



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 $1.62 \pm 0.89 \mu\text{g m}^{-3}$, comprising $2.23 \pm 0.5\%$ 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 ($\delta^{13}\text{C}$) 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 C₃ plants and fossil fuel combustion.

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

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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 Ramanathan, 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-ethylhexyl) (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; Jenkin and Clementshaw, 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 ($\delta^{13}\text{C}$) in aerosols allows estimating the relative contributions of C_3 (Calvin-Benson cycle) versus C_4 plants (Hatch-Slack cycle) (Cachier, 1989). Plants using the Calvin-Benson cycle, so-called C_3 carbon fixation plants, have $\delta^{13}\text{C}$ 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 C_3 plants. Meanwhile, plants using the Hatch-Slack (or dicarboxylic acid) cycle, so-called C_4 carbon fixation plants, have $\delta^{13}\text{C}$ 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 ^{13}C or ^{12}C 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 $\delta^{13}\text{C}$ values close to the mean values of C_3 plants ($-26 \pm 2\text{‰}$) (Sackett, 1989). Thus, the $\delta^{13}\text{C}$ 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 rainforest 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

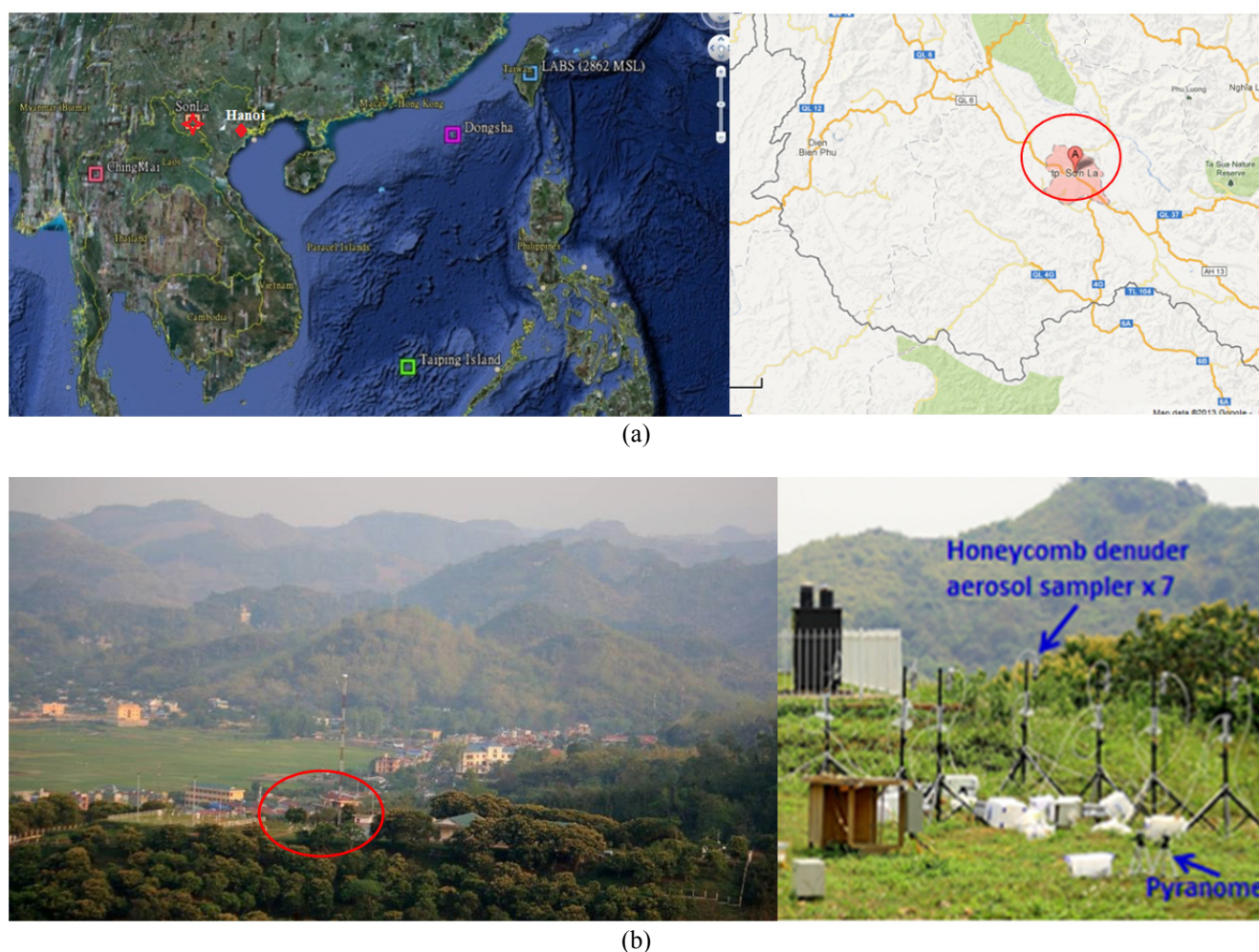
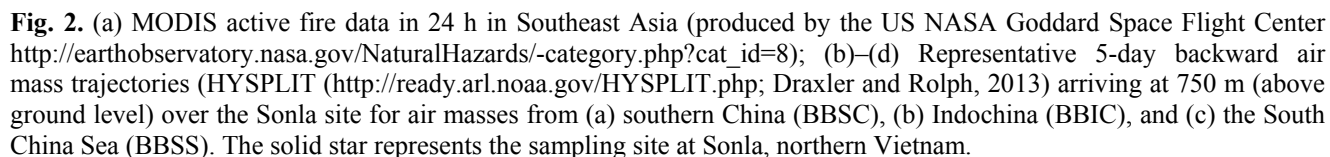


Fig. 1. (a) Geographic location of the Sonla site (star) in Sonla province, Vietnam. The right panel illustrates a closer look of the site of the left panel; (b) Sonla sampling site (circle) and a closer look of the sampler deployment site.

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 μ L of N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA, Sigma-Aldrich) containing 1% trimethylsilyl chloride and 10 μ L of



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 $\text{ng } \mu\text{L}^{-1}$ of internal standard (C_{13} *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 \times 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 $^{\circ}\text{C min}^{-1}$ and then to 300°C at 5 $^{\circ}\text{C min}^{-1}$ 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 better than 80% except for polyacids and pinonic acid, whose recoveries were around 60%. Relative standard deviations of the concentrations based on duplicate analysis were generally < 10% (Fu *et al.*, 2014). Concentrations were not corrected for the recoveries. The field and laboratory blank filters were also analyzed by the procedure described above for quality assurance. The results showed that contamination levels were less than 5% of real samples for any species detected. All the data reported here were corrected for field blanks. For more details regarding the GC-MS analysis procedure, see Fu *et al.* (2012).

Stable Carbon Isotope Measurements

For the measurements of isotopic compositions, a punch (1.54 cm^2) 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 $\delta^{13}\text{C}$ values were defined as:

$$\delta^{13}\text{C} (\text{‰}) = \left[\left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{sample}} / \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{standard}} - 1 \right] \times 1000 \quad (1)$$

Before running the real samples for the determination of $\delta^{13}\text{C}$, 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 $\delta^{13}\text{C}$ measurement based on repeated analyses of atmospheric aerosol samples were within 0.2‰ (Kawamura *et al.*, 2004). $\delta^{13}\text{C}$ 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 $\text{PM}_{2.5}$ for the whole study period and the groups of organic compounds for the selected 14 samples according to the three different trajectory types. The $\text{PM}_{2.5}$ mass concentration was on average $69 \pm 33 \mu\text{g m}^{-3}$ for the selected samples. The average $\text{PM}_{2.5}$ concentrations in the different trajectories were $47 \pm 3 \mu\text{g m}^{-3}$ ($N = 4$), $98 \pm 18 \mu\text{g m}^{-3}$ ($N = 7$), and $30 \pm 14 \mu\text{g m}^{-3}$ ($N = 3$) 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 $\text{PM}_{2.5}$, indicating the influence of BB on the selected samples. Levoglucosan comprised on average 2.23% of $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$, 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 $\text{PM}_{2.5}$ 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.

