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Aircraft measurements of polar organic tracer compounds in tropospheric particles (PM_{10}) over Central China

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Abstract

Atmospheric aerosol samples were collected by aircraft at low to middle altitudes (0.8–3.5 km a.g.l.) over Central East to West China during summer 2003 and spring 2004. The samples were analyzed for polar organic compounds using a technique of solvent extraction/BSTFA derivatization/gas chromatography-mass spectrometry. Biogenic secondary organic aerosol (SOA) tracers from the oxidation of isoprene were found to be more abundant in summer (3.3–138 ng m^{-3}, mean 39 ng m^{-3}) than in spring (3.2–42 ng m^{-3}, 15 ng m^{-3}), while α/β-pinene and β-caryophyllene SOA tracers showed similar abundance between these two seasons. A strong positive correlation ($R^2 = 0.83$) between levoglucosan and β-caryophyllinic acid was found in the spring samples versus a weak correlation ($R^2 = 0.17$) in the summer samples, implying substantial contributions from biomass burning to the β-caryophyllinic acid production in spring. Two organic nitrogen species (oxamic acid and carbamide) were detected in the aircraft aerosol samples and their concentrations were comparable to those of biogenic SOA tracers. Most of the POA and SOA tracers were less abundant at higher altitudes, suggesting they are of ground surface origin, either being directly emitted from anthropogenic/natural sources on the ground surface, or rapidly formed through photooxidation of their precursors emitted from the ground surface and then diluted during uplifting into the troposphere. This study demonstrates that primary biological aerosols, biogenic SOA, and organic nitrogen species are important components of organic aerosols in the troposphere over Central China.

1 Introduction

Primary organic aerosols (POA, particles directly emitted from sources such as plant material, soil dust, biomass and fossil fuel burning) and secondary organic aerosols (SOA, particles formed by the oxidation of gas-phase precursors in the atmosphere) are ubiquitous in the Earth's atmosphere (Kanakidou et al., 2005; Robinson et al., 2007;

Zhang et al., 2007; de Gouw and Jimenez, 2009; Hallquist et al., 2009). They can influence the radiative balance, chemical composition and water cycle in the atmosphere (Ramanathan et al., 2001). Particular attention has been paid to atmospheric chemical studies in East Asia (e.g., ACE-Asia campaign) because anthropogenic emissions of gas and aerosols in this region are significant on a global scale (Huebert et al., 2003; Seinfeld et al., 2004). This is especially true for China that has been facing a serious air pollution problem due to significant industrial emissions, coal and biofuel burning, vehicular exhaust emission, waste incineration, and soil dust originated from the deserts in the north/west regions. Furthermore, field burning of agriculture residues (e.g., wheat straw) sometimes causes serious air pollution in the North China Plain (Li et al., 2007; Fu et al., 2008).

In addition to high loadings of POA emitted from biomass burning and fossil fuel combustion in China (Wang et al., 2006), biogenic SOA from the oxidation of biogenic volatile organic compounds (BVOCs) should also substantially contribute to organic aerosol in this region. For example, East China is one of the most important source regions of isoprene in the world during summertime (Guenther et al., 1995). Further, the aerosol accumulation mode number concentrations in this region are postulated to be highest in the world (Andreae and Rosenfeld, 2008). Up to date, several studies have been conducted in urban and forest areas from North to South China, focusing on the SOA tracers from the oxidation of BVOCs such as isoprene, monoterpenes and sesquiterpenes (Hu et al., 2008; Wang et al., 2008; Fu et al., 2010; Gao et al., 2012). During the ACE-Asia campaign, remarkably high organic carbon concentrations (mean 4 µgC m^{-3} up to 6.5 km altitude) in the free troposphere were obtained by aircraft measurements (Huebert et al., 2003). Modeling studies (Heald et al., 2005; Henze and Seinfeld, 2006) found that SOA, especially isoprene oxidation products, was the dominant component of aerosol mass in the free troposphere over East Asia. A recent field measurement also reported that isoprene SOA tracers such as 2-methyltetrols (2.2–457 ng m^{-3}, mean 110 ng m^{-3}) were very abundant in the day-/night-time aerosols collected at the summit of Mt. Tai (1534 m a.s.l.) in the North China Plain in early summer

(Fu et al., 2010). These studies highlight the need to better understand the sources and organic molecular composition of atmospheric aerosols at high altitudes, especially for biogenic SOA tracers.

In a previous study, Wang et al. (2007) have reported the molecular composition of primary organic aerosols including *n*-alkanes, fatty acids, sugars, and polycyclic aromatic hydrocarbons (PAHs) in fine aerosol particles ($PM_{2.5}$) over China. $PM_{2.5}$ exclude most of the primary biological aerosol particles (PBAPs) such as fungal spores and airborne pollen grains that contain a large amount of sugar compounds in the coarse mode. In this study, we report the abundances and sources of polar organic tracers, including biogenic POA and SOA tracers in aerosol particles (PM_{10}) collected by two aircraft campaigns over Central China. Vertical distributions of various organic compounds and their seasonal differences (spring/summer) are discussed. To our knowledge, this is the first airborne measurement of biogenic SOA tracers together with two organic nitrogen-containing compounds (oxamic acid and carbamide) over China, which adds to the increasing datasets for the chemical characterization of organic aerosols in the troposphere.

2 Experimental section

2.1 Sample collection

Two aircraft campaigns were conducted over Central East to West China during the summer of 2003 (8 August–13 September) and the spring of 2004 (19 May–10 June) using Yun-12 and Yun-5 airplanes, respectively. Fourteen and sixteen PM_{10} aerosol samples were collected during the summer and spring campaigns, respectively, from low to middle altitudes (0.8–3.5 km a.g.l.) (see Table 1). Detailed sampling information and flight tracks are illustrated in Fig. 1. Aerosol samples were collected on precombusted (450 °C for 6 h) quartz filters (Φ90 mm) using a medium-volume air sampler (Beijing Geological Instrument Factory, China) at a flow rate of 78 $\mathrm{L\,min^{-1}}$. After the sampling, each filter was placed in a pre-combusted (450 °C for 6 h) glass vial with a Teflon-lined cap and stored at −20 °C in the dark prior to analyses.

2.2 Extraction, derivatization, and GC-MS analyses

Aliquots (1/4) of the aerosol sample and blank filters were extracted with 10 mL of dichloromethane/methanol (2 : 1; *v* / *v*) under ultrasonication (10 min) for three times. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated in a rotary evaporator, and then air dried with pure nitrogen gas. The extracts were derivatized with 50 µL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1 % trimethylsilyl chloride and 10 µL pyridine for 3 hours at 70 °C. After the reaction, the derivatives were diluted by the addition of 140 µL *n*-hexane containing 1.43 ng μL^{-1} internal standard (C_{13} *n*-alkane) prior to the determination by gas chromatography-mass spectrometry (GC-MS).

