https://doi.org/10.1016/j.atmosenv.2015.08.095

Anthropogenic and biogenic organic compounds in summertime fine aerosols (PM2.5) in Beijing, China

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Abstract

Ambient fine aerosol samples ($PM_{2.5}$) were collected at an urban site (PKU) in Beijing and its upwind suburban site (Yufa) during the CAREBEIJING-2007 field campaign. Organic molecular compositions of the $PM_{2.5}$ samples were studied for seven organic compound classes (sugars, lignin/resin acids, hydroxy-/polyacids, aromatic acids, biogenic SOA tracers, fatty acids and phthalates) using capillary GC/MS to better understand the characteristics and sources of organic aerosol pollution in Beijing. More than 60 individual organic species were detected in $PM_{2.5}$ and were grouped into different compound classes based on their functional groups. Concentrations of total quantified organics at Yufa (469–1410 ng m^{-3}, average 1050 ng m^{-3}) were slightly higher than those at PKU (523–1390 ng m^{-3}, 900 ng m^{-3}). At both sites, phthalates were found as the most abundant compound class. Using a tracer-based method, the contributions of the biogenic secondary organic carbon (SOC) to organic carbon (OC) were 3.1% at PKU and 5.5% at Yufa, among which isoprene-SOC was the dominant contributor. In addition, most of the measured organic compounds were higher at Yufa than those at PKU, indicating a more serious pollution in its upwind region than in urban Beijing.

Key words: Secondary organic aerosol; Biomass burning; Levoglucosan; 2-Methyltetrols; Phthalates

1. Introduction

Fine aerosol particles ($PM_{2.5}$, <2.5 µm in aerodynamic diameter) are the major air pollutant in most megacities in China during the past decade (Chan and Yao, 2008). They are a complicated mixture of inorganic substances (e.g. metal ions, sulfate, ammonium, nitrate) and hundreds of organic compounds (e.g. fatty acids, *n*-alkanes, dicarboxylic acids, sugar compounds, and biogenic SOA tracers). Organic aerosols, which are essential components in the atmosphere (de Gouw and Jimenez, 2009), are the largest contributor to the atmospheric fine particles in highly industrialized cities (Xu et al., 2005; Feng et al., 2006). Considerable efforts have been devoted during the last decade to understand the sources and formation processes of organic aerosols in the atmosphere (Kanakidou et al., 2005; Hallquist et al., 2009). Generally, organic particles are comprised of primary organic aerosols (POA) and secondary organic aerosols (SOA). POA are directly emitted from sources such as higher plants, soil dust, biomass and fossil fuel burning (Simoneit et al., 1999; de Gouw and Jimenez, 2009; Chen et al., 2013; Pavuluri et al., 2013), while SOA are formed by the oxidation of gas-phase precursors in situ or through long-range transport in the atmosphere (Hallquist et al., 2009; Kundu et al., 2010; Aggarwal et al., 2013).

Biomass burning is a significant source of atmospheric gases and particles on a regional to global scale (Simoneit et al., 1999; Andreae and Merlet, 2001; Engling et al., 2006; Chen et al., 2013; Li et al., 2013; Pavuluri et al., 2013). Particles derived by biomass burning can influence the global climate by absorbing radiation and acting as cloud condensation nuclei (CCN) (Mochida and Kawamura, 2004). Plastics are versatile polymeric materials produced and used worldwide (Simoneit et al., 2005). Phthalic acid esters (phthalates) are widely manufactured as plasticizers and also used in cosmetics, lubricants, and other products (Thuren and Larsson, 1990). Health and environmental hazards of the esters are associated with potential carcinogenic and endocrine disrupting properties, which have been the subject of scientific discussion and public concern (Xie et al., 2007). Plants and microbial activities release a lot of organic matter into the aerosols, such as sugars and sugar alcohols, fatty acids and so on. Biogenic volatile organic compounds (VOCs) that are released from vegetation include isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons such as alcohols, aldehydes and ketones (Guenther et al., 2006). The VOC-derived organics account for up to 70% of the fine aerosol mass, and potentially control the physicochemical properties of atmospheric particles (Kanakidou et al., 2005). Isoprene (2-methyl-1, 3-butadiene, C_5H_8) is highly reactive due to the presence of C=C bonds, which makes it susceptible to react with oxidants. The global emissions of biogenic terpenes and anthropogenic hydrocarbons are both far lower than that of isoprene (500–750 Tg yr^{-1}) (Guenther et al., 2006).

Beijing is the capital of China and is one of the major metropolises in the world. With the growing urbanization, rapid economic development and large energy consumption, Beijing has been suffering with serious air pollution over the past two decades. Both anthropogenic and biogenic sources contribute to the atmospheric fine particles ($PM_{2.5}$), which is the most serious environmental issue in Beijing nowadays (Guo et al., 2012; Sun et al., 2013; Huang et al., 2014); About 40–60% of the fine aerosol mass is composed of organic materials (He et al., 2001; Huang et al., 2014). Many organic constituents in $PM_{2.5}$ are recognized as mutagenic or carcinogenic compounds, which are generated from anthropogenic sources. Given the high aerosol loading in China, a better understanding of aerosol composition and sources in the polluted atmosphere can effectively contribute to help policy makers to reduce aerosol loadings on a regional scale.

The objective of this study is to investigate the daily variations of both POA and SOA components in $PM_{2.5}$ samples collected at an urban site (PKU) and a suburban site (Yufa) in Beijing during summertime. Here, we report the concentrations, molecular distributions and temporal variations of seven organic compound classes (more than 60 organic species) in the fine aerosols. A tracer-based method (Kleindienst et al., 2007) was used to estimate the contributions of SOC from photooxidation of isoprene, monoterpenes, and β-caryophyllene to aerosol OC. Based on the molecular distributions, we report their possible sources, formation processes, and the contributions of different organic compounds to OC in the PM$_{2.5}$ samples.

2. Experimental Section

2.1 Aerosol sampling

Fine aerosol particles (PM$_{2.5}$) were collected at Peking University (PKU, 39°59′21″N, 116°18′25″E, the urban site) and Yufa (39°30′49″N, 116°18′15″E, the upwind suburban site) simultaneously during the CAREBeijing-2007 (Campaigns of Air quality REsearch in BEIJING and surrounding regions during August 3–31, 2007). There are less industrial facilities and more farmlands and residential areas near Yufa than PKU. Yufa has very weak local emissions except for domestic coal and biomass burning. PM$_{2.5}$ samples were collected on preheated (800°C, 3 hours) quartz-fiber filters (47 mm, Whatman) by mini-volume air samplers (Airmetrics, Eugene, Oregon) at a flow rate of 5 L min^{-1} for 24 hours. One field blank filter was prepared for each site. After the sampling, each filter was placed in a clean glass jar with a Teflon-lined screw cap and stored in a dark freezer room at –20°C prior to analysis.

