

# Diurnal variations of polar organic tracers in summer forest aerosols: A case study of a *Quercus* and *Picea* mixed forest in Hokkaido, Japan

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We investigated the summertime formation of secondary organic aerosols (SOA) via the oxidation of isoprene,  $\alpha/\beta$ -pinene and  $\beta$ -caryophyllene in a *Quercus crispula* and *Picea glehnii* mast mixed forest located at Hokkaido University Uryu Experimental Forest in Japan. Biogenic SOA tracers and other polar organic compounds (e.g., sugars and aromatic acids) in time-resolved (4 h) aerosol samples (13–15 August, 2001) were characterized using gas chromatography-mass spectrometry. Isoprene SOA tracers including 2-methyltetrols and C<sub>5</sub>-alkane triols were found to be the most abundant compound class (32–219 ng m<sup>-3</sup>, average 113 ng m<sup>-3</sup>), followed by sugars/sugar alcohols. A strong diurnal variation of isoprene oxidation products was observed with higher concentrations during late afternoon-early evening. However, there were no clear trends for  $\alpha/\beta$ -pinene and  $\beta$ -caryophyllene oxidation products. The daytime formation of isoprene SOA correlated well with increased temperature and solar radiation, suggesting a temperature- and/or light-dependent emission of isoprene in the forest followed by photochemical oxidation. Levoglucosan, a biomass burning tracer, showed no correlation with biogenic SOA tracers, indicating that biomass burning contribute little to the formation of biogenic SOA at the sampling site. A significant decrease in the concentrations of biogenic SOA tracers and other polar organic tracers was found during a fog event. Using a tracer-based method, we conclude that the contributions of secondary organic carbon (SOC) from isoprene oxidation products to organic carbon were more significant than those of  $\alpha/\beta$ -pinene and  $\beta$ -caryophyllene oxidation products. The total SOC accounts for 5.7–34% (average 17%) of OC. This suggests that the emission of biogenic volatile organic compounds followed by subsequent oxidation plays an important role in the formation of SOA over the *Quercus* and *Picea* mixed forest.

Keywords: secondary organic aerosol, isoprene, 2-methyltetrols, levoglucosan, BVOCs

## INTRODUCTION

Vegetation releases a variety of biogenic volatile organic compounds (BVOCs) into the atmosphere, including isoprene, monoterpenes, sesquiterpenes, as well as oxygenated hydrocarbons (e.g., acetone and methanol) (Guenther *et al.*, 1995). On a global scale, the emissions of BVOCs have been estimated to be 1150 Tg yr<sup>-1</sup>, among which isoprene is the most important species with an estimated emission rate of *ca.* 600 Tg yr<sup>-1</sup> (Guenther *et al.*, 2006). Modeling studies have shown that isoprene could be a significant source of atmospheric organic matter globally (Henze and Seinfeld, 2006). Liao *et al.* (2007) reported that 58.2% and 37.3% of biogenic SOA in the United States are formed from the oxidation of isoprene and monoterpenes, respectively.

Although there are evidences for marine production of isoprene (Bonsang *et al.*, 1992; Yokouchi *et al.*, 1999) and monoterpenes (Yassaa *et al.*, 2008), terrestrial veg-

etation is the main source of BVOCs in the atmosphere. Their emissions vary geographically depending on vegetation type (Guenther *et al.*, 2006). Measurements of BVOC emissions have been conducted on several hundred individual species (Kesselmeier and Staudt, 1999; Duhl *et al.*, 2008). For example, isoprene emission has been reported from both broad-leaved (e.g., *Quercus*, *Populus*, and *Eucalyptus*) and needle-leaved (e.g., *Picea* and *Abies*) trees (see Pacifico *et al.*, 2009 and references therein), which are generally C3 plants. The emission of isoprene is mainly controlled by light intensity and temperature (Yokouchi and Ambe, 1988; Guenther *et al.*, 1995). The light-dependence distinguishes isoprene emission from monoterpene emissions, which continue during nighttime (Pacifico *et al.*, 2009).

In the past decade, considerable efforts have been devoted to understand secondary organic aerosol (SOA) formation from the photooxidation of BVOCs because SOA is an important component in the Earth's atmosphere (Hallquist *et al.*, 2009 and references therein). SOA can influence the atmospheric radiation budget directly by scattering sunlight and indirectly by acting as cloud condensation nuclei (CCN) (Kanakidou *et al.*, 2005). Polar

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organic tracers (e.g., 2-methyltetrols, pinic acid, 3-hydroxyglutaric acid, and  $\beta$ -caryophyllinic acid) from the oxidation of BVOCs have been characterized in smog chamber experiments (Inuma *et al.*, 2004; Sato, 2008) and widely reported in ambient samples (e.g., Yu *et al.*, 1999; Claeys *et al.*, 2004a; Plewka *et al.*, 2006; Szmigielski *et al.*, 2007; Hu *et al.*, 2008; Kourtchev *et al.*, 2008b; Wang *et al.*, 2008; Fu *et al.*, 2009, 2010).

Moreover, studies have reported that oligomers (e.g., Kalberer *et al.*, 2004) and other high molecular weight organic substances such as organosulfates (e.g., Liggio and Li, 2006; Inuma *et al.*, 2007) and humic-like substances (HULIS) may also contribute to SOA in the atmosphere. Recently, Jaoui *et al.* (2010) reported two new nitrogen-containing compounds (the structures are not identified) from isoprene oxidation under acidic conditions, which could be potentially served as tracers for isoprene SOA formation. In addition, highly time-resolved characterization of organic aerosol by using aerosol mass spectroscopy (AMS) (e.g., Hodzic *et al.*, 2009) has been often reported in urban and rural sites as well as a continuous measurement of water-soluble organic carbon (WSOC) coupled to a particle-into-liquid sampler (PILS) (Miyazaki *et al.*, 2006). These studies provide insights into the sources and processes that influence SOA production and their spatial and seasonal distributions. Aerosol organic carbon in forests is believed to be dominated by biogenic SOA, especially in summer when biological activities are maximized under intense sunlight and high ambient temperature conditions. However, studies on time-resolved diurnal variations of ambient SOA at a molecular level in the forest atmosphere are limited (Kavouras *et al.*, 1999).

