH radical under low-NO_x conditions. Therefore, C₅-alkene triols exhibited a positive correlation with 2-methyltetrols throughout the whole sampling period ($R > 0.6$) (Fig. 5). Such a strong correlation was also observed in Shanghai, China (Ren *et al.*, 2018), and high Arctic region (Fu *et al.*, 2009). Chamber experiments and field observations have suggested that 2-methylglyceric acid is produced from the oxidation of isoprene under high-NO_x conditions and is promoted into the particle phase in the low humid atmosphere (Zhang *et al.*, 2011; Li *et al.*, 2013a; Ren *et al.*, 2018). Therefore, the concentration of 2-methylglyceric acid was higher during daytime than that during nighttime due to the lower relative humidity in daytime (Table 1).

Monoterpene SOA Tracers

Four kinds of monoterpene SOA tracers, including *cis*-pinonic acid, *cis*-pinic acid, 3-hydroxyglutaric acid and MBTCA were determined in the PM_{2.5} samples of Mt. Tai (Table 2 and Fig. 4). The total concentrations of monoterpene SOA tracers in daytime (47.1 ± 26.1 ng m⁻³) were around 1.2 times higher than those in nighttime (40.0 ± 22.6 ng m⁻³), which was consistent with the diurnal variations of isoprene SOA tracers. Among the measured tracers of monoterpene oxidation products, 3-hydroxyglutaric acid was the dominant species and accounted for 63% and 64% of the total monoterpene SOA tracers during daytime and nighttime, respectively, followed by MBTCA (Table 2 and Fig. 3). The molecular distributions at Mt. Tai were also found in other regions such as oceans (Fu *et al.*, 2011; Hu *et al.*, 2013), mountains (Hong *et al.*, 2019; Ren *et al.*, 2019) and continents (Yuan *et al.*, 2018). Previous studies have suggested that both *cis*-pinonic acid and *cis*-pinic acid can be further photodegraded into MBTCA (Szmigielski *et al.*, 2007; Ding *et al.*, 2012). Therefore, the ratio of P/M (*cis*-pinonic acid plus *cis*-pinic acid to MBTCA) can be regarded as an indicator for organic aerosols aging (Szmigielski *et al.*, 2007; Hu *et*

al., 2008; Ding *et al.*, 2011). The higher ratio of P/M indicates the fresher monoterpene SOA, and the lower ratio reflects the older monoterpene SOA. Compared with that in nighttime, the smaller ratio of P/M was observed in daytime, again suggesting that the daytime photochemical modification of aerosols is stronger because of the stronger solar radiation and the higher temperature. In this study, the average ratio of P/M (1.45 ± 0.88) at Mt. Tai was much lower than Chinese cities such as Xi'an (22.2), Shanghai (16.5), Chengdu (24.6), Guangzhou (19.9) and Urumqi (33.8) and Qinghai Lake (53.3) (Ren *et al.*, 2018), a continental background site in the Tibetan Plateau during the summertime, suggesting that the monoterpene SOA were relatively aged in the mountainous atmosphere, largely due to the stronger solar radiation on the peak of Mt. Tai (Meng *et al.*, 2018; Zhu *et al.*, 2018a).

β-Caryophyllene SOA Tracers

Among a great deal of BVOCs determined to date, sesquiterpenes have been the least studied because of their low vapor pressure and high reactivity (Fu *et al.*, 2009). However, sesquiterpenes might be the main source of SOA due to the high reactivity and aerosol yields (Fu *et al.*, 2009; Ren *et al.*, 2018). β-caryophyllene is one of the dominant sesquiterpenes, and most usually studied in various environments (Duhl *et al.*, 2008; Xu *et al.*, 2018; Zhu *et al.*, 2018a). β-caryophyllinic acid was produced either by the ozonolysis or photooxidation of β-caryophyllene (Jaoui *et al.*, 2007; Yuan *et al.*, 2018), which was measured in all PM_{2.5} samples of Mt. Tai. Being similar to the diurnal characteristics of isoprene and monoterpene SOA tracers, the concentration of β-caryophyllinic acid in daytime (20.8 ± 8.2 ng m⁻³) was observed to be higher than that in nighttime (11.7 ± 6.3 ng m⁻³) (Table 2 and Fig. 4).