2.2 Extraction, derivatization and GC/MS analysis

Detailed analytical method has been described in the supporting material. Briefly, filter aliquots were extracted with dichloromethane/methanol (2:1; v/v) under ultrasonication. The solvent extracts were concentrated by the use of a rotary evaporator, and then blown down to dryness with pure nitrogen gas. The extracts were then reacted with 50 µl of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 µl of pyridine at 70°C for 3 h. After reaction, the derivatives were diluted with *n*-hexane prior to GC/MS injection.

GC/MS analyses were performed on a Hewlett-Packard model 6890 GC coupled to

Hewlett-Packard model 5973 MSD. Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data (Kleindienst et al., 2007; Fu et al., 2008; Hu et al., 2008). Its relative standard deviation based on these two methods was <5%. Two field blank filters were treated as the real samples for quality assurance. Target compounds were not detected in the blanks. Recoveries for the authentic standards or surrogates were generally better than 80%. The data reported here were not corrected for the recoveries. Relative standard deviation of the concentrations based on duplicate sample analysis was generally <15%.

3. Results and Discussion

Seven organic compound classes were detected in the Beijing $PM_{2.5}$ aerosols based on functional groups and sources, i.e., fatty acids, sugars/sugar alcohols, lignin and resin products, hydroxyl and aromatic acids, plasticizers, polyacids, and biogenic SOA tracers (Fig. 1). Table 1 presents the concentrations of organic compounds detected in this study. Among them, phthalates, fatty acids and sugars/sugar alcohols are the major compound classes, while other compound classes were relatively minor. As a single compound detected (on average), di-(2-ethylhexyl) phthalate (DEHP) was the most abundant, followed by $C_{16:0}$ fatty acid, di-n-butyl (DnBP), diisobutyl phthalate (DiBP) and levoglucosan.

3.1 Plant emission and microbial input

Many organic compounds such as sugars and sugar alcohols originate from plant emission and microbial activity. They have been proposed as tracers for primary biological aerosol particles including developing leaves, pollen, fungi and bacteria (Yttri et al., 2007; Fu et al., 2012a). The concentrations of sugars in $PM_{2.5}$ samples from PKU and Yufa ranged from 88 to 275 ng m^{-3} and 121 to 300 ng m^{-3}, respectively. The average concentrations of total sugars/sugar alcohols at Yufa (203±63 ng m^{-3}) were more abundant than at PKU (142±54 ng m^{-3}) (Table S1), suggesting higher biological activities due to more vegetation at the suburban site.

Fungal spores are important sources of primary organic carbon. For example, Bauer et al. (2008) reported that arabitol and mannitol are tracers the quantification of airborne fungal spores. Trehalose is present in a variety of microorganisms (fungi, bacteria and yeast), a few higher plants and invertebrates (Medeiros et al., 2006). In the present study, the concentrations of these three tracers at Yufa were higher than at PKU (Fig. 2), indicating an enhanced biogenic source at Yufa. The high peak concentrations of arabitol and mannitol at Yufa preceded those at PKU (Fig. 2). This is reasonable that Yufa is an upwind suburban site; more plant emissions and microbial input occur at countryside. Their temporal patterns are similar to that of levoglucosan (Fig. 3a), suggesting that biomass-burning activities may enhance the emission of sugar alcohols. Another explanation is that fungal spores and other primary bioaerosols may be adsorbed onto smoke aerosols to be co-transported to the sampling site. The ratios of mannitol to arabitol were 0.70–3.0 (average 1.3) at PKU and 0.72–1.5 (1.0) at Yufa. Besides, a relatively weak correlation was observed between arabitol and mannitol (R^2=0.33 at PKU; R^2=0.30 at Yufa), which may imply a high diversity of fungal spores in $PM_{2.5}$ in Beijing. Different fungal species may contain various levels of arabitol and mannitol. The discharge of fungal spores into the atmosphere from different fungi is highly variable, depending on location, season, weather, as well as time of day (Burshtein et al., 2011). Rather, a recent study has reported that the global diversity of fungal spores in soils (Tedersoo et al., 2014); fungi may emit into the atmosphere through soil resuspension.

Fatty acids were measured in $PM_{2.5}$ samples including $C_{12:0}$–$C_{30:0}$ and unsaturated acids (e.g. $C_{16:1}$ and $C_{18:1}$) (Fig. 1a). Higher molecular weight (HMW, $C_{20:0}$–$C_{30:0}$) fatty acids are derived from terrestrial higher plant wax whereas lower molecular weight (LMW, <$C_{20:0}$) fatty acids have multiple sources such as vascular plants, microbes, marine phytoplankton, as well as kitchen emissions (Simoneit and Mazurek, 1982a; Schauer et al., 2001). The concentration ratios of LMW/HMW fatty acids were 16.9±7.23 at PKU versus

17.2±10.0 at Yufa. These values are much higher than those reported in Mt. Tai aerosols (LMW/HMW were 1.0±0.80) in Central East China (Fu et al., 2012b) and even higher than those in tropical Indian PM_{10} aerosols (5.3±1.8) during summertime (Fu et al., 2010). Thus, our results suggest that much more LMW fatty acids are emitted from microbial sources in Beijing in summer, especially at the suburban site. Besides saturated fatty acids, two unsaturated fatty acids, oleic ($C_{18:1}$) and palmitoleic ($C_{16:1}$) acids were found in the $PM_{2.5}$ samples. The presence of unsaturated fatty acids in aerosols is indicative of recent biogenic inputs from higher plants and microbial/marine sources. In urban environments, cooking, motor vehicles, and biomass burning can also be the major anthropogenic sources of these acids (Rogge et al., 1993, 1996). Oleic acid is unstable and can be rapidly oxidized and degraded in the atmosphere (Kawamura and Gagosian, 1987). Thus $C_{18:1}/C_{18:0}$ is often used as an indicator for the aging of aerosol or aerosol reactivity (Rudich et al., 2007). The ratios of oleic acid to stearic acid ($C_{18:1}/C_{18:0}$) at PKU and Yufa ranged from 0–0.17 (0.08) and 0.01–0.07 (0.04), respectively. Low ratios of $C_{18:1}/C_{18:0}$ indicate that photo-oxidation of unsaturated fatty acids in Beijing region is significant under strong radiation conditions in summer.