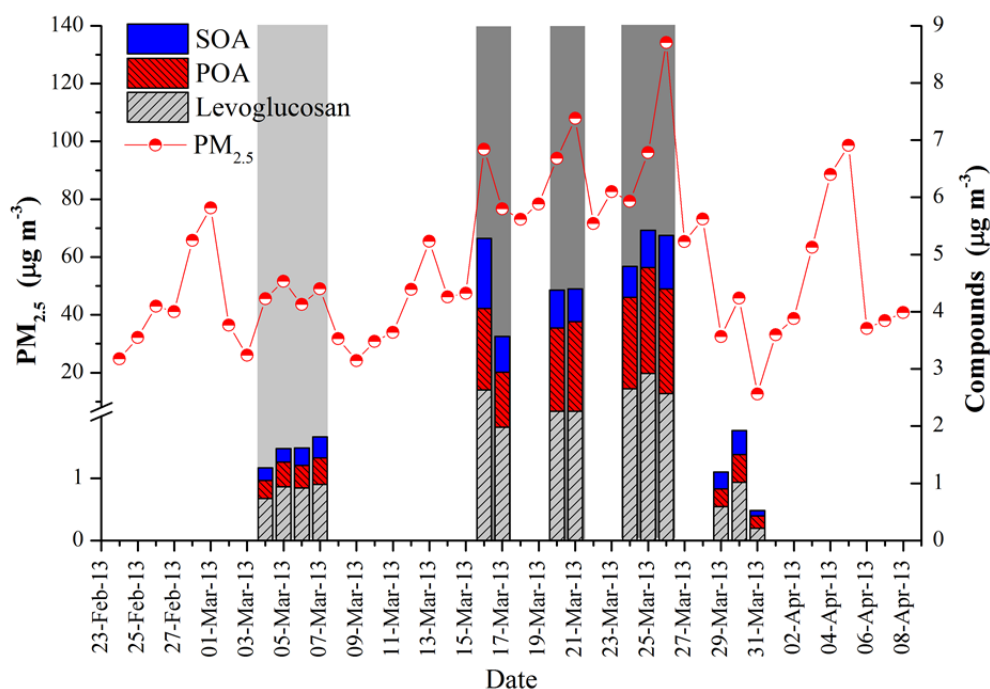


Fig. 3. Time-series of $PM_{2.5}$ aerosol mass concentrations from late February to early April 2013 and the resolved levoglucosan, primary organic aerosols (POA), and secondary organic aerosols (SOA) for backward trajectory types from southern China (BBSC) (light grey area, $n = 4$), Indochina (BBIC) (dark grey area, $n = 7$), and the South China Sea (BBSS) (white background, $n = 3$) collected at Sonla, Vietnam.

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. $1620 \pm 893 \text{ ng m}^{-3}$, 2.3% of $PM_{2.5}$ mass), indicating a significant impact of BB on the ambient aerosols. Concentrations of levoglucosan from the BBIC trajectory type were highest (ave. $2468 \pm 292 \text{ ng m}^{-3}$, 2.6% of $PM_{2.5}$ mass), while the average concentrations from the BBSC and BBSS types were $895 \pm 94 \text{ ng m}^{-3}$ (1.9% of $PM_{2.5}$ mass) and $610 \pm 329 \text{ ng m}^{-3}$ (1.9% of $PM_{2.5}$ 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; 2013), as they are signature compounds released by burning of wood and other biomass material. The major markers for lignin and resin burning are (i) dehydroabietic acid from conifer wood, (ii) 4-hydroxybenzoic acid from grasses and other non-woody vegetation, (iii) vanillic acid from softwood and hardwood, and (iv) syringic acid from hardwood (Oros

and Simoneit, 2001; Simoneit, 2002; Sheesley *et al.*, 2003; Fu *et al.*, 2013). 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 ($6 \pm 3 \text{ ng m}^{-3}$), 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 $30 \pm 25 \text{ ng m}^{-3}$, 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 $\text{PM}_{2.5}$ for the resolved molecular organic compounds in the fourteen representative $\text{PM}_{2.5}$ samples from Sonla, northern Vietnam with three types of 5-day backward air mass trajectories.

| Trajectory Types Number of Samples | BBSC | | BBIC | | BBSS | |
|---|------------------|------------------------|-------------------|------------------------|-------------------|------------------------|
| | 4 | | 7 | | 3 | |
| | Mean \pm SD | % in $\text{PM}_{2.5}$ | Mean \pm SD | % in $\text{PM}_{2.5}$ | Mean \pm SD | % in $\text{PM}_{2.5}$ |
| <i>PM</i> _{2.5} | 47000 \pm 3000 | 100 | 98000 \pm 18000 | 100 | 30000 \pm 14000 | 100 |
| <i>Levoglucosan (POA)</i> | 895 \pm 94 | 1.90 | 2468 \pm 292 | 2.60 | 610 \pm 329 | 1.90 |
| <i>Lignin/Resin Products (POA)</i> | 30 \pm 6 | 0.062 | 149 \pm 31 | 0.157 | 18 \pm 12 | 0.056 |
| Dehydroabietic acid | 4 \pm 1 | 0.009 | 8 \pm 2 | 0.008 | 2 \pm 1 | 0.007 |
| Syringic acid | 11 \pm 2 | 0.024 | 59 \pm 13 | 0.063 | 4 \pm 3 | 0.014 |
| Vanillic acid | 6 \pm 1 | 0.013 | 30 \pm 8 | 0.032 | 4 \pm 2 | 0.012 |
| 4-hydroxybenzoic acid | 8 \pm 1 | 0.017 | 53 \pm 15 | 0.054 | 8 \pm 6 | 0.023 |
| <i>Sugars (POA)</i> | 17 \pm 1 | 0.036 | 48 \pm 13 | 0.049 | 19 \pm 11 | 0.061 |
| Fructose | 4 \pm 1 | 0.01 | 15 \pm 6 | 0.015 | 5 \pm 2 | 0.013 |
| Glucose | 12 \pm 2 | 0.026 | 34 \pm 9 | 0.034 | 14 \pm 9 | 0.047 |
| <i>Sugar alcohols (POA)</i> | 55 \pm 7 | 0.116 | 119 \pm 29 | 0.122 | 41 \pm 13 | 0.147 |
| Arabitol | 5 \pm 1 | 0.01 | 15 \pm 7 | 0.014 | 4 \pm 2 | 0.011 |
| Mannitol | 3 \pm 1 | 0.006 | 12 \pm 7 | 0.011 | 3 \pm 1 | 0.009 |
| Inositol | 2 \pm 0 | 0.004 | 7 \pm 1 | 0.008 | 2 \pm 1 | 0.006 |
| Erythritol | 14 \pm 1 | 0.029 | 31 \pm 7 | 0.032 | 8 \pm 4 | 0.093 |
| Glycerol | 31 \pm 10 | 0.066 | 54 \pm 12 | 0.056 | 24 \pm 5 | 0.028 |
| <i>Fatty Acids (POA)</i> | 241 \pm 44 | 0.506 | 1090 \pm 223 | 1.121 | 202 \pm 70 | 0.741 |
| LMW ($\leq \text{C}_{19}$) | 181 \pm 31 | 0.38 | 349 \pm 38 | 0.365 | 202 \pm 70 | 0.741 |
| HMW ($\geq \text{C}_{20}$) | 60 \pm 21 | 0.126 | 741 \pm 260 | 0.756 | n.d. | n.d. |
| <i>Phthalate esters (POA)</i> | 59 \pm 10 | 0.124 | 121 \pm 12 | 0.127 | 55 \pm 9 | 0.222 |
| Diethyl phthalate (DEP) | 21 \pm 7 | 0.045 | 4 \pm 2 | 0.005 | 3 \pm 4 | 0.023 |
| Di-iso-butyl phthalate (DiBP) | 10 \pm 2 | 0.021 | 30 \pm 9 | 0.032 | 13 \pm 3 | 0.050 |
| Di-n-butyl phthalate (DnBP) | 15 \pm 3 | 0.033 | 49 \pm 10 | 0.051 | 26 \pm 4 | 0.103 |
| Di-(2-ethylhexyl) phthalate (DEHP) | 12 \pm 4 | 0.025 | 38 \pm 9 | 0.038 | 13 \pm 6 | 0.046 |
| <i>Aromatic acids (SOA)</i> | 73 \pm 9 | 0.155 | 158 \pm 30 | 0.161 | 62 \pm 25 | 0.208 |
| o-phthalic acid | 30 \pm 4 | 0.063 | 65 \pm 16 | 0.066 | 32 \pm 11 | 0.113 |
| m-phthalic acid | 3 \pm 1 | 0.007 | 10 \pm 2 | 0.010 | 3 \pm 1 | 0.008 |
| p-phthalic acid | 40 \pm 10 | 0.085 | 82 \pm 17 | 0.085 | 27 \pm 14 | 0.086 |
| <i>Polyacids (SOA)</i> | 108 \pm 20 | 0.228 | 311 \pm 101 | 0.319 | 106 \pm 59 | 0.326 |
| DL-tartalic acid | 10 \pm 2 | 0.021 | 29 \pm 12 | 0.029 | 11 \pm 7 | 0.034 |
| Citric acid | 1 \pm 1 | 0.003 | 7 \pm 3 | 0.008 | 3 \pm 2 | 0.007 |
| DL-malic acid | 65 \pm 15 | 0.137 | 190 \pm 66 | 0.196 | 66 \pm 36 | 0.204 |
| Glyceric acid | 32 \pm 2 | 0.067 | 85 \pm 22 | 0.086 | 26 \pm 14 | 0.081 |
| <i>Isoprene oxidation (SOA)</i> | 38 \pm 18 | 0.082 | 118 \pm 66 | 0.148 | 47 \pm 24 | 0.121 |
| 2-methylthreitol | 6 \pm 2 | 0.012 | 15 \pm 8 | 0.015 | 6 \pm 3 | 0.020 |
| 2-methylerythritol | 13 \pm 7 | 0.027 | 36 \pm 22 | 0.036 | 16 \pm 8 | 0.050 |
| ΣC_5 -Alkene triols | 16 \pm 9 | 0.033 | 54 \pm 36 | 0.057 | 20 \pm 12 | 0.060 |
| 2-methylglyceric acid | 4 \pm 1 | 0.009 | 13 \pm 3 | 0.014 | 5 \pm 1 | 0.017 |
| <i>α-pinene oxidation (SOA)</i> | 62 \pm 14 | 0.100 | 158 \pm 47 | 0.164 | 54 \pm 27 | 0.172 |
| 3-HGA | 62 \pm 14 | 0.100 | 158 \pm 47 | 0.164 | 54 \pm 27 | 0.172 |