GC-MS analyses of the derivatized fraction were performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 MSD. The GC was equipped with a split/splitless injection and a DB-5ms fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). GC oven temperature was 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 isothermal hold at 300 °C for 16 min. The MS was operated on the electron ionization (EI) mode at 70 eV and scanned from 50 to 650 Da. GC-MS response factors were determined using authentic standards. Recoveries for the standards including urea and oxamic acid were generally better than 80 %. Because of the lack of authentic standards for some SOA tracers, 2-methylglyceric acid, 3-MeTHF-3,4-diols, 3-methyl-1,2,3-butanetricarboxylic acid and *β*-caryophyllinic acid were estimated using glyceric acid, *meso*-erythritol, malic acid and pinic acid as surrogate standards, respectively. Field blank filters were treated as real samples for quality assurance. The results showed no contamination for any target species.

3 Results and discussion

3.1 Overview

Eight compound classes, i.e., anhydrosugars, sugars/sugar alcohols, lignin and resin products, sterols, polyacids, aromatic acids, biogenic SOA tracers, and two organic nitrogen-containing compounds (oxamic acid and urea) were detected in the aerosol samples with a total concentration range of 93–685 ng m^{-3} (mean 299 ng m^{-3}) in summer and 105–939 ng m^{-3} (257 ng m^{-3}) in spring (Fig. 2 and Table 2). Figure 3 shows the major resolved organic components of total aerosol extracts. Table 2 presents the concentrations of all the identified organic compounds. In summer, anhydrosugars, sugars/sugar alcohols, lignin and resin acids, biogenic SOA tracers, hydroxy-/polyacids, and organic nitrogen compounds were the major compound classes, while sterols and aromatic acids were relatively minor (Fig. 3). In spring, however, lignin and resin acids became minor along with sterols and aromatic acids (Fig. 3). Dehydroabietic acid (on average) was the most abundant single compound in summer, followed by levoglucosan, urea, 2-methyltetrols and malic acid. In contrast, levoglucosan was the most abundant single compound in spring, followed by urea and malic acid (Table 2).

3.2 Biomass burning tracers

Biomass burning is an important source of atmospheric gases and particles on both regional and global scales. Particles produced by biomass burning can influence the global climate by scattering and absorbing radiation or acting as cloud condensation nuclei (CCN). Levoglucosan, produced during pyrolysis of cellulose, has been recognized as a key tracer for biomass burning (Simoneit, 2002). In the present study, levoglucosan was detected sometimes very abundantly (up to 305 ng m^{-3}) in the springtime aerosols, indicating a potential impact of biomass burning to the regional air quality and climate in Central China.

Galactosan (G) and mannosan (M), the isomers of levoglucosan (L), were also detected in aerosol samples. They are also tracers for the burning of cellulose/hemicellulose (Simoneit, 2002). Fabbri et al., (2009) reported that the emission factors of levoglucosan and mannosan from burning of lignites are similar to those from burning of extant biomass fuels, while galactosan cannot be detected in lignite smoke. The isomeric ratios of levoglucosan/mannosan (L/M) ranged from 5.5–23 (mean 15) in summer to 5.8–25 (mean 14) in spring (Table 2). These values are similar to those found for wood smokes (0.6–32), rice straw burning aerosols (15–61) (Engling et al., 2013), and within the generic range (3.5–75) for ambient aerosols (Sheesley et al., 2003; Fu et al., 2008; Fabbri et al., 2009; Sang et al., 2013). In general, hardwood smoke aerosols show higher L/M ratios (3.3–32) than softwood smoke aerosols (0.6–13.8) (Fabbri et al., 2009). The ratios of L/(G+M) ranged from 3.7–14 (mean 8.9) in summer and 4.4–15 (mean 8.8) in spring, which are also similar to those (3.2–14) reported in ambient aerosols (Fabbri et al., 2009).

Three lignin and resin acids (4-hydroxybenzoic, vanillic, and dehydroabietic acids) were detected in the samples with a total concentration of 64 ± 33 ng m^{-3} in summer versus 8.7 ± 4.7 ng m^{-3} in spring (Table 2). These acids have been found in both smoke particles (Oros and Simoneit, 2001; Simoneit, 2002) and ambient aerosols (Simoneit, 2002; Fu et al., 2008, 2013). Vanillic acid is a specific source tracer for conifers. Dehydroabietic acid is a diterpenoid that is present in vegetation smoke, both as natural and thermally altered products (Medeiros and Simoneit, 2008).

Cholesterol is a tracer for smoke particles generated from meat cooking and also has been proposed as a source marker of marine organisms (Simoneit and Elias, 2000). Its concentration was higher in summer (3.1–23 ng m^{-3}, mean 10 ng m^{-3}) than in spring (0.52–13 ng m^{-3}, 5.5 ng m^{-3}). β-Sitosterol is present in terrestrial higher plants and emitted to the air via biomass burning (Simoneit, 2002). The abundant presence of sterols, lignin and resin acids, and anhydrosugars in the troposphere over Central China indicates that biomass/biofuel burning is an important source of organic aerosols in this region.

3.3 Water-soluble sugars and sugar alcohols

Primary saccharides consisting of arabinose, fructose, glucose, sucrose, maltose, and trehalose, as well as some saccharide polyols (including arabitol, mannitol and inositol), were detected in the samples (Fig. 4). Positive correlations between arabitol and mannitol were found in both spring and summer seasons (Fig. 5a–b), supporting the idea that they are tracers for airborne fungal spores (Lewis and Smith, 1967; Bauer et al., 2008). Higher concentrations of arabitol and mannitol were observed in spring than in summer (Table 2). This is reasonable because, besides airborne fungal spores, biogenic emissions of arabitol and mannitol as pollen may also be significant due to enhanced activities of vegetation during spring blossom season.

Fructose, glucose and sucrose originate from plant materials such as pollen, fruits, and their fragments (Speranza et al., 1997; Pacini, 2000). In addition, they may also result from biomass burning (Medeiros and Simoneit, 2008). A strong positive correlation ($R^2 = 0.67$, $p<0.01$) was obtained for fructose and glucose in spring. However, no significant correlation ($R^2 = 0.07$, $p<0.01$) was found in the summertime samples, indicating that fructose and glucose may have different sources and/or photooxidation pathways. Trehalose (glucose + glucose) is present in a variety of microorganisms (fungi, bacteria and yeast), and a few higher plants and invertebrates (Medeiros et al., 2006). Trehalose is the most abundant saccharide in soils, and is proposed as a tracer for the resuspension of surface soil and unpaved road dust (Simoneit et al., 2004a).

