Comprehensive PM$_{2.5}$ Organic Molecular Composition and Stable Carbon Isotope Ratios at Sonla, Vietnam: Fingerprint of Biomass Burning Components

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ABSTRACT

This study presents measurements of aerosol chemical properties at Sonla, northern Vietnam (675 m a.s.l.) during spring time, when biomass burning (BB) was very active in the northern Indochina Peninsula, as part of the 7-SEAS (Seven South East Asian Studies) campaign in 2013. The gas chromatography-mass spectrometry (GC-MS) analysis of BB markers in 14 selected samples indicated that mixed softwood, hardwood, grass, and non-woody vegetation were burned. More than 50 organic compounds including levoglucosan, lignin and resin products, sugar and sugar alcohol compounds, fatty acids, phthalate esters, aromatic acids, poly-acids, and biogenic oxidation products (e.g., 2-methyltetrols, alkene triols, 3-hydroxyglutaric acid) were measured in PM$_{2.5}$. Levoglucosan, a BB tracer, was the predominant species among aerosol sugars, with an average concentration of 1.62 ± 0.89 µg m$^{-3}$, comprising 2.23 ± 0.5% of PM$_{2.5}$ mass. For the collection period of the selected samples, backward air mass trajectories were classified into the source regions of Indochina (BBIC), southern China (BBSC), and the South China Sea (BBSS). All resolved molecular compounds show their dominance on the trajectory from BBIC, verifying the BB smoke origin of that region. Trajectory classification provides additional information, such as higher level of diethyl phthalate associated with BBSC trajectory, revealing urban or industrial influence, and more low-molecular-weight than high-molecular-weight fatty acids, indicating distributions with more microbial and lesser plant wax/vegetation burning contributions along the BBSC trajectory. In addition, we report, for the first time, stable carbon isotopic data ($\delta^{13}$C) for PM$_{2.5}$ aerosols in northern Vietnam, which ranged from –26.6 to –25.4‰ in PM$_{2.5}$, indicating contributions from burning of C$_3$ plants and fossil fuel combustion.

Keywords: Indochina; Fine aerosol particles; Biomass burning; Organic molecular markers; $\delta^{13}$C isotope.

INTRODUCTION

Atmospheric aerosols affect the Earth’s climate via profound impacts on the thermodynamic and radiative energy budgets of the Earth (Andreae et al., 2005). Airborne particulates also play important roles in atmospheric chemistry and biogeochemical cycles via participation in heterogeneous chemical reactions (Andreae and Crutzen, 1997). Exposure to fine atmospheric particulates has been associated with adverse impacts on human health (Chow et al., 2006; Pope and Dockery, 2006). Among several sources of atmospheric aerosols, biomass burning (BB) is an...
important source contributing to atmospheric trace gases and particles (Andreae and Merlet, 2001). After emission and transformations, the properties of aged particles in regional hazes become significantly different from fresh plumes due to chemical and physical transformations, dry deposition and/or conversion of less volatile oxidation products to particulate matter (Rudich et al., 2007; Hennigan et al., 2011). The changes in chemical composition have a large impact on the physical and optical properties of the aerosol, which give much challenge to the chemists interested in chemical characterization as well as scientists who run climate models (Andreae, 2009; Andreae and Ramathan, 2013). In addition, these pollutants can be transported many thousands of kilometers downwind from the source areas; therefore, they have extensive implications on climate and human health over a vast region (Engling et al., 2011; Lee et al., 2011).

BB produces a large amount of fine particles, which are mainly composed of carbonaceous matter and water-soluble inorganic ions, and are transported long distances from source to receptor regions (Lee et al., 2011; Chuang et al., 2013). These BB fine particles have implications on atmospheric chemistry by transformation, growth, and serving as cloud condensation nuclei (Reid et al., 2005). Thus, understanding the characteristics of the chemical composition especially for near-source BB aerosol is crucial. Organic aerosol characterization provides information on specific target compounds that are potentially toxic and can be used as important source tracers. The main classes of organic source tracers include compounds such as saccharides and sugar alcohols that are tracers for primary biogenic aerosol (Simoneit et al., 2004a; Tsai et al., 2013); fatty acids as tracers for biological emissions (plants, microbes and phytoplankton) (Simoneit and Mazurek, 1982; Kawamura et al., 2003); aromatic and poly-acids as tracers for BB and secondary organic aerosol (SOA) (Claeys et al., 2004b; Fine et al., 2004; Simoneit et al., 2004b; Fu et al., 2008; 2009; Kundu et al., 2010b; Fu et al., 2012); phthalate esters (phthalates) including diethyl (DEP), di-isobutyl (DiBP), di-n-butyl (DnBP), and di(2-ethylhelyxyl) (DEHP) esters as tracers for anthropogenic sources (Wang et al., 2006; Fu et al., 2012, 2013; Tsai et al., 2013). Moreover, oxidation products of isoprene and α/β-pinene have been reported as tracers for vegetation/forest emissions (Guenther et al., 1995; Jenkins and Clementsaw, 2000; Andreae and Merlet, 2001; Claeys et al., 2004a; b; Claeys et al., 2007; Lewandowski et al., 2007; Kourtchev et al., 2008a, b; Schurgers et al., 2009; Cohen et al., 2010; Fu et al., 2012).

In addition to the above-mentioned organic compounds, stable carbon isotopes in aerosols can reveal valuable information about the sources of aerosol organic carbon (Turekian et al., 2003; Wozniak et al., 2012). Use of this isotopic composition has been demonstrated in studies related to aerosols from BB activities (Ulevicius et al., 2010; Fu et al., 2012). Analysis of stable carbon isotope abundance (δ13C) in aerosols allows estimating the relative contributions of C3 (Calvin-Benson cycle) versus C4 plants (Hatch-Slack cycle) (Cachier, 1989). Plants using the Calvin-Benson cycle, so-called C3 carbon fixation plants, have δ13C values in the range of –23 to –34‰ (Gelencser, 2004). Virtually all trees, most shrubs, mid-latitude and boreal grasses, and sedges belong to the class of C3 plants. Meanwhile, plants using the Hatch-Slack (or dicarboxylic acid) cycle, so-called C4 carbon fixation plants, have δ13C values in the range of –12 to –14‰. These plants comprise warm-season grasses and sedges, thus they can be found predominantly in tropical savannas, temperate grasslands, and semi-deserts (Schidlowski, 1987; Rommerskirchen et al., 2006). The variation in the carbon isotopic ratios among different plant types has been attributed to the preferential uptake of 13C or 12C isotopes during the photosynthesis process (Huang et al., 2010; Ceburnis et al., 2011). In addition, the isotopic differences may also occur via fractionation during cellulose and lignin synthesis and or during vegetation combustion (Turekian et al., 1998; Loader et al., 2003; Garbaras et al., 2015). Fossil fuels, such as petroleum, have δ13C values close to the mean values of C3 plants (–26 ± 2‰) (Sackett, 1989). Thus, the δ13C value is a potent index for source apportionment of biogenic and anthropogenic sources.