Comparison of BSOA Tracers with Previous Studies

The concentrations of isoprene, monoterpene and β-caryophyllene oxidation products at Mt. Tai during the

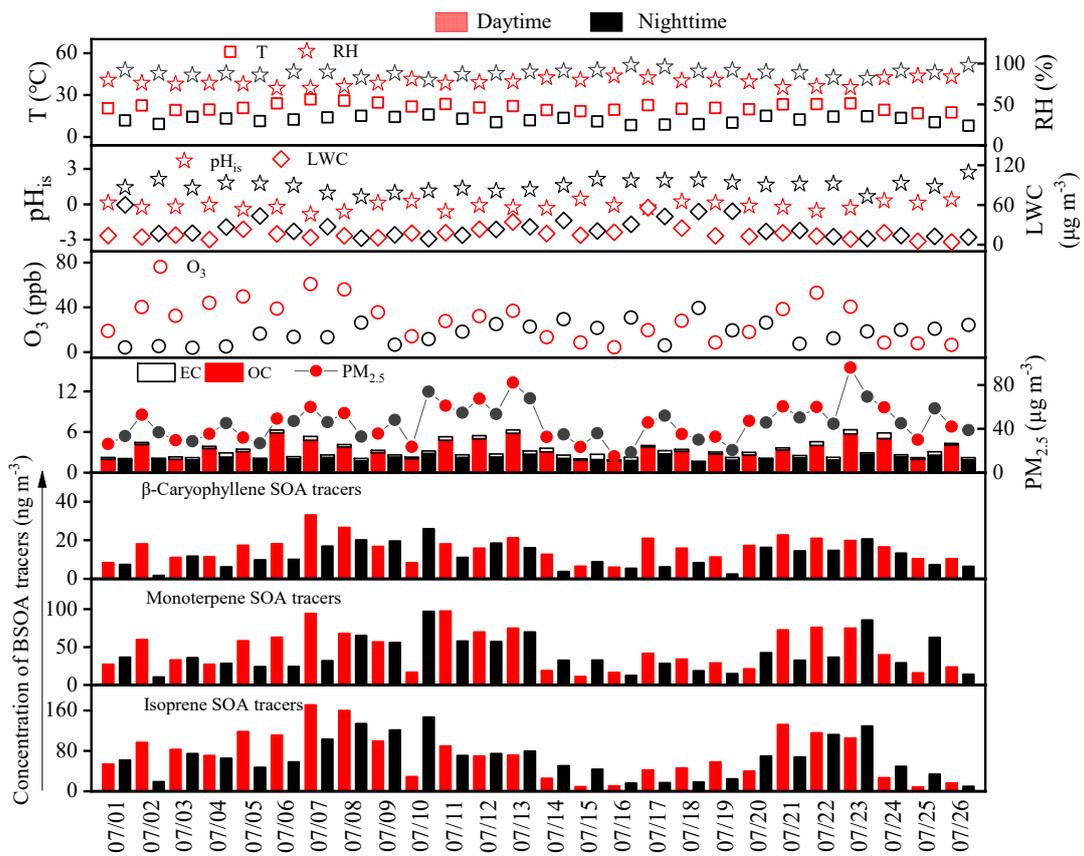
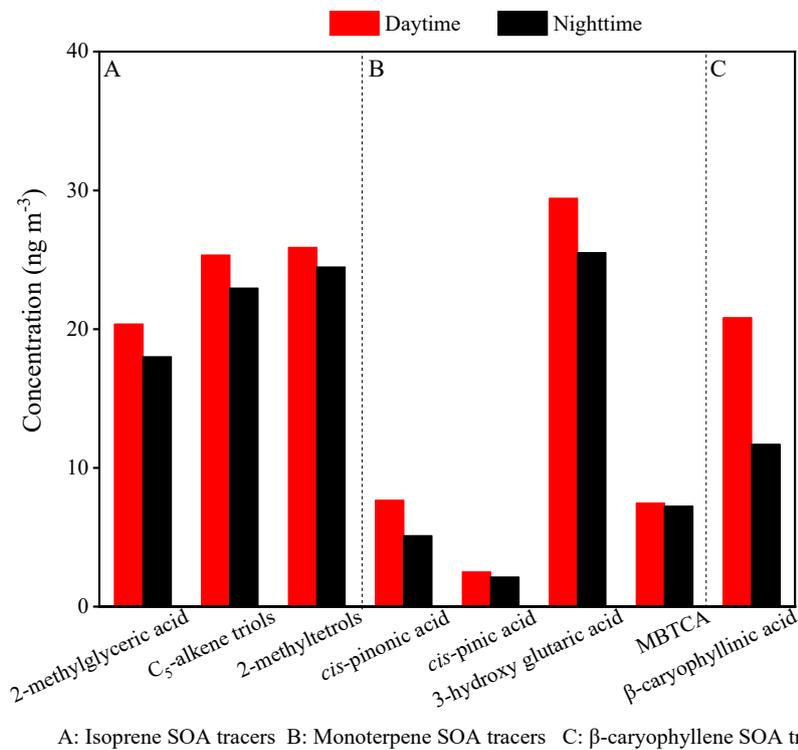