3.4 Biogenic SOA tracers in the troposphere

Eight compounds were identified as isoprene SOA tracers in the samples, including 2-methyltetrols (2-methylthreitol and 2-methylerythritol), 2-methylglyceric acid (2-MGA), C_5-alkene triols, and *cis*- and *trans*-3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4-diols) (Table 2). In summer, concentration ranges of 2-methylthreitol and 2-methylerythritol were 0.51–34 ng m^{-3} (8.0 ng m^{-3}) and 1.0–71 ng m^{-3} (17 ng m^{-3}), respectively. They are more than twice higher than those (2.3 ± 1.7 ng m^{-3} for 2-

methylthreitol and 6.3 ± 6.0 ng m^{-3} for 2-methylerythritol) in spring. A recent study (Nozière et al., 2011) has shown that the primary emission of 2-methyltetrols from plants should be considered. Based on observed positive correlation between 2-methyltetrols and sugars, Cahill et al. (2006) suggested that 2-methyltetrols are directly emitted from a similar biological source in addition to the photochemical production. Here, the correlation efficient (R^2) for 2-methylthreitol and 2-methylerythritol is 0.98 in summer (Fig. 5c), suggesting a photochemical origin of these compounds rather than direct emission from plants. Interestingly, the correlation between 2-methylthreitol and 2-methylerythritol is slightly weaker in spring (R^2 = 0.87, Fig. 5d) than in summer, possibly due to a potential contribution from biological sources in spring.

Under low-NO_x conditions, gas-phase isoprene epoxydiols (IEPOX) that formed from the oxidation of isoprene hydroxyhydroperoxides (ISOPOOH) are likely to be key intermediates for isoprene SOA (Paulot et al., 2009). 3-MeTHF-3,4-diols can be formed from IEPOX via acid-catalyzed intermolecular rearrangement (Lin et al., 2012). Concentrations of 3-MeTHF-3,4-diols were higher in summer (0.03–0.79 ng m^{-3}, mean 0.29 ng m^{-3}) than those in spring (0–0.38 ng m^{-3}, 0.13 ng m^{-3}) (Table 2). These values were much lower than that (27 ng m^{-3}) reported in the ambient $PM_{2.5}$ sample collected in Yorkville, GA during the summer of 2010 (Lin et al., 2012), while they were about one order of magnitude higher than those (0.001–0.070 ng m^{-3}, mean 0.013 ng m^{-3}) reported in marine aerosols collected during the France-Canada-USA joint Arctic campaign, MALINA, which was conducted in the Southern Beaufort Sea, Canadian Arctic in summer 2009 (Fu et al., 2013).

Concentration ranges of C_5-alkene triols were 1.2–50 ng m^{-3} (11 ng m^{-3}) in summer and 0.32–7.0 ng m^{-3} (2.6 ng m^{-3}) in spring, much lower than those reported in subtropical Hong Kong (50 ng m^{-3}) (Hu et al., 2008) and Mount Tai in the North China Plain (2.6–64 ng m^{-3}, 18 ng m^{-3}) (Fu et al., 2010). 2-MGA can be formed by the oxidation of methacrolein and methacrylic acid, two major gas-phase oxidation products of isoprene. The levels of 2-MGA were lower in summer (0.55–6.2 ng m^{-3}, 2.7 ng m^{-3}) than in spring (0.88–9.7 ng m^{-3}, 3.5 ng m^{-3}), opposite to the trends of 2-methyltetrols and C_5-alkene triols.

The detected α/β-pinene oxidation products include pinonic, pinic, 3-hydroxyglutaric, and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). These species have been used to evaluate the role of monoterpene oxidation in the formation of SOA (Kavouras et al., 1999; Kleindienst et al., 2007). Monoterpenes account for 35 % of the global emissions of biogenic VOCs (Griffin et al., 1999). Both 3-hydroxyglutaric acid (3-HGA) and MBTCA can be produced by irradiating monoterpenes, e.g., α-pinene, in the presence of NO_x(Claeys et al., 2007; Szmigielski et al., 2007). The summertime concentrations of 3-hydroxyglutaric acid and MBTCA were 1.2–24 ng m^{-3} (8.5 ng m^{-3}) and 0.06–8.7 ng m^{-3} (1.9 ng m^{-3}), respectively. These values are similar to those in spring (Table 2).

β-Caryophyllinic acid, formed either by ozonolysis or by photo-oxidation of β-caryophyllene (Jaoui et al., 2007), was identified in all samples (0.08–5.2 ng m^{-3}) without any seasonal difference. These values were about ten times lower than those (1.2–39 ng m^{-3}, 12 ng m^{-3}) reported in tropospheric aerosols collected at the summit of Mt. Tai in the North China Plain in summer (Fu et al., 2010). Interestingly, β-caryophyllinic acid and levoglucosan showed a positive correlation ($R^2 = 0.83$) during the spring 2004 campaign (Fig. 5f), indicating that biomass burning may release β-caryophyllinic acid and/or its precursor followed by atmospheric oxidation and the biomass burning products are uplifted to the upper troposphere over China. This correlation was also found for the above-mentioned Mt. Tai aerosols (Fu et al., 2010), which were heavily influenced by the field burning of wheat straw in the North China Plain after the harvest in early June. In contrast, no correlation was found during the summer 2003 campaign (Fig. 5e). Similarly, such a seasonal difference was also found for the correlations between levoglucosan and non-sea-salt potassium (nss-K^+). nss-K^+ is an inorganic tracer of biomass burning. It correlated well with levoglucosan in spring ($R^2 = 0.86$), indicating a common emission from biomass burning. However, no correlation ($R^2 = 0.04$) was found in summer (Fig. 5g–h), suggesting that levoglucosan and nss-K^+ may have different sources and/or different atmospheric behaviors under strong solar irradiation in summer.

3.5 Hydroxy-/poly-acids

Both glycolic acid (hydroxyacetic acid) and salicylic acid (2-hydroxybenzoic acid) were detected in the aerosol samples. Glycolic acid is the smallest α-hydroxy acid that is hygroscopic and highly water-soluble. Interestingly, strong positive correlations were found between glycolic acid and 2-MGA ($R^2 = 0.88$ in summer and 0.80 in spring), suggesting that they have similar sources. Similar positive correlations ($R^2 = 0.72$ and 0.94, respectively) were previously reported in the Sierra Nevada Mountains of California (Cahill et al., 2006) and the Canadian high Arctic regions (Fu et al., 2009). These results suggest that glycolic acid and 2-MGA might be of the same origin because these two compounds are structurally very similar. It should be noted that in this study, the concentrations of glycolic acid were approximately 3–6 times higher than those of 2-MGA. In the Arctic aerosols, glycolic acid (0.33–4.3 ng m^{-3}, 2.0 ng m^{-3}) was about 10 times more abundant than 2-methylglyceric acid, and vice versa in the Sierra Nevada Mountain aerosols (Cahill et al., 2006). Besides, malic acid correlated well with 2-MGA (R^2>0.59) and 3-HGA (R^2>0.98) in the troposphere in both summer and spring aerosols, indicating a similar source.

3.6 Organic nitrogen species

Organic nitrogen (ON) is ubiquitous in the atmosphere and is an important component of wet and dry deposition, including amino acids, urea, organic nitrates, nitro-aromatics, humic-like substances, and others (Cornell et al., 1998; Zhang et al., 2002; Mace et al., 2003; González Benítez et al., 2010; Shi et al., 2010). Two nitrogen-containing organic compounds (carbamide and oxamic acid) were detected here. The levels of carbamide, generally known as urea, are 0.52–99 ng m^{-3} (mean 36 ng m^{-3}) in summer, which are similar to those in spring (9.1–80 ng m^{-3}, 39 ng m^{-3}). These values are higher than those (0–40 ng m^{-3}) reported in aircraft samples over the northwestern Pacific during the ACE-Asia campaign (Simoneit et al., 2004b). Urea could be primarily emitted from agricultural activities in Central China. However, urea may also be a secondary product from atmospheric reactions (Simoneit et al., 2004b).