3.2 Plastic emissions

Phthalates are semi-volatile organic compounds and have been widely used as plasticizers to enhance the flexibility of polyvinyl chloride (PVC) products. Because of their inverse health effects, phthalates have been intensively investigated in both ambient and indoor air (Wang et al., 2006; Fu et al., 2008; Fu et al., 2012b; Xu et al., 2015). Five phthalates were detected in this study, i.e., dimethyl (DMP), diethyl (DEP), diisobutyl (DiBP), di-n-butyl (DnBP), and di-(2-ethylhexyl) (DEHP) phthalates. Total concentrations of phthalates were 178–631 ng m^{-3} (387 ng m^{-3}) at PKU versus 140–557 ng m^{-3} (378 ng m^{-3}) at Yufa (Table S1). DEHP was generally the dominant species at both PKU and Yufa, followed by DnBP at PKU and DiBP at Yufa. In addition, the predominance of DEHP has also been reported in urban and rural aerosols in China (Wang et al., 2006). In this study, concentrations of DiBP and DnBP showed a strong positive linear correlation ($R^2 = 0.83$ at PKU and 0.91 at Yufa), suggesting that these compounds are commonly used plasticizers and simultaneously emitted from the plastics into the atmosphere by evaporation. Interestingly, the temporal patterns of bisphenol A (BPA) (Fig. 1h), an intermediate in the production of epoxy resins and polycarbonate plastics (Fu and Kawamura, 2010), were different from those of phthalates (Fig. 1g), suggesting that they are derived from different plastics and/or have different atmospheric behaviors.

3.3 Biomass burning

Levoglucosan is considered as a key tracer for biomass burning (Simoneit et al., 1999). Levoglucosan was found to be one of the dominant compounds among the individually identified compounds with a concentration range of 37–148 ng m^{-3} at PKU versus 34–149 ng m^{-3} at Yufa, indicating a significant impact of biomass burning to the summertime aerosols in Beijing. The ratio of levoglucosan to OC (levoglucosan/OC) has been used to estimate the contribution from biomass burning to the aerosol OC (Puxbaum et al., 2007; Mochida et al., 2010). The levoglucosan/OC ratio was generally higher at Yufa than at PKU (Fig. 4). The ratio in $PM_{2.5}$ at Yufa was the highest on August27. However at PKU, it peaked on August 5 and August 27. It should be noted that the levoglucosan/OC ratios might suffer a large variability due to different combustion sources.

Galactosan and mannosan, the isomers of levoglucosan, are produced by the pyrolysis of cellulose/hemicelluloses during biomass burning (Simoneit, 2002). Mean concentrations of galactosan and mannosan at PKU were 3.4 ng m^{-3} and 6.4 ng m^{-3}, respectively; they were lower than those at Yufa (5.3 ng m^{-3} for galactosan, 7.8 ng m^{-3} for mannosan) (Table S1), suggesting that biomass-burning emissions are more important at the suburban site. Statistically strong correlations among the individual compounds and levoglucosan (Fig. S1) were observed at PKU and Yufa, pointing out their similar sources or formation processes.

Fabbri et al. (2008) reported that mannosan was not detected by analytical pyrolysis of lignites, while it was detected at low levels in the smoke of lignites (Fabbri et al., 2009). They suggested mannosan as a more diagnostic marker for recent biomass. Thus, the isomeric ratio of levoglucosan to other anhydrosugars could be used as a more specific tracer for biomass burning. Here the mass concentration ratios of levoglucosan to mannosan (L/M) were 8.71–12.7 (10.1) at PKU. At Yufa, this ratio was slightly higher, ranging from 8.2 to 16.5 (10.8). The higher L/M ratios observed at Yufa than PKU agree with those for straw burning smokes (Sheesley et al., 2003; Engling et al., 2009). Hall et al. (2012) used a combustion chamber to burn sugarcane in controlled conditions and calculated the emission of several compounds per unit of mass, including levoglucosan and mannosan. Using their reported average concentration, the calculated L/M ratio was 10, which is very close to the values obtained from PKU and Yufa.

Vanillic and dehydroabietic acids were detected in the $PM_{2.5}$ with a total concentration of 1.4±0.53 ng m^{-3} at PKU versus 1.4±0.66 ng m^{-3} at Yufa (Table S1). Vanillic acid is produced during the burning of both softwood and hardwood. It is a source specific tracer for conifer burning. Dehydroabietic acid, a more specific biomass-burning tracer of conifer resin, is often detected in urban, rural, and marine aerosols (Simoneit and Mazurek, 1982b; Wang et al., 2006; Fu et al., 2011). Levoglucosan and dehydroabietic acid showed similar temporal trends with higher concentrations on August 5 (Fig. 3). The abundance of anhydrosugars, hydroxybenzoic acids, as well as lignin products, in the fine aerosols indicates that biomass burning is an important source of organic aerosols in this region.

3.4 Secondary oxidation products

Polyacids such as malic and tartaric acids are considered as secondary oxidation products of precursor organic compounds. Six hydroxy-/polyacids were detected in the Beijing samples, including glycolic, glyceric, malic, tartaric, citric, and tricarballylic acids. Glycolic acid is the most abundant species at both PKU and Yufa. The concentration range of glycolic acid was 25–68 ng m^{-3} (43 ng m^{-3}) at PKU, which was slightly higher than those (15–57 ng m^{-3}, 38 ng m^{-3}) at Yufa. This is one of the few compounds that were more abundant at PKU than Yufa. Glycolic acid was previously reported in the high Arctic aerosols (0.35–4.3 ng m^{-3}, 2.0 ng m^{-3}) (Fu et al., 2009) and marine aerosols collected in the North Pacific Ocean (4.8±2.6 ng m^{-3} and 8.5±5.6 ng m^{-3} during periods of low and high biological activities, respectively) (Miyazaki et al., 2014), which were several to ten times lower than those in the Beijing aerosols.