The Indochina Peninsula, consisting of Myanmar, Thailand, Cambodia, Laos, and Vietnam, is known as an area of intense seasonal BB. Yet, the BB activities in this region, specifically in northern Vietnam, are typically not fully detected by satellite sensors due to a thick aerosol-cloud system that may shield the fires below (Hsu et al., 2003). There have been many studies conducted to chemically characterize the BB plumes in the African Savanna or Brazilian Amazonian rainbowforest in the past decades (Yamasoe et al., 2000; Mayol-Bracero et al., 2002; Gao et al., 2003; Li et al., 2003; Sinha et al., 2003; Iinuma et al., 2007). However, in the Indochina Peninsula, there have been few systematic studies investigating the chemical properties of BB aerosol, such as those conducted at rural sites in Thailand to investigate the implications of burnt materials as well as burning phase, through the 7-SEAS campaign (Li et al., 2012; Chuang et al., 2013; Lin et al., 2013; Tsai et al., 2013). Aerosol concentrations typically peak associated with BB activity and contribute considerably to the vast area with enormous regional implications (Carmichael et al., 2003; Streets et al., 2003; Streets et al., 2009; Gautam et al., 2012), which can be evidenced in Chiang Mai and Phimai, Thailand (Li et al., 2012; Chuang et al., 2013), Hong Kong and the southeastern Tibetan Plateau, China (Chan et al., 2003; Engling et al., 2011), Mt. Lulin in central Taiwan (Lee et al., 2011), and the Philippine Sea (Song et al., 2005). The mechanism of the high-altitude long-range transport pathway associated with the prevailing westerlies best represents the observed BB plume at several locations along the transport pathway (Lin et al., 2013).

During the aerosol evolution process with gas-to-particle conversion during transport, formation of SOA occurs, which is an area of vast uncertainty from region to region, in terms of the understanding of the chemical and physical properties of organic aerosol, and subsequently in estimating global and regional radiative forcing. Thus, understanding the fresh smoke properties and aging processes is crucial to reduce these uncertainties, especially in the northern Indochina Peninsula for which very few reports are available.
This study was designed to provide comprehensive chemical characterization of near-source BB aerosol with special reference to organic compounds and stable carbon isotope measurements in northern Vietnam, in order to shed more light on the source contributions in the region. Here, we compare the tracer results of aerosol samples classified with different air mass histories for better understanding the influence of BB and other emission sources.

METHODS

Sampling Site and Sampling Collection
The sampling site (21°19'55"N, 103°54'18"E, 675 m a.s.l.) is located at the Sonla atmospheric observatory station, Sonla province, Northern Vietnam (Figs. 1(a)–1(b)). The site is 302 km northwest of Hanoi, 140 km south of the border to China, and 110 km east of the Lao border. The province covers a vast area of 14,174 km², and the population is estimated to be approximately 1.15 million inhabitants as of 2013 (Vietnam Demographics Profile, 2014 – Available from http://www.gso.gov.vn/), with a density of about 80 persons per km². The site is located at on a hill in the outskirts of Sonla city and surrounded by grass areas and trees.

The aerosol collectors were operated for 24 hours, starting from 8:00 am local time during typical sampling days. PM$_{2.5}$ (particulates with aerodynamic diameters equal to or less than 2.5 µm) samples were collected on quartz-fiber filters (TISSUQUARTZ 2500QAT-UP, PALL Life Sciences, Inc., Ann Arbor, MI, USA) using collocated R&P ChemComb Model 3500 Speciation Sampling Cartridges (Thermo Fisher Scientific Co, Inc., Waltham MA, USA) following Chuang et al. (2013). For the determination of PM$_{2.5}$ mass concentrations, Teflon filters were adopted for separate aerosol collection. The Teflon filters were conditioned for at least 72 h and then weighed using a Mettler MX5 Microbalance (Mettler Toledo Co., Inc., Greifensee, Switzerland) with a sensitivity of ± 1 µg in a stable environment with a temperature of 22°C ± 1°C and a relative humidity of 30–35%.

MODIS Fire Image and Backward Trajectory Observation Using HYSPLIT
The field observations were arranged by tracking possible sources of BB activities with MODIS satellite fire counts (produced by the US NASA Goddard Space Flight Center http://earthobservatory.nasa.gov/NaturalHazards/-category.php?cat_id=8) (Fig. 2(a)). Five-day backward trajectory data

Fig. 1. (a) Geographic location of the Sonla site (star) in Sonla province, Vietnam. The right panel illustrates a closer look of the site of the left panel; (b) Sonla sampling site (circle) and a closer look of the sampler deployment site.
from HYSPLIT (http://ready.arl.noaa.gov/HYSPLIT.php; Draxler and Rolph, 2013) website were computed to establish the classification of different trajectories arriving at the sampling site, including BB Indochina (BBIC), BB Southern China (BBSC), and BB South China Sea (BBSS) (Figs. 2(b)–2(d)). Since all the collected samples were under the influence of BB activities, the three trajectory types were all named with “BB” as a prefix.

**Chemical Analysis**

PM$_{2.5}$ Filter Sample Extraction and Derivatization for the Analysis of Organic Compounds Using GC-MS

Fourteen samples were selected to represent the different trajectory types and sent to the Laboratory of Atmospheric Chemistry and Organic Geochemistry, Institute of Low Temperature Science, Hokkaido University, Japan. Filter samples were extracted three times with dichloromethane/methanol (2:1, v/v) for 10 min under ultra-sonic agitation. The solvent extracts were filtered through quartz wool packed into a Pasteur pipette, concentrated by the use of a rotary evaporator, and then blown down to dryness under pure nitrogen gas. The extracts were reacted with 50 µL of N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA, Sigma-Aldrich) containing 1% trimethylsilyl chloride and 10 µL of

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**Fig. 2.** (a) MODIS active fire data in 24 h in Southeast Asia (produced by the US NASA Goddard Space Flight Center http://earthobservatory.nasa.gov/NaturalHazards/-category.php?cat_id=8); (b)–(d) Representative 5-day backward air mass trajectories (HYSPLIT [http://ready.arl.noaa.gov/HYSPLIT.php; Draxler and Rolph, 2013] arriving at 750 m (above ground level) over the Sonla site for air masses from (a) southern China (BBSC), (b) Indochina (BBIC), and (c) the South China Sea (BBSS). The solid star represents the sampling site at Sonla, northern Vietnam.
pyridine at 70°C for 3 h. After the reaction, the derivatives were diluted by addition of 140 μL of n-hexane containing 1.43 ng μL–1 of internal standard (C13- n-alkane) prior to gas chromatography/mass spectrometry (GC/MS) analysis (Fu et al., 2012).

