



Seasonal variations of biogenic secondary organic aerosol tracers in ambient aerosols from Alaska



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HIGHLIGHTS

- This study presents distinct seasonal variations of SOA tracers in Alaskan aerosols.
- BVOCs (isoprene, α - β -pinene and β -caryophyllene) significantly contribute to SOC (14.4% of OC).
- Isoprene is a more important contributor for biogenic SOA than α - β -pinene and β -caryophyllene in subarctic Alaska.

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ABSTRACT

We investigated total suspended particles (TSP) collected from central Alaska, USA for molecular compositions of secondary organic aerosol (SOA) derived from the oxidation of biogenic volatile organic compounds (BVOCs). Isoprene-, α - β -pinene- and β -caryophyllene-SOA tracers were determined using gas chromatography-mass spectrometry. The concentration ranges of isoprene, α - β -pinene and β -caryophyllene oxidation products were 0.02–18.6 ng m⁻³ (ave. 4.14 ng m⁻³), 0.42–8.24 ng m⁻³ (2.01 ng m⁻³) and 0.10–9 ng m⁻³ (1.53 ng m⁻³), respectively. Isoprene-SOA tracers showed higher concentrations in summer (ave. 8.77 ng m⁻³), whereas α - β -pinene- and β -caryophyllene-SOA tracers exhibited highest levels in spring (3.55 ng m⁻³) and winter (4.04 ng m⁻³), respectively. β -Caryophyllinic acid and levoglucosan showed a positive correlation, indicating that biomass burning may be a major source for β -caryophyllene. We found that mean contributions of isoprene oxidation products to organic carbon (OC) and water-soluble organic (WSOC) (0.56% and 1.2%, respectively) were higher than those of α - β -pinene (0.31% and 0.55%) and β -caryophyllene (0.08% and 0.13%). Using a tracer-based method, we estimated the concentrations of secondary organic carbon (SOC) produced from isoprene, α - β -pinene and β -caryophyllene to be 0.66–718 ngC m⁻³ (ave. 159 ngC m⁻³), 7.4–143 ngC m⁻³ (35 ngC m⁻³) and 4.5–391 ngC m⁻³ (66.3 ngC m⁻³), respectively. Based on SOA tracers, this study suggests that isoprene is a more important precursor for the production of biogenic SOA than α - β -pinene and β -caryophyllene in subarctic Alaska.

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1. Introduction

Secondary organic aerosol (SOA) is produced via the oxidation of biogenic volatile organic compounds (BVOCs) with O₃, OH and NO₃ radicals (Atkinson and Arey, 1998). Vegetation can release huge amounts of BVOCs, including isoprene, monoterpenes, sesquiterpenes and oxygenated hydrocarbons (Goldstein and Galbally, 2007;

Guenther et al., 1995). Oxygenated VOCs contribute to particle growth processes over boreal forests (Kourtchev et al., 2008a). Biogenic emissions are the dominant source of reduced organic gases to the atmosphere (Holzinger et al., 2005). These BVOCs play an important role in local, regional, and global climate change. SOA can affect the earth's radiative balance (Hoyle et al., 2009) and leads to visibility reduction that can affect the global climate (Kleindienst et al., 2007). Oxidation products of biogenic SOA are polar and thus hygroscopic (Virkkula et al., 1999).

Isoprene is a significant source of organic aerosol in the atmosphere, with emissions estimated to be 440–660 TgC yr⁻¹

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(Surratt et al., 2010). On a global budget, emissions of biogenic VOCs (1150 Tg yr^{-1}) are suggested to be one order of magnitude higher than those of anthropogenic VOCs (Guenther et al., 2006), whereas emission of isoprene is 44% of total emissions of BVOCs (Ding et al., 2014). Recent study suggested that oxidation of isoprene leads to the formation of SOA in the atmosphere via heterogeneous reactions (Kroll et al., 2006). However, various factors such as different oxidants (OH, O_3 and NO_3), heterogeneous reactions, NO_x concentration, etc. can play a role in SOA formation (Kroll et al., 2006). Contribution of photo-oxidation products of isoprene is significant to boreal forest aerosols (Kourtchev et al., 2005). Aerosol characterization studies from different forest sites indicated that SOA compounds from the photo-oxidation of isoprene (i.e., 2-methyltetrols and 2-methylglyceric acid) are important constituents (Cahill et al., 2006; Claeys et al., 2004; Edney et al., 2005; Ion et al., 2005). 2-Methyltetrols were first identified in the Amazonian rainforest (Claeys et al., 2004) and subsequently detected in ambient aerosols from many sites in the world (Clements and Seinfeld, 2007; Ion et al., 2005; Edney et al., 2005; Chan et al., 2010).

Monoterpenes and sesquiterpenes are also believed to be important sources of biogenic SOA. Monoterpenes are mainly emitted from conifer forest, with annual emission of 127 Tg , considering α -pinene as major terpene (Claeys et al., 2007). Several studies of organic aerosol composition have focused on monoterpene photo-oxidation products at coniferous forest sites (Kavouras et al., 1998; Yu et al., 1999; Pio et al., 2001) and the emissions of monoterpene are believed to be important in these environments (Jobson et al., 1994; Lamanna and Goldstein, 1999; Hakola et al., 2000). Monoterpene-SOA tracers have been used to evaluate the role of monoterpene in the formation of SOA; monoterpenes contribute about 35% of the global emissions of BVOCs (Griffin et al., 1999a). High SOA yields from monoterpene were also observed in laboratory experiments (Griffin et al., 1999b). The SOA tracers are useful to estimate SOA v.s. primary OA (Stone et al., 2012). Moreover, the compositions of SOA tracers can give additional information on the process and sources (Ding et al., 2014).