The purpose of this study is to characterize the SOA tracers that are derived from the atmospheric oxidation of isoprene,  $\alpha/\beta$ -pinene, and  $\beta$ -caryophyllene in an experimental forest dominated by *Quercus crispula* and *Picea glehnii mast* in Hokkaido, Japan. Diurnal trends of biogenic SOA tracers are compared with meteorological parameters and other polar organic compounds such as primary saccharides, hydroxyacids and biomass burning tracers (e.g., levoglucosan).

## SAMPLES AND METHODS

### Sample collection

Total suspended particles (TSP) were collected from 13 to 15 August 2001 at a rural site in the Uryu Experimental Forest of Hokkaido University (44.35°N, 142.25°E, approximately 200 km north of Sapporo). Dominant plant species in the experimental forest are *Quercus crispula* (oak tree) and *Picea glehnii mast* (spruce tree). The sampling site is located approximately 1 km inside the nearest forest boundary. Time-resolved aero-

sol particles were collected onto precombusted (450°C, 6 h) quartz fiber filters (20 × 25 cm, Pallflex 2500QAT-UP) every 4 h (00:15–03:45, 04:15–07:45, 08:15–11:45, 12:15–15:45, 16:15–19:45 and 20:15–23:45, local time) using a high-volume air sampler with a flow rate of 1.0 m<sup>3</sup> min<sup>-1</sup>. The sampler was set at 3.5 m above the ground level where the canopy height was approximately 15 m. The sample filter was placed in a precombusted clean glass jar with a Teflon-lined screw cap and stored in a dark freezer room at -20°C prior to analysis.

### Extraction, derivatization, and GC/MS determination

Filter aliquots were extracted three times for 10 min each with dichloromethane/methanol (2:1; v/v) under ultrasonication. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated by the use of a rotary evaporator, and blown down to dryness with pure nitrogen gas. The extracts were then derivatized with 50  $\mu$ l of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10  $\mu$ l of pyridine at 70°C for 3 h. After the reaction, derivatives were diluted by addition of 140  $\mu$ l of *n*-hexane containing 1.43 ng  $\mu$ l<sup>-1</sup> of the internal standard (C<sub>13</sub> *n*-alkane) prior to GC/MS injection. GC/MS analyses of the samples were performed on a Hewlett-Packard model 6890 GC coupled to Hewlett-Packard model 5973 mass-selective detector (MSD). The derivatized sample was injected to GC in a splitless mode at an injector temperature of 280°C. The GC separation was carried out on a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25  $\mu$ m film thickness) with the GC oven temperature programmed from 50°C (2 min) to 120°C at 15°C min<sup>-1</sup> and then to 300°C at 5°C min<sup>-1</sup> with final isothermal hold at 300°C for 16 min. The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV and scanned in the *m/z* range 50–650. Data were processed with the Chemstation software. Individual compounds (TMS derivatives) were identified by comparison of mass spectra with those of authentic standards or literature data.

For the quantification of biomass burning tracers and some other polar organic tracers (hydroxy-/polyacids, aromatic acids, sugars and sugar alcohols, 3-hydroxyglutaric, pinonic, norpinic, and pinic acids), their GC/MS response factors were determined using authentic standards. The concentrations of  $\beta$ -caryophyllinic acid (a diacid similar to pinic acid) were calculated assuming that the response factor of this acid is equivalent to that of pinic acid (Jaoui *et al.*, 2007). Following fragment ions were used for the identification of biogenic SOA tracers: *m/z* 219 and 277 for 2-methyltetrols, *m/z* 231 for C<sub>5</sub>-alkene triols, *m/z* 219 and 203 for 2-methylglyceric acid, *m/z* 171 for pinic and pinonic acids, *m/z* 349 for 3-hydroxyglutaric acid, *m/z* 405 for 3-methyl-1,2,3-butanetricarboxylic acid

(MBTCA), and  $m/z$  383 for  $\beta$ -caryophyllinic acid. MBTCA, 2-methylglyceric acid,  $C_5$ -alkene triols, and 2-methyltetrols were quantitatively determined with a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m  $\times$  0.2 mm i.d., 0.50  $\mu$ m film thickness), and a flame ionization detector (FID). The identification of the organic compounds by GC/FID was confirmed by GC/MS analysis. *Meso*-erythritol, a surrogate compound that was generally used for the quantification of 2-methyltetrols (e.g., Claeys *et al.*, 2004a; Wang *et al.*, 2008), was quantitatively determined by both GC/MS and GC/FID. The analytical error for the GC/MS and GC/FID analysis of *meso*-erythritol was <5%. Field blank filters were treated as real samples for quality assurance. The results showed no serious contamination (less than 1% of real samples). Recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz filters ( $n = 3$ ) and treated as a real sample were generally better than 80%. The data reported here were corrected for the blanks but not for recoveries. Relative standard deviation of the concentrations based on duplicate analysis was generally <10%.

Organic carbon (OC) was measured using a Sunset Lab carbon analyzer, following the Interagency Monitoring of Protected Visual Environments (IMPROVE). Duplicate analyses of filter samples showed uncertainties of  $\pm 10\%$ .

## RESULTS

### Meteorological condition and general results

During the sampling period, clear sky conditions were maintained without rainfall, although a fog event occurred in the morning of 15 August when the light intensity (wave length: approximately 300–2800 nm) remained lower for *ca.* 1.5 hours (Fig. 1(a)). Ambient temperatures ranged from 9.3°C to 29.5°C, whereas relative humidity (RH) ranged from 31.3% to 92.1% (see Fig. 1(b)). The wind speeds recorded at 3.5 m above ground level were <0.01  $m s^{-1}$ , whereas at 10 m they ranged from 0.12 to 0.84  $m s^{-1}$  (average 0.42  $m s^{-1}$ ) (Matsunaga *et al.*, 2003). Such a low wind speed indicates that local influences are rather more important than long-range atmospheric transport. Concentrations of organic carbon in the forest aerosols ranged from 1.6 to 6.7  $\mu g m^{-3}$  (4.3  $\mu g m^{-3}$ ). The diurnal

Fig. 1. Diurnal variations of polar organic tracers detected in forest aerosols from northern Japan. (a) light intensity, (b) relative humidity (RH), ambient temperature (T), and organic carbon (OC), (c) biogenic secondary organic aerosol tracers for isoprene, monoterpene and sesquiterpene oxidation, (d) sugars and sugar alcohols, (e) other polar organic acids (hydroxylpolyacids and aromatic acids), and (f) biomass burning tracers. Shadows in the plots indicate nighttime.