Fig. 3. Diurnal variations of temperature (T), relative humidity (RH), liquid water content (LWC) and *in situ* acidity of particles (pH_{is}), the concentrations of OC and EC (organic and elemental carbon), $\text{PM}_{2.5}$, biogenic secondary organic aerosols.



A: Isoprene SOA tracers B: Monoterpene SOA tracers C: β -caryophyllene SOA tracers

Fig. 4. Diurnal variations of relative abundance of BSOA productions from Mt. Tai in summer (^aMBTCA: 3-methyl-1,2,3-butanetricarboxylic acid).

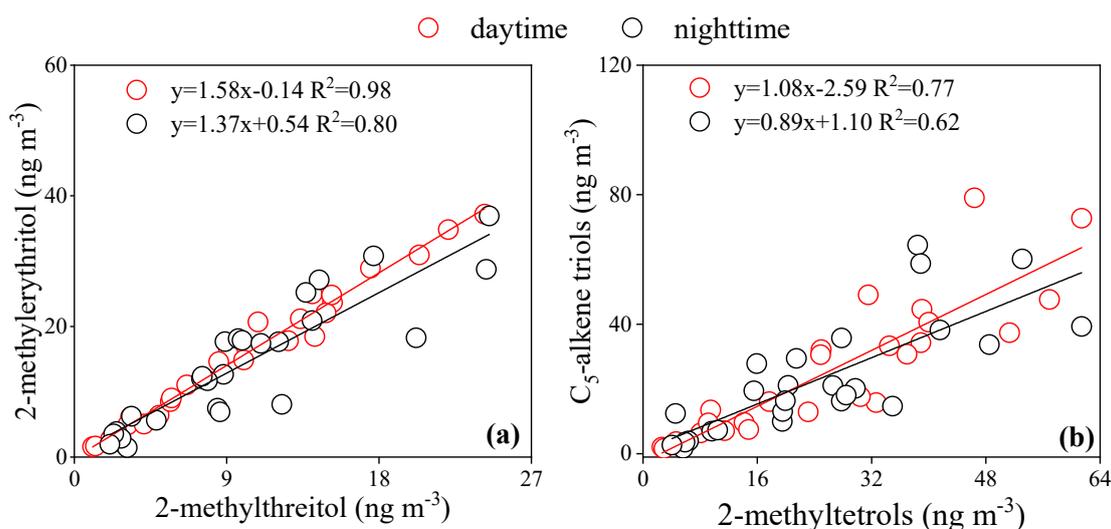


Fig. 5. Correlations between 2-methylthreitol and 2-methylerythritol, 2-methyltetrols and C₅-alkene triols in Mt. Tai during summer.

summertime of 2016 and from other previous studies are shown in Table 3. In order to investigate the unique characteristics of aerosols at Mt. Tai in the summer, a comparison of chemical compositions of aerosols in highland, mountainous and urban regions was made. All BSOA tracers presented 14–26 times higher concentrations than those observed in the Qinghai Lake, China (Li *et al.*, 2013b). However, the total concentrations of BSOA tracers in the summer of 2016 at Mt. Tai were about 1.4 times lower than those in 2006 (Fu *et al.*, 2010). It is worth noting that the concentration levels of isoprene SOA tracers in this study were significantly lower than 10 years ago. Different meteorology factors between 2006 and 2016 may partially explain the decreased concentrations, as well as the different sampling periods.