Notes:

- ΣC_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 ($17 \pm 14 \text{ ng m}^{-3}$). In contrast, syringic acid (associated mainly with hardwood) was observed with an average concentration of $34 \pm 27 \text{ ng m}^{-3}$. 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 arabitol, mannitol, inositol,

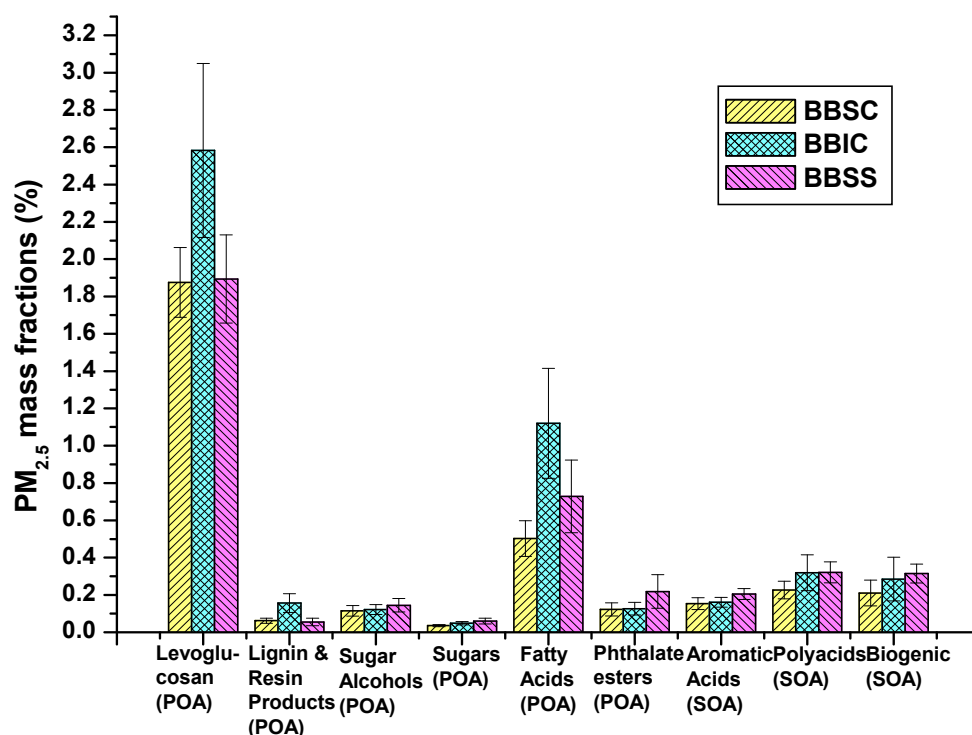


Fig. 4. Comparison of PM_{2.5} mass fractions of the organic compound groups among three different backward trajectory types from southern China (BBSC, $n = 4$), Indochina (BBIC, $n = 7$), and the South China Sea (BBSS, $n = 3$) at Sonla, Vietnam, from early to late March 2013.

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 ($167 \pm 53 \text{ ng m}^{-3}$), which is nearly double of those for the BBSC ($72 \pm 15 \text{ ng m}^{-3}$) and BBSS trajectories ($60 \pm 24 \text{ ng m}^{-3}$). 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 Simoneit (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 ($R^2 = 0.95$, $n = 14$, 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 Simoneit, 2001). The average concentrations of low-molecular-weight (LMW, $\leq C_{19}$) fatty acids were $181 \pm 31 \text{ ng m}^{-3}$ in the BBSC trajectories and $202 \pm 70 \text{ ng m}^{-3}$ in the BBSS trajectories, whereas those of high-molecular-weight (HMW, $\geq C_{20}$) fatty acids were $60 \pm 21 \text{ ng m}^{-3}$ 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 (C_{18:1} and C_{18:2}) 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, DnBP, 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 (Stailes *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 BBIC trajectories are approximately three times higher than those from the BBSC 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) ΣC_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 ΣC_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-puszt, 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 or non-acidic seeding condition (Claeys *et al.*, 2007; Lewandowski *et al.*, 2007; Kourtchev *et al.*, 2008b). While 2-methyltetrols are formed under various NO_x regimes, ΣC_5 -alkene triols require low- NO_x conditions, and 2-methylglyceric acid is enhanced under high- NO_x conditions (Surratt *et al.*, 2006). Claeys *et al.* (2004b) reported that in the Amazon Basin forest isoprene is oxidized by OH radical in the presence of low NO_x ($NO + NO_2$) concentrations; in contrast, the enhancement of photo-oxidation takes place in anthropogenically influenced regions with high NO_x and SO_2 concentrations (Lewandowski *et al.*, 2007; Kourtchev *et al.*, 2008a).