Little is known about oxamic acid (H_2N-CO-COOH) in the atmosphere. Oxamic acid is amino-substituted glyoxylic acid; the latter has been reported in aerosols as abundant species following oxalic acid (Kawamura, 1993; Kawamura and Yasui, 2005). One potential source of atmospheric oxamic acid could be the photooxidation of nitrogen-containing organic compounds that are derived from both anthropogenic and natural sources, e.g., paracetamol (Yang et al., 2009) and acetamide (Karpel Vel Leitner et al., 2002). Concentrations of oxamic acid were higher (0–46 ng m^{-3}, 10 ng m^{-3}) in the springtime samples than those (0–14 ng m^{-3}, 4.9 ng m^{-3}) in summer, suggesting that oxamic acid and/or its precursors may be emitted into the atmosphere in larger amounts in spring. Another possibility is that oxamic acid can be efficiently oxidized under stronger solar irradiation over Central China in summer. Further oxidation of oxamic acid yields nitrate ions (Karpel Vel Leitner et al., 2002) and small organic acids such as glyoxylic and oxalic acids (Emilio et al., 2005).

3.7 Vertical distribution of POA and SOA tracers

Figure 6 shows the vertical profiles of major organic species among the identified organics. It is noticeable that with increasing altitude, concentrations of most organic species (e.g., levoglucosan, mannitol, phthalic acid, MBTCA, and pinic acid) decrease in both seasons, owing to the atmospheric dilution during upward transport. During the ACE-Asia campaign, a large organic carbon aerosol source was observed in the free troposphere over the downwind regions of China (Heald et al., 2005), which is proposed to be mainly from isoprene-derived SOA (Henze and Seinfeld, 2006). However, in the present study, high concentrations of both primary (e.g., sucrose, trehalose and cholesterol) and secondary organic aerosol tracers (e.g., 2-methyltetrols, pinonic acid), as well as urea, are occasionally observed at a high altitude up to 3 km (Fig. 6). As mentioned earlier, sucrose is a tracer for airborne pollen and trehalose for soil resuspension. Cholesterol can be emitted into the atmosphere from marine biota and meat cooking. These POA tracer profiles suggest that in addition to SOA, primary organic aerosols can also be uplifted to the upper troposphere.

Furthermore, the mass concentration ratios of some biogenic SOA tracers to sulfate (SO_4^{2-}) showed an intriguing ">-shape" vertical profile during the summer 2003 campaign (Fig. 7); the concentration ratios increased with altitude up to ca. 2 km, and then decreased with increasing altitude. These SOA tracers include 2-MGA, 3-HGA and MBTCA, which are considered as higher-generation products from the oxidation of isoprene and α/β-pinene (Kourtchev et al., 2009). Malic acid (Fig. 7g) and tricarballylic acid (Fig. 7i) also showed similar vertical profiles.

However, no ">-shape" pattern was observed during the spring 2004 campaign. Interestingly, such vertical patterns were not found for POA tracers including biomass burning tracers (e.g., levoglucosan), fungal spore tracers (arabitol and mannitol), sucrose, trehalose, as well as some biogenic SOA tracers such as 2-methyltetrols and pinonic acid during both campaigns; 2-methyltetrols and pinonic acid are first-generation products from the oxidation of isoprene and α/β-pinene, respectively. It should be noted that the concentrations of sulfate were much higher in summer (1720–7140 ng m^{-3}, mean 3270 ng m^{-3}) than those (29.6–305 ng m^{-3}, 86.8 ng m^{-3}) in spring, while the concentrations of biogenic SOA tracers were similar in both seasons.

The observed ">-shape" profiles for higher-generation SOA tracers indicate that under high sulfate conditions in summer, some unique photochemical pathways (aging processes) may have occurred during the upward transport of biogenic SOA and/or their precursors from the lower to free troposphere over Central China. Ervens et al. (2011) reported that under the conditions of higher relative humidity and higher loadings of biogenic VOC and NO_x, SOA can be significantly formed in cloud droplets and aqueous particles. Thus, cloud processing may enhance the formation of higher-generation SOA tracers at an altitude around 2 km over Central China, a point that warrants further study. The observed decreasing trend in the ratios of organic species to sulfate at elevation above 2 km may be explained by less efficient wet removal of SO_2 than those of preexisting aerosols and oxidized VOCs during air mass lifting (Dunlea et al., 2009). The further processing of the resulting air mass may thus lead to the formation of particles relatively enriched with sulfate compared to organics. Indeed, in a study performed at Whistler Peak in western Canada, the highest sulfate to organic aerosol ratios (> 10) were observed in highly aged air masses that descended from above 3 km (Sun et al., 2009).

3.8 Relative abundances of levoglucosan, fungal spore tracers, SOA tracers and urea below and above 2 km

As mentioned above, levoglucosan is a specific tracer for biomass burning; arabitol and mannitol are tracers for fungal spores in the atmosphere; urea is a organic-nitrogen containing compound that may be derived from both primary emission and photooxidation. The SOA tracers detected here include isoprene-, monoterpene- and sesquiterpene-oxidation products as listed in Table 2. The relative abundances of these POA and SOA tracers are shown in Fig. 8, which are briefly categorized into two groups for both summer and spring campaigns: above and below 2 km a.s.l. In general, SOA tracers were relatively more abundant in summer (43.4 % and 38.3 % below and up 2 km, respectively) than in spring (26.6 % and 23.4 % below and above 2 km, respectively). However, fungal spore tracers and levoglucosan showed higher percentages in spring than those in summer. In average, biomass-burning-, fungal spore- and SOA-tracers were more abundant near the ground surface (< 2 km) than those > 2 km, again suggesting that POA, SOA and their precursors are uplifted to the mid-troposphere from the ground surface. Interesting, urea was relatively more abundant at altitudes > 2 km than those < 2 km for both summer and spring campaigns, which may highlight the importance of secondary production of urea in the mid-troposphere.