GC-MS Analysis

GC-MS analyses were performed with a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 mass-selective detector (MSD) (Fu et al., 2012). The GC was equipped with a split/splitless injection system and a DB-5MS fused silica capillary column (30 m × 0.25 mm in diameter, 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 a final hold at 300°C for 16 min. Helium was used as the carrier gas at a flow rate of 1.0 mL min–1. The sample was injected in splitless mode with the injector temperature set at 280°C. 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 acquired and processed with the ChemStation software. GC-MS response factors were determined using authentic standards. For some biogenic SOA tracers whose standards were not commercially available, their concentrations were estimated using surrogate compounds.

Recovery experiments were performed by spiking certain quantities of authentic standards onto pre-combusted quartz-fiber filters and were analyzed like real samples. Recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz filters were generally around 60%. Relative standard deviations of the recoveries were better than 80% except for polyacids and pinonic acid, whose recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz-fiber filters and were analyzed like real samples. Replicate analyses were not conducted due to the small size of available sample filters. A reproducibility test using other ambient aerosol filters were performed. The analytical errors for δ13C measurement based on repeated analyses of atmospheric aerosol samples were within 0.2‰ (Kawamura et al., 2004). δ13C values were corrected for the field blanks using an isotopic mass balance equation.

RESULTS AND DISCUSSIONS

Overview of Molecular Tracers

Fig. 3 shows the time-series of mass concentrations of PM2.5 for the whole study period and the groups of organic compounds for the selected 14 samples according to the three different trajectory types. The PM2.5 mass concentration was on average 69 ± 33 μg m–3 for the selected samples. The average PM2.5 concentrations in the different trajectories were 47 ± 3 μg m–3 (N = 4), 98 ± 18 μg m–3 (N = 7), and 30 ± 14 μg m–3 (N = 3) for BBSC, BBIC, and BBSS, respectively (Table 1). Since the resolved organic compounds are present in trace amounts, they are grouped into levoglucosan, primary organic aerosol (POA), and SOA. Levoglucosan is singled out from POA in Fig. 3, as it is a recognized BB tracer (Simoneit, 2002) and dominant among the resolved compounds. POA and levoglucosan varied consistently with the associated PM2.5, indicating the influence of BB on the selected samples. Levoglucosan comprised on average 2.23% of PM2.5 mass (Table 1), which was comparable to 2.6% of total resolved organic components in deciduous tree smoke from controlled burning (Oros and Simoneit, 2001). In the present study, more than 50 organic compounds were detected and classified into 10 compound classes depending on functional groups and sources, as shown in Table 1. The comparison of PM2.5 mass fractions of the organic compound groups among the three different backward trajectory types is depicted in Fig. 4. The BB marker groups including levoglucosan, lignin and resin products, and fatty acids from the BBIC trajectory type accounted for the highest fractions in PM2.5, compared to the other two types, indicating the contribution of BB from this region was much higher. POA includes BB tracers such as levoglucosan, a product of cellulose and hemicellulose burning, sugar compounds, sugar alcohols, fatty acids, and phthalate esters. SOA includes aromatic acids, polyacids, and oxidation products of isoprene and α-pinene. Concentrations of most organic species were found to be elevated in the BBIC trajectory type with an exception of diethyl phthalate ester. Molecular tracers in the POA group are mainly BB products with minor anthropogenic and marine inputs. On the other hand, molecular tracers in the SOA group are mainly photo-oxidation products of biogenic organic compounds. As far as percent PM2.5 mass fraction is concerned with respect to each of the organic species, levoglucosan and fatty acids are dominant in the BBIC trajectory, whereas phthalate esters and aromatic acids are more abundant in the BBSS trajectory. The remaining organic compound groups did not show significant differences in mass fractions among different trajectories.

Stable Carbon Isotope Measurements

For the measurements of isotopic compositions, a punch (1.54 cm²) of each quartz filter sample was used. The filter punch was rounded using a pair of flat-tip tweezers, placed into a tin cup, and then caked into a ball. Beforehand, tin cups were cleaned with acetone under ultra-sonication to remove organic and other contaminants (Kawamura et al., 2004). The samples (filter plus tin cup) were then analyzed for isotopic composition using an EA/isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus). Isotope data reported as δ13C values were defined as:

\[ \delta^{13}C (\%) = \frac{[^{13}C/^{12}C]_{\text{sample}}/[^{13}C/^{12}C]_{\text{standard}} - 1} \times 1000 \]  

(1)

Before running the real samples for the determination of δ13C, the instrument conditions were checked three times with an empty tin cup and also evaluated with a five-point calibration curve using acetanilide standard with the procedural blanks. Replicate analyses were not conducted due to the small size of available sample filters. A reproducibility test using other ambient aerosol filters were performed. The analytical errors for δ13C measurement based on repeated analyses of atmospheric aerosol samples were within 0.2‰ (Kawamura et al., 2004). δ13C values were corrected for the field blanks using an isotopic mass balance equation.
Levoglucosan and Lignin/Resin Products as Biomass-Burning Tracers

BB results in emissions of gases and particles into the atmosphere, which have been ascribed as an important source of organic aerosols (Simoneit and Elias, 2001; Simoneit, 2002; Chen et al., 2013). Levoglucosan, produced by pyrolysis of cellulose, is a well-established tracer for BB (Simoneit, 2002). In the present study, we found levoglucosan to be the single most abundant organic compound (ave. 1620 ± 893 ng m⁻³, 2.3% of PM₂.₅ mass), indicating a significant impact of BB on the ambient aerosols. Concentrations of levoglucosan from the BBIC trajectory type were highest (ave. 2468 ± 292 ng m⁻³, 2.6% of PM₂.₅ mass), while the average concentrations from the BBSC and BBSS types were 895 ± 94 ng m⁻³ (1.9% of PM₂.₅ mass) and 610 ± 329 ng m⁻³ (1.9% of PM₂.₅ mass), respectively (Table 1). These values clearly indicate a reasonable classification of trajectory types with the dominance of BB in the BBIC trajectories and less influence of BB on the other air mass trajectories. Additional BB tracers detected in the present samples include four lignin and resin products (dehydroabietic, syringic, vanillic, and 4-hydroxybenzoic acids) as listed in Table 1.

These BB products have been reported in atmospheric aerosols and smoke particulates in several studies (e.g., Oros and Simoneit, 2001; Simoneit, 2002; Fu et al., 2008; Fu et al., 2012). Dehydroabietic acid is a phenolic compound emitted by the burning of resin from conifers (Simoneit, 2002; Fu et al., 2012). Simoneit et al. (1999) indicated that this acid is detected at comparable quantity with levoglucosan in smoke particles from conifer fuel types. In our samples, dehydroabietic acid is detected at very low levels (6 ± 3 ng m⁻³), suggesting less significant contribution from burning of conifer trees in this part of the Indochina Peninsula. The total forest cover in Vietnam in 2010 was 13.8 million ha or 44% of the total land area (FAO, 2010). The Sonla province had a forest-coverage of 41.2% of total land area (DoFP, 2009, 2010). The dominance of deciduous trees has been reported in Vietnam where the dominant forest types are tropical semi-deciduous broad-leaved forest and tropical deciduous broad-leaved forest (Chien, 2006). Approximately 75% of deciduous trees are estimated to be in tropical deciduous broad-leaved forests (Chan and Dung, 1992). In tropical semi-deciduous broad-leaved forests, the deciduous trees represent 25 to 75% of all trees (Chan and Dung, 1992; Linh, 1996).