In the present study, mean concentrations of 2-methylthreitol were 6 ± 2 ng m⁻³, 15 ± 8 ng m⁻³, and 6 ± 3 ng m⁻³ in the aerosol samples associated with the BBSC, BBIC, and BBSS trajectories, respectively, while those of 2-methylerythritol were 13 ± 7 ng m⁻³, 36 ± 22 ng m⁻³, and 16 ± 8 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 Hyytiälä, 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 ΣC_5 -alkene triols were 16 ± 9 ng m⁻³, 54 ± 36 ng m⁻³, and 20 ± 12 ng m⁻³ in the BBSC, BBIC, and BBSS trajectories, respectively (Table 1). During the intensive BB period, these triols 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 ΣC_5 -alkene triols were found to be higher than individual 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- NO_x 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; Szmigielski *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- NO_x 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- NO_x condition. Thus, 2-methylglyceric acid can act as a tracer for SOA formation from isoprene photo-oxidation under high NO_x during BB periods. In this study, 2-methylglyceric acid was detected as the lowest among all isoprene-SOA tracers. The concentrations varied from 4 ± 1 ng m⁻³ in early March in the BBSC trajectories to 13 ± 3 ng m⁻³ in the BBIC trajectories, and 5 ± 1 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 ΣC_5 -alkenes to that of 2-methyltetrols in the marine and coastal aerosols were found to be < 0.1 (Fu *et al.*, 2011) and ≤ 0.66 (Cahill *et al.*, 2006), respectively. In the present study, the ratio of ΣC_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 (Claeys *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-methylerythritol 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-methyltetrosols 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.

α -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 (Schurgers *et al.*, 2009). Oxidation of monoterpenes in the atmosphere contributes to the production of O_3 in the presence of NO_x (Jenkin and Clemitshaw, 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 α -pinene oxidation products include 3-hydroxyglutaric acid (3-HGA), which has been observed both in smog chamber experiments with UV-irradiated α -pinene in the presence of NO_x (Claeys *et al.*, 2007) and field studies from marine to mountainous sites (Lewandowski *et al.*, 2007; Kourchev *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 $54 \pm 27 \text{ ng m}^{-3}$, respectively, whereas that for the BBIC trajectories is $158 \pm 47 \text{ ng m}^{-3}$ (Table 1). The mean concentration for the 14 samples is $108 \pm 61 \text{ ng m}^{-3}$, which is highest among those reported in other studies for forests, e.g., Mt. Tai, Mt. Hyttiala, K-puszt, and Amazon forest (Claeys *et al.*, 2004b; Claeys *et al.*, 2007; Kourchev *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 α -pinene.

Stable Carbon Isotope Ratio ($\delta^{13}\text{C}$): 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 $\delta^{13}\text{C}$ value in fossil fuel is reported to be $-26 \pm 2\text{‰}$ (Sackett, 1989). Although $\delta^{13}\text{C}$ values have been used to assess the sources for carbon in aerosol, there is overlap in the range of $\delta^{13}\text{C}$ values for each defined source. Due to the $\delta^{13}\text{C}$ overlap between the major pollution sources, it is not straightforward to delineate the pollution sources using only $\delta^{13}\text{C}$ values. Previous studies used $\delta^{13}\text{C}$ values along with the air mass transport patterns (Cachier *et al.*, 1985). In our study, the $\delta^{13}\text{C}$ values were on average $-25.49 \pm 0.10\text{‰}$, $-26 \pm 0.43\text{‰}$, and $-26.15 \pm 0.09\text{‰}$ in the aerosol samples that have been assigned to the BBSC, BBIC, and BBSS trajectories, respectively. Based on the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values among the three trajectory types. Interestingly, the spatial distributions of $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values of bulk aerosol carbon in comparison to those of individual diacids and attributed such increase in $\delta^{13}\text{C}$ values of diacids to the photochemical processing of the organic aerosol particles.

CONCLUSIONS

This study reports comprehensive $\text{PM}_{2.5}$ organic molecular composition and stable carbon isotope ratios of BB smoke at Sonla, Vietnam from early to late March 2013. Fourteen representative $\text{PM}_{2.5}$ samples were analyzed for more than 50 organic compounds, including POA components such as anhydrosugars, lignin and resin products, sugars, sugar alcohols, fatty acids, and phthalate esters; and SOA components such as aromatic acids, polyacids, and biogenic oxidation products (e.g., 2-methyltetrosols, ΣC_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 $\text{PM}_{2.5}$ 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 hardwood than softwood 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

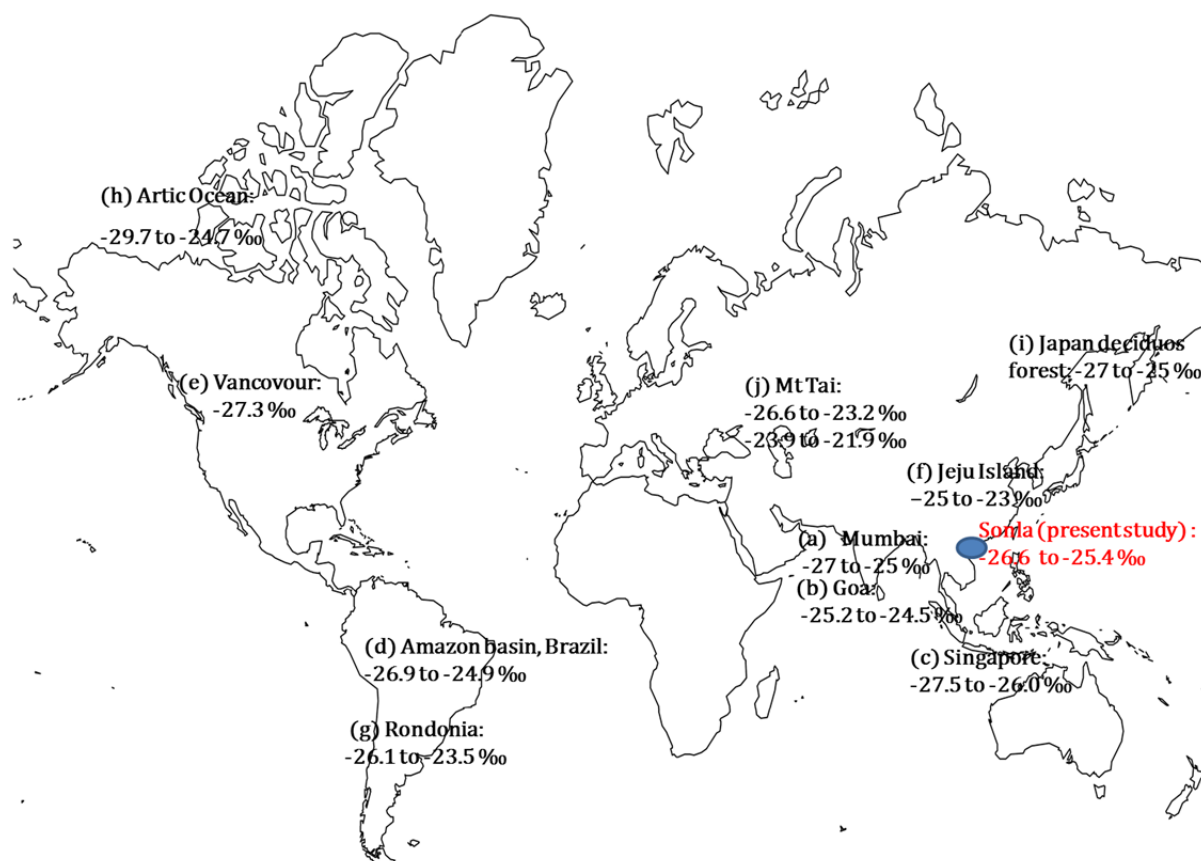


Fig. 5. Distribution of $\delta^{13}\text{C}$ values on a global map (<http://imgkid.com/flat-globe-map.shtml>). (a) Agarwal *et al.* (2013); (b) Agnihotri *et al.* (2011); (c) Narukawa *et al.* (1999); (d) Martinelli *et al.* (2002); (e) Huang *et al.* (2006); (f) Kawamura *et al.* (2004); (g) Kundu *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 ΣC_5 -alkene triols and 2-methyltetrols could be explained by O_3 -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 $\delta^{13}\text{C}$ values ranged from -26.6 to -25.4‰ in $\text{PM}_{2.5}$ at Sonla, Vietnam, indicating that carbonaceous aerosols were derived from both C_3 plant burning and fossil fuel combustion. There is less significant variation in $\delta^{13}\text{C}$ values among the three trajectory types and other places in the world, reflecting global distributions of $\delta^{13}\text{C}$ values to be relatively narrow.