As shown in Table 3, the total concentration of isoprene SOA tracers at Mt. Tai was about 1.4–1.9 times lower compared with some Chinese mountains such as Mt. Gongga in 2011 and Mt. Changbai in 2007 (Wang *et al.*, 2008). Interestingly, the concentration levels of isoprene SOA tracers were observed to be almost equivalent to those reported in Mt. Fuji, Japan (Fu *et al.*, 2014), mainly because the latitudes and altitudes of both sampling sites are similar and both mountains are dominated by the broadleaved forests (Meng *et al.*, 2018). Furthermore, the O₃ concentration at Mt. Tai in the whole sampling campaign is also comparable to that at Mt. Fuji increasing from a few ppb at night to about 60 ppb at noon (Mochizuki *et al.*, 2017), indicating that the oxidizing capacity at both sites during the observation periods is similar. Thus, the concentration of SOA tracers derived from isoprene were equal at these two mountainous regions. However, the total concentration of isoprene SOA tracers were higher than those in some Chinese mountains such as Mt. Wuyi (Ren *et al.*, 2019), Mt. Hua (Li *et al.*, 2013a) and Mt. Himalayas (Stone *et al.*, 2012), and also higher than those observed in Chinese urban areas such as Shanghai (Zhu *et al.*, 2018a), Xi'an (Ren *et al.*, 2018) and Chengdu (Ren *et al.*, 2018). The average concentrations of monoterpene SOA tracers at Mt. Tai ($43.5 \pm 24.4 \text{ ng m}^{-3}$) were comparable

to those measured in Mt. Changbai (Wang *et al.*, 2008) and Mt. Wuyi (Ren *et al.*, 2019), China, and Mt. Fuji, Japan (Fu *et al.*, 2014), and lower than Chinese urban areas (e.g., Xi'an and Chengdu) (Ren *et al.*, 2018), but higher than Mt. Hua and Mt. Gongga, China (Li *et al.*, 2013a; Li *et al.*, 2018a). The concentration of β -caryophyllinic acid was comparable to those measured in Mt. Wuyi (Ren *et al.*, 2019) and the Research Triangle Park, North Carolina, USA (11.5 ng m^{-3}) (Lewandowski *et al.*, 2007), but was much higher than Ya'an, China (1.6 ng m^{-3}) (Li *et al.*, 2013c); Okinawa Island, Japan (0.2 ng m^{-3} ; Zhu *et al.*, 2016); and Alaska, USA (0.62 ng m^{-3} ; Haque *et al.*, 2016).