Burning of grasses and other non-woody vegetation or Gramineae plants is the source of 4-hydroxybenzoic acid (a methoxy-phenol compound) (Simoneit, 2002). 4-Hydroxybenzoic acid, detected at a level of 30 ± 25 ng m⁻³, can be attributed to agricultural residue burning in the Indochina Peninsula during the pre-monsoon period. Phenolic acids produced upon burning of wood lignin include vanillic and syringic acids. Vanillic acid is produced from grasses, softwood, and hardwood combustion (Simoneit et al., 2002; Fu et al., 2012). In the present study, vanillic acid...
Table 1. Mean values with associated standard deviation (ng m\(^{-3}\)) and relative abundance (%) in PM\(_{2.5}\) for the resolved molecular organic compounds in the fourteen representative PM\(_{2.5}\) samples from Sonla, northern Vietnam with three types of 5-day backward air mass trajectories.

<table>
<thead>
<tr>
<th>Trajectory Types</th>
<th>Number of Samples</th>
<th>BBSC (4)</th>
<th>BBIC (7)</th>
<th>BBSS (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± SD</td>
<td>% in PM(_{2.5})</td>
<td>Mean ± SD</td>
<td>% in PM(_{2.5})</td>
</tr>
<tr>
<td>(\text{PM}_{2.5})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Levoglucosan (POA)</td>
<td>895 ± 94</td>
<td>1.70</td>
<td>2468 ± 292</td>
<td>2.60</td>
</tr>
<tr>
<td>Lignin/Resin Products (POA)</td>
<td>30 ± 6</td>
<td>0.062</td>
<td>149 ± 31</td>
<td>0.157</td>
</tr>
<tr>
<td>Dehydroabietic acid</td>
<td>6 ± 1</td>
<td>0.013</td>
<td>8 ± 2</td>
<td>0.008</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>6 ± 1</td>
<td>0.013</td>
<td>38 ± 13</td>
<td>0.032</td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>5 ± 1</td>
<td>0.011</td>
<td>2 ± 1</td>
<td>0.002</td>
</tr>
<tr>
<td>4-hydroxybenzoic acid</td>
<td>8 ± 1</td>
<td>0.017</td>
<td>60 ± 15</td>
<td>0.054</td>
</tr>
<tr>
<td>Sugars (POA)</td>
<td>17 ± 1</td>
<td>0.036</td>
<td>15 ± 1</td>
<td>0.022</td>
</tr>
<tr>
<td>Fructose</td>
<td>12 ± 2</td>
<td>0.026</td>
<td>9 ± 4</td>
<td>0.011</td>
</tr>
<tr>
<td>Glucose</td>
<td>17 ± 1</td>
<td>0.036</td>
<td>5 ± 2</td>
<td>0.013</td>
</tr>
<tr>
<td>Sugar alcohols (POA)</td>
<td>55 ± 7</td>
<td>0.116</td>
<td>119 ± 29</td>
<td>0.122</td>
</tr>
<tr>
<td>Arabinol</td>
<td>5 ± 1</td>
<td>0.01</td>
<td>3 ± 1</td>
<td>0.007</td>
</tr>
<tr>
<td>Mannitol</td>
<td>3 ± 1</td>
<td>0.006</td>
<td>12 ± 7</td>
<td>0.011</td>
</tr>
<tr>
<td>Inositol</td>
<td>2 ± 0</td>
<td>0.004</td>
<td>7 ± 1</td>
<td>0.008</td>
</tr>
<tr>
<td>Erythritol</td>
<td>14 ± 1</td>
<td>0.029</td>
<td>31 ± 7</td>
<td>0.032</td>
</tr>
<tr>
<td>Glycerol</td>
<td>31 ± 10</td>
<td>0.066</td>
<td>54 ± 12</td>
<td>0.056</td>
</tr>
<tr>
<td>Fatty Acids (POA)</td>
<td>241 ± 44</td>
<td>0.506</td>
<td>1090 ± 223</td>
<td>1.21</td>
</tr>
<tr>
<td>LMW (≤ C(_{19}))</td>
<td>181 ± 31</td>
<td>0.38</td>
<td>349 ± 38</td>
<td>0.365</td>
</tr>
<tr>
<td>HMW (≥ C(_{20}))</td>
<td>60 ± 21</td>
<td>0.126</td>
<td>741 ± 260</td>
<td>0.756</td>
</tr>
<tr>
<td>Phthalate esters (POA)</td>
<td>59 ± 10</td>
<td>0.124</td>
<td>121 ± 12</td>
<td>0.127</td>
</tr>
<tr>
<td>Diethyl phthalate (DEP)</td>
<td>21 ± 7</td>
<td>0.045</td>
<td>4 ± 2</td>
<td>0.005</td>
</tr>
<tr>
<td>Di-isobutyl phthalate (DiBP)</td>
<td>10 ± 2</td>
<td>0.021</td>
<td>30 ± 9</td>
<td>0.032</td>
</tr>
<tr>
<td>Di-n-butyl phthalate (DnBP)</td>
<td>15 ± 3</td>
<td>0.033</td>
<td>49 ± 10</td>
<td>0.051</td>
</tr>
<tr>
<td>Di-(2-ethylhexyl) phthalate (DEHP)</td>
<td>12 ± 4</td>
<td>0.025</td>
<td>38 ± 9</td>
<td>0.038</td>
</tr>
<tr>
<td>Aromatic acids (SOA)</td>
<td>73 ± 9</td>
<td>0.155</td>
<td>158 ± 30</td>
<td>0.161</td>
</tr>
<tr>
<td>o-phthalic acid</td>
<td>30 ± 4</td>
<td>0.063</td>
<td>65 ± 16</td>
<td>0.066</td>
</tr>
<tr>
<td>m-phthalic acid</td>
<td>3 ± 1</td>
<td>0.007</td>
<td>10 ± 2</td>
<td>0.010</td>
</tr>
<tr>
<td>p-phthalic acid</td>
<td>40 ± 10</td>
<td>0.085</td>
<td>82 ± 17</td>
<td>0.085</td>
</tr>
<tr>
<td>Polyacids (SOA)</td>
<td>108 ± 20</td>
<td>0.228</td>
<td>311 ± 101</td>
<td>0.319</td>
</tr>
<tr>
<td>DL-tartaric acid</td>
<td>10 ± 2</td>
<td>0.021</td>
<td>29 ± 12</td>
<td>0.029</td>
</tr>
<tr>
<td>Citric acid</td>
<td>1 ± 1</td>
<td>0.003</td>
<td>7 ± 3</td>
<td>0.008</td>
</tr>
<tr>
<td>DL-malic acid</td>
<td>65 ± 15</td>
<td>0.137</td>
<td>190 ± 66</td>
<td>0.196</td>
</tr>
<tr>
<td>Glyceric acid</td>
<td>32 ± 2</td>
<td>0.067</td>
<td>85 ± 22</td>
<td>0.086</td>
</tr>
<tr>
<td>Isoprene oxidation (SOA)</td>
<td>38 ± 18</td>
<td>0.082</td>
<td>118 ± 66</td>
<td>0.148</td>
</tr>
<tr>
<td>2-methylthreitol</td>
<td>6 ± 2</td>
<td>0.012</td>
<td>15 ± 8</td>
<td>0.015</td>
</tr>
<tr>
<td>2-methylerythritol</td>
<td>13 ± 7</td>
<td>0.027</td>
<td>36 ± 22</td>
<td>0.036</td>
</tr>
<tr>
<td>(\Sigma)C(_{5})-Alkene triols</td>
<td>16 ± 9</td>
<td>0.033</td>
<td>54 ± 36</td>
<td>0.057</td>
</tr>
<tr>
<td>2-methylglyceric acid</td>
<td>4 ± 1</td>
<td>0.009</td>
<td>13 ± 3</td>
<td>0.014</td>
</tr>
<tr>
<td>(\alpha)-pinene oxidation (SOA)</td>
<td>62 ± 14</td>
<td>0.100</td>
<td>158 ± 47</td>
<td>0.164</td>
</tr>
<tr>
<td>3-HGA</td>
<td>62 ± 14</td>
<td>0.100</td>
<td>158 ± 47</td>
<td>0.164</td>
</tr>
</tbody>
</table>