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REFERENCES

- Aggarwal, S.G., Kawamura, K., Umarji, G.S., Tachibana, E., Patil, R.S. and Gupta, P.K. (2013). Organic and inorganic markers and Stable C-, N-isotopic compositions of tropical coastal aerosols from megacity Mumbai: sources of organic aerosols and atmospheric processing. *Atmos. Chem. Phys.* 13: 4667–4680.
- Agnihotri, R., Mandal, T.K., Karapurkar, S.G., Naja, M., Gadi, R., Nazeer, Y.A., Kumar, A., Saud, T. and Saxena, M. (2011). Stable carbon and nitrogen isotopic composition of bulk aerosols over India and northern Indian Ocean. *Atmos. Environ.* 45: 2828–2835.
- Andreae, M.O. and Crutzen, P.J. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science* 276: 1052–1058.
- Andreae, M.O. and Merlet, P. (2001). Emission of trace gases and aerosols from biomass burning. *Global*

- Biogeochem. Cycles* 15: 955–966.
- Andreae, M.O. (2009). A new look at aging aerosols. *Science* 326: 1493–1494.
- Andreae, M.O., Jones, C.D. and Cox, P.M. (2005). Strong present-day aerosol cooling implies a hot future. *Nature* 435: 1187–1190.
- Andreae, M.O. and Ramanathan, V. (2013). Climate's dark forcings. *Science* 340: 280–281.
- Bauer, H., Claeys, M., Vermeylen, R., Schueller, E., Weinke, G., Berger, A. and Puxbaum, H. (2008). Arabitol and mannitol as tracers for the quantification of airborne fungal spores. *Atmos. Environ.* 42: 588–593.
- Burshtein, N., Lang-Yona, N. and Rudich, Y. (2011). Ergosterol, arabitol and mannitol as tracers for biogenic aerosols in the eastern Mediterranean. *Atmos. Chem. Phys.* 11: 829–839.
- Cachier, H., Buat-Menard, P. and Frontugne, M. (1985). Source terms and source strength of the carbonaceous aerosol in the tropics. *J. Atmos. Chem.* 3: 469–489.
- Cachier, H. (1989). Isotopic characterization of carbonaceous aerosols. *Aerosol Sci. Technol.* 10: 379–385.
- Cahill, T.M., Seaman, V.Y., Charles, M.J., Holzinger, R. and Goldstein, A.H. (2006). Secondary organic aerosols formed from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains of California. *J. Geophys. Res.* 111: D16312, doi: 10.1029/2006JD007178.
- Carmichael, G.R., Tang, Y., Kurata, G., Uno, I., Streets, D., Woo, J.H., Huang, H., Yienger, J., Lefer, B., Shetter, R., Blake, D., Atlas, E., Fried, A., Apel, E., Eisele, F., Cantrell, C., Avery, M., Barrick, J., Sachse, G., Brune, W., Sandholm, S., Kondo, Y., Singh, H., Talbot, R., Bandy, A., Thornton, D., Clarke, A. and Heikes, B. (2003). Regional-scale chemical transport modeling in support of the analysis of observations obtained during the TRACE-P experiment. *J. Geophys. Res.* 108: 8812, doi: 10.1029/2002JD003200.
- Ceburnis, D., Garbaras, A., Szidat, S., Rinaldi, M., Fahrni, S., Perron, N., Wacker, L., Leinert, S., Remeikis, V. and Facchini, M. (2011). Quantification of the carbonaceous matter origin in submicron marine aerosol by ^{13}C and ^{14}C isotope analysis. *Atmos. Chem. Phys.* 11: 8593–8606.
- Chan, C.Y., Chan, L.Y., Harris, J.M., Oltmans, S.J., Blake, D.R., Qin, Y., Zheng, Y.G. and Zheng, X.D. (2003). Characteristics of biomass burning emission sources, transport, and chemical speciation in enhanced springtime tropospheric ozone profile over Hong Kong. *J. Geophys. Res.* 108: 8800, doi: 10.1029/2003JD003427.
- Chan, L.M. and Dung, V.V. (1992). *Forest Tree Textbook*. Vietnam Forestry University. Xuan Mai.
- Chen, J., Kawamura, K., Liu, C.Q. and Fu, P.Q. (2013). Long-term observations of saccharides in remote marine aerosols from the western North Pacific: A comparison between 1990–1993 and 2006–2009 periods. *Atmos. Environ.* 67: 448–458.
- Chen, T.C., Yen, M.C., Huang, W.R. and Gallus, W.A. (2002). An East Asian cold surge: Case study. *Mon. Weather Rev.* 130: 2271–2290.
- Chow, J.C., Watson, J.G., Mauderly, J.L., Costa, D.L., Wyzga, R.E., Vedal, S., Hidy, G.M., Altshuler, S.L., Marrack, D., Heuss, J.M., Wolff, G.T., Pope, C.A., 3rd and Dockery, D.W. (2006). Health effects of fine particulate air pollution: Lines that connect. *J. Air Waste Manage. Assoc.* 56: 1368–1380.
- Chuang, M.T., Chou, C.C.K., Sopajareepom, K., Lin, N.H., Wang, J.L., Sheu, G.R., Chang, Y.J. and Lee, C.T. (2013). Characterization of aerosol chemical properties from near-source biomass burning in the northern Indochina during 7-SEAS/Dongsha experiment. *Atmos. Environ.* 78: 72–81.
- Claeys, M., Wang, W., Ion, A.C., Kourtchev, I., Gelencser, A. and Maenhaut, W. (2004a). Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide. *Atmos. Environ.* 38: 4093–4098.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P. and Maenhaut, W. (2004b). Formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303: 1173–1176.
- Claeys, M., Szmigielski, R., Kourtchev, I., Van der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H. and Edney, E.O. (2007). Hydroxydicarboxylic acids: Markers for secondary organic aerosol from the photooxidation of alpha-pinene. *Environ. Sci. Technol.* 41: 1628–1634.
- Cohen, D.D., Crawford, J., Stelcer, E. and Bac, V.T. (2010). Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008. *Atmos. Environ.* 44: 320–328.
- Department of Forest Protection (DoFP) (2010). Data of Changes in the Forest of Vietnam from 2002 to 2009. <http://www.kiamlam.org.vn/Desktop.aspx/News/So-lieu-dien-bien-rung-hang-nam/>. Last Access: 7 August 2011.
- Draxler, R.R. and Rolph, G.D. (2013). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website, (<http://www.arl.noaa.gov/HYSPLIT.php>), NOAA Air Resources Laboratory, College Park, MD.
- Engling, G., Zhang, Y.N., Chan, C.Y., Sang, X.F., Lin, M., Ho, K.F., Li, Y.S., Lin, C.Y. and Lee, J.J. (2011). Characterization and sources of aerosol particles over the southeastern Tibetan Plateau during the Southeast Asia biomass-burning season. *Tellus Ser. B* 63: 117–128.
- FAO (2010). Global Forest Resources Assessment 2010 – Vietnam Country Report, www.fao.org/docrep/013/al664e/al664e.pdf. Last Access: 31 December 2015.
- Fine, P.M., Cass, G.R. and Simoneit, B.R.T. (2001). Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. *Environ. Sci. Technol.* 35: 2665–2675.
- Fine, P.M., Chakrabarti, B., Krudysz, M., Schauer, J.J. and Sioutas, C. (2004). Diurnal variations of individual organic compound constituents of ultrafine and accumulation mode particulate matter in the Los Angeles basin. *Environ. Sci. Technol.* 38: 1296–1304.
- Frohlich-Nowoisky, J., Burrows, S.M., Xie, Z., Engling, G., Solomon, P.A., Fraser, M.P., Mayol-Bracero, O.L., Artaxo, P., Begerow, D., Conrad, R., Andreae, M.O., Després,