Seven aromatic acids, i.e., three phthalic acids (*o*-, *m*-, and *p*-isomers), three hydroxybenzoic acid (2-hydroxybenzoic acid, 3-hydroxybenzoic acid and 4-hydroxybenzoic acid) and 3, 4-dihydroxybenzoic acid, were detected in the samples. The total concentrations of hydroxy and aromatic acids were 27±8.8 ng m^{-3} at PKU versus 37±11 ng m^{-3} at Yufa. Phthalic acids (8.43–33.7 ng m^{-3}, mean 21.5 ng m^{-3} at PKU; 6.91–37.9 ng m^{-3}, 25.2 ng m^{-3} at Yufa), which may be derived from the oxidation of naphthalene or other polycyclic aromatic hydrocarbons (PAHs) (Fine et al., 2004), have been proposed as a surrogate for the contributions of secondary oxidation to an ambient aerosol sample, although primary sources such as biomass burning and fossil fuel combustion cannot be excluded (Kawamura and Yasui, 2005). Their isomeric composition was characterized by the predominance of phthalic acid, being consistent with those reported in aerosols from other studies (Wang et al., 2006).

Six isoprene SOA tracers were identified in the samples, including 2-methylglyceric acid, C_5-alkene triols, and 2-methyltetrols (2-MT, the sum of 2-methylthreitol and 2-methylerythritol). Their concentrations were higher at the suburban site (Table S1). 2-Methylerythritol was about 2.5-fold more abundant than 2-methylthreitol at both PKU and Yufa. This ratio is similar to those observed in other studies (Claeys et al., 2004; Ion et al., 2005; Cahill et al., 2006; Fu et al., 2010; Fu et al., 2013), implying that this ratio may be relatively constant at different geographical locations.

A good correlation was found between 2-methylthreitol and 2-methylerythritol (R^2 = 0.94 at PKU and R^2 = 0.97 at Yufa) (Fig. S2a), suggesting that their formation pathway is similar in terms of the oxidation of isoprene. C_5-Alkene triols, which are also photooxidation products of isoprene (Wang et al., 2005; Surratt et al., 2006), were detected in all the $PM_{2.5}$ samples with a concentration range of 3.0–35 ng m^{-3} (13 ng m^{-3}) at PKU versus 1.4–20 ng m^{-3} (11 ng m^{-3}) at Yufa. However, their concentrations are lower than those reported in Hong Kong (about 50 ng m^{-3}) (Hu et al., 2008). A good correlation was also found between 2-methyltetrols and C_5-alkene triols in the Beijing $PM_{2.5}$ samples (Fig. S2b). 2-Methylglyceric acid is possibly formed by further oxidation of methacrolein and methacrylic acid in aqueous medium (Griffin et al., 1999; Claeys et al., 2004; Surratt et al., 2006). The concentration ranges of 2-methylglyceric acid were 1.90–14.9 ng m^{-3} (6.80 ng m^{-3}) at PKU and 1.31–15.2 ng m^{-3} (8.77 ng m^{-3}) at Yufa. Its concentrations were lower than those of 2-methyltetrols and C_5-alkene triols (Table S1). The temporal pattern of 2-methylglyceric acid was similar to those of 2-methyltetrols and C_5-alkene triols (Fig. 5).

Monoterpenes contribute about 35% of the global emissions of biogenic VOCs (Griffin et al., 1999). Four α/β-pinene oxidation products, including pinonic acid, pinic acid, 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1, 2, 3-butanetricarboxylic acid (MBTCA), were detected in the $PM_{2.5}$ samples. Pinonic and pinic acids are produced by the oxidation of α/β-pinene via reactions with O_3 and OH radicals (Hoffmann et al., 1997; Yu et al., 1999; Iinuma et al., 2007). Concentrations of pinic and pinonic acids were similar at Yufa, while the concentrations of pinonic acid were higher than those of pinic acid at PKU. 3-HGA was the most abundant species among the α/β-pinene oxidation products (15 ng m^{-3} at PKU and 19 ng m^{-3} at Yufa). Both 3-HGA and MBTCA can be generated from UV-irradiated α-pinene in the presence of NO_x (Claeys et al., 2007; Szmigielski et al., 2007). They are later-generation photooxidation products of α/β-pinene. These two species were well correlated each other ($R^2 = 0.71$ at PKU, $R^2 = 0.79$ at Yufa). The formation of MBTCA can be explained by further reaction of *cis*-pinonic acid with OH radical (Szmigielski et al., 2007). However, MBTCA (1.9 ng m^{-3} at PKU and 2.2 ng m^{-3} at Yufa) was found to be a minor species among the monoterpene SOA tracers, which may indicate a relatively short atmospheric lifetime of MBTCA.

Sesquiterpenes could be a major source of SOA because their reactivity and aerosol yields are high (Griffin et al., 1999). β-Caryophyllinic acid, formed either by ozonolysis or photooxidation product of β-caryophyllene (Jaoui et al., 2007), was slightly lower at PKU (2.7±1.0 ng m^{-3}) than that at Yufa (3.9±1.5 ng m^{-3}).

Figure 5 presents the diurnal variations of biogenic SOA tracers. Two peaks were observed on August 15 and 19 at both PKU and Yufa (Fig. 5a–c); another peak was found on August 7 at Yufa. Biogenic SOA was more abundant at Yufa on August 3, but the generally occurring south wind reduced them at Yufa and then carried them to the downwind site of PKU, where the levels of biogenic SOA tracers increased on August 5. A similar pattern occurred on August 7 and 9.

Figure 6a–b shows the temporal trends of the total biogenic SOA tracers. Isoprene oxidation products were found to be the most abundant BVOCs, followed by α/β-pinene and β-caryophyllene oxidation products. The total concentrations of biogenic SOA tracers were 23–189 ng m^{-3} (92 ng m^{-3}) at PKU versus 18–203 ng m^{-3} (110 ng m^{-3}) at Yufa (Table S1). Contributions of these BVOCs to OC were examined to better understand the chemical composition of SOA in Beijing (Fig. 6c–d). Contributions of total SOA tracers to OC at PKU (0.25±0.11%) were lower than those at Yufa (0.37±0.13%) (Table 2). Mean contributions of isoprene oxidation products to OC (0.15% at PKU, 0.24% at Yufa) were about 2 times higher than those of monoterpene oxidation products (0.09% at PKU and 0.11% at Yufa) (Table 2). The relative abundances of β-caryophyllene SOA tracer in OC are similar at PKU and Yufa (Fig. 6c–d), which suggest that there is no significant regional difference for the emissions of sesquiterpenes in Beijing during summertime.