Notes:
- \(\Sigma\)C\(_{5}\)-Alkene triols consist 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
- 3-HGA: 3-hydroxyglutaric acid
- n.d.: not detected

is detected at moderate levels (17 ± 14 ng m\(^{-3}\)). In contrast, syringic acid (associated mainly with hardwood) was observed with an average concentration of 34 ± 27 ng m\(^{-3}\). Based on the relative abundance of resin acids and lignin products, BB smoke contributions appear to be predominantly from hardwood combustion. These results are comparable with those reported for intensive BB aerosols in Rondonia, Brazil (Kundu et al., 2010b).

**Sugars and Sugar Alcohols: Tracers of Bioaerosols**

Sugar compounds, including glucose and fructose as well as some sugar alcohols such as arabinol, mannitol, inositol,
erythritol, and glycerol, were detected in the aerosols collected at the Sonla site (Table 1). In our study, total sugars and sugar alcohols showed the highest levels for the BBIC trajectories (167 ± 53 ng m⁻³), which is nearly double of those for the BBSC (72 ± 15 ng m⁻³) and BBSS trajectories (60 ± 24 ng m⁻³). The sources for glucose and fructose can be assigned to plant materials such as pollen, fruits, and debris (Speranza et al., 1997; Pacini, 2000). Medeiros and Simonet (2008) suggested that BB also emits such sugars into the atmosphere. The sugars and sugar alcohols detected in aerosol samples have been used as tracers for primary biogenic aerosol, such as pollen and fungal spores (Graham et al., 2003; Bauer et al., 2008) and re-suspension of surface soil from agricultural activities (Simoneit et al., 2004a; Tsai et al., 2013).

A strong positive correlation was found between the concentrations of arabitol and mannitol (R² = 0.95, n = 14, not shown as a figure), indicating that they may be derived from the same source, i.e., fungal spores (Lewis and Smith, 1967; Bauer et al., 2008), although previous studies have shown these fungal spore tracers to be present predominantly (up to 90%) in the coarse mode of ambient aerosol. Abundant presence of mannitol over the Arctic Ocean was attributed to terrestrial fungal spores by Fu et al. (2013) as the most preferred habitats of fungi are present in soils or dead plant matter, while oceans have been assigned as insignificant source of spores (Burshtein et al., 2011; Frohlich-Nowoisky et al., 2012). Glycerol (highest amount among all sugar alcohols) and erythritol constituted about 70% of total sugar alcohols, suggesting that particles emitted from BB of slashed vegetation are associated with agricultural activities that release soil biota from farmland soils (Simoneit et al., 2004a; Tsai et al., 2013). Airborne pollen and fungal spores have been estimated to constitute 12–22% of total organic carbon in ambient aerosols (Womiloju et al., 2003), which was later supported by Jaenicke (2005) who reported that primary bioaerosols such as plant fragments and pollen in the Lake Baikal region (Russia) and Mainz (Germany) contributed up to 30% of the total atmospheric particles. Airborne fungal spores can be associated with smoke particles and then transported with BB particles (Fu et al., 2012; Yang et al., 2012). Therefore, sugars and sugar alcohols can have primary plant origin in the form of pollens and fungi as well as from combustion of cellulose (when biomass is burned) which are basic cell wall materials of plants.

**Fatty Acids: Tracers of Plant Waxes and Marine Input**

During BB events, lipid class compounds that are originally present as leaf-waxes can be emitted to the air together with smoke particles via volatilization, absorption, and trapped onto particulate matter without severe oxidative degradation. Consequently, smoke particles produced by smoldering and especially flaming combustion process may be uplifted by convection and transported over long distances (Oros and Simonet, 2001). The average concentrations of low-molecular-weight (LMW, ≤ C₁₉) fatty acids were 181 ± 31 ng m⁻³ in the BBSC trajectories and 202 ± 70 ng m⁻³ in the BBSS trajectories, whereas those of high-molecular-weight (HMW, ≥ C₂₀) fatty acids were 60 ± 21 ng m⁻³ in the BBSC trajectories. However, HMW fatty acids were not detected in the BBSS trajectories. In contrast, LMW and HMW
fatty acids from the BBIC types were observed at relatively higher concentrations, i.e., 349 ± 38 and 741 ± 260 ng m⁻³, respectively (Table 1). As for the BBIC trajectories, much higher concentrations of HMW fatty acids with the predominance of C₂₆ and C₂₈ could be explained by the intensive vegetation burning, which can serve as an additional indicator for BB activity (Fu et al., 2012). HMW fatty acids are derived from terrestrial higher plant waxes (Simoneit and Mazurek, 1982; Kawamura et al., 2003). Recently, Fu et al. (2012) and Wang et al. (2009) reported high concentrations of HMW fatty acids during intensive BB periods influenced by wheat straw burning in northern China and East China, suggesting that BB may enhance the HMW fatty acid levels in ambient aerosols.