In order to obtain further information on the relative abundances of secondary organic aerosols from the photooxidation of isoprene, monoterpenes and sesquiterpenes, a tracer-based method were used to estimate the secondary organic carbon (SOC) (Kleindienst et al., 2007). The carbon mass fraction of SOA tracers in SOC (f_{soc}) for an individual precursor is defined as=

$$f_{\mathrm{soc}} = \frac{\sum_i [\mathrm{tracer}_i]}{[\mathrm{SOC}]} \tag{1}$$

where $\sum_i[\mathrm{tracer}_i]$ is the sum of the concentrations of the selected suite of tracers for a same BVOC precursor. The laboratory-derived tracer mass fraction (f_{soc}) factors of 0.155 ± 0.039 for isoprene, 0.231 ± 0.111 for α-pinene and 0.0230 ± 0.0046 for β-caryophyllene (Kleindienst et al., 2007) were used in the present study. As shown in Fig. 9, the total SOC concentrations were several times higher in aerosols collected below 2000 m in both summer (566 ng m^{-3}) and spring (364 ng m^{-3}) than those up 2000 m in both seasons (153 ng m^{-3} and 98.9 ng m^{-3} in summer and spring, respectively). The isoprene-derived SOC contributed more than half of the total SOC in summer 2003, followed by monoterpene- and sesquiterpene SOC. The relative abundances of isoprene-, monoterpene- and sesquiterpene-SOC showed little difference in aerosols collected < 2 km and > 2 km in summer. In spring, however, the contribution of isoprene-SOC was less than that in summer; isoprene-SOC was comparable with monoterpene-SOC. In addition, sesquiterpene-SOC in the springtime aerosols could contribute 30.2 % and 20 % to total SOC below and above 2 km, respectively, indicating the importance of sesquiterpene-SOC in aerosol chemistry over Central China in spring.

The estimated isoprene-SOC concentrations ranged from 13.6 to 717 ng m^{-3} (179 ng m^{-3}) in summer and 18.6 to 242 ng m^{-3} (77.7 ng m^{-3}) in spring, which were slightly lower than those (10–2190 ng m^{-3}) reported in urban and rural sites in the Pearl River Delta region (Hu et al., 2008; Ding et al., 2012) and those (160–1120 ng m^{-3}, mean 540 ng m^{-3}) in summertime aerosols from a *Quercus* and *Picea* mixed forest in North Japan (Fu and Kawamura, 2011). Nevertheless, our results were similar to those (0–1380 ng m^{-3}, mean 250 ng m^{-3}) reported in Research Triangle Park, NC in 2006 (Offenberg et al., 2011), and also similar to those reported at the ground surface in

China. For example, Wang et al. (2008) investigated the summertime SOC levels from isoprene oxidation in four forests in East China; the estimated isoprene-SOC concentrations were 320 ng m^{-3} for Changbai Mountain, 30 ng m^{-3} for Chongming, 160 ng m^{-3} for Dinghu, and 270 ng m^{-3} for Hainan. Such a similarity strongly suggests the presence of a large amount of biogenic SOA not only near the ground surface, but also aloft in the troposphere over Central China.

4 Conclusions

Eight organic compound classes were determined in the tropospheric aerosols collected at the altitudes of 0.5–3.5 km by two aircraft campaigns over Central China with similar total concentrations in summer (299 ± 173 ng m^{-3}) to those in spring (257 ± 210 ng m^{-3}). The atmospheric levels of organic nitrogen compounds (oxamic acid and urea) are comparable to those of biogenic SOA tracers in both spring and summer. Concentrations of the measured organic species decreased with an altitude, suggesting that they are emitted from primary sources and/or produced by secondary oxidation of their precursors on the ground surface. High abundances of anhydrosugars, lignin/resin acids, and β-sitosterol suggest that biomass burning is an important source of organic aerosols in the troposphere over Central China. Further, primary biological aerosols and biogenic SOA can also significantly contribute to the tropospheric aerosols over Central China.

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Table 1. Information on sample identification (ID) number, sample duration, flight altitude (above ground level, a.g.l.), and air volume of each sample collected during two aircraft campaigns. Complete flight tracks are shown in Fig. 1.

Sample ID	Date	Time (hh:mm)	Altitude (km)	Air volume (m^3)
Summer 2003				
H1	8 Aug	07:08–11:18	2.35	19.3
H3	21 Aug	08:38–10:51	2.68	10.3
H5	21 Aug	10:58–12:34	0.89	7.42
H7	23 Aug	08:45–11:33	2.31	13.0
H9	23 Aug	11:38–13:11	0.85	7.19
H11	26 Aug	08:53–12:33	2.97	17.0
H15	4 Sep	08:30–09:58	2.72	6.81
H17	4 Sep	10:02–11:33	1.36	7.04
H19	5 Sep	08:48–11:13	2.57	11.2
H21	5 Sep	11:17–12:47	1.56	6.96
H23	10 Sep	10:11–15:16	2.78	23.6
H25	11 Sep	08:56–13:43	2.69	22.2
H27	13 Sep	12:37–14:47	2.42	10.1
H29	13 Sep	15:00–16:35	0.84	7.35
Spring 2004				
H-1	19 May	02:30–06:35	1.85	19.0
H-2	20 May	01:12–04:26	3.15	15.1
H-3	21 May	01:29–03:47	2.80	10.7
H-4	21 May	03:57–05:16	1.25	6.08
H-5	27May	00:07–02:08	2.60	9.31
H-6	27 May	02:12–03:34	1.40	6.36
H-7	28 May	04:29–08:10	3.50	17.1
H-8	30–31 May	23:56–02:04	2.40	9.85
H-9	31 May	02:08–03:28	0.95	6.20
H-10	31 May	17:24–18:58	2.70	7.29
H-11	31 May	19:04–20:19	0.85	5.82
H-12	7 Jun	01:02–04:11	2.50	14.7
H-13	9 Jun	03:54–05:44	1.30	8.56
H-14	9 Jun	05:48–07:05	2.60	5.93
H-15	10 Jun	01:37–03:41	2.60	9.64
H-16	10 Jun	03:45–05:28	0.85	7.99

Table 2. Average concentrations and concentration ranges for polar organic species detected in the aerosol samples (PM_{10}) collected by aircraft over Central China ($ng\,m^{-3}$).

Organic compounds	Summer 2003 (*n* = 14)				Spring 2004 (*n* = 16)			
	min	max	mean	std[a]	min	max	mean	std
I. Anhydrosugars								
galactosan (G)	0.08	7.9	1.6	2.1	0.29	9.3	2.1	2.8
mannosan (M)	0.22	11	2.3	3.1	0.68	14	3.1	3.6
levoglucosan (L)	2.4	197	38	55	7.1	305	52	77
subtotal	3.0	216	42	60	8.3	328	57	83
L/M ratio	5.5	23	15	4.7	5.8	25	14	6.0
L/(G+M) ratio	3.7	14	8.9	2.8	4.4	15	8.8	3.5
II. Sugars/sugar alcohols								
arabinose	1.7	15	6.4	3.7	0.57	10	2.0	2.4
arabitol	0.72	6.0	2.3	1.8	0.99	15	5.7	5.1
fructose	0.83	9.0	4.4	2.4	0.95	7.2	2.8	1.8
glucose	5.7	74	16	17	3.2	19	9.8	5.7
mannitol	0.83	12	4.1	3.4	0.75	19	5.5	5.1
inositol	0.13	4.4	1.1	1.2	0.20	1.4	0.66	0.42
sucrose	0.76	6.6	3.6	1.9	0.48	5.4	2.2	1.5
maltose	0.09	1.7	0.64	0.43	0.17	3.2	0.72	0.77
trehalose	0.50	3.6	1.6	1.1	0.61	3.2	1.5	0.76
subtotal	14	86	40	20	10	63	31	20
III. Lignin and resin acids								
4-hydroxybenzoic acid	0.87	12	4.2	3.8	1.9	13	5.7	3.4
vanillic acid	0.53	4.6	2.3	1.3	0.26	2.9	1.3	0.87
dehydroabietic acid	14	125	58	32	0.60	3.2	1.7	0.75
subtotal	16	134	64	33	3.8	18	8.7	4.7
IV. Sterols								
cholesterol	3.1	23	10	5.4	0.52	13	5.5	3.4
β-sitosterol	nd	5.2	2.0	1.7	nd	4.4	1.0	1.5
subtotal	3.6	27	12	6.5	0.52	13	6.6	3.7

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Table 2. Continued.