The boreal forest covers more than $1.2 \times 10^7 \text{ km}^2$ spanning North America and Eurasia (Baumgartner, 1979; Stocks and Lynham, 1996). Two-thirds of the boreal forest area are located in Eurasia and the remaining is located primarily in Canada and Alaska (Hare and Ritchie, 1972). Tundra and boreal forests are also available in Russia, Alaska and Canada. Thus, BVOC emissions from these ecosystems are considered to make a significant contribution to SOA mass. High loading of natural aerosols over boreal forests was proposed in northern Europe (Tunved et al., 2006). As a large fraction of organic carbon (OC), water-soluble organic carbon (WSOC) has the potential role to modify the hygroscopic properties of particles (Saxena et al., 1995), in which WSOC is often associated with oxygenated polar compounds and closely related to SOA formation (Weber et al., 2007). Although many studies have been conducted for the understanding the compositions, sources and formation mechanisms of SOA for the last decade, it is still needed to expand the knowledge on the SOA formation in the high latitudinal atmosphere.

The objective of this study is to characterize the abundance and seasonal variations of SOA tracers that are generated from atmospheric oxidation of isoprene, α -/ β -pinene, and β -caryophyllene in the ambient aerosols from Fairbanks, Alaska. Contributions of SOA tracers to organic carbon (OC), water-soluble organic carbon (WSOC) and secondary organic carbon (SOC) are also evaluated in the ambient aerosols over central Alaska. The current study presents for the first time one-year observation on biogenic SOA tracers in the subarctic region.

2. Experimentals

2.1. Sample collection

Total suspended particles (TSP, $n = 32$) were collected on the rooftop of the International Arctic Research Centre (IARC), University of Alaska Fairbanks ($64^\circ 51' \text{N}$; $147^\circ 51' \text{W}$), Alaska, USA during June 2008–June 2009 using a low-volume air sampler (NIER) at a flow rate of 16.7 L/min . TSP were collected roughly every one week to three weeks onto pre-combusted (450°C for 6 h) quartz fiber filters (47 mm, HEPA, Pall Corporation, USA). The samples were stored in a pre-combusted glass vial (50 mL) with a Teflon-lined screw cap in darkness at -20°C until the analysis.

2.2. Extraction and derivatization

Filter aliquots (disk diameter of 20 mm) were extracted three times with 7 mL of dichloromethane/methanol (2:1; v/v) under ultrasonication. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated using rotary evaporator under vacuum and then blown down to dryness with pure nitrogen gas. The extracts were then derivatized with 50 μL of N,O -bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 μL of pyridine at 70°C for 3 h (Fu et al., 2009). After the reaction, the derivatives were diluted with 40 μL of n -hexane containing the internal standard (C_{13} n -alkane, $1.43 \text{ ng}/\mu\text{L}$) prior to determination by gas chromatography/mass spectrometry (GC/MS).

2.3. Gas chromatography-mass spectrometry (GC/MS)

GC/MS analyses of the samples were performed on a Hewlett–Packard model 6890 GC coupled to a Hewlett–Packard model 5973 MSD. The GC was equipped with a split/splitless injector and a DB-5MS fused silica capillary column ($30 \text{ m} \times 0.25 \text{ mm i.d.}$, $0.25 \mu\text{m}$ film thickness). The mass spectrometer was operated on electron ionization mode at 70 eV and scanned from 50 to 650 Da. Data were acquired and processed with Chemstation software. Individual compounds of TMS derivatives were identified by comparison of mass spectra with those of authentic standards or literature data (Fu et al., 2010).

For the quantification of *cis*-pinonic, pinic and 3-hydroxyglutaric acids, their GC–MS response factors were determined using authentic standards. Owing to a lack of standards, concentrations of 2-methylglyceric acid, C_5 -alkene triols and 2-methyltetrols were estimated using the response factor of *meso*-erythritol (Wang et al., 2008; Kourtchev et al., 2008b). Meanwhile 3-methyl-1,2,3-butanetricarboxylic (MBTCA) and β -caryophyllinic acids were quantified using the response factors of pinic acid (Jaoui et al., 2007; Ding et al., 2011), respectively. It should be noted that surrogate standards do not represent exactly the ionization and mass fragmentation of target SOA tracers. Thus, the measured values of SOA tracers that used surrogate standards may have substantial uncertainties. We estimated the uncertainties caused by using different surrogate standards based on the method of Stone et al. (2012). In this study, the uncertainties of 2-methylglyceric acid, C_5 -alkene triols, 2-methyltetrols, MBTCA, and β -caryophyllinic acid were found to be 10, 85, 15, 32, and 136%, respectively. Field blank filters ($n = 3$) were analyzed as a real sample for quality assurance. Target compounds were not detected in the blank filters. The authentic standards or surrogates were spiked into precombusted quartz filters ($n = 3$), whose recoveries were $99 \pm 4.5\%$ for *meso*-erythritol, $98 \pm 1.6\%$ for *cis*-pinonic acid, $80 \pm 4.9\%$ for pinic acid and $83 \pm 5.9\%$ for 3-hydroxyglutaric acid. Relative standard deviations for the target compounds in duplicate samples were generally $<10\%$.

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