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Characteristics and source apportionment of $PM_{2.5}$-bound saccharides and carboxylic acids in Central Shanghai, China

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ABSTRACT

$PM_{2.5}$-bound of a group of thirty-six polar organic compounds including seventeen saccharides and nineteen carboxylic acids and $PM_{2.5}$ were analyzed for the abundance and potential sources at three sites in central Shanghai, China from September 2015 to August 2016. The annual average concentrations of the total saccharides in the $PM_{2.5}$ was 184.9 ng/m^3 with concentrations ranging from 15.3–873.4 ng/m^3 for all samples. Principal component analysis coupled with multiple linear regression (PCA-MLR) revealed that 53% of saccharides in Shanghai were derived from biomass combustion emission, 25% from fungal spore emission and 22% from plant emission. The annual average concentration of total acids concentration was 122.5 ng/m^3. Pollutants showed seasonal variations with significant higher concentrations of the dicarboxylic acid, anhydrosugar and sugar alcohol in winter and primary sugar such as fructose and sucrose in spring and summer. Lower ratios of adipic acid (C6)/azelaic acid (C9) and phthalic acid (Ph)/C9 indicated that aerosols in Shanghai are more influenced by biogenic sources. Three PCA factors explained 84% of the variance of the studied carboxylic acids data. The PCA results showed that secondary aerosols(both from anthropogenic and biogenic sources)and biomass burning emissions were the most important sources of carboxylic acids in Shanghai.

1. Introduction

Fine particulate matter ($PM_{2.5}$, aerodynamic diameter less than or equal to 2.5 μm) pollution is still the major air pollution problem in China's mega cities (Yang et al., 2016). $PM_{2.5}$ has important impacts on global climate, atmospheric visibility and human health (Li et al., 2017; Liu et al., 2019b). It contains inorganic substances (e.g. metal ions, sulfate, ammonium, nitrate) and hundreds of organic compounds (e.g. fatty acids, polycyclic aromatic hydrocarbons, dicarboxylic acids, and sugar compounds) (Yang et al., 2016; Yin et al., 2018). Organic aerosols (OA) typically contribute 20–50% of the total atmospheric aerosol mass, in which 40–80% of the organic aerosols are water soluble (Saxena and Hildemann, 1996; Zhang et al., 2016). Polar organic compounds (POCs) is one of the most abundant water-soluble organic compounds in aerosols. Due to their water solubility and hygroscopicity, POCs play an important role in atmospheric chemistry through atmospheric processing (e.g., secondary aerosol formation) and in Earth's climate by enhancing the ability of organic aerosols to act as cloud condensation nuclei (Kawamura and Bikkina, 2016; Kumar et al., 2003; Peng et al., 2001).

Previous studies suggested that POCs could be directly emitted from primary sources including natural sources (e.g., plant emission, soil and dust suspension, fungal spores, metabolism of microorganisms, and sea spray) and anthropogenic sources (e.g. industrial emissions, traffic emissions and biomass burning) (Balla et al., 2018; Simoneit et al., 2004a; Wang et al., 2011). They can also be formed by secondary photochemical oxidation in the atmosphere (Fu et al., 2016; Kawamura et al., 1996). Various POCs can serve as tracers for specific pollution sources. Levoglucosan (Lev) and related anhydrosugar isomers, produced from the pyrolysis of cellulose and ranked as the most abundant species in biomass burning emissions, have been recognized as a specific molecular marker for biomass burning sources. Arabitol and

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mannitol are released by fungal spores and are considered as possible tracers of this source (Bauer et al., 2008). Fructose and sucrose detected in the atmosphere are often associated with biological sources (eg, plants, soil resuspension) (Chen et al., 2013; Jia and Fraser, 2011). Diacid and related compounds can serve as tracers for secondary organic aerosol (SOA) and could be good markers for evaluating the changes of SOA concentrations and their climatic relevance in the atmosphere (Balla et al., 2018; Fu et al., 2013; Popovicheva et al., 2014). Adipic acid (C6) and phthalic acid (pH) are produced by the oxidation of anthropogenic cyclohexene and aromatic hydrocarbons (Hatakeyama et al., 1985; Kawamura and Ikushima, 1993). Azelaic acid (C9) is produced by the oxidation of biogenic unsaturated fatty acid (UFAs) (Kawamura and Kaplan, 1987; Tedetti et al., 2007). C6/C9 and Ph/C9 ratios can be used as indicators of the impact of anthropogenic and biogenic precursors to SOA production (Kawamura and Yasui, 2005).