Organic compounds	Summer 2003 (n = 14)				Spring 2004 (n = 16)			
	min	max	mean	std[a]	min	max	mean	std
V. Biogenic SOA tracers								
2-methylglyceric acid	0.55	6.2	2.7	2.3	0.88	9.7	3.5	2.8
3-MeTHF-3,4-diols[c]	0.03	0.79	0.29	0.26	nd	0.38	0.13	0.12
C_5-alkene triols[d]	1.2	50	11	14	0.32	7.0	2.6	2.0
2-methylthreitol	0.51	34	8.0	8.7	0.43	6.1	2.3	1.7
2-methylerythritol	1.0	71	17	18	1.3	25	6.3	6.0
3-hydroxyglutaric acid	1.2	24	8.5	7.7	2.5	64	11	15
pinonic acid	0.87	7.7	3.6	2.3	0.76	7.1	2.2	1.7
pinic acid	0.57	5.4	2.3	1.4	0.37	10	2.7	2.4
MBTCA[e]	0.06	8.7	1.9	2.4	0.13	8.3	1.7	2.0
β-caryophyllinic acid	0.15	3.4	1.2	1.1	0.08	5.2	1.4	1.6
subtotal	7.5	168	57	49	8.6	128	34	30
Σisoprene SOA tracers	3.3	138	39	38	3.2	42	15	11
Σα/β-pinene SOA tracers	3.9	38	16	13	4.6	90	18	21
VI. Aromatic acids								
phthalic acid	1.7	14	7.0	4.7	2.4	47	10	11
isophthalic acid	0.06	2.3	0.66	0.64	0.09	1.6	0.41	0.42
terephthalic acid	0.01	1.8	0.58	0.49	0.04	6.1	0.85	1.5
subtotal	1.8	17	8.3	5.5	2.6	55	11	13
VII. Hydroxy-/poly-acids								
glycolic acid	0.75	20	8.0	6.9	4.9	55	21	13
glyceric acid	1.9	17	6.3	4.8	2.7	71	12	16
malic acid	3.9	49	17	15	5.5	124	22	29
tartaric acid	0.09	4.1	0.75	1.0	0.34	29	2.9	7.0
citric acid	0.03	1.1	0.34	0.28	0.15	3.3	0.66	0.74
tricarballylic acid	0.15	4.4	1.6	1.4	0.33	9.5	1.8	2.3
subtotal	7.4	88	34	27	16	291	60	66
VIII. Organic nitrogen compounds								
oxamic acid	nd	14	4.9	4.7	nd	46	10	13
carbamide (urea)	0.52	99	36	30	9.1	80	39	24
subtotal	0.54	102	41	33	12	88	49	25
Total measured organics	93	685	299	173	105	939	257	210

[a] std: standard deviation; [b] nd: not detected; [c] 3-MeTHF-3,4-diols: the sum of *trans*- and *cis*-isomers. [d] C_5-alkene triols: the sum of *cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene; [e] MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

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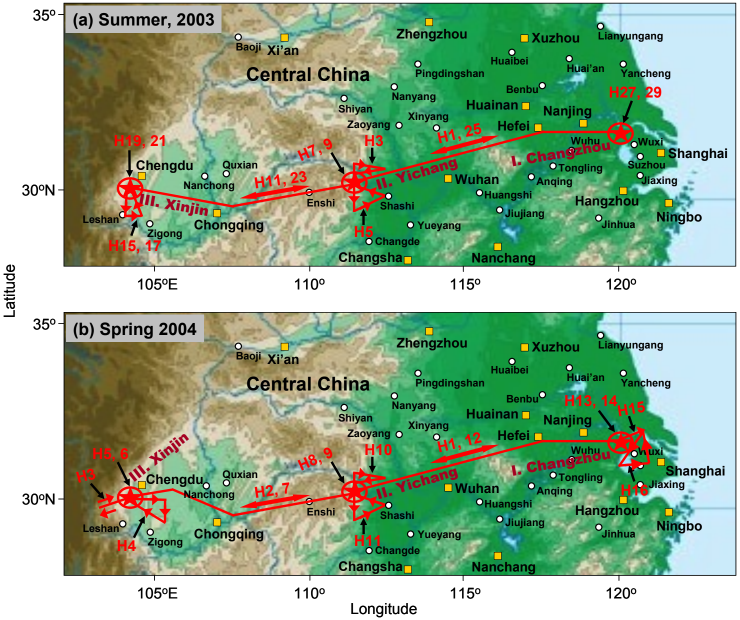

Fig. 1. Flight tracks during **(a)** summer of 2003 (8 August–13 September) and **(b)** spring of 2004 (19 May–10 June) over Central East to West China. The hovering flights (H7,9, H19,21, and H27,29 in **(a)**, and H5,6, H8,9, and H13,14 in **(b)**) over local cities were named as O-shape flight and shown as circles. Flights H3, H5, and H15,17 in **(a)**, and flights H3, H4, H10, H11, H15, and H16 in **(b)** were also designed for local cities (named as L-shape flight). Capital cities with populations more than one million are shown in yellow squares.

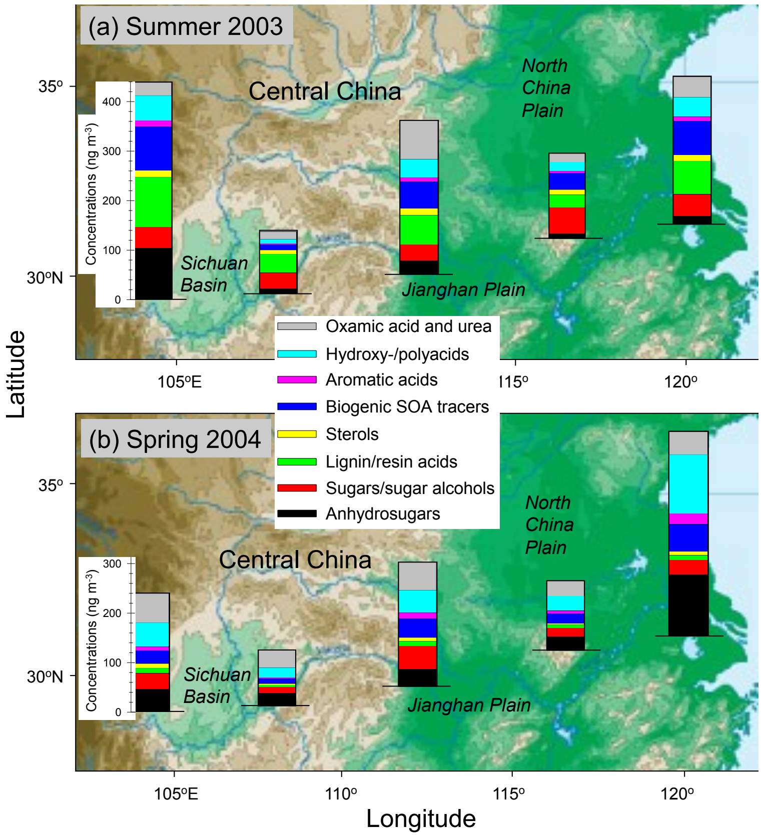

Fig. 2. Spatial distributions of organic compound classes measured in the aerosol samples (PM_{10}) collected over Central China. Concentrations of organic species from flights over local cities are averaged for their local abundances, while concentrations of organic compounds in the samples collected during the round flights between two cities are averaged and shown as a column in the middle of the cities.