Effects of Meteorological Factors and Anthropogenic Pollutants on BSOA

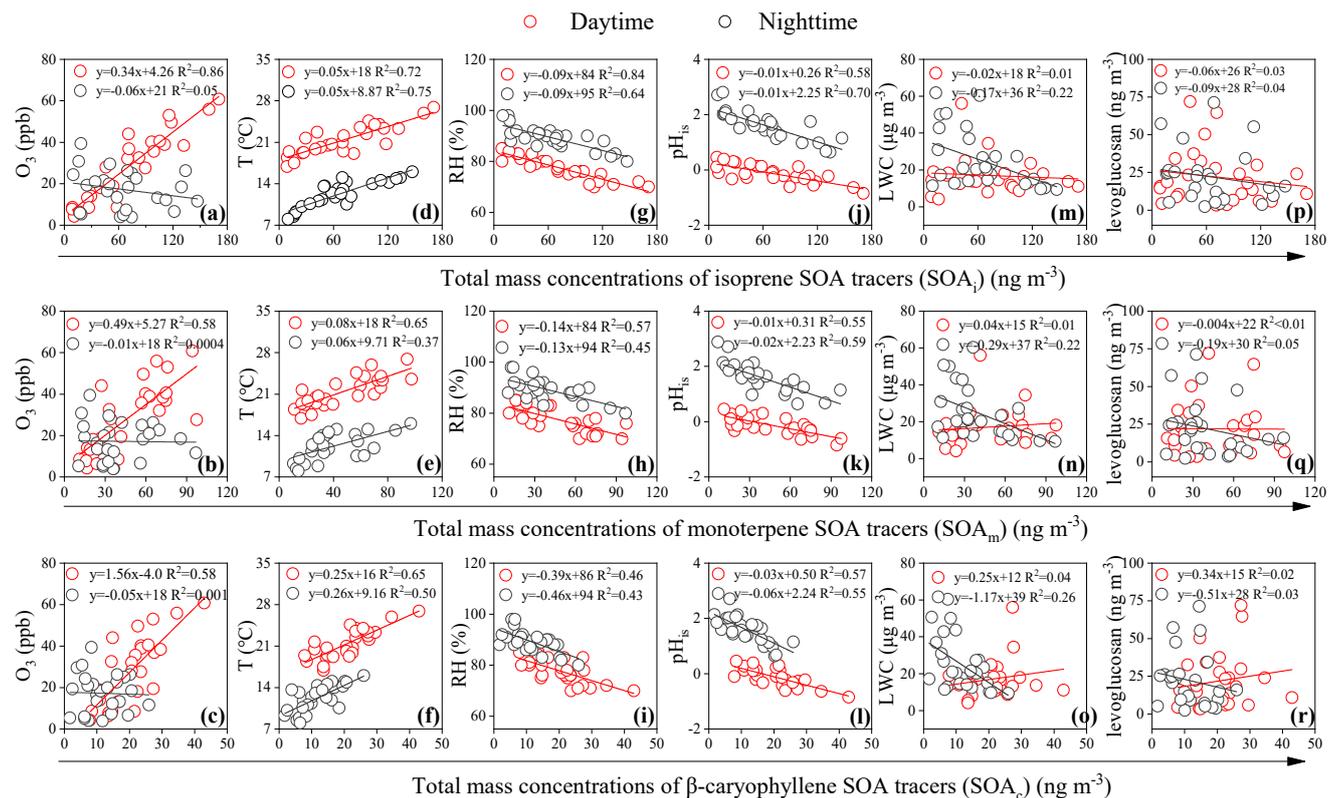
Temporal variations of BSOA tracers, meteorological factors and O₃ concentration were present in Fig. 3. In this study, a significantly positive correlation ($R^2 = 0.58\text{--}0.86$) of the mass concentrations of BSOA produced by isoprene (SOA_i), monoterpene (SOA_m) and β -caryophyllene (SOA_c) with O₃ was observed for the daytime, respectively, but no clear linear correlation ($R^2 < 0.10$) was found for the nighttime (Figs. 6(a)–6(c)). OH radicals (Fan and Zhang, 2004) and O₃ (He *et al.*, 2014) are major oxidants in the atmosphere reacted with the BVOCs in daytime, whereas the dominant oxidant is NO₃ radicals in nighttime (Warneke *et al.*, 2004). These results suggested that the daytime BSOA at the summit of Mt. Tai were largely produced by O₃ and OH radical oxidation of BVOCs, while the nighttime BSOA might be derived from NO₃ radical and other oxidizing agents (H₂O₂) (Meng *et al.*, 2018). In addition, the titration of O₃ by the residual NO in the atmosphere at night can be proposed as an alternate explanation for the lack of correlation between BSOA tracers and O₃ in nighttime (Edwards *et al.*, 2017).

As shown in the Figs. 6(d)–6(f), the concentrations of SOA_i, SOA_m and SOA_c correlated strongly with temperature (T) ($R^2 \geq 0.37$) during daytime and nighttime, respectively, indicating that both the emissions of BVOCs and production of

Table 3. Concentrations (ng m^{-3}) of BSOA in Mt. Tai and other regions in the world during summer.