Fu et al. (2013) reported LMW fatty acids in the marine aerosols collected over the Arctic Ocean. Similar observations had also been reported in Canadian high Arctic aerosols at Alert (Fu et al., 2009). Few unsaturated fatty acids (C₁₈:₁ and C₁₉:₂) detected in the marine aerosols over the Arctic Ocean have been proposed to be derived from the cell membranes of marine phytoplankton and from terrestrial plants by direct emission via leaf or wood burning (Fine et al., 2001; Fu et al., 2013). LMW fatty acids have been assigned to multiple sources such as vascular plants, microbes, and marine phytoplankton (Simoneit and Mazurek, 1982; Rogge et al., 1993; Kawamura et al., 2003). Therefore, the BBSC trajectories with higher LMW versus HMW fatty acid concentrations indicate more influence from microbial sources and less from plant wax/vegetation burning. As for the BBSS type, the shift in atmospheric circulation patterns from westerly to easterly regimes may explain the high levels of LWM fatty acids with the predominance of C₁₆ and C₁₈ that are mainly contributed from marine organisms.

Phthalate Esters: Tracers of Plastic Burning Emissions

Various phthalate esters (phthalates) were detected in the present study, including DEP, DiBP, DinBP, and DEHP (Table 1). Phthalates are used in industrial applications such as plasticizers, cosmetics, lubricants, and others (Thuren and Larsson, 1990). They can be emitted into the atmosphere by evaporation from polymers depending on ambient temperature, because they are not chemically bonded to the polymer (Wang et al., 2006; Fu et al., 2012). The controlling factors for the emission of phthalates include (i) temperature-dependence, due to their low vapor pressures, evidenced by the observation of higher phthalate concentrations in urban aerosols in summer (Wang et al., 2006; Fu et al., 2012), and (ii) photodegradation (Stales et al., 1997).

In our study, the average concentration of total detected phthalates is 89 ± 52 ng m⁻³. Our data reveal that DBPs are dominant, followed by DEHP and DEP. Concentrations of phthalates observed in this study are higher than those reported for marine sites (2.6 ± 3.5 ng m⁻³, Fu et al., 2013), but are comparable with those reported for the Chiang Mai Basin, Thailand during the BB period (92 ± 56 ng m⁻³, Tsai et al., 2013). However, our concentration levels are lower than those reported for Mt. Tai during summer in northern China (109 ng m⁻³ in early June, influenced by BB with lower ambient temperatures, and 400 ng m⁻³ from late June with higher ambient temperatures) (Fu et al., 2012). Wang et al. (2006) observed high concentrations of phthalates in 14 Chinese megacities in summer and reported specifically high concentrations of phthalates in summer for Hong Kong (403 ng m⁻³) and Guangzhou (432 ng m⁻³). DBPs and DEHP from the BBIC trajectories are higher by approximately two to three times than those from the BBSC and BBSS trajectories. However, interestingly, DEP from the BBSC trajectories is more abundant by five and seven times than those from the BBIC and BBSS trajectories, respectively, indicating the role of DEP as a potential urban or industrial tracer. In Southeast Asian countries, especially rural areas, burning of garbage, including plastic bags, is common, enhancing the levels of phthalates in the ambient air.

Aromatic and Polyacids: Tracers of Secondary Organic Aerosol

Phthalic acids such as o-phthalic, m-phthalic, and p-phthalic acids were detected in the Solna aerosol samples. Phthalic acids are generally derived from the oxidation of anthropogenic cyclohexene and aromatic hydrocarbons (Kawamura and Ikushima, 1993; Fine et al., 2004). These aromatic acids are directly emitted from combustion sources (Kawamura and Kaplan, 1987; Koebel and Elsener, 1998) and/or formed in the atmosphere by atmospheric degradation of aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993). In the present study, concentrations of o-, m-, and p-phthalic acids (ave. 113 ± 53 ng m⁻³, n = 14) are higher than those reported from aircraft measurements over China (17 ± 13 ng m⁻³ in summer) (Wang et al., 2007) and the northwestern Pacific (ave. 1.5 ng m⁻³) (Simoneit et al., 2004b), and from wheat straw BB smoke at Mt. Tai in China (32 ± 17 ng m⁻³) (Fu et al., 2012). A similar pattern of phthalic acid distributions with the predominance of o-and p-phthalic acids, has been reported in the BB aerosols in Rondonia, Brazil, by Kundu et al. (2010b). The isomer distribution of aromatic acids may be considered as a fingerprint of BB smoke. The average concentration of phthalic acids from the BBIC trajectories was 158 ± 30 ng m⁻³, while those from the BBSC and BBSS trajectories were on average 73 ± 9 ng m⁻³ and 62 ± 25 ng m⁻³, respectively (Table 1). The concentrations from the BBSC trajectories are approximately three times higher than those from the BBIC and BBSS trajectories.

Polyacids are considered as secondary oxidation products of precursor organic compounds (Claeys et al., 2004b; Simoneit et al., 2004b; Kundu et al., 2010b; Fu et al., 2012). In our study, average concentrations of total polyacids were 210 ± 130 ng m⁻³ with the greatest abundance of malic acid (128 ± 80 ng m⁻³), followed by glyceric (57 ± 33 ng m⁻³), tartaric (20 ± 13 ng m⁻³), and citric acids (5 ± 4 ng m⁻³). Abundances of malic and glyceric acids from the BBIC trajectories were 190 ± 66 and 85 ± 22 ng m⁻³, respectively (Table 1), which are two-fold higher than those of the BBSC and BBSS trajectories, confirming the contribution of intensive BB activity to aged organic aerosols. Fu et al. (2012) observed a strong correlation between malic acid and levoglucosan in the aerosol samples from Mt. Tai during the BB period, suggesting that malic acid could be produced by...
the photochemical oxidation of BB-derived organic matter in the atmosphere. Kundu et al. (2010b) had attributed BB as a source for polyacids and their precursors. Claeys et al. (2004b) suggested that isoprene photo-oxidation results in the formation of malic and tartaric acids in pristine aerosols from the Amazonian rain forest during the wet season. In addition, Simoneit et al. (2004b) suggested, during the ACE-Asia aircraft campaign, that glyceric and malic acids may be secondary oxidation products of saccharides from soil dust/soil re-suspension by agriculture tilling.

Isoprene- and α-Pinene-Oxidation Products: Biogenic Secondary Organic Aerosols

Molecular characterization of individual SOA constituents derived from the photo-oxidation of biogenic volatile organic compounds (BVOCs) such as isoprene and α/β-pinene are considered as suitable tracers for organic aerosol characterization (Hallquist et al., 2009). Isoprene, which is mainly emitted by broadleaf vegetation and is the most abundant non-methane hydrocarbon in the atmosphere (500 Tg C per year), plays an important role in atmospheric chemistry (Guenther et al., 1995). Isoprene oxidation products so far reported as SOA tracers include (i) 2-methyltetrols (2-methylthreitol and 2-methylerythritol), (ii) \( \Sigma C_5 \)-alkene triols, and (iii) 2-methylglyceric acid (Claeys et al., 2004a, b; Wang et al., 2004). These tracers were detected in our aerosol samples with different trajectories with the highest concentrations in the BBIC trajectories (Table 1).