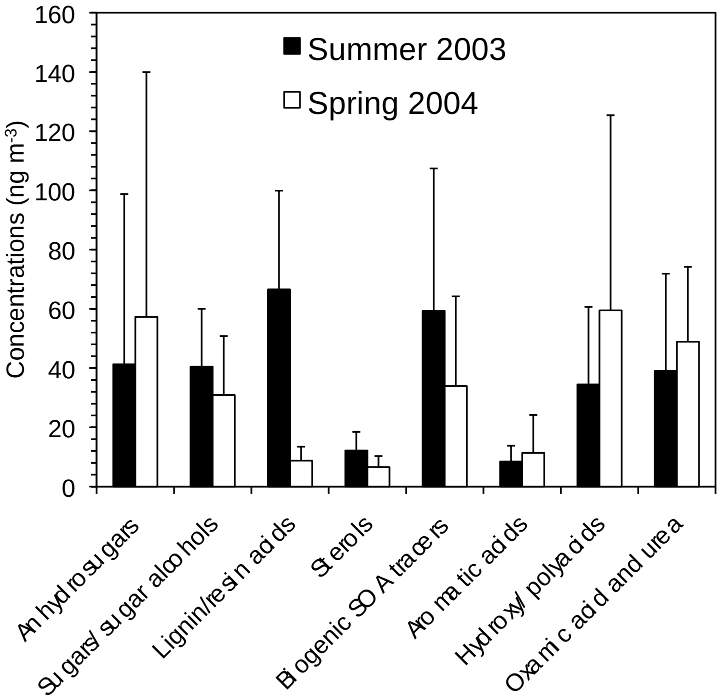

Fig. 3. Total concentrations of organic compound classes detected during two aircraft campaigns. Anhydrosugars, aromatic acids, hydroxy/polyacids and oxamic acid and urea were lower in summer than in spring, while sugars/sugar alcohols, lignin/resin acids, sterols and biogenic secondary organic aerosol (SOA) tracers showed higher levels in summer than in spring.

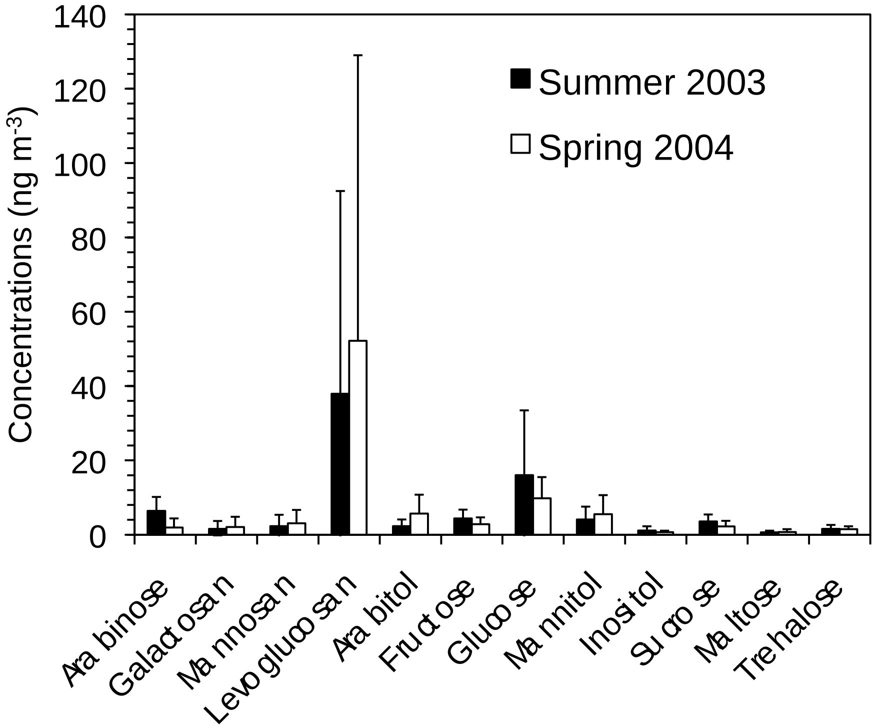

Fig. 4. Molecular distributions of sugar compounds detected in the aerosol (PM_{10}) samples collected during aircraft campaigns in summer 2003 and spring 2004.

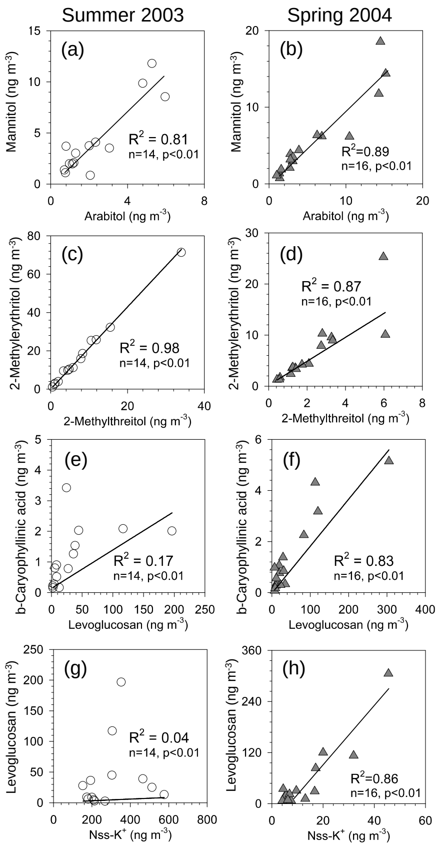

Fig. 5. Relationships between the concentrations of the chemical species identified in the aerosol samples. Circles represent the samples collected in summer 2003 (left), while triangles represent those collected in spring 2004 (right).