Location	Aerosols type	Isoprene SOA tracers	Monoterpene SOA tracers	β -caryophyllene SOA tracers	Reference
Mt. Tai, China	PM _{2.5}	65.4	42.5	12.5	This study
Mt. Tai, China	TSP	171	30	12	(Fu et al., 2010)
Qinghai Lake, China	PM _{2.5}	2.5	3.0	0.9	(Li et al., 2013b)
Mt. Hua, China	PM ₁₀	13	6.6	2.2	(Li et al., 2013a)
Mt. Wuyi, China	PM _{2.5}	21	36	11	(Ren et al., 2019)
Himalays, China	PM _{2.5}	30.7	13.2	1.7	(Stone et al., 2012)
Mt. Fuji, Japan	TSP	69	39	0.4	(Fu et al., 2014)
Mt. Gongga, China	PM _{2.5}	89	3.6	0.13	(Li et al., 2018a)
Changbai, China	PM _{2.5}	127	40	NA	(Wang et al., 2008)
Shanghai, China	PM _{2.5}	17.6	3.6	0.6	(Zhu et al., 2018a)
Xi'an, China	TSP	20	58	NA	(Ren et al., 2018)
Chengdu, China	TSP	23	88	NA	(Ren et al., 2018)
Triangle Park, North Carolina, USA	PM _{2.5}	NA	NA	11.5	(Lewandowski et al., 2007)
Ya'an, China	PM _{2.5}	71.1	5.8	1.6	(Li et al., 2013c)
Okinawa Island, Japan	TSP	2.12	1.43	0.20	(Zhu et al., 2016)
Alaska, USA	TSP	8.8	2.4	0.62	(Haque et al., 2016)

*NA: not available.

**Fig. 6.** Linear regressions of BSOA tracers with O₃, temperature (T), relative humidity (RH), *in situ* pH (pH_{is}), liquid water content (LWC) and levoglucosan.

BSOA can be promoted under higher-temperature conditions (Meng et al., 2018; Yuan et al., 2018). The Arrhenius equation has demonstrated that high temperature can speed up the reaction rates (Ding et al., 2016). Such a phenomenon was also observed in other regions such as Qinghai Lake (Li et al., 2013b), Mt. Wuyi (Ren et al., 2019) and Mt. Hua in

China (Li et al., 2013a), and Germany (Zhang et al., 2010). Temperature measured at the summit of Mt. Tai during the sampling time only indicates the local weather conditions rather than the regional meteorological conditions. Thus, significant correlations between BSOA tracers and temperature can only be found when BSOA are mostly originated from

the local oxidation of BVOCs emissions rather than long-distance transport. In addition, the higher O₃ concentration in the daytime suggested that oxidation potential was stronger at the top of Mt. Tai during the daytime than during the nighttime. Trees are the only emission of isoprene in daytime. Therefore, the higher concentrations of BSOA tracers in daytime can be explained by the stronger photochemical oxidation and enhancements in BVOCs emissions. In this study, the concentration of BSOA tracers showed a significant negative correlation with RH ($R^2 \geq 0.43$) (Figs. 6(g)–6(i)) in daytime and nighttime, respectively. Chamber experiment (Zhang *et al.*, 2011) and field measurements (Li *et al.*, 2013a; Ren *et al.*, 2019) have demonstrated that lower-RH conditions can favor the formation of BSOA from isoprene and other BVOCs by the photochemical oxidation. In contrast, 2-methyltetrols did not change dramatically as RH varied (Riva *et al.*, 2016). Moreover, a strong negative correlation was also observed for BSOA tracers and pH_{is} ($R^2 \geq 0.55$) (Figs. 6(i)–6(l)) in the whole sampling campaign, suggesting that the acidic condition is favorable for the formation of BSOA and their precursors. Previous studies pointed that aerosol acidity can promote the formation of BSOA derived from the acid-catalyzed heterogeneous oxidation BVOCs (Ding *et al.*, 2011; Li *et al.*, 2013a). Nguyen *et al.* (2011) reported that the increased RH was the foremost factors controlling the BSOA formation, mainly attributed to the suppression of condensation and addition reactions such as hemiacetal formation and aldol formation. High RH conditions can restrain the acid-catalyzed formation of BSOA because of the dilution of aerosol acidity (Li *et al.*, 2013a). Therefore, BSOA negatively correlated with both RH and pH_{is}.