2-Methyltetrols and \( \Sigma C_5 \)-alkene triols were discovered in the Amazon rainforest (Claeys et al., 2004b), while 2-methylglyceric acid was firstly detected in aerosol collected from a mixed deciduous/coniferous forest in K-puszta, Hungary (Claeys et al., 2004a). There are many laboratory and field studies showing that SOA markers can be formed from photochemical oxidation and ozonolysis in acidic and non-acidic seeding condition (Claeys et al., 2007; Lewandowski et al., 2007; Kourtchev et al., 2008b). While 2-methyltetrols are formed under various \( \Sigma NO \) regimes, \( \Sigma C_5 \)-alkene triols require low-\( \Sigma NO \) conditions, and 2-methylglyceric acid is enhanced under high-\( \Sigma NO \) conditions (Surratt et al., 2006). Claey et al. (2004b) reported that in the Amazon Basin forest isoprene is oxidized by OH radical in the presence of low NOx (NO + \( \Sigma NO \)) concentrations; in contrast, the enhancement of photo-oxidation takes place in anthropogenically influenced regions with high NOx and SO2 concentrations (Lewandowski et al., 2007; Kourtchev et al., 2008a).

In the present study, mean concentrations of 2-methylthreitol were \( 6 \pm 2 \text{ ng m}^{-3} \), \( 15 \pm 8 \text{ ng m}^{-3} \), and \( 6 \pm 3 \text{ ng m}^{-3} \) in the aerosol samples associated with the BBSC, BBIC, and BBSS trajectories, respectively, while those of 2-methylerythritol were \( 13 \pm 7 \text{ ng m}^{-3} \), \( 36 \pm 22 \text{ ng m}^{-3} \), and \( 16 \pm 8 \text{ ng m}^{-3} \), respectively (Table 1). In general, the mean concentrations of the 2-methyltetrols are lower than those found at other forested sites during summer periods, such as Mt. Tai with BB influence (Fu et al., 2012), and Hyytiala, Finland (Kourtchev et al., 2008a) and Research Triangle Park, USA with acidic conditions (Lewandowski et al., 2007), but comparable to those found in Sapporo (Miyazaki et al., 2012). Good correlation was found between 2-methylerythritol and 2-methylthreitol (\( R^2 = 0.95, n = 14 \), not shown as a figure) for the whole period, suggesting a similar photochemical formation process by the oxidation of isoprene, as suggested by Fu et al. (2012).

The concentrations of \( \Sigma C_5 \)-alkene triols were \( 16 \pm 9 \text{ ng m}^{-3} \), \( 54 \pm 36 \text{ ng m}^{-3} \), and \( 20 \pm 12 \text{ ng m}^{-3} \) in the BBSC, BBIC, and BBSS trajectories, respectively (Table 1). During the intensive BB period, these tris were explicitly enhanced, nearly three times those observed during other periods in early and late March. The average concentration is much higher than those from a Californian pine forest (3.5 ng m\(^{-3}\), USA (Cahill et al., 2006), mixed deciduous forest (2–5 ng m\(^{-3}\)) in Julich, western Germany (Kourtchev et al., 2008b), and middle European spruce forest (0.5–15.7 ng m\(^{-3}\)) in northeastern Bavaria, Germany (Plewka et al., 2006). At the same time, the values are comparable to those (50 ng m\(^{-3}\)) reported in subtropical Hong Kong (Hu et al., 2008). In the present study, concentrations of \( \Sigma C_5 \)-alkene triols were found to be higher than that of 2-methyltetrols. These results are in good agreement with the observations reported in Hong Kong, but opposite to those observed at Mt. Tai (Fu et al., 2012) and Julich, Germany (Kourtchev et al., 2008b).

2-Methylglyceric acid is formed under high-NOx condition and is a key monomeric unit while the residues are formed by esterification of hydroxyl groups with acetic and/or formic acid (Surratt et al., 2006; Szmielski et al., 2007). This observation was later confirmed by Jaoui et al. (2008) who also observed the esterification of two 2-methylglyceric acid residues in the ambient aerosol under high-NOx conditions. Moreover, Lin et al. (2013) recently suggested that 2-methylglyceric acid may originate from oxidation of methacrolein and methacrylic acid, which are oxidation products of isoprene under high-NOx condition. Thus, 2-methylglyceric acid can act as a tracer for SOA formation from isoprene photo-oxidation under high NOx during BB periods. In this study, 2-methylglyceric acid was detected as the lowest among all isoprene-SOA tracers. The concentrations varied from \( 4 \pm 1 \text{ ng m}^{-3} \) in early March in the BBSC trajectories to \( 13 \pm 3 \text{ ng m}^{-3} \) in the BBIC trajectories, and \( 5 \pm 1 \text{ ng m}^{-3} \) in the BBSS trajectories.

Wang et al. (2013) conducted a chamber study at with initial condition of isoprene/O\(_3\) and observed high SOA yield from C\(_5\)-alkene triols and 2-methyltetrols with their ratio close to unity, whereas the ratio of 2-methylthreitol to 2-methylerythritol was about 0.45. The above mentioned ratios of isoprene oxidation products in our study are comparable with the results of Wang et al. (2013) from the oxidation of isoprene by O\(_3\). The ratios of \( \Sigma C_5 \)-alkenes to that of 2-methyltetrols in the marine and coastal aerosols were found to be \(< 0.1 \) (Fu et al., 2011) and \( \leq 0.66 \) (Cahill et al., 2006), respectively. In the present study, the ratio of \( \Sigma C_5 \)-alkenes to 2-methyltetrols in all three trajectories is approximately unity, suggesting lesser influence of marine input. Similarly, concentrations of 2-methylerythritol were 1.5–2.5 times higher than those of 2-methylthreitol in the forest aerosol (Claey et al., 2004b; Cahill et al., 2006), whereas lower ratios in the range of 0.76–2.1 have been reported in marine aerosol (Fu et al., 2013). In our study,
the ratio of 2-methylerthritol to 2-methylthreitol is approximately 2 in all three trajectories, suggesting greater influence of biogenic emissions rather than anthropogenic or marine contributions. Moreover, Cahill et al. (2006) suggested that aside from photochemical oxidation, 2-methyltetrols may have primary biological sources, being similar to the case of sugars. Hu et al. (2008) also observed the triols as high as 426 ng m\(^{-3}\) on regional pollution days with high concentrations of O\(_3\). Thus, aside from NO\(_x\), O\(_3\) may also play a key role in favor of the formation of triols.