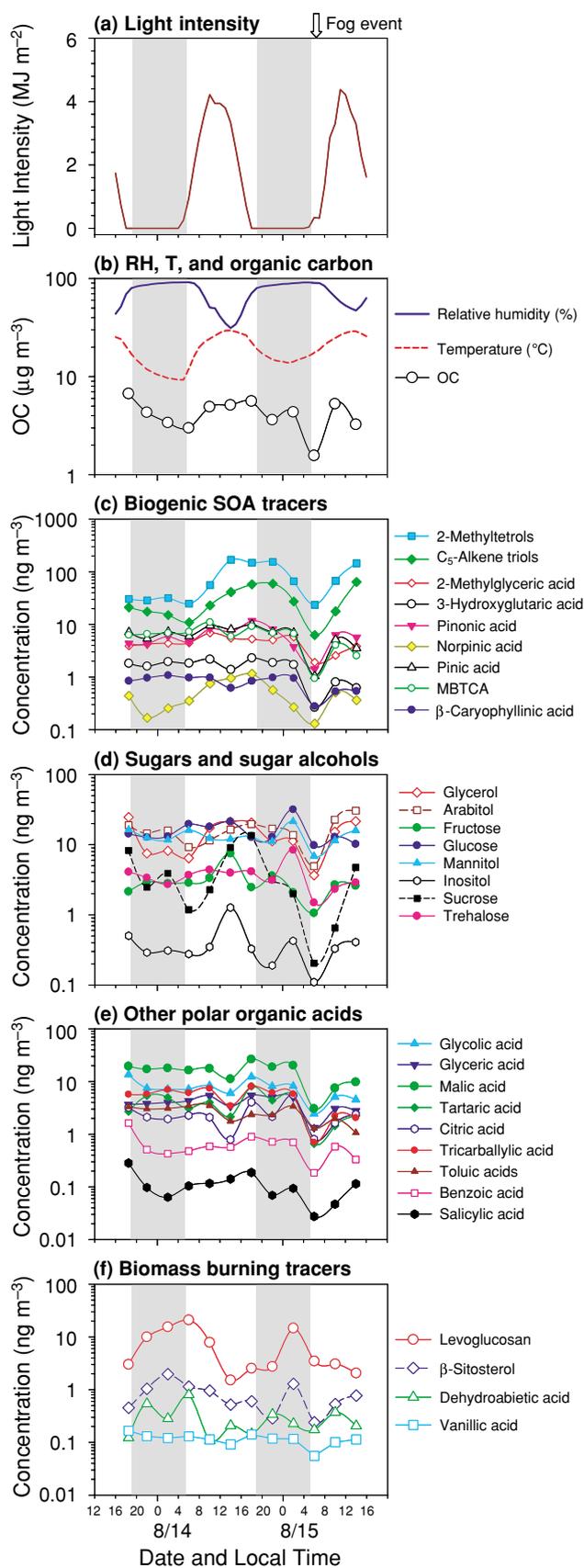


Fig. 1.

Table 1. Concentrations of biogenic secondary organic aerosol tracers and other polar organic compounds detected in the time-resolved atmospheric aerosols, ( $\text{ng m}^{-3}$ )

Compound	mean	std <sup>a</sup>	min	max	Compound	mean	std <sup>a</sup>	min	max
<b>Isoprene SOA tracers</b>					<b>Biomass burning tracers</b>				
2-Methylglyceric acid	4.5	1.4	1.9	6.9	Levogluconan	7.3	6.5	1.5	21
$\Sigma\text{C}_5$ -alkene triols <sup>b</sup>	30	20	6.3	64	Galactosan	0.3	0.3	0.04	0.9
2-Methylthreitol	24	18	7.1	55	Mannosan	1.0	0.5	0.2	2.0
2-Methylerythritol	54	40	15	113	Vanillic acid	0.1	0.03	0.06	0.2
Subtotal	113	77	32	219	Dehydroabiatic acid	0.3	0.2	0.1	0.8
<b><math>\alpha/\beta</math>-Pinene SOA tracers</b>					<b><math>\beta</math>-Sitosterol</b>				
3-Hydroxyglutaric acid	9.2	3.8	1.6	14	Subtotal	9.7	7.8	3.4	26
Pinonic acid	6.0	2.7	1.4	12	<b>Sugars and sugar alcohols</b>				
Norpinic acid	0.5	0.3	0.1	1.2	Glycerol	14	7.0	3.7	25
Pinic acid	6.4	2.5	1.0	10	Arabitol	16	6.6	4.9	30
MBTCA <sup>c</sup>	6.2	2.7	0.9	11	Fructose	3.0	1.6	1.1	7.5
Subtotal	28	11	5.1	46	Glucose	16	6.1	9.8	32
<b><math>\beta</math>-Caryophyllene SOA tracer</b>					<b>Mannitol</b>				
$\beta$ -Caryophyllinic acid	0.8	0.3	0.3	1.1	Inositol	0.4	0.3	0.1	1.3
Total biogenic SOA tracers	142	81	37	258	Sucrose	4.3	4.0	0.2	13
<b>Hydroxy-/polyacids</b>					<b>Trehalose</b>				
Glycolic acid	7.8	3.1	2.4	14	Subtotal	71	19	28	93
Salicylic acid	0.1	0.1	0.03	0.3	<b>SOC yields<sup>d</sup> (<math>\mu\text{gC m}^{-3}</math>)</b>				
Glyceric acid	4.1	1.2	1.3	5.5	Isoprene-derived SOC	0.54	0.38	0.16	1.12
Malic acid	16	6.3	3.0	26	$\alpha$ -Pinene-derived SOC	0.12	0.05	0.02	0.20
Tartaric acid	3.8	2.1	0.7	8.2	$\beta$ -Caryophyllene-derived SOC	0.03	0.01	0.01	0.05
Citric acid	2.5	1.2	0.8	5.6	Subtotal	0.69	0.39	0.20	1.28
Tricarballic acid	5.2	2.3	0.7	8.1	<b>OC (<math>\mu\text{g m}^{-3}</math>)</b>				
Subtotal	39	15	9.0	65	SOC in OC (%)	17	9.2	5.7	34
<b>Aromatic acids</b>									
Benzoic acid	0.6	0.2	0.4	1.0					
<i>o</i> -Toluic acid	0.2	0.1	0.03	0.3					
<i>m</i> -Toluic acid	0.4	0.2	0.1	1.0					
<i>p</i> -Toluic acid	0.1	0.1	0.05	0.4					
Subtotal	1.3	0.5	0.6	2.7					

<sup>a</sup>std = standard deviation.