RH and aerosol hygroscopic composition are key factors controlling the aerosol LWC (Bikkina *et al.*, 2017). However, the total concentration of SOA_i, SOA_m and SOA_c did not show any correlation with LWC in daytime and nighttime, respectively (Figs. 6(m)–6(o)). The higher LWC can promote the partitioning of water-soluble semi-volatile organic precursors of BSOA into the aqueous phase, and further improves the formation of BSOA (McNeill *et al.*, 2012). Nevertheless, LWC can reduce particle acidity, which suppresses the formation of BSOA via acid-catalyzed reactions (Riva *et al.*, 2016). Thus, there was no correlation between LWC and the concentration of SOA_i, SOA_m and SOA_c in the aerosols of Mt. Tai. Furthermore, there was no correlation between BSOA tracers and anthropogenic pollutants such as levoglucosan, SO₄²⁻, NO₃⁻ and EC during daytime and nighttime, respectively (Figs. 6(p)–6(r), Table S1), which is consistent with our discussions above. Such a phenomenon was also observed in Mt. Hua, China, where the effect of anthropogenic pollutants was no significant correlation in summer (Li *et al.*, 2013a). Levoglucosan was acknowledged as a remarkable tracer of biomass burning, which formed by hemicellulose and the pyrolysis of cellulose (Fu *et al.*, 2016). In this work, no correlation ($R^2 \leq 0.05$) was found between BSOA tracers and levoglucosan during the whole sampling campaign, indicating the effect of biomass burning on the formation of BSOA is minor. Previous study has observed that biomass burning (field burning of wheat straws) was mainly performed during May to June in the

North China Plain (Fu *et al.*, 2012). The observation campaign in this study was conducted in July when the field burning of wheat straw residue was rarely observed. Therefore, BSOA tracers did not show any correlation with levoglucosan at Mt. Tai, clearly suggesting that the BSOA formation was mostly originated from the oxidation of BVOCs rather than biomass burning.

Consequently, these results clearly demonstrated that BSOA derived from isoprene, monoterpene and β-caryophyllene in the summertime atmosphere of Mt. Tai during the campaign were mostly originated from the local oxidation of BVOCs rather than the anthropogenic emissions from the lowlands by long-distance transport. Such a conclusion highlighted the important role of the BVOCs emissions in the formation process of BSOA in the forested highland region when the emission of BVOCs was dominant in the summertime atmosphere of Mt. Tai.

CONCLUSIONS

The profiles of eleven kinds of BSOA tracers derived from isoprene, monoterpene and β-caryophyllene in PM_{2.5} samples from the top of Mt. Tai (1534 m a.s.l.) during the summer, along with the EC, OC, WSOC, levoglucosan and inorganic ions, were determined. The average concentrations of the isoprene, monoterpene and β-caryophyllene oxidation products were $68.5 \pm 42.6 \text{ ng m}^{-3}$, $43.5 \pm 24.4 \text{ ng m}^{-3}$ and $16.3 \pm 8.6 \text{ ng m}^{-3}$, respectively. The concentrations were almost 1.4 times lower than those recorded in 2006, which were influenced by biomass burning, but equal to those observed on Mt. Fuji, Japan, due to the similarity in latitude, altitude and vegetation type. The concentrations of all of the BSOA tracers were higher during the day than at night, suggesting that the higher diurnal temperatures and solar radiation favored the emission of BVOCs and formation of BSOA. The concentrations of the BSOA tracers and O₃ displayed significantly positive correlations during the daytime, but no clear linear correlation was found for nighttime. The temperature was positively correlated with all of the BSOA tracers over the whole campaign, as higher temperatures can promote BVOCs emission and BSOA formation. Conversely, RH and pH_{is} exhibited significantly negative correlations with the concentrations of the BSOA tracers during the daytime and nighttime because higher RH can reduce the *in situ* particle acidity, which further suppresses the effect of acid catalysis on BSOA formation. However, the concentrations of the BSOA tracers did not show any correlation with the LWC regardless of the time. Moreover, no significant linear correlation between the BSOA tracers and anthropogenic pollutants, such as levoglucosan, SO₄²⁻, NO₃⁻ and EC, was observed over the entire observation period, which indicates that BSOA in the typical summertime atmosphere of Mt. Tai mainly originates from the local oxidation of BVOCs rather than long-range-transported anthropogenic pollutants.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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