3.5 Contributions of organic compound classes to OC

Contributions of each compound class to OC in the samples were examined in this study (Table 2). Sugar compounds accounted for 0.35% of OC at PKU and 0.67% of OC at Yufa. They are lower than those reported in urban aerosols from Hong Kong (average 1.3%) (Wan and Yu, 2007). Contributions of biomass burning tracers (such as anhydrosugars) to OC at Yufa are twice higher than at PKU, indicating that biomass burning is more significant in the countryside than in urban regions. The total organics identified in Beijing aerosols accounted for 3.3±0.77% of OC at PKU versus 7.8±3.7% at Yufa with a maximum of 15.2%.

The contributions of biogenic secondary sources to OC were estimated using a tracer-yield method reported by Kleindienst et al. (2007). Using the measured concentrations of tracer compounds in $PM_{2.5}$ samples and the laboratory-derived tracer mass fraction (f_{soc}) factors of 0.155±0.039 for isoprene, 0.231±0.111 for monoterpenes, and 0.0230±0.0046 for β-caryophyllene, we calculated the contributions of these precursor hydrocarbons to ambient OC. Although certain uncertainties remained in this method (Yttri et al., 2011), the tracer-based method was proved to be useful in estimating biogenic SOA contributions (Hu et al., 2008; Stone et al., 2010; Ding et al., 2012; Feng et al., 2012; Fu et al., 2014). As shown in Figure S3, isoprene-SOC was the major contributor to SOC in Beijing. The isoprene-derived SOC at PKU and Yufa were 54.8–599 ngC m^{-3} and 36.3–867 ngC m^{-3}, respectively. The contributions of monoterpenes and β-caryophyllene to SOC ranged from 44.3 to 248 ngC m^{-3} and 62.3 to 186 ngC m^{-3} at PKU versus 37.6 to 231 ngC m^{-3} and 93.9 to 293 ngC m^{-3} at Yufa, respectively (Fig. S3). The contributions of the biogenic SOC to OC were 3.1% at PKU, among which 1.7% from isoprene, 0.76% from α-pinene, and 0.69% from β-caryophyllene. At Yufa, the biogenic SOC were responsible for 5.5% of OC with the dominance of isoprene (3.2%). A comparison of biogenic SOC in Beijing and other regions is summarized in Table S2. The contributions of biogenic SOC to OC at Beijing are among the low to middle levels from different geographical locations, which may be affected by many factors including local vegetation cover, meteorological conditions, oxidative capacity of the troposphere and so on.

4. Conclusions

Seven organic compound classes were measured in $PM_{2.5}$ collected at PKU and Yufa, Beijing. Concentrations of total quantified organic compounds were higher at Yufa (469–1410 ng m^{-3}, 1050 ng m^{-3}) than at PKU (523–1390 ng m^{-3}, 900 ng m^{-3}). The total identified organics accounted for 2.1–4.4% (0.77%) and 4.5–15.2% (3.7%) of OC at PKU and Yufa, respectively. The abundances of anhydrosugars and lignin products in the aerosol samples suggest that biomass burning is an important source of organic aerosols in Beijing. Distributions of biogenic SOA tracers in the $PM_{2.5}$ were characterized by a predominance of isoprene and α/β-pinene oxidation products, while β-caryophyllene oxidation was a minor contributor. The concentrations of almost all organic compounds measured at Yufa during the study were higher than those at PKU, indicating that biogenic emissions and pollution levels are more serious in upwind suburban areas. However, among the measured organics, fatty acids were dominant at Yufa, while phthalates were found to be the dominant species at PKU, which suggests the serious influence of plastic emissions in urban regions. Further study is needed to characterize the seasonal variation and size distribution of organic aerosols and to better evaluate the relative contributions of primary bioaerosols and biogenic SOA in Beijing.

Acknowledgements. This study was in part supported by the Environment Research and Technology Development Fund (B-0903) of the Japanese Ministry of the Environment, the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (Grant No. XDB05030306), National Natural Science Foundation of China (No. 41475117), and Research Grants Council of Hong Kong (PolyU 152083/14E). P.F. appreciates the “One Hundred Talents” program of Chinese Academy of Sciences.

Appendix A. Supplementary data

Supplementary data to this article can be found online.

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Table 1. Concentrations (ng m^{-3}) of the identified organic compounds $PM_{2.5}$ samples collected at urban (PKU) and suburban (Yufa) sites during 2007 CAREBeijing campaign.

Compounds	PKU (n=10)				Yufa (n=10)			
	min	max	mean	std[a]	min	max	mean	std
I. Sugars/sugar alcohols	88	275	142	54	121	300	203	63
II. Lignin/resin acids	0.53	2.6	1.4	0.53	0.31	2.7	1.4	0.66
III. Hydroxy-/polyacids	37	103	65	22	34	124	73	30
IV. Aromatic acids	12	41	27	8.8	10	46	31	11
V. Biogenic SOA tracers								
∑isoprene SOA tracers	11	128	59	32	7.0	153	75	43
∑*a*-pinene SOA tracers	10	57	30	14	8.7	53	32	14
β-caryophyllinic acid	1.4	4.3	2.7	1.0	2.2	6.8	3.9	1.5
subtotal	23	189	92	46	18	203	110	57
VI. Fatty acids	110	260	188	48	122	492	248	106
VII. Phthalate esters	178	631	387	137	140	557	378	127
Total detected organics (ng m^{-3})	523	1390	900	264	469	1410	1050	291
OC (μgC m^{-3})	14.3	21.5	17.1	2.5	6.5	18.9	13.1	3.7

[a] std: standard deviation. Detailed concentrations of individual species are listed in Table S1 in Appendix A.

Table 2. Contributions of organic compound classes to organic carbon (%) in the $PM_{2.5}$ samples.