<sup>b</sup> $\text{C}_5$ -alkene triols: *cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene.

<sup>c</sup>MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

<sup>d</sup>The total mass concentrations of SOC produced by isoprene (2-methylglyceric acid and 2-methyltetrols were used),  $\alpha/\beta$ -pinene, and  $\beta$ -caryophyllene were calculated using a tracer-based method reported by Kleindienst *et al.* (2007).

variation of OC was characterized by a major peak during daytime and a sharp drop during the fog event (Fig. 1(b)). Table 1 presents the detected organic compounds including oxidation products of BVOCs. Isoprene SOA tracers were found to be the most abundant compound class (32–219  $\text{ng m}^{-3}$ , average 113  $\text{ng m}^{-3}$ ), followed by sugars/sugar alcohols (28–93  $\text{ng m}^{-3}$ , 71  $\text{ng m}^{-3}$ ).

#### Biogenic SOA tracers

Isoprene (2-methyl-1,3-butadiene,  $\text{C}_5\text{H}_8$ ) is emitted by many deciduous trees during daytime. It is highly reactive because of the C=C bonds, which makes it susceptible to react with oxidants (e.g., OH,  $\text{O}_3$ , and  $\text{NO}_3$ ). Six

compounds were so far identified as isoprene SOA tracers in the forest aerosols, including 2-methylglyceric acid, three  $\text{C}_5$ -alkene triols, and two diastereoisomeric 2-methyltetrols (2-methylthreitol and 2-methylerythritol). Concentration ranges of 2-methyltetrols were 22–168  $\text{ng m}^{-3}$  (78  $\text{ng m}^{-3}$ ) with 2-methylerythritol being more abundant than 2-methylthreitol by 2.2-fold (Table 1). This ratio is similar to those observed in other studies (Claeys *et al.*, 2004a; Ion *et al.*, 2005; Cahill *et al.*, 2006). The levels of 2-methyltetrols reported here are comparable to those of mid-latitude mountain aerosols from China (Wang *et al.*, 2008).  $\text{C}_5$ -Alkene triols, which are also photooxidation products of isoprene (Wang *et al.*, 2005),

were detected in all the samples with an average of  $30 \pm 20 \text{ ng m}^{-3}$ . This level is higher than those reported in other studies from a Californian pine forest, USA ( $3.47 \text{ ng m}^{-3}$ ) (Cahill *et al.*, 2006), and Jülich, Germany ( $1.6\text{--}4.9 \text{ ng m}^{-3}$ ) (Kourtchev *et al.*, 2008b). It is 2–3 orders of magnitude higher than those reported in the Arctic aerosols (Fu *et al.*, 2009). Concentrations of 2-methylglyceric acid were  $1.9\text{--}6.9 \text{ ng m}^{-3}$  ( $4.5 \text{ ng m}^{-3}$ ). This acid is a possible oxidation product of methacrolein and methacrylic acid that are derived from isoprene (Claeys *et al.*, 2004b; Surratt *et al.*, 2006).

Pinonic, norpinic, and pinic acids are produced by the photooxidation of  $\alpha/\beta$ -pinene via reactions with  $\text{O}_3$  and OH radicals. Concentrations of pinonic, norpinic and pinic acids in this study ranged from  $1.4\text{--}12 \text{ ng m}^{-3}$ ,  $0.1\text{--}1.2 \text{ ng m}^{-3}$  and  $1.0\text{--}10 \text{ ng m}^{-3}$ , respectively (Table 1). Two novel compounds were recently identified in aerosols as 3-hydroxyglutaric acid (3-HG) (Claeys *et al.*, 2007) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski *et al.*, 2007). Both 3-HG and MBTCA can be generated in smog chamber experiments of  $\alpha$ -pinene under the irradiation of UV in the presence of  $\text{NO}_x$ . They are considered as later-generation products of the photooxidation of  $\alpha/\beta$ -pinene (Szmigielski *et al.*, 2007; Kourtchev *et al.*, 2009). Concentration ranges of 3-HG and MBTCA were  $1.6\text{--}14 \text{ ng m}^{-3}$  ( $9.2 \text{ ng m}^{-3}$ ) and  $0.9\text{--}11 \text{ ng m}^{-3}$  ( $6.2 \text{ ng m}^{-3}$ ), respectively.

$\beta$ -Caryophyllene is one of the most abundant sesquiterpenes emitted from the plants and the most frequently reported (Duhl *et al.*, 2008).  $\beta$ -Caryophyllinic acid, an ozonolysis or photo-oxidation product of  $\beta$ -caryophyllene (Jaoui *et al.*, 2007), was identified in the forest samples ranging from  $0.3$  to  $1.1 \text{ ng m}^{-3}$  ( $0.8 \text{ ng m}^{-3}$ ).

#### *Biomass burning tracers and sugar compounds*

Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose), specifically formed by the pyrolysis of cellulose above  $300^\circ\text{C}$ , has been recognized as an excellent tracer of biomass-burning (Simoneit *et al.*, 1999). The concentration range of levoglucosan was  $1.5\text{--}21 \text{ ng m}^{-3}$  ( $7.3 \text{ ng m}^{-3}$ ). In addition to levoglucosan, another two anhydrosugars (galactosan and mannosan) were identified in all the samples. The concentration ranges of galactosan and mannosan were  $0.04\text{--}0.9 \text{ ng m}^{-3}$  ( $0.3 \text{ ng m}^{-3}$ ) and  $0.2\text{--}2.0 \text{ ng m}^{-3}$  ( $1.0 \text{ ng m}^{-3}$ ), respectively. Vanillic acid is a biomass-burning tracer that can be detected in both hard and soft woods (Fine *et al.*, 2001; Hays *et al.*, 2005). Dehydroabietic acid is a diterpenoid, which is present in vegetation smoke both as natural and thermally altered products (Medeiros and Simoneit, 2008).  $\beta$ -Sitosterol is present in terrestrial higher plant leaves and can be emitted to the air via biomass burning processes (Simoneit, 2002).