- V.R. and Poschl, U. (2012). Biogeography in the air: Fungal diversity over land and oceans. *Biogeosciences* 9: 1125–1136.
- Fu, P.Q., Kawamura, K., Okuzawa, K., Aggarwal, S.G., Wang, G.H., Kanaya, Y. and Wang, Z.F. (2008). Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain. *J. Geophys. Res.* 113: D19107, doi: 10.1029/2008JD009900.
- Fu, P.Q., Kawamura, K. and Barrie, L.A. (2009). Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring. *Environ. Sci. Technol.* 43: 286–292.
- Fu, P.Q., Kawamura, K. and Miura, K. (2011). Molecular characterization of marine organic aerosols collected during a round-the-world cruise. *J. Geophys. Res.* 116: D13302, doi: 10.1029/2011JD015604.
- Fu, P.Q., Kawamura, K., Chen, J., Li, J., Sun, Y.L., Liu, Y., Tachibana, E., Aggarwal, S.G., Okuzawa, K., Tanimoto, H., Kanaya, Y. and Wang, Z.F. (2012). Diurnal variations of organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain: an influence of biomass burning. *Atmos. Chem. Phys.* 12: 8359–8375.
- Fu, P.Q., Kawamura, K., Chen, J., Charriere, B. and Sempere, R. (2013). Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. *Biogeosciences* 10: 653–667.
- Fu, P.Q., Kawamura, K., Chen, J. and Miyazaki, Y. (2014). Secondary production of organic aerosols from biogenic VOCs over Mt. Fuji, Japan. *Environ. Sci. Technol.* 48: 8491–8497.
- Gao, S., Hegg, D.A., Hobbs, P.V., Kirchstetter, T.W., Magi, B.I. and Sadilek, M. (2003). Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution. *J. Geophys. Res.* 108: 8491, doi: 10.1029/2002JD002324.
- Garbaras, A., Masalaite, A., Garbariene, I., Ceburnis, D., Krugly, E., Remeikis, V., Puida, E., Kvietkus, K. and Martuzevicius, D. (2015). Stable carbon fractionation in size-segregated aerosol particles produced by controlled biomass burning. *J. Aerosol Sci.* 79: 86–96.
- Gautam, R., Christina Hsu, N., Eck, T.F., Holben, B.N., Janjai, S., Jantarach, T., Tsay, S.C. and Lau, W.K. (2012). Characterization of aerosols over the Indochina peninsula from satellite-surface observations during biomass burning pre-monsoon season. *Atmos Environ.* 78: 51–59.
- Gelencser, A. (2004). *Carbonaceous Aerosol*. Springer, New York.
- Graham, B., Guyon, P., Taylor, P.E., Artaxo, P., Maenhaut, W., Glovsky, M.M., Flagan, R.C. and Andreae, M.O. (2003). Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography-mass spectrometry. *J. Geophys. Res.* 108: 4766, doi: 10.1029/2003JD003990.
- Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P. (1995). A global-model of natural volatile organic-compound emissions. *J. Geophys. Res.* 100: 8873–8892.
- Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A. H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th.F., Monod, A., Prévôt, A.S.H., Seinfeld, J. H., Surratt, J.D., Szmigielski, R. and Wildt, J. (2009). The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9: 5155–5236.
- Hennigan, C.J., Miracolo, M.A., Engelhart, G.J., May, A.A., Presto, A.A., Lee, T., Sullivan, A.P., McMeeking, G.R., Coe, H., Wold, C.E., Hao, W.M., Gilman, J.B., Kuster, W.C., de Gouw, J., Schichtel, B.A., Collett, J.L., Kreidenweis, S.M. and Robinson, A.L. (2011). Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber. *Atmos. Chem. Phys.* 11: 7669–7686.
- Hoffmann, T., Odum, J.R., Bowman, F., Collins, D., Klockow, D., Flagan, R.C. and Seinfeld, J.H. (1997). Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem.* 26: 189–222.
- Hsu, N.C., Herman, J.R. and Tsay, S.C. (2003). Radiative impacts from biomass burning in the presence of clouds during boreal spring in Southeast Asia. *Geophys. Res. Lett.* 30: 1224, doi: 10.1029/2002GL016485.
- Hu, D., Bian, Q., Li, T. W.Y., Lau, A.K.H. and Yu, J.Z. (2008). Contributions of isoprene, monoterpenes, beta-caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006. *J. Geophys. Res.* 113: D22206, doi: 10.1029/2008JD010437.
- Huang, J., Kang, S., Shen, C., Cong, Z., Liu, K., Wang, W. and Liu, L. (2010). Seasonal variations and sources of ambient fossil and biogenic-derived carbonaceous aerosols based on ¹⁴C measurements in Lhasa, Tibet. *Atmos. Res.* 96: 553–559.
- Huang, L., Brook, J.R., Zhang, W., Li, S.M., Graham, L., Ernst, D., Chivulescu, A. and Lu, G. (2006). Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment. *Atmos. Environ.* 40: 2690–2705.
- Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M.O., Helas, G., Parmar, R. and Herrmann, H. (2007). Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat. *J. Geophys. Res.* 112: D08209, doi: 10.1029/2006JD007120.
- Jaenicke, R. (2005). Abundance of cellular material and proteins in the atmosphere. *Science* 308: 73.
- Jaoui, M., Edney, E.O., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., Surratt, J.D. and Seinfeld, J.H. (2008). Formation of secondary organic aerosol from irradiated -pinene/toluene/NO_x mixtures and the effect of isoprene and sulfur dioxide. *J. Geophys. Res.* 113:

- D09303, doi: 10.1029/2007JD009426.
- Jenkin, M.E. and Clemittshaw, K.C. (2000). Ozone and other secondary photochemical pollutants: Chemical processes governing their formation in the planetary boundary layer. *Atmos. Environ.* 34: 2499–2527.
- Kawamura, K. and Kaplan, I.R. (1987). Motor exhaust emission as a primary source for dicarboxylic acids in Los Angeles ambient air. *Environ. Sci. Technol.* 21: 105–110.
- Kawamura, K. and Ikushima, K. (1993). Seasonal-changes in the distribution of dicarboxylic-acids in the urban atmosphere. *Environ. Sci. Technol.* 27: 2227–2235.
- Kawamura, K., Ishimura, Y. and Yamazaki, K. (2003). Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific. *Global Biogeochem. Cycles*. 17: 1003. doi: 10.1029/2001GB001810.
- Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T. and Lee, M. (2004). In *Geochemical Investigation in Earth and Space Science: A Tribute to Issac R. Kaplan*, Hill, R.J., Leventhal, J., Aizenshtat, Z., Baedeker, M.J., Glaypool, G., Eganhouse, R., Goldhaber, M. and Peters K. (Eds.), Elsevier, The Geochemical Society, Saint Louis, pp. 243–265.
- Kawamura, K., Ono, K., Tachibana, E., Charrière, B. and Sempéré, R. (2012). Distributions of low molecular weight dicarboxylic acids, ketoacids and α -dicarbonyls in the marine aerosols collected over the Arctic Ocean during late summer. *Biogeosciences* 9: 4725–4737.
- Koebel, M. and Elsener, M. (1998). Oxidation of diesel-generated volatile organic compounds in the selective catalytic reduction process. *Ind. Eng. Chem. Res.* 37: 3864–3868.
- Kourtchev, I., Ruuskanen, T., Keronen, P., Sogacheva, L., Dal Maso, M., Reissell, A., Chi, X., Vermeylen, R., Kulmala, M. and Maenhaut, W. (2008a). Determination of isoprene and α - β -pinene oxidation products in boreal forest aerosols from Hyytiälä, Finland: diel variations and possible link with particle formation events. *Plant Biology*. 10: 138–149.
- Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T. and Claeys, M. (2008b). Polar organic marker compounds in PM_{2.5} aerosol from a mixed forest site in western Germany. *Chemosphere* 73: 1308–1314.
- Kundu, S., Kawamura, K. and Lee, M. (2010a). Seasonal variation of the concentrations of nitrogenous species and their nitrogen isotopic ratios in aerosols at Gosan, Jeju Island: Implications for atmospheric processing and source changes of aerosols. *J. Geophys. Res.* 115: D20305, doi: 10.1029/2009JD013323.
- Kundu, S., Kawamura, K., Andreae, T.W., Hoffer, A. and Andreae, M.O. (2010b). Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondonia, Brazil. *J. Aerosol Sci.* 41: 118–133.
- Lee, C.T., Chuang, M.T., Lin, N.H., Wang, J.L., Sheu, G.R., Chang, S.C., Wang, S.H., Huang, H., Chen, H.W., Liu, Y.L., Weng, G.H., Lai, H.Y. and Hsu, S.P. (2011). The enhancement of PM_{2.5} mass and water-soluble ions of biomass transported from Southeast Asia over the Mountain Lulin site in Taiwan. *Atmos. Environ.* 45: 5784–5794.
- Lewandowski, M., Jaoui, M., Kleindienst, T.E., Offenberg, J.H. and Edney, E.O. (2007). Composition of PM_{2.5} during the summer of 2003 in Research Triangle Park, North Carolina. *Atmos. Environ.* 41: 4073–4083.
- Lewis, D.H. and Smith, D.C. (1967). Sugar alcohols (polyols) in fungi and green plants: 1. Distributions, physiology and metabolism. *New Phytol.* 66: 143–184.
- Li, C., Tsay, S.C., Hsu, N.C., Kim, J.Y., Howell, S.G., Huebert, B.J., Ji, Q., Jeong, M.J., Wang, S.H., Hansell, R.A. and Bell, S.W. (2012). Characteristics and composition of atmospheric aerosols in Phimai, central Thailand during BASE-ASIA. *Atmos. Environ.* 78: 60–71.
- Li, J., Posfai, M., Hobbs, P.V. and Buseck, P.R. (2003). Individual aerosol particles from biomass burning in southern Africa: 2, Compositions and aging of inorganic particles. *J. Geophys. Res.* 108: 8484, doi: 10.1029/2002JD002310.
- Lin, N.H., Tsay, S.C., Maring, H.B., Yen, M.C., Sheu, G.R., Wang, S.H., Chi, K.H., Chuang, M.T., OuYang, C.F., Fu, J.S., Reid, J.S., Lee, C.T., Wang, L.C., Wang, J.L., Hsu, C.N., Sayer, A.M., Holben, B.N., Chu, Y.C., Nguyen, X.A., Sopajaree, K., Chen, S.J., Cheng, M.T., Tsuang, B.J., Tsai, C.J., Peng, C.M., Schnell, R.C., Conway, T., Chang, C.T., Lin, K.S., Tsai, Y.I., Lee, W.J., Chang, S.C., Liu, J.J., Chiang, W.L., Huang, S.J., Lin, T.H. and Liu, G.R. (2013). An overview of regional experiments on biomass burning aerosols and related pollutants in Southeast Asia: From BASE-ASIA and the Dongsha Experiment to 7-SEAS. *Atmos. Environ.* 78: 1–19.
- Linh, V.B. (1996). Dry open Dipterocarpus in Vietnam. In *Vietnamese Studies*, Quang, M.L. (Eds.). Ha Noi. pp. 53–68.
- Liu, C.G., Zhang, P., Wang, Y.F., Yang, B. and Shu, J.N. (2012). Heterogeneous reactions of particulate methoxyphenols with NO₃ radicals: Kinetics, products, and mechanisms. *Environ. Sci. Technol.* 46: 13262–13269.
- Loader, N., Robertson, I. and McCarroll, D. (2003). Comparison of stable carbon isotope ratios in the whole wood, cellulose and lignin of oak tree-rings. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 196: 395–407.
- Martinelli, L.A., Camargo, P.B., Lara, L.B.L.S., Victoria, R.L. and Artaxo, P. (2002). Stable carbon and nitrogen isotopic composition of bulk aerosol particles in a C₄ plant landscape of southeast Brazil. *Atmos. Environ.* 36: 2427–2432.
- Mayol-Bracero, O.L., Guyon, P., Graham, B., Roberts, G., Andreae, M.O., Decesari, S., Facchini, M.C., Fuzzi, S. and Artaxo, P. (2002). Water-soluble organic compounds in biomass burning aerosols over Amazonia - 2. Apportionment of the chemical composition and importance of the polyacidic fraction. *J. Geophys. Res.* 107: LBA 59-1–LBA 59-15.