Compound class [a]	PKU			Yufa		
	range	mean	std	range	mean	std
Fatty acids	0.45−1.0	0.82	0.18	1.4−11.6	4.3	3.7
Anhydrosugars	0.12−0.36	0.19	0.08	0.19−0.66	0.34	0.15
Sugars/sugar alcohols	0.12−0.20	0.16	0.03	0.18−0.59	0.33	0.12
Biogenic SOA tracers	0.06−0.36	0.22	0.09	0.11−0.55	0.32	0.11
Isoprene SOA tracers	0.03−0.27	0.15	0.07	0.05−0.45	0.24	0.10
α/β-Pinene SOA tracers	0.03−0.14	0.09	0.03	0.07−0.14	0.11	0.03
2-Methyltetrols	0.02−0.18	0.10	0.05	0.03−0.35	0.17	0.08
Hydroxy-/polyacids	0.02−0.07	0.04	0.02	0.05−0.19	0.09	0.05
Aromatic acids	0.10−0.21	0.18	0.04	0.17−0.31	0.24	0.04
Lignin/resin acids	0.002−0.009	0.006	0.002	0.003−0.013	0.007	0.002
Phthalates	0.83−2.4	1.6	0.52	1.6−3.2	2.1	0.53
Total measured organics	2.1−4.4	3.3	0.77	4.5−15.2	7.8	3.7

[a] Compound concentrations (ngC m^{-3}) were calculated for each species and were divided by OC. Values are given in percent (%).

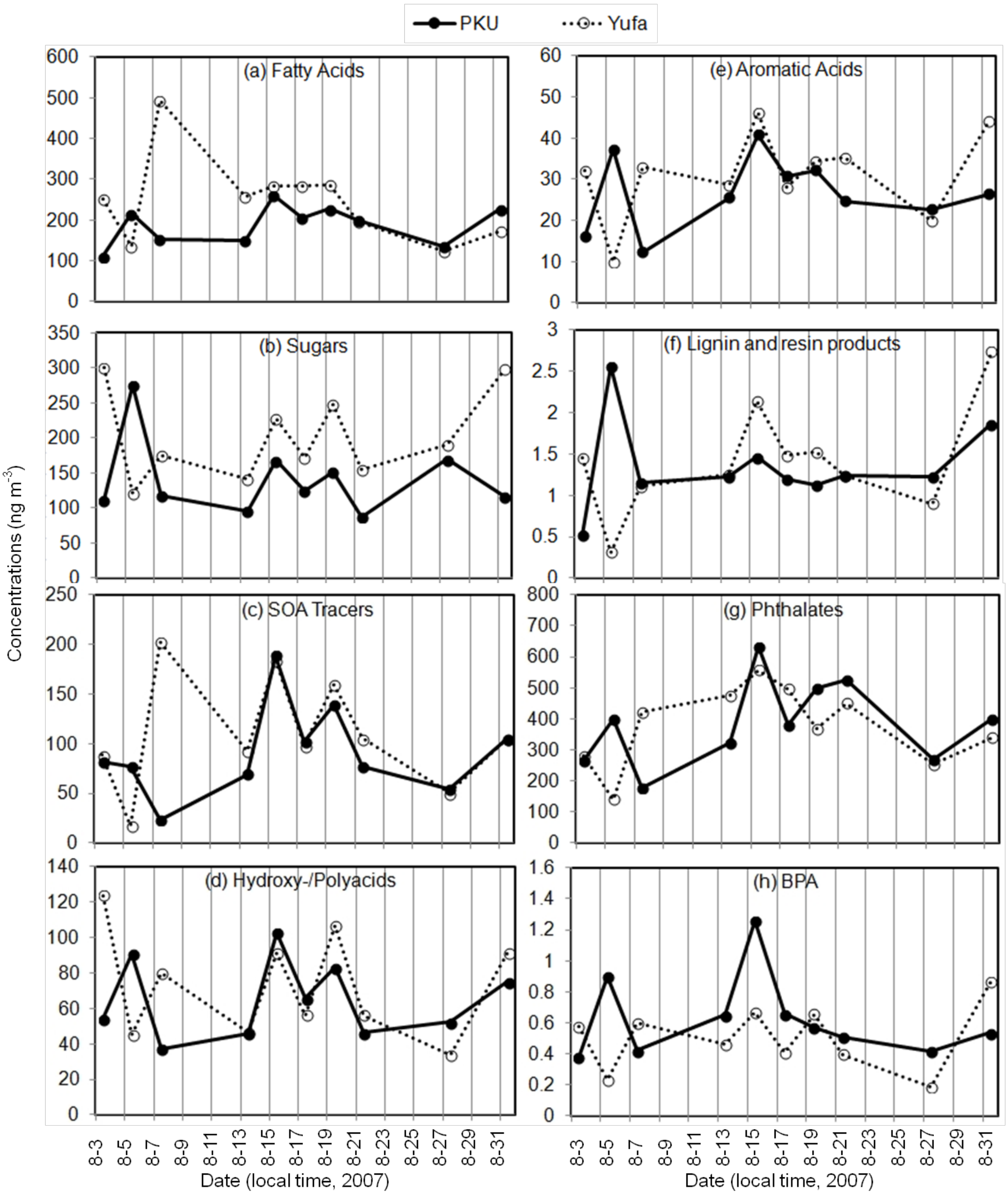


Fig. 1. Temporal variations in the concentrations of aliphatic lipids and other organic compound classes detected in the Beijing $PM_{2.5}$ aerosols. The data of bisphenol A (BPA) are from Fu and Kawamura (2010).

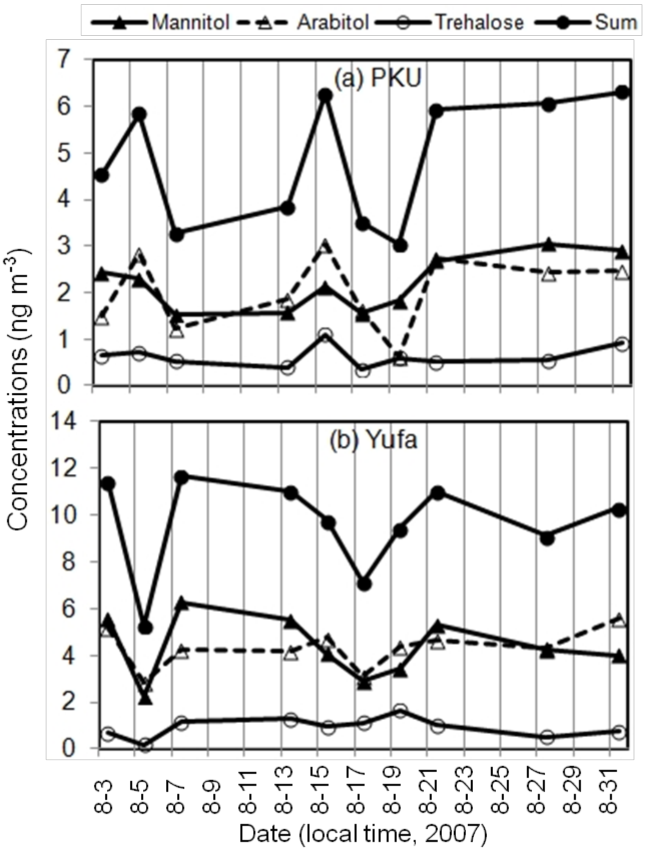


Fig. 2. Temporal variations in the concentrations of tracers for primary bioaerosols detected in the Beijing $PM_{2.5}$ aerosols.