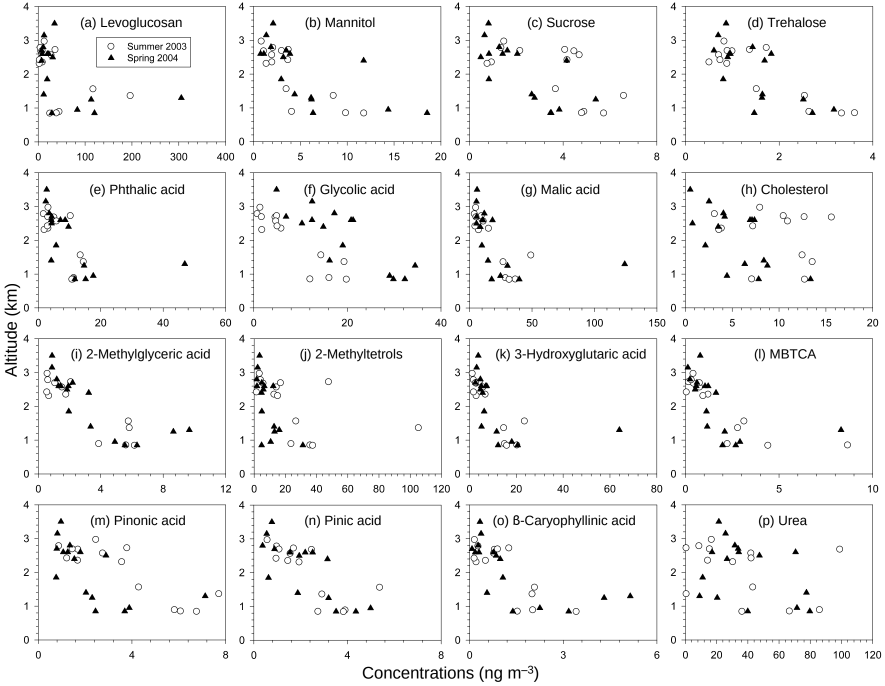

Fig. 6. Vertical profiles of polar organic tracers in aerosol particulate matter (PM$_{10}$) collected during two aircraft campaigns over Central China in summer 2003 and spring 2004, respectively.

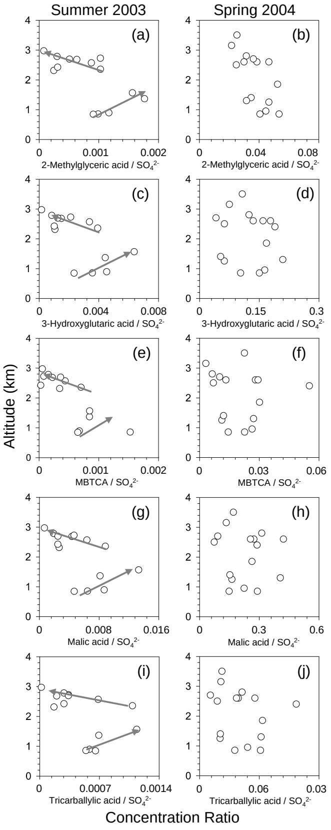

Fig. 7. Vertical profiles of mass concentration ratios of SOA tracers to sulfate (SO_4^{2-}) in the aerosols samples (PM_{10}) collected during the summer 2003 (left) and spring 2004 (right) aircraft campaigns over Central China.

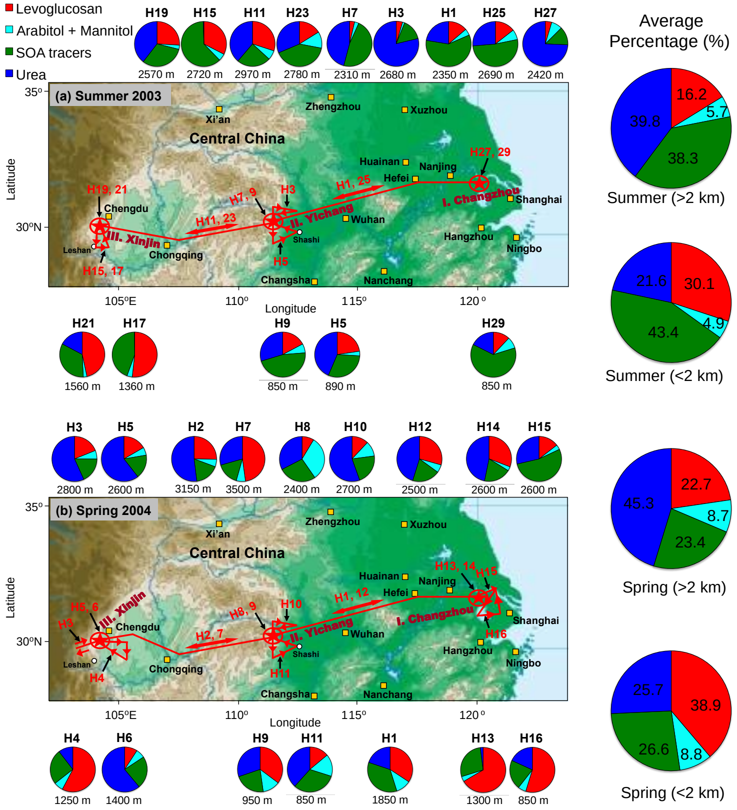

Fig. 8. Relative abundances (%) of POA and SOA tracers in the tropospheric aerosol particles (PM_{10}) over Central China. The right-side pie diagrams with percentage values (%) show the averaged relative abundances for aerosol samples collected at relatively high (> 2 km) and low (< 2 km) altitudes in both seasons.

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Aircraft measurements of polar organic tracer compounds

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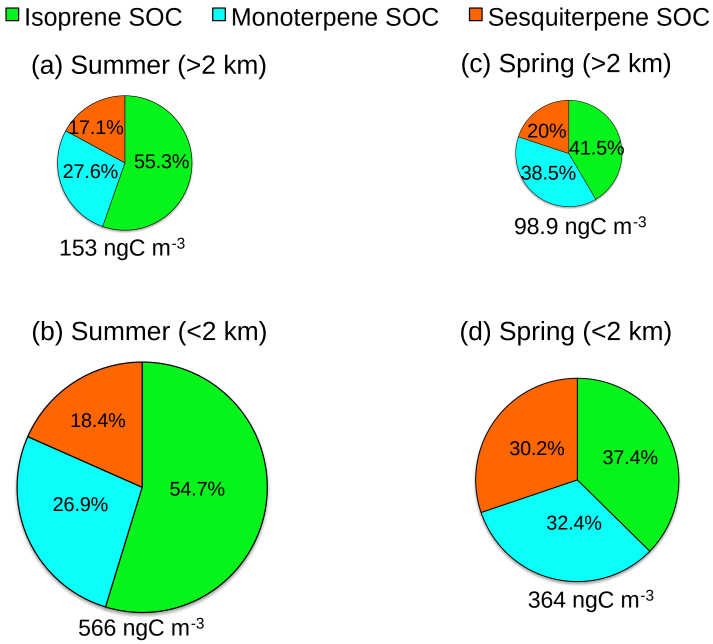

Fig. 9. Averaged concentrations of secondary organic carbon (SOC) and the relative abundances of SOA from the oxidation of isoprene, monoterpene and sesquiterpene in the aerosol samples collected at relatively high (> 2 km) and low (< 2 km) altitudes in both seasons. SOC values are estimated using a tracer-based method by Kleindienst et al. (2007). The sizes of the pie diagrams are proportional to the averaged total SOC concentrations for each category.