Eight primary saccharides (glycerol, arabitol, fructose, glucose, mannitol, inositol, sucrose, and trehalose) were detected in the forest aerosols. Total concentrations of primary saccharides ranged from  $28$  to  $93 \text{ ng m}^{-3}$  ( $71 \text{ ng m}^{-3}$ ) with the predominance of arabitol and glucose (Table 1). They have been used as tracers for primary biological aerosol particles (Graham *et al.*, 2003; Medeiros *et al.*, 2006; Bauer *et al.*, 2008) and soil resuspension (Simoneit *et al.*, 2004). Resuspended soil particles contain biological materials including pollen, fungi and bacteria.

#### *Other polar organic acids*

Seven hydroxy- or poly-acids were detected in the forest aerosols, including glycolic, salicylic, glyceric, malic, tartaric, citric, and tricarballylic acids with the dominance of malic acid. Glycolic acid (hydroxyacetic acid), the smallest  $\alpha$ -hydroxy acid, is hygroscopic and highly water-soluble. Salicylic acid (2-hydroxybenzoic acid) is a known plant hormone and can be directly emitted from plants into the atmosphere (Heiden *et al.*, 1999). It is highly CCN active (Hartz *et al.*, 2006), although its solubility is low. In the present study, the concentration range of salicylic acid was  $0.03\text{--}0.3 \text{ ng m}^{-3}$  ( $0.1 \text{ ng m}^{-3}$ ), which are lower than those reported in the tropical Indian aerosols ( $0.1\text{--}1.1 \text{ ng m}^{-3}$ ) (Fu *et al.*, 2010). However, they are much higher than those in the Arctic aerosols ( $0.002\text{--}0.1 \text{ ng m}^{-3}$ , average  $0.04 \text{ ng m}^{-3}$ ) (Fu *et al.*, 2009). Glyceric, malic, tartaric and citric acids are suggested as secondary oxidation products. For example, malic acid can be formed by the photo-oxidation of unsaturated fatty acids (Kawamura *et al.*, 1996). The concentration range of tricarballylic acid was  $0.7\text{--}8.1 \text{ ng m}^{-3}$  ( $5.2 \text{ ng m}^{-3}$ ), being similar to those reported in the tropical Indian aerosols (Fu *et al.*, 2010).

Benzoic acid and three toluic acid isomers (*o*-, *m*-, and *p*-) were detected in the samples. Toluic acids can also be directly emitted from motor vehicular exhausts (Kawamura *et al.*, 2000) or derived by the oxidation of xylene (Forstner *et al.*, 1997). The total concentrations of these aromatic acids ranged from  $0.6$  to  $2.7 \text{ ng m}^{-3}$  (Table 1).

## DISCUSSION

### *Diurnal variations of biogenic SOA tracers: Predominance of isoprene SOA formation and influence of a fog event*

Figure 1(c) presents diurnal variations of the biogenic SOA tracers. 2-Methyltetrols and  $\text{C}_5$ -alkene triols showed very similar patterns with a continuous increase from early morning to late afternoon. Such an increase during daytime should be caused by the local emissions of isoprene followed by the photochemical oxidation. Matsunaga *et al.*

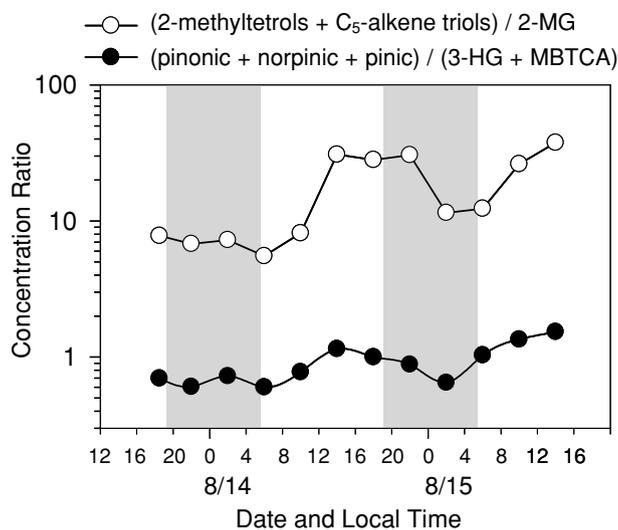


Fig. 2. Diurnal variations in the concentration ratios of isoprene and  $\alpha/\beta$ -pinene oxidation tracers.

*al.* (2003) reported diurnal variations of glycolaldehyde and hydroxyacetone in both gas and particle phases at the same sampling site during the same period. They found that the gaseous concentrations of these two compounds minimized early in the morning (02:00–06:00, local time) and increased rapidly to the maxima around noontime, suggesting that these semi-volatile carbonyls were vigorously produced and/or released in the forest atmosphere at daytime. The diurnal patterns of 2-methyltetrols and  $C_5$ -alkene triols (Fig. 1(c)) are similar to those of particulate glycolaldehyde and hydroxyacetone measured during the same campaign (Matsunaga *et al.*, 2003). They also reported a time lag of several hours between the peak concentrations of these carbonyls in gas and particle phases, indicating a gas-to-particle conversion probably through condensation and adsorption of gaseous compounds onto the pre-existing particles. The condensation/adsorption processes should be accelerated in the evening when the ambient temperature decreased.

A good correlation between the concentrations of 2-methyltetrols and  $C_5$ -alkene triols ( $R^2 = 0.84$ ) was obtained in this study. Such a positive correlation has been reported in other studies (e.g., Cahill *et al.*, 2006; Fu *et al.*, 2010).  $C_5$ -Alkene triols can be formed by acid-catalyzed ring opening of epoxydiol derivatives of isoprene (Wang *et al.*, 2005). They can be converted to 2-methyltetrols through acid-catalyzed hydrolysis.