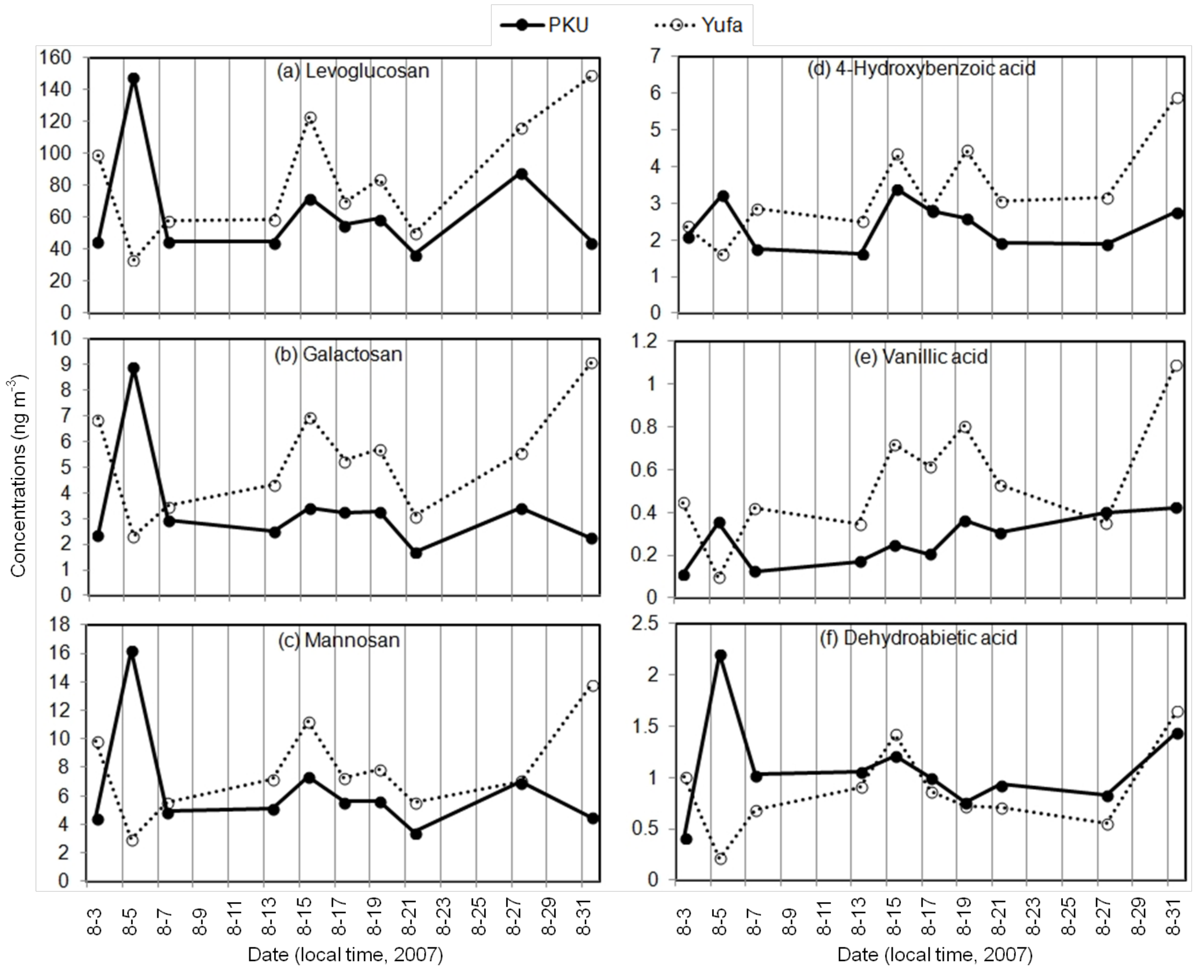


Fig. 3. Temporal variations in the concentrations of biomass burning tracers detected in the Beijing $PM_{2.5}$.