\(\alpha\)-Pinene is the dominant monoterpene species mainly emitted from conifers, whose annual global emission rate is estimated to be 127 Tg (Guenther et al., 1995). The emissions of monoterpenes from terrestrial vegetation are known to be highly dependent on temperature (Schrurgers et al., 2009). Oxidation of monoterpenes in the atmosphere contributes to the production of \(O_3\) in the presence of NO\(_x\) (Jenkin and Clemsthat, 2000). Monoterpenes also react with \(O_3\), forming low volatility oxidation products that are important sources of SOA (Hoffmann et al., 1997). In addition, aerosol acidity appears to have a much stronger influence on the SOA formation (Lewandowski et al., 2007). The \(\alpha\)-pinene oxidation products include 3-hydroxyglutaric acid (3-HGA), which has been observed both in smog chamber experiments with UV-irradiated \(\alpha\)-pinene in the presence of NO\(_x\) (Claeys et al., 2007) and field studies from marine to mountainous sites (Lewandowski et al., 2007; Kourtchev et al., 2008a; Fu et al., 2011, 2012, 2013). Hence, 3-HGA is suggested as an evolutionary tracer for SOA. Mean concentrations of 3-HGA from the BBSC and BBSS trajectories were 62 ± 14 and 54 ± 27 ng m\(^{-3}\), respectively, whereas that for the BBIC trajectories is 158 ± 47 ng m\(^{-3}\) (Table 1). The mean concentration for the 14 samples is 108 ± 61 ng m\(^{-3}\), which is highest among those reported in other studies for forests, e.g., Mt. Tai, Mt. Hyytiala, K-puszta, and Amazon forest (Claeys et al., 2004b; Claeys et al., 2007; Kourtchev et al., 2008a; Fu et al., 2012). It is likely that rising temperatures during the pre-monsoon season have contributed to the enhanced SOA formation by photo-oxidation of \(\alpha\)-pinene.

**Stable Carbon Isotope Ratio (\(\delta^{13}C\)) Signature for Plants with Different Carbon Fixations**

Stable carbon isotope ratios have a wide range, i.e., –23 to –34‰ for \(C_3\) plants, and –12 to –14‰ for \(C_4\) plants (Schidlowski, 1987; Gelencser, 2004; Rommerskirchen et al., 2006), while the \(\delta^{13}C\) value in fossil fuel is reported to be –26 ± 2‰ (Sackett, 1989). Although \(\delta^{13}C\) values have been used to assess the sources for carbon in aerosol, there is overlap in the range of \(\delta^{13}C\) values for each defined source. Due to the \(\delta^{13}C\) overlap between the major pollution sources, it is not straightforward to delineate the pollution sources using only \(\delta^{13}C\) values. Previous studies used \(\delta^{13}C\) values along with the air mass transport patterns (Cachier et al., 1985). In our study, the \(\delta^{13}C\) values were on average –25.49 ± 0.10‰, –26 ± 0.43‰, and –26.15 ± 0.09‰ in the aerosol samples that have been assigned to the BBSC, BBIC, and BBSS trajectories, respectively. Based on the \(\delta^{13}C\) values, sources of carbonaceous aerosol collected during the sampling period can be attributed to the burning of \(C_3\) plants and fossil fuel combustion. Garbaras et al. (2015) carried out a study to assess the carbon isotope fractionation in aerosol from different biomass fuel types and reported that isotopic signatures in aerosols from BB activities reflect not only the isotopic content of biomass but are also affected by particle size and combustion efficiency. Therefore, the observations and findings of the present study need further investigation with a larger sample size.

Vietnam has a wide range of vegetation types, dominated by \(C_3\) plants, with about 2084 native species, due to its diverse climatic and soil conditions (Stibig et al., 2004; Phuong, 2007). We found less significant variations in \(\delta^{13}C\) values among the three trajectory types. Interestingly, the spatial distributions of \(\delta^{13}C\) values reported around the globe are also within close proximity to each other (Fig. 5). The less significant variations can also be attributed to the differences in the concentrations of individual components of the organic aerosols. Kawamura et al. (2012) reported lower \(\delta^{13}C\) values of bulk aerosol carbon in comparison to those of individual diacids and attributed such increase in \(\delta^{13}C\) values of diacids to the photochemical processing of the organic aerosol particles.

**CONCLUSIONS**

This study reports comprehensive PM\(_{2.5}\) organic molecular composition and stable carbon isotope ratios of BB smoke at Sonla, Vietnam from early to late March 2013. Fourteen representative PM\(_{2.5}\) samples were analyzed for more than 50 organic compounds, including POA components such as anhydro sugars, lignin and resin products, sugars, sugar alcohols, fatty acids, and phthalate esters; and SOA components such as aromatic acids, polycyclics, and biogenic oxidation products (e.g., 2-methyltetros, \(\Sigma C_5\)-alkenes triols, and 3-hydroxyglutaric acid). During the study period, backward air mass trajectories were classified into the BBIC (Indochina), BBSC (South China), and BBSS (South China Sea) trajectory types. Most of the resolved molecular species showed their dominance in the BBIC trajectory type, verifying the BB smoke origin of the ambient aerosol in this region. Levoglucosan was found as the single most abundant organic species in all the PM\(_{2.5}\) samples for the three trajectory types, confirming the prevailing influence of BB on the Sonla site. Although the sampling site was under the dominant influence of BB emissions, trajectory classification still provides additional source information, such as higher DEP levels in the BBSC trajectories revealing urban or industrial influence. In contrast, higher levels of LMW fatty acids compared to HMW fatty acids indicate burning emissions associated with the BBSC trajectories with contributions of more microbial sources and less from plant wax/vegetation.

The abundance of 4-hydroxybenzoic and vanillic acids indicates that burned materials were non-woody vegetation and mixed wood, yet with more hard wood than soft wood contributions. Moreover, the abundant presence of glycerol and erythritol confirms the importance of agricultural activities, whereas arabitol and mannitol provide evidence of the contribution of fungal spores to aerosol mass in the
Fig. 5. Distribution of δ^{13}C values on a global map (http://imgkid.com/flat-globe-map.shtml). (a) Agarwal et al. (2013); (b) Agnihotri et al. (2011); (c) Narukawa et al. (1999); (d) Martinelli et al. (2002); (e) Huang et al. (2006); (f) Kawamura et al. (2004); (g) Kundu et al. 2010a); (h) Kawamura et al. (2012); (i) Miyazaki et al. (2012); (j) Fu et al. (2012) and the present study at the Sonla site.

Area. The presence of phthalic acids indicates atmospheric degradation of aromatic hydrocarbons and SOA formation. The dominance of o- and p-phthalic acids among the phthalic acid isomers agrees with other literature findings, suggesting their role as potential fingerprints of BB smoke. Similarly, considerable amounts of the ΣC₅-alkene triols and 2-methyltetrols could be explained by O₃-initiated photo-oxidation of isoprene. Also, concentrations of 3-hydroxyglutaric acid were found to be high, indicating that rising temperatures during the pre-monsoon BB season may have caused the increase in SOA compounds formed by photo-oxidation of α-pinene.

This study also presents for the first time the stable carbon isotopic ratios of aerosol carbon, whose δ^{13}C values ranged from –26.6 to –25.4‰ in PM_{2.5} at Sonla, Vietnam, indicating that carbonaceous aerosols were derived from both C₃ plant burning and fossil fuel combustion. There is less significant variation in δ^{13}C values among the three trajectory types and other places in the world, reflecting global distributions of δ^{13}C values to be relatively narrow.

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