Currently, China's research on POCs mainly focused on the PRD (Ho et al., 2011), Beijing (Zhao et al., 2018; Liang et al., 2015) and Hong Kong (Ho et al., 2006). As a mega city, Shanghai is one of the six largest cities in the world. The Source and chemical transformations of POCs in Shanghai are very complicated. However, previous studies on organic aerosol characteristics in Shanghai and surrounding regions are limited and the limited information are primarily focused on a few aerosol species or a handful of organic compound classes (Feng et al., 2006; Li et al., 2013). In this study, one-year $PM_{2.5}$ samples were collected at three selected locations in central of Shanghai, and polar compounds such as saccharides and diacid and related compounds were measured in each sample. The objective of this study was to study the spatial and seasonal characteristics of typical polar compounds in Shanghai during the year, combined with principal component analysis (PCA) and multiple linear regression (MLR) to promote our current understanding of their sources.

2. Experimental section

2.1. Sites and sampling

Twenty-four hour $PM_{2.5}$ samples were collected simultaneously every 8–10 days at three sampling stations in downtown Shanghai, China. A total of 108 samples were collected from September 2015 to August 2016 on pre-baked (550 °C for 5.5 h) quartz fiber filters using a high-volume air sampler (XT-1025, Shanghai Xintuo Analytical Instruments) at a flow rate of 1 m^3/min. Details of the three sampling sites are shown in Fig. 1. Field blanks were prepared by loading a blank filter to the sampler in the absence of air-flow for 24 h. After sampling, the filters were packaged with aluminum foil and stored at −20 °C prior to instrumental analysis.

2.2. Sample preparation and instrumental analysis

Before extraction, partial of air filter samples were spiked with known amounts of internal standards (d_{31}-palmitic acid and methyl β-D-galactopyranoside (mxp)). The filter samples were extracted by ultrasonication three times with 4 mL, 2 mL, and 2 mL dichloromethane/methanol (4:1; *v*/*v*) for 10 min each. To prevent the solvent evaporation and decomposition of organic components associated with the temperature rise from ultrasonication, an appropriate amount of ice was added to the ultrasonic bath to keep temperatures below 30 °C. After extraction, extracts were passed through a syringe filter to remove insoluble particles and filter debris, and then dried with pure nitrogen gas. The extracts were then derivatized with *N*,*O*-bis-(trimethylsilyl) trifluoroacetamide at 70 °C for > 2 h. Following derivatization, each derivatized sample was injected into the GC/MS for identification and quantification.

The determination of studied compounds was performed with a gas chromatograph mass spectrometer (GC/MS-QP 2010 Ultra, Shimadzu Corporation, Japan). The GC was fitted with a DB-5MS column (30 m × 0.25 mm × 0.25 μm, J&W Scientific, USA). Ultra-pure helium was used as carrier gas under constant flow mode at a flow rate of 1.1 mL/min. Automatic injections (1uL) were made in t split mode with a split ratio of 10:1. The injection temperature was set at 280 °C. The gas chromatographic conditions were as follows. Initial column temperature was held at 80 °C for 1 min, and then programmed to 200 °C at 3 °C min^{-1} (held for 2 min), and to 310 °C at 10 °C min^{-1} (held for 15 min). The GC/MS interface temperature was 275 °C. The MS was operated in electron ionization (EI+) scan mode with the scan ranging from 50 to 500 amu.

Field blanks and laboratory blanks were treated in the same way as the ambient samples for quality assurance. Calibration standards were prepared by spiking different volumes of a standard solution mixture onto ambient filter samples and analyzed following the same analytical procedure as that for ambient $PM_{2.5}$ filter samples. This approach has the advantage of taking into account the matrix effect. All of the samples were quantified using the calibration curves by this standard addition method.

2.3. Data analysis

All the analyses of this research were performed using SPSS statistical software package, version 23.0 (SPSS Inc., Chicago, IL, USA). The

