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Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over Mt. Tai, Central East China

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ABSTRACT

To better understand the contribution of biogenic volatile organic compounds to the formation of secondary organic aerosol (SOA) in high mountain regions, ambient aerosols were collected at the summit of Mt. Tai (1534 m, a.s.l.), Central East China (CEC) during the Mount Tai Experiment 2006 campaign (MTX2006) in early summer. Biogenic SOA tracers for the oxidation of isoprene, α/β-pinene, and β-caryophyllene were measured using gas chromatography/mass spectrometry. Most of the biogenic SOA tracers did not show clear diurnal variations, suggesting that they are formed during long-range atmospheric transport or over relatively long time scales. Although isoprene- and α/β-pinene-derived SOA tracers did not correlate with levoglucosan (a biomass burning tracer), β-caryophyllinic acid showed a good correlation with levoglucosan, indicating that crop residue burning may be a source for this acid. Total concentrations of isoprene oxidation products are much higher than those of α/β-pinene and β-caryophyllene oxidation products. The averaged ratio of isoprene to α/β-pinene oxidation products ($R_{iso/pine}$) was 4.9 and 6.7 for the daytime and nighttime samples, respectively. These values are among the highest in the aerosols reported in different geographical regions, which may be due to the large isoprene fluxes and relatively high levels of oxidants such as OH in CEC. Using a tracer-based method, we estimated the concentrations of secondary organic carbon (SOC) derived from isoprene, α/β-pinene, and β-caryophyllene to be 0.42–3.1 μgC m^{-3} (average 1.6 μgC m^{-3}) during the daytime and 0.11–4.2 μgC m^{-3} (1.7 μgC m^{-3}) during the nighttime. These values correspond to 2.9–23% (10%) and 3.2–28% (9.8%) of the total OC concentrations, in which isoprene-derived SOC accounts for 58% and 63% of total SOC during the daytime and nighttime, respectively. This study suggests that isoprene is a more significant precursor for biogenic SOA than α/β-pinene and β-caryophyllene at high altitudes in CEC.

1. Introduction

Vegetation releases large amounts of biogenic volatile organic compounds (BVOCs), including isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons (Guenther et al., 1995; Goldstein and Galbally, 2007). On a global scale, emissions of biogenic VOCs (1150 Tg yr^{-1}) are suggested to be one order of magnitude larger than those of anthropogenic VOCs (Guenther et al., 2006). Considerable efforts have been devoted in the last decade to understand secondary organic aerosol (SOA) formation from the photooxidation of BVOCs (Hallquist et al., 2009 and references therein), because SOA is an important component in the Earth's atmosphere. For example, it may provide surfaces for heterogeneous reactions in the atmosphere, and can have an impact on the atmospheric radiation budget directly by scattering sunlight and indirectly by acting as cloud condensation nuclei (Kanakidou et al., 2005).

Isoprene is the most abundant non-methane hydrocarbon emitted into the Earth's atmosphere. Its annual global emission is estimated to be in the range of 400–600 Tg of carbon (Tg C) (Guenther et al., 2006; Arneth et al., 2008). Despite its large flux, isoprene had not been generally considered to be an SOA precursor due to the high volatility of its known reaction products. However, Claeys et al. (2004) first identified two diastereoisomeric 2-methyltetrols in Amazonian rain forest aerosols as isoprene oxidation products. Since then, isoprene has been believed to be a large biogenic source of SOA mass. Monoterpenes and sesquiterpenes are also believed to be the major biogenic sources of SOA mass. Global bottom-up model estimates for biogenic SOA are in the range of 9–50 Tg C yr^{-1} (Kanakidou et al., 2005), while recent top-down estimates, including isoprene SOA, are as high as 185 Tg C yr^{-1} (Hallquist et al., 2009).

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In forested areas, biogenic emissions may govern the air chemistry and SOA formation in summer when intense sunlight and high ambient temperatures are common. High loading of natural aerosols over boreal forests was reported in northern Europe (Tunved et al., 2006). In the past decade, the identification of SOA tracers of isoprene, monoterpenes, and sesquiterpene oxidation products has been conducted in chamber experiments (e.g., Hoffmann et al., 1997; Yu et al., 1999; Iinuma et al., 2007; Jaoui et al., 2007; Sato, 2008) and ambient aerosols from urban (e.g., Hu et al., 2008; Fu et al., 2010; Stone et al., 2010), forested or mountain areas (e.g., Kavouras et al., 1998; Claeys et al., 2004; Cahill et al., 2006; Kleindienst et al., 2007; Lewandowski et al., 2007; Wang et al., 2008; Kourtchev et al., 2009), as well as the Arctic region (Fu et al., 2009). These studies provide insights into sources and processes that influence SOA production and their spatial and seasonal distributions.

However, information with regard to the BVOC oxidation products at high altitudes remains limited. High mountains may provide a unique situation for atmospheric chemistry because they sometimes exist in the free troposphere (FT) due to the downward movement of the planetary boundary layer (PBL) during the nighttime. Heald et al. (2005) reported a large, sustained source of SOA in the FT from the oxidation of long-lived volatile organic compounds. Henze and Seinfeld (2006) reported that inclusion of isoprene as a source of SOA in a global model substantially increases SOA concentrations in the FT, because isoprene, and especially its oxidation products, has much greater concentrations at higher altitudes than other biogenic SOA precursors. These studies highlight the need to investigate the organic molecular composition of atmospheric aerosols at high altitudes.