2-Methylglyceric acid did not show a clear diurnal variation although a significant decrease was seen in the morning of 15 August when the fog event occurred (Fig. 1). A similar drop was observed for OC and other organic compounds, suggesting that the suspended particles in the

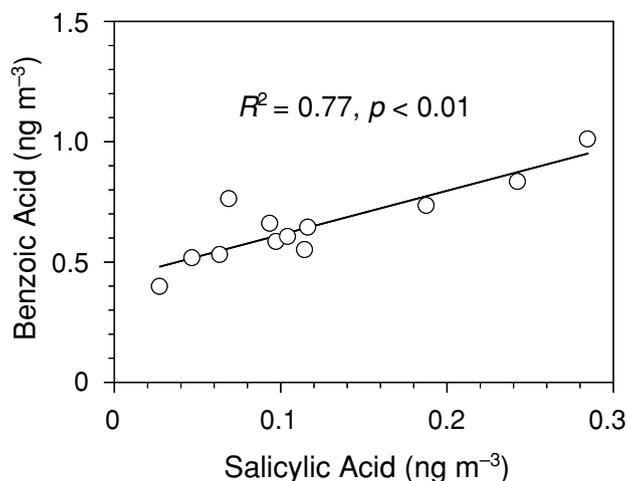


Fig. 3. A positive correlation between salicylic acid and benzoic acid detected in the forest aerosols.

forest atmosphere could be efficiently removed via wet deposition of fog droplets. The diurnal pattern of 2-methylglyceric acid was different from those of 2-methyltetrols and  $C_5$ -alkene triols even though they are all derived from isoprene oxidation. Claeys *et al.* (2004b) pointed out that the formation of 2-methyltetrols can be explained through acid-catalyzed reaction of isoprene with hydrogen peroxide, while 2-methylglyceric acid can be formed by further oxidation of methacrolein and methacrylic acid, both gas-phase oxidation products of isoprene, via acid-catalyzed reaction with hydrogen peroxide in aqueous medium. Chamber experiments demonstrate that these polyols are mainly detected under low- $NO_x$  conditions (below 1 ppb), while 2-methylglyceric acid is a major product under high- $NO_x$  conditions (Surratt *et al.*, 2006).

3-Hydroxyglutaric, pinonic, pinic, 3-methyl-1,2,3-butanetricarboxylic, and  $\beta$ -caryophyllinic acids show similar diurnal trends without daytime maxima (Fig. 1(c)). These diurnal patterns are different from those of isoprene SOA tracers such as 2-methyltetrols and  $C_5$ -alkene triols except 2-methylglyceric acid (Fig. 1(c)). No clear diurnal variations were observed for  $\alpha/\beta$ -pinene SOA tracers, being in agreement with previous studies (Kourtchev *et al.*, 2008a). Although the emissions of monoterpenes are temperature-dependant, they can also be emitted during nighttime and oxidized by  $NO_3$ . Another possibility is that the formation of a shallow stable layer near the ground over the forest during nighttime may in part contribute to enhance the atmospheric levels of organic aerosols.

The concentration ratios of earlier- (pinic, pinonic and norpinic acids) to later-generation products (3-HG and MBTCA) of  $\alpha/\beta$ -pinene increased from early morning to

late afternoon, and then decreased toward nighttime (Fig. 2), suggesting that the earlier-generation products or their precursors are continuously oxidized at night. Although the diurnal patterns of  $\alpha/\beta$ -pinene oxidation products are different from those of isoprene oxidation products, the concentration ratios of the sum of 2-methyltetrols and C<sub>5</sub>-alkene triols to 2-methylglyceric acid (2-MG) showed a very similar trend to that of  $\alpha/\beta$ -pinene SOA tracers (Fig. 2). As mentioned above, the formation pathway of 2-MG is different from that of polyols. Such a diurnal pattern suggests that 2-MG may be a relatively later product of isoprene oxidation compared to 2-methyltetrols and C<sub>5</sub>-alkene triols. However, the formation mechanisms of isoprene SOA tracers are not completely understood yet (Carlton *et al.*, 2009; Paulot *et al.*, 2009; Claeys, 2010). It should be noted that there is a large difference in the concentrations of biogenic SOA tracers such as 2-methyltetrols was observed between the nights of 13–14 August and 14–15 August. This suggests that the SOA yields in the ambient atmosphere depend on a number of factors such as the mixing ratios of BVOCs, OH and NO<sub>x</sub> levels, organic aerosol loading, and the degree of oxidation (Carlton *et al.*, 2009; Hallquist *et al.*, 2009).

Hydroxy-/polyacids also showed diurnal patterns similar to those of  $\alpha/\beta$ -pinene SOA tracers (Fig. 1(e)). Interestingly, the diurnal pattern of salicylic acid was different from polyacids such as malic acid. A positive correlation was found between benzoic acid and salicylic acid (Fig. 3), indicating an intrinsic relation between these two aromatic acids. As mentioned earlier, salicylic acid can be directly emitted from plants (Heiden *et al.*, 1999). Nakajima *et al.* (2008) reported that one possible source for salicylic acid in the atmosphere is the reaction of benzoic acid with hydroxyl radicals. Benzoic acid is emitted as a primary pollutant from fossil fuel combustion of motor vehicles (Kawamura and Kaplan, 1987; Rogge *et al.*, 1993; Kawamura *et al.*, 2000) and is produced by the photochemical oxidation of aromatic hydrocarbons (e.g., toluene) emitted from automobiles (Suh *et al.*, 2003).

#### *Diurnal variations of primary saccharides*

Primary saccharides are an important class of organic compounds in atmospheric aerosols (Medeiros *et al.*, 2006; Wan and Yu, 2007; Yttri *et al.*, 2007; Fu *et al.*, 2008). They are completely water-soluble and thus contribute to WSOC in aerosol. Sugar compounds are generally found to be more abundant in coarse fraction than the fine one (Fuzzi *et al.*, 2007; Yttri *et al.*, 2007), supporting that they are likely derived from primary biological aerosol particles. Graham *et al.* (2003) reported that fructose, sucrose and glucose showed higher daytime concentrations, which were explained by the specific daytime release of pollen, fern spores and other “giant” bioaerosols. Sucrose is the predominant sugar in the

phloem of plants and is important in developing flower buds (Bielecki, 1995). Pashynska *et al.* (2002) reported that the atmospheric levels of inositol and sucrose and their contributions to OC were highest in early summer (June) owing to the developing leaves. As shown in Fig. 1(d), glycerol, arabinol, fructose, inositol and sucrose exhibited diurnal trends with daytime maxima. Thus, these sugars and sugar alcohols may be associated with specific daytime release of primary biological aerosol particles (PBAP) in the forest.

