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Seasonal variations of biogenic secondary organic aerosol tracers in Cape Hedo, Okinawa

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HIGHLIGHTS

- Maximum isoprene-SOA in summer is controlled by local source.
- Monoterpene- and sesquiterpene-SOA are related to the continental outflow.
- Biogenic SOC accounts for 0.01–9.8% of aerosol organic carbon.

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ABSTRACT

Secondary organic aerosol (SOA) substantially contributes to particulate organic matter affecting the regional and global air quality and the climate. Total suspended particle (TSP) samples were collected in October 2009 to February 2012 on a weekly basis at Cape Hedo, Okinawa, Japan in the western North Pacific Rim, an outflow region of Asian aerosols and precursors. The TSP samples were analyzed for SOA tracers derived from biogenic volatile organic compounds (BVOCs). Total isoprene-SOA tracers showed a maximum in summer (2.12 ± 2.02 ng m^{-3}) and minimum in winter (1.16 ± 0.92 ng m^{-3}). This seasonality is mainly controlled by isoprene emission from the local subtropical forest, followed by regional scale emission of isoprene from the surrounding seas and long-range transported air masses. Total monoterpene-SOA tracers peaked in March (3.38 ± 2.03 ng m^{-3}) followed by October (2.95 ± 1.62 ng m^{-3}). In contrast, sesquiterpene-SOA tracer, β-caryophyllinic acid, showed winter maximum (1.63 ± 1.18 ng m^{-3}) and summer minimum (0.20 ± 0.46 ng m^{-3}). The variations of the monoterpene- and sesquiterpene-SOA tracers are likely related to the continental outflow of oxidation products of BVOC. Using a tracer-based method, we estimated the total biogenic SOC of 0.25 −157 ng m^{-3} (mean 35.8 ng m^{-3}) that accounts for 0.01–9.8% (mean 2.7%) of aerosol organic carbon. Our study suggests that SOA formation in the western North Pacific Rim is involved with not only local but also regional emissions followed by long-range atmospheric transport.

1. Introduction

Organic aerosols (OA), which are composed of numerous compounds derived from both natural and anthropogenic sources, could be categorized into primary organic aerosols (POA) and secondary organic aerosols (SOA). POA is directly emitted from biomass burning, soil dust re-suspension, plant debris and fungal spore, as well as fossil fuel combustion (Aiken et al., 2008). In contrast, SOA is formed through photochemical oxidation of volatile organic compounds (VOCs) by oxidants such as hydroxyl radical (OH), ozone (O_3), and nitrate radical (NO_3), followed by partitioning in gas and particle phases (Atkinson and Arey, 2003). Oxidation of POA in particle phase also contributes to SOA formation (Zhang et al., 2007). SOA accounts for a substantial fraction of organic aerosol, depending on regions and landscapes with varying source strengths of anthropogenic and biogenic VOC (BVOC) and oxidizing processes (Ait-Helal et al., 2014).

Biogenic emissions account for ~90% of non-methane hydrocarbons globally, while anthropogenic VOCs deserve more attention in highly populated regions (Atkinson and Arey, 2003; Goldstein and Galbally, 2007). Being emitted mainly from terrestrial ecosystems and partly from ocean, isoprene (C_5H_8) is the largest source of VOCs (~50% of total) with global emission of

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309–706 Tg C yr^{-1} (Acosta Navarro et al., 2014; Guenther et al., 2006). However, the importance of isoprene in its contribution to SOA formation did not draw attention in the community until the discovery of its oxidation products, 2-methyltetrols, being first identified in aerosols from the Amazon forest (Claeys et al., 2004). Subsequent studies revealed that the oxidizing pathways of isoprene depend on the NO_x levels, while low NO_x conditions favor the isoprene epoxydiols (IEPOX) pathway (causing aerosol phase products of 2-methyltetrols) and high NO_x conditions favor the methacrylic acid epoxide (MAE) pathway (causing aerosol phase product of 2-methylglyceric acid), leading to an SOA yield of 1–29% (Kroll et al., 2006; Surratt et al., 2006; Worton et al., 2013).

Monoterpenes ($C_{10}H_{16}$, ~10% of total VOCs) are another group of important SOA precursors (Ziemann and Atkinson, 2012). In the atmosphere, monoterpenes can be oxidized by OH/O_3 in daytime and by NO_3 in nighttime (Hallquist et al., 2009; Kristensen et al., 2014), whose products with lower vapor pressure undergo gas-to-particle conversion, causing SOA formation (Kroll and Seinfeld, 2008). Although being less reported than isoprene and monoterpenes, sesquiterpenes ($C_{15}H_{24}$) constitute an appreciable portion of BVOC (Helmig et al., 2006). Laboratory studies indicated that sesquiterpenes were readily ozonlyzed to form SOA (Tang et al., 2012). The most common sesquiterpene detected in boreal forests is β-caryophyllene (Tarvainen et al., 2005). In $PM_{2.5}$ samples collected in North Carolina, USA, β-caryophyllinic acid was identified as an SOA tracer of β-caryophyllene, raising the importance to quantify the SOA fraction from sesquiterpene oxidation (Jaoui et al., 2007).