The objective of this research was to characterize the chemical compositions and abundance of SOA tracers produced by the oxidation of isoprene, α/β-pinene and β-caryophyllene, and to evaluate their contributions to organic carbon in the tropospheric aerosols over Mount Tai, Central East China (CEC).

2. Experimental section

2.1. Aerosol sampling

Mt. Tai (36.25°N and 117.10°E, 1534 m above sea level) is located in Shandong Province, Central East China (CEC, 30°N–40°N and 110°E–130°E), where the elevations in most of the flat region are less than 200 m. It lies in a deciduous forest zone, in which about 80% of the land is covered with vegetation. Almost 1000 species are known to grow in the mountain area (http://en.wikipedia.org/wiki/Mount_Tai). However, vegetation at the mountaintop is limited to bushes, and the ground surfaces are mostly rocks. As part of the MTX2006 campaign, daytime/nighttime and 3-h aerosol samplings were performed from May 28 to June 28, 2006 at the balcony of the 2nd floor of the observatory (~10 m, above ground level) on the top of Mt. Tai using pre-combusted (450 °C for 6 h) quartz fiber filters and a high-volume air sampler at a flow rate of 1.0 m^3 min^{-1}. Eighty-one aerosol samples (including 5 whole-day, 19 daytime (6:00–18:00, local time), 20 nighttime (18:00–6:00), and 37 3-h samples) were collected during the campaign. Among them the results of daytime/nighttime samples ($n = 39$) were presented here. The PBL height at Mt. Tai was estimated using a WRF/Chem model. The results showed that the PBL height reached a maximum of c.a. 4000 m at midday and a minimum of 200 m during the night to early morning period, with averages of 2200 m and 600 m during the campaign (Takigawa et al., unpublished data).

2.2. Extraction, derivatization, and GC/MS determination

Details of the sample extraction and derivatization have been presented elsewhere (Fu et al., 2008). Briefly, filter aliquots were extracted with dichloromethane/methanol (2:1, v/v), followed by TMS derivatization with 50 μl N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in the presence of 1% trimethylsilyl chloride and 10 μl of pyridine prior to GC/MS injection. GC/MS analyses of samples were performed on a Hewlett–Packard model 6890 GC coupled to Hewlett–Packard model 5973 mass-selective detector (MSD). The GC instrument was equipped with a split/splitless injection and a DB-5MS fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) with the GC oven temperature programmed from 50 °C (2 min) to 120 °C at 15 °C min^{-1} and then to 300 °C at 5 °C min^{-1} 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 range of 50–650 Da. Data were acquired and processed with the Chemstation software.

Individual compounds (TMS derivatives) were identified by comparison of mass spectra with those of authentic standards or literature data (Claeys et al., 2004; Jaoui et al., 2007; Hu et al., 2008). Following fragment ions were used: m/z 219 and 277 for 2-methyltetrols, m/z 231 for C_5-alkene triols, m/z 219 and 203 for 2-methylglyceric acid, m/z 171 for pinic acid, m/z 349 for 3-hydroxyglutaric acid, m/z 405 for 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), and m/z 383 for β-caryophyllinic acid. Quantification was conducted using calibration curves by analyzing aliquots of a stock solution of authentic standards that had been derivatized using the procedure mentioned above. For the quantification of 3-hydroxyglutaric, *cis*-pinonic, and pinic acids, their GC/MS response factors were determined using authentic standards. *cis*-Norpinic acid was quantified using the response factor of *trans*-norpinic acid. β-Caryophyllinic acid (a diacid similar to pinic acid) was estimated using the response factor of pinic acid (Jaoui et al., 2007). 2-Methylglyceric acid, C_5-alkene triols, 2-methyltetrols and 3-methyl-1,2,3-butanetricarboxylic acid were quantitatively determined with a capillary GC (Hewlett–Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m × 0.2 mm i.d., 0.50 μm film thickness), and a flame ionization detector (FID). The identification of the organic compounds quantified by GC-FID was confirmed by GC/MS analysis. The standard of *meso*-erythritol, a surrogate compound generally used for the quantification of 2-methyltetrols (e.g., Claeys et al., 2004; Ding et al., 2008; Kourtchev et al., 2009), was quantitatively determined by both GC/MS and GC-FID. The analytical error in the quantification of *meso*-erythritol between the two methods was <5%.

Field blank filters were treated as real samples for quality assurance. Target compounds were not detected in the blanks. Recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz filters ($n = 3$) were 94 ± 2.6% for *meso*-erythritol, 91 ± 5.5% for 3-hydroxyglutaric acid, 64 ± 5.9% for *cis*-pinonic acid, 93 ± 2.3% for *trans*-norpinic acid, and 79 ± 2.3% for pinic acid. Relative standard deviation of the concentrations based on duplicate sample analysis was generally <10%.

OC was determined using a Sunset Lab EC/OC Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol. The concentrations of OC reported here are corrected for the field blanks. Duplicate analyses of filter samples showed uncertainties of ±10%.

3. Results and discussion

3.1. Isoprene, α/β-pinene, and β-caryophyllene oxidation products

Six compounds were identified as isoprene SOA tracers in the tropospheric aerosols over Mt. Tai, including 2-methylglyceric acid, three C_5-alkene triols, and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol) (Table 1). Concentration ranges of 2-methyltetrols were 17–268 ng m^{-3} (average 98 ng m^{-3}) during the