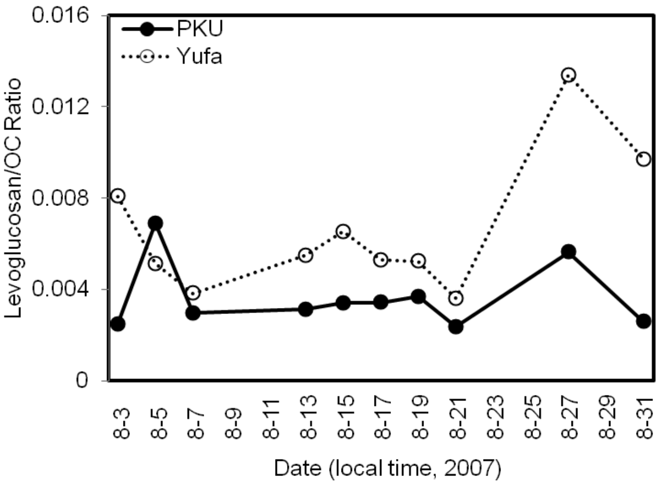
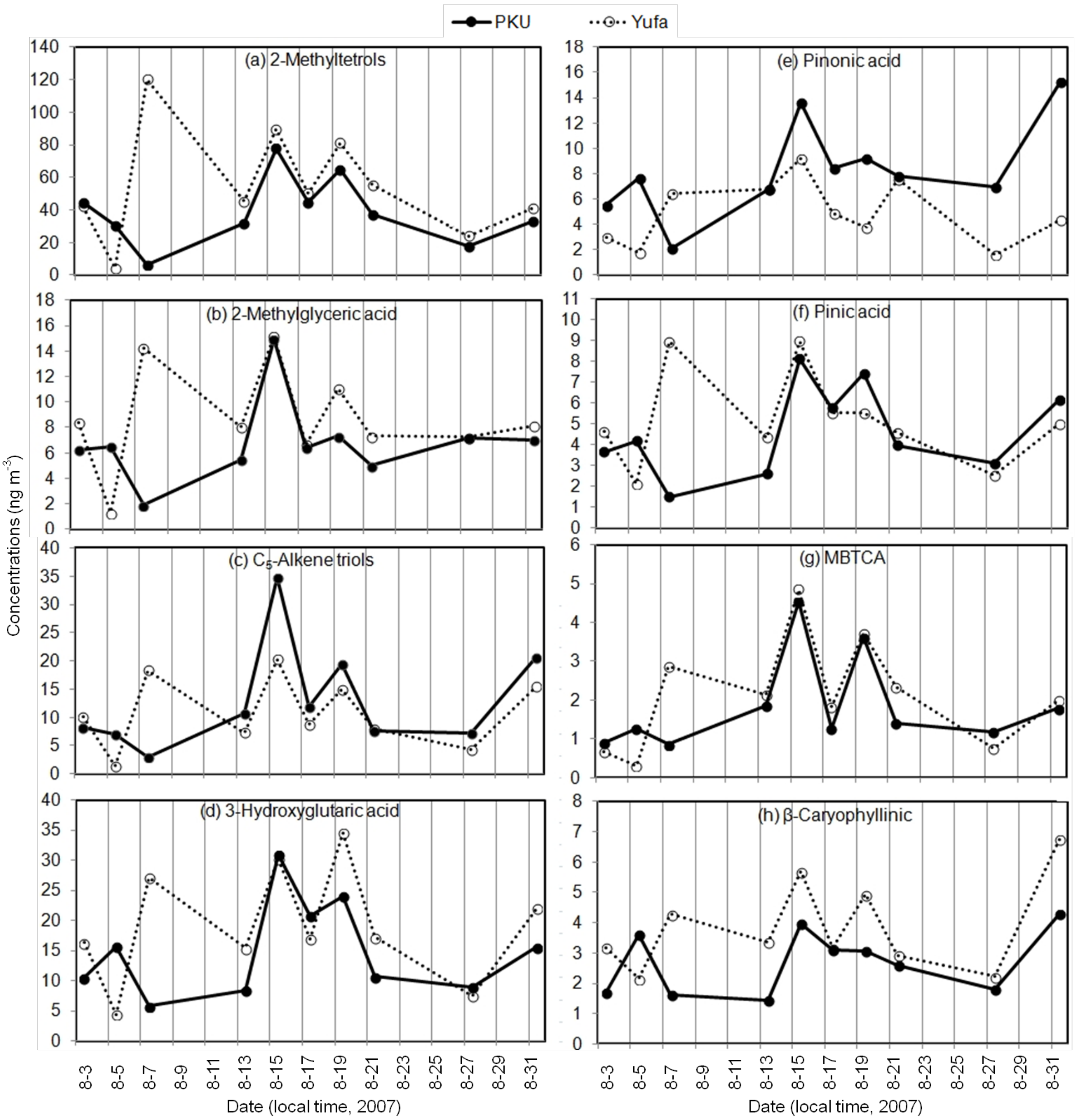


Fig. 4. Temporal variation levoglucosan/OC concentration ratios in the $PM_{2.5}$ samples in Beijing during the summertime.



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684

685 **Fig. 5.** Temporal variations in the concentrations of biogenic secondary organic aerosol
686 tracers detected in the Beijing $PM_{2.5}$ aerosols.

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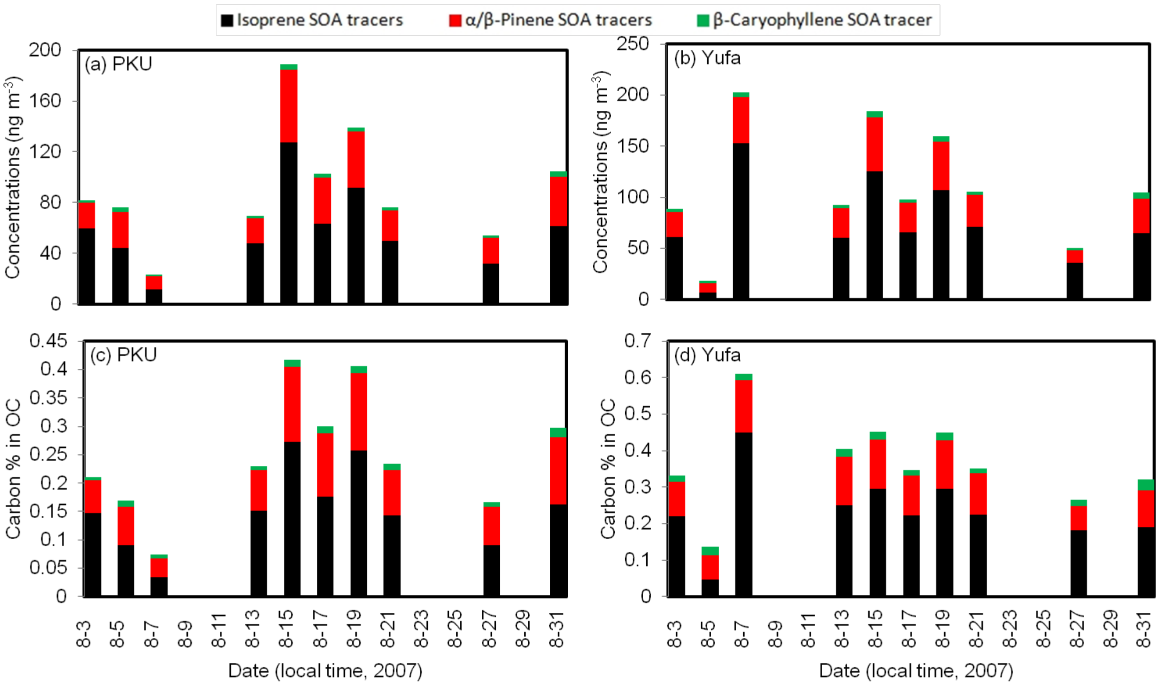

Fig. 6. Temporal variations of the total concentrations of isoprene-, α/β-pinene- and β-caryophyllene-SOA tracers at **(a)** PKU and **(b)** Yufa; the carbon percentage of biogenic SOA tracers in Organic Carbon (OC) in $PM_{2.5}$ at **(c)** PKU and **(d)** Yufa.