On the contrary, mannitol, glucose and trehalose didn't show clear diurnal patterns, which can be explained by the continuous emission of these compounds from microorganisms even at night. For example, mannitol, together with arabinol, has been reported as tracers for the airborne fungal spores (Bauer *et al.*, 2008). Trehalose is present in a large variety of microorganisms (fungi, bacteria and yeast), and a few higher plants and invertebrates (Medeiros *et al.*, 2006).

#### *Evaluation of the potential impact of biomass burning on SOA formation*

Biomass burning, together with biogenic SOA formation, is one of the major sources of organic aerosols in the atmosphere (de Gouw and Jimenez, 2009). Levoglucosan and other pyrolysis products of cellulose can be used as specific tracers for the emissions from biomass burning in atmospheric aerosols (Simoneit *et al.*, 1999). In the present study, the concentration range of levoglucosan was 1.5–21 ng m<sup>-3</sup> (7.3 ng m<sup>-3</sup>). Such a level is even lower than those reported in marine aerosols over the western North Pacific (average 14 ng m<sup>-3</sup>) and off the Coast of East Asia (15 ng m<sup>-3</sup>) (Mochida *et al.*, 2003), suggesting that the effect of biomass burning on the forest aerosols was negligible during the sampling period. Furthermore, the temporal variations of biomass burning tracers (Fig. 1(f)) showed patterns different from those of biogenic SOA tracers. For example, levoglucosan showed a minimum concentration during daytime when concentrations of 2-methyltetrols and other isoprene oxidation products maximized. This difference again suggests that the effect of biomass burning on SOA formation was minor.

#### *Contributions of polar organic tracers to OC*

To better understand the SOA formation in the forest atmosphere, the contributions of isoprene,  $\alpha/\beta$ -pinene and  $\beta$ -caryophyllene oxidation products, and other polar organic compounds to OC were examined (Fig. 4). The contributions of isoprene SOA tracers to OC ranged from 0.4% to 3.0% (1.3%), which were 4 times higher than those of  $\alpha/\beta$ -pinene SOA tracers (0.2–0.5%, 0.3%). Those of  $\beta$ -caryophyllenic acid to OC ranged from 0.007% to 0.02% (0.01%). Total SOA tracers are the most abundant

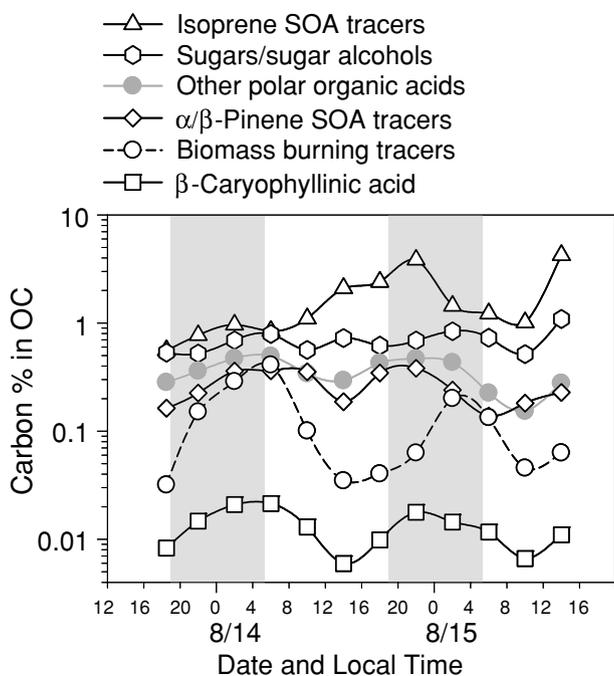


Fig. 4. Diurnal variations of the carbon % of different organic compound classes in OC.

among the organic compound classes detected in this study. The mean contributions of total SOA tracers to OC were  $1.6 \pm 0.9\%$  with a maximum of 3.3%. These values are similar to those (1.7% in average) reported in the boreal forest aerosols in Finland (Kourtschev *et al.*, 2008a). Although the SOA tracers studied are oxidation products of biogenic VOCs, there are many unidentified organic compounds that can contribute to the formation of SOA (Hallquist *et al.*, 2009), suggesting that the above contributions are only the minimum estimate and the actual contribution of BVOC to SOA should be much larger.

As shown in Fig. 4, the temporal variations of biomass burning tracers,  $\alpha/\beta$ -pinene SOA tracers,  $\beta$ -caryophyllinic acid, and other polar organic acids (hydroxy, aromatic and polyacids as mentioned in Table 1) relative to OC showed similar diurnal patterns each other with nighttime maxima and daytime minima. Such a trend suggests that during nighttime, higher relative humidity may favor the liquid phase formation of some polar organic compounds through heterogeneous reactions and that lower ambient temperature may enhance the condensation/adsorption processes. In contrast, the contributions of isoprene SOA tracers to OC exhibited a daytime maximum, while primary saccharides rather showed a flat pattern. These differences again suggest that isoprene oxidation products and primary biological particles are substantial components of forest organic aerosols in summer, particularly during daytime.