Due to the high reactivity, contributions of BVOCs to SOA and/or secondary organic carbon (SOC) had been mostly studied in laboratory oxidation experiments (e.g., Surratt et al., 2010). Site observation of SOA compound is meaningful for better understanding OA chemical properties and its implications to air quality and future climate. Okinawa is located in the western North Pacific Rim in the outflow region of the Asian continent. Previous studies suggested that Okinawa aerosols are contributed by continental outflow of emissions from fossil fuel combustion (Takami et al., 2007) and biomass burning (Zhu et al., 2015a). Our recent study indicated that emissions of primary biological aerosol particles from local vegetation contribute to a notable fraction of TSP (Zhu et al., 2015b). Emissions of BVOC from the local vegetation and the Asian continent could contribute to SOA in Okinawa aerosols. In this work, we report the abundances and the seasonal variations of biogenic SOA tracers in Okinawa aerosols. We also estimate the biogenic SOC masses and their contributions to OC.

2. Experimental section

2.1. Sample collection

Aerosol samples were collected at the Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) (26.9°N, 128.2°E) in the northern edge of Okinawa Island, Japan. The region close to CHAAMS is characterized by a maritime subtropical climate. In a meteorological station (Oku, ~6 km to CHAAMS, maintained by Japan Metrological Agency, JMA), the monthly mean temperatures ranged from 17.3 °C in January to 30.3 °C in August in 2010, with the annual mean temperature of 20.7 °C. The total precipitation was 3500.5 mm in 2010. Okinawa is frequently affected by typhoon in July to October. The northern part of the island is mostly covered with subtropical evergreen broadleaf forest. Around the sampling site, the dominant species of vegetation are *Castanopsis sieboldii* and *Schima wallichii* (Enoki, 2003).

From October 2009 to February 2012, total suspended particulate (TSP) samples were collected on a weekly basis (n = 112) using baked (450 °C, > 3 h) quartz filters (Pallflex 2500QAT-UP, 20 cm × 25 cm) and a high–volume air sampler (Kimoto AS-810B) at a flow rate of 50–60 m^3 h^{-1}. Each of the samples was kept in a baked (450 °C, >3 h) glass jar with a Teflon–lined screw cap and stored in darkness at −20 °C. Filters were placed in a desiccator for 24–72 h until constant weight was obtained before weighing and analysis. Two field blanks were collected on November 2009 and March 2011, following all the collection procedures except for the operation of sampling pump.

2.2. Extraction and derivatization

Aliquots of the filters (ca. 10 cm^2) were extracted three times with dichloromethane/methanol (2:1, v/v) under ultrasonication for 10 min (~7 ml × 3). The extracts were concentrated using a rotary evaporator under vacuum and blown down to dryness with pure nitrogen gas. The extracts were then derivatized by 50 μl of N,O-bis-(trimethylsilyl)trifluoroacetamide containing 1% trimethylsilyl chloride and 10 μl of pyridine for 3 h at 70 °C to convert OH groups to trimethylsilyl ethers and COOH groups to esters (Simoneit et al., 2004). Internal standard (C_{13} *n*-alkane) was added to each derivative to quantify compounds before gas chromatography-mass spectrometry quantification.

2.3. Gas chromatography-mass spectrometry

Organic compounds were quantified by gas chromatography/mass spectrometry (GC/MS) analyses of the derivatized total extracts using an Agilent 7890A GC equipped with HP-5 ms capillary column (30 m × 0.25 mm × 0.25 μm) coupled to Agilent 5975C mass-selective detector. The GC oven temperature was programmed from 50 (2 min) to 120 °C at 15 °C min^{-1} and then to 305 °C at 5 °C min^{-1} with a final isothermal hold at 305 °C for 15 min. Two μl of each extract were injected into the GC in splitless mode with the injector temperature at 280 °C. The mass spectrometer was operated in the electron ionization mode at 70 eV and scanned over the *m/z* range of 50–650 Da. GC/MS response factors of monoterpene-SOA tracers, namely pinic acid, pinonic acid and 3-hydroxyglutaric acid, were determined using authentic standards (cis-pinic acid and cis-pinonic acid: Sigma–Aldrich, St. Louis, USA; 3-hydroxyglutaric acid: Wako Pure Chemical Industries, Osaka, Japan). For other biogenic SOA tracers whose standards were not commercially available, surrogate standards were applied (Fu et al., 2010). By adding standards to blank filters followed by extraction and derivatization, recoveries of pinic and 3-hydroxyglutaric acids were determined to be better than 70%, whereas the recovery for pinonic acid was ~60%. No peak for biogenic SOA tracer was found in the field and laboratory blanks. The laboratory analytical errors by duplicate analyses were less than 15%.

2.4. Organic carbon analysis

Organic carbon (OC) was determined using a thermal/optical carbon analyzer (Sunset Laboratory Inc., USA) (Birch and Cary, 1996), following the Interagency Monitoring Protected Visual Environments thermal evolution protocol. The analytical error in replicate analyses was within 8%. Samples were corrected for field blanks, in which OC level was <5% of the samples. OC data for the first year was from Kunwar and Kawamura (2014).

3. Results and discussions

3.1. Seasonal variations of biogenic SOA tracers

Temporal variations and monthly means of biogenic SOA tracers