- Medeiros, P.M. and Simoneit, B.R.T. (2000). Source profiles of organic compounds emitted upon combustion of green vegetation from temperate climate forests. *Environ. Sci. Technol.* 42: 8310–8316.
- Miyazaki, Y., Jung, J., Fu, P., Mizoguchi, Y., Yamanoi, K. and Kawamura, K. (2012). Evidence of formation of submicrometer water-soluble organic aerosols at a deciduous forest site in northern Japan in summer. *J. Geophys. Res.* 117: D19213, doi: 10.1029/2012JD018250.
- Narukawa, M., Kawamura, K., Takeuchi, N. and Nakajima, T. (1999). Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires. *Geophys. Res. Lett.* 26: 3101–3104.
- Oros, D.R. and Simoneit, B.R. (2001). Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 1. Temperate climate conifers. *Appl. Geochem.* 16: 1513–1544.
- Pacini, E. (2000). From anther and pollen ripening to pollen presentation. *Plant Syst. Evol.* 222: 19–43.
- Puong, V.T. (2007). Forest Environment of Vietnam: Features of Forest Vegetation and Soils. In *Forest Environments in the Mekong River Basin*, Springer, New York, pp. 189–200.
- Plewka, A., Gnauk, T., Brüggemann, E. and Herrmann, H. (2006). Biogenic contributions to the chemical composition of airborne particles in a coniferous forest in Germany. *Atmos. Environ.* 40: 103–115.
- Pope, C.A., 3rd and Dockery, D.W. (2006). Health effects of fine particulate air pollution: lines that connect. *J. Air Waste Manage. Assoc.* 56: 709–742.
- Reid, J.S., Koppmann, R., Eck, T.F. and Eleuterio, D.P. (2005). A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* 5: 799–825.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R. and Simoneit, B.R.T. (1993). Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation. *Atmos. Environ.* 27: 1309–1330.
- Rommerskirchen, F., Plader, A., Eglinton, G., Chikaraishi, Y. and Rullkotter, J. (2006). Chemotaxonomic significance of distribution and stable carbon isotopic composition of long-chain alkanes and alkan-1-ols in C₄ grass waxes. *Organic Geochem.* 37: 1303–1332.
- Rudich, Y., Donahue, N.M. and Mentel, T.F. (2007). Aging of organic aerosol: Bridging the gap between laboratory and field studies. *Annu. Rev. Phys. Chem.* 58: 321–352.
- Sackett, W. (1989). Stable carbon isotope studies on organic matter in the marine environment. In *Handbook of Environmental Isotope Geochemistry*, Vol. 3, Fritz, P. and Fontes, J.Ch. (Eds.), pp. 139–169.
- Schidlowski, M. (1987). Application of stable carbon isotopes to early biochemical evolution on Earth. *Annu. Rev. Earth Plan. Sci.* 15: 47–72.
- Schurgers, G., Arneth, A., Holzinger, R. and Goldstein, A.H. (2009). Process-based modelling of biogenic monoterpene emissions combining production and release from storage. *Atmos. Chem. Phys.* 9: 3409–3423.
- Sheesley, R.J., Schauer, J.J., Chowdhury, Z., Cass, G.R. and Simoneit, B.R.T. (2003). Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. *J. Geophys. Res.* 108: 4285, doi: 10.1029/2002JD002981.
- Simoneit, B.R.T. and Mazurek, M.A. (1982). Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16: 2139–2159.
- Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F. and Cass, G.R. (1999). Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.* 33: 173–182.
- Simoneit, B.R.T. and Elias, V.O. (2001). Detecting organic tracers from biomass burning in the atmosphere. *Mar. Pollut. Bull.* 42: 805–810.
- Simoneit, B.R.T. (2002). Biomass burning - A review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 17: 129–162.
- Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F. and Didyk, B.M. (2004a). Sugars - Dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. *Environ. Sci. Technol.* 38: 5939–5949.
- Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K. and Huebert, B.J. (2004b). Aerosol particles collected on aircraft flights over the northwestern Pacific region during the ACE-Asia campaign: Composition and major sources of the organic compounds. *J. Geophys. Res.* 109: D19S09, doi: 10.1029/2004JD004565.
- Sinha, P., Hobbs, P.V., Yokelson, R.J., Bertschi, I.T., Blake, D.R., Simpson, I.J., Gao, S., Kirchstetter, T.W. and Novakov, T. (2003). Emissions of trace gases and particles from savanna fires in southern Africa. *J. Geophys. Res.* 108: 8487, doi: 10.1029/2002JD002325.
- Song, C.H., Ma, Y., Orsini, D., Kim, Y.P. and Weber, R.J. (2005). An investigation into the ionic chemical composition and mixing state of biomass burning particles recorded during TRACE-P P3B Flight#10. *J. Atmos. Chem.* 51: 43–64.
- Speranza, A., Calzoni, G.L. and Pacini, E. (1997). Occurrence of mono- or disaccharides and polysaccharide reserves in mature pollen grains. *Sex. Plant. Reprod.* 10: 110–115.
- Stales, C.A., Peterson, D.R., Parkerton, T.F. and Adams, W.J. (1997). The environmental fate of phthalate esters: a literature review. *Chemosphere* 35: 667–749.
- Stibig, H.J., Achard, F. and Fritz, S. (2004). A new forest cover map of continental southeast Asia derived from SPOT-VEGETATION satellite imagery. *Appl. Veg. Sci.* 7: 153–162.
- Streets, D.G., Yan, F., Chin, M., Diehl, T., Mahowald, N., Schultz, M., Wild, M., Wu, Y. and Yu, C. (2009). Anthropogenic and natural contributions to regional trends in aerosol optical depth, 1980–2006. *J. Geophys. Res.* 114: D00D18, doi: 10.1029/2008JD011624.
- Streets, D.G., Yarber, K.F., Woo, J.H. and Carmichael, G.R. (2003). Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions. *Global Biogeochem.*

- Cycles 17: 1099, doi: 10.1029/2003GB002040.
- Surratt, J.D., Murphy, S.M., Kroll, J.H., Ng, N.L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R.C. and Seinfeld, J.H. (2006). Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. *J. Phys. Chem. A* 110: 9665–9690.
- Szmigielski, R., Surratt, J.D., Vermeylen, R., Szmigielska, K., Kroll, J.H., Ng, N.L., Murphy, S.M., Sorooshian, A., Seinfeld, J.H. and Claeys, M. (2007). Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry. *J. Mass Spectrom.* 42: 101–116.
- Thuren, A. and Larsson, P. (1990). Phthalate esters in the Swedish atmosphere. *Environ. Sci. Technol.* 24: 554–559.
- Tsai, Y.I., Sopajaree, K., Chotruksa, A., Wu, H.C. and Kuo, S.C. (2013). Source indicators of biomass burning associated with inorganic salts and carboxylates in dry season ambient aerosol in Chiang Mai Basin, Thailand. *Atmos. Environ.* 78: 93–104.
- Turekian, V.C., Macko, S.A., Ballentine, D., Swap, R.J. and Garstang, M. (1998). Causes of bulk carbon and nitrogen isotopic fractionations in the products of vegetation burns: laboratory studies. *Chem. Geol.* 152: 181–192.
- Turekian, V.C., Macko, S.A. and Keene, W.C. (2003). Concentrations, isotopic compositions, and sources of size-resolved, particulate organic carbon and oxalate in near-surface marine air at Bermuda during spring. *J. Geophys. Res.* 108: 4157, doi: 10.1029/2002JD002053.
- Ulevicius, V., Bycenkienė, S., Remeikis, V., Garbaras, A., Kecorius, S., Andriejauskienė, J., Jasinevičienė, D. and Mocnik, G. (2010). Characterization of pollution events in the East Baltic region affected by regional biomass fire emissions. *Atmos. Res.* 98: 190–200.
- Wang, G.H., Kawamura, K., Lee, S., Ho, K.F. and Cao, J.J. (2006). Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. *Environ. Sci. Technol.* 40: 4619–4625.
- Wang, G.H., Kawamura, K., Hatakeyama, S., Takami, A., Li, H. and Wang, W. (2007). Aircraft measurement of organic aerosols over China. *Environ. Sci. Technol.* 41: 3115–3120.
- Wang, G.H., Kawamura, K., Xie, M.J., Hu, S.Y., Cao, J.J., An, Z.S., Waston, J.G. and Chow, J.C. (2009). Organic molecular compositions and size distributions of chinese summer and autumn aerosols from Nanjing: characteristic haze event caused by wheat straw burning. *Environ. Sci. Technol.* 43: 6493–6499.
- Wang, W., Vas, G., Dommissie, R., Loones, K. and Claeys, M. (2004). Fragmentation study of diastereoisomeric 2-methyltetrols, oxidation products of isoprene, as their trimethylsilyl ethers, using gas chromatography/ion trap mass spectrometry. *Rapid Commun. Mass Spectrom.* 18: 1787–1797.
- Wang, W., Iinuma, Y., Kahnt, A., Ryabtsova, O., Mutzel, A., Vermeylen, R., Van der Veken, P., Maenhaut, W., Herrmann, H. and Claeys, M. (2013). Formation of secondary organic aerosol marker compounds from the photooxidation of isoprene and isoprene-derived alkene diols under low-NO_x conditions. *Faraday Discuss.* 165: 261–272.
- Womiloju, T.O., Miller, J.D., Mayer, P.M. and Brook, J.R. (2003). Methods to determine the biological composition of particulate matter collected from outdoor air. *Atmos. Environ.* 37: 4335–4344.
- Wozniak, A.S., Bauer, J.E., Dickhut, R.M., Xu, L. and McNichol, A.P. (2012). Isotopic characterization of aerosol organic carbon components over the eastern United States. *J. Geophys. Res.* 117: D13303, doi: 10.1029/2011JD017153.
- Yamasoe, M.A., Artaxo, P., Miguel, A.H. and Allen, A.G. (2000). Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. *Atmos. Environ.* 34: 1641–1653.
- Yang, Y.H., Chan, C.Y., Tao, J., Lin, M., Engling, G., Zhang, Z.S., Zhang, T. and Su, L. (2012). Observation of elevated fungal tracers due to biomass burning in the Sichuan Basin at Chengdu City, China. *Sci. Total Environ.* 431: 68–77.

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