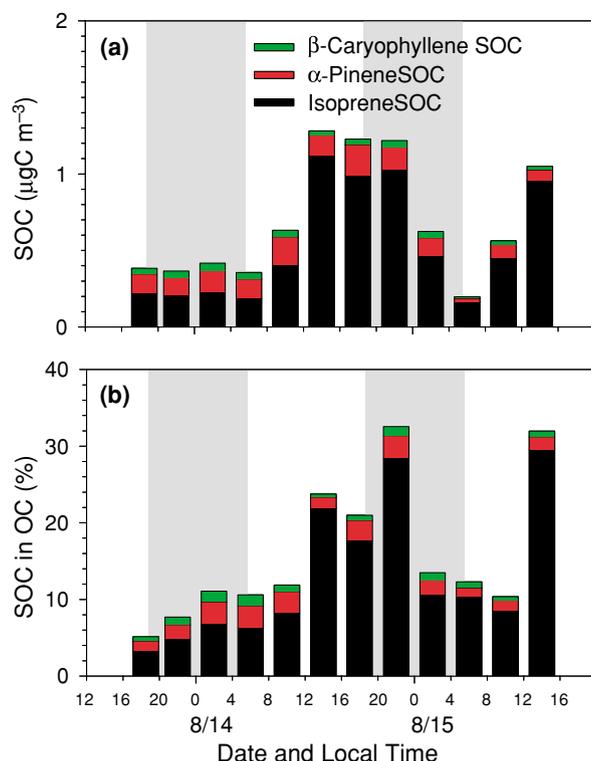


Fig. 5. Contributions of different hydrocarbon precursors to secondary organic carbon (SOC), and the percentages of SOC in ambient OC in individual samples.

#### Estimates of ambient SOC, and SOC in OC

Based on the present dataset, we estimated the contributions of BVOCs to secondary organic carbon (SOC) using a tracer-based method proposed by Kleindienst *et al.* (2007). With the measured concentrations of tracer compounds in the forest aerosols and the laboratory-derived tracer mass fraction ( $f_{\text{soc}}$ ) factors of  $0.155 \pm 0.039$  for isoprene,  $0.231 \pm 0.111$  for  $\alpha$ -pinene and  $0.0230 \pm 0.0046$  for  $\beta$ -caryophyllene (Kleindienst *et al.*, 2007), the contributions of these precursors to aerosol OC were calculated by the following equation:

$$f_{\text{soc}} = \frac{\sum_i [\text{tracer}_i]}{[\text{soc}]} \quad (1)$$

where  $\sum_i [\text{tracer}_i]$  is the sum of the concentrations of the selected suite of tracers for a same BVOC precursor in  $\mu\text{g m}^{-3}$ . Although this technique was developed using a series of smog chamber experiments under relatively high  $\text{NO}_x$  conditions (0.11–0.63 ppm) (Kleindienst *et al.*, 2007), the  $f_{\text{soc}}$  of  $0.155 \pm 0.039$  for isoprene is similar to those ( $f_{\text{soc, isoprene}}$  from 0.117 to 0.231, average 0.156) in the absence of  $\text{NO}_x$  (Kleindienst *et al.*, 2009). The simi-

lar values suggest that the tracer-based method is applicable to the forest aerosols where the ambient  $\text{NO}_x$  levels are generally low. Although little is known about the differences of  $f_{\text{soc}}$  values for  $\alpha$ -pinene and  $\beta$ -caryophyllene between high and low  $\text{NO}_x$  levels, we consider that the tracer-based method is the best technique available at present.

As shown in Table 1 and Fig. 5, the isoprene-based tracers (2-methylglyceric acid and 2-methyltetrols) were calculated to be 0.16 to 1.12  $\mu\text{gC m}^{-3}$  (0.54  $\mu\text{gC m}^{-3}$ ). The contributions of  $\alpha$ -pinene and  $\beta$ -caryophyllene to SOC ranged from 0.02 to 0.20  $\mu\text{gC m}^{-3}$  and 0.01 to 0.05  $\mu\text{gC m}^{-3}$ , respectively. These calculations show that isoprene was the major contributor to SOC in the *Quercus* and *Picea* mixed forest aerosols, which is reasonable because *Quercus* is a strong emitter of isoprene, although *Picea* emits both isoprene and monoterpenes (Pacífico *et al.*, 2009 and references therein). The total SOC in the present forest aerosols ranged from 0.20 to 1.28  $\mu\text{gC m}^{-3}$  (average 0.69  $\mu\text{gC m}^{-3}$ ), which correspond to 5.7–34% (17%) of the aerosol OC. It should be noted that Kleindienst *et al.* (2007) derived mass fractions of SOA tracers by using ketopinic acid as the surrogate for all the SOA tracers. In this study, the SOA tracers were quantified using authentic standards together with some surrogates that were further quantified using GC/FID (see the Section of Samples and Methods). Nevertheless, we believe that the uncertainties between the two quantification methods should be minimal in terms of the uncertainties raised by the tracer-based approach itself (20–48%) due to the standard deviation of  $f_{\text{soc}}$  mentioned above (Kleindienst *et al.*, 2007). Another point is that the isoprene and  $\beta$ -caryophyllene SOA tracers used in the tracer-based method are exactly same as those in Kleindienst *et al.* (2007). For the  $\alpha/\beta$ -pinene SOA tracers, however, five organic species were detected in this study, that is, 3-hydroxyglutaric, pinonic, norpinic, pinic and 3-methyl-1,2,3-butanetricarboxylic acids, although Kleindienst *et al.* (2007) reported a few additional  $\alpha/\beta$ -pinene SOA tracers, which were either undetectable or minor species in this study. The uncertainty raised by this point is estimated to be less than 30%.

## CONCLUSIONS

Biogenic SOA tracers, that is, the oxidation products of isoprene,  $\alpha/\beta$ -pinene and  $\beta$ -caryophyllene, together with other polar organic tracers, were determined in the aerosols collected from the mixed forest of *Quercus crispula* and *Picea glehnii* mast. 2-Methyltetrols and related isoprene oxidation products were found to be the dominant species among the identified organic compounds, especially during daytime. Total biogenic SOA tracers contributed  $1.6 \pm 0.9\%$  of the OC with a maxi-

um of 3.3% in daytime. Contribution of biomass burning to SOA production was found to be minor. However, primary saccharides could contribute  $0.7 \pm 0.2\%$  of the OC with a maximum of 1.1%. In addition, secondary organic carbon that was estimated by a tracer-based method can contribute up to 34% (average 17%) of OC in the forest aerosols, among which isoprene SOC was evaluated as the major contributor (average 13%). This study demonstrates that the BVOC emission and its SOA formation processes play an important role in aerosol chemistry over a *Quercus* and *Picea* mixed forest in mid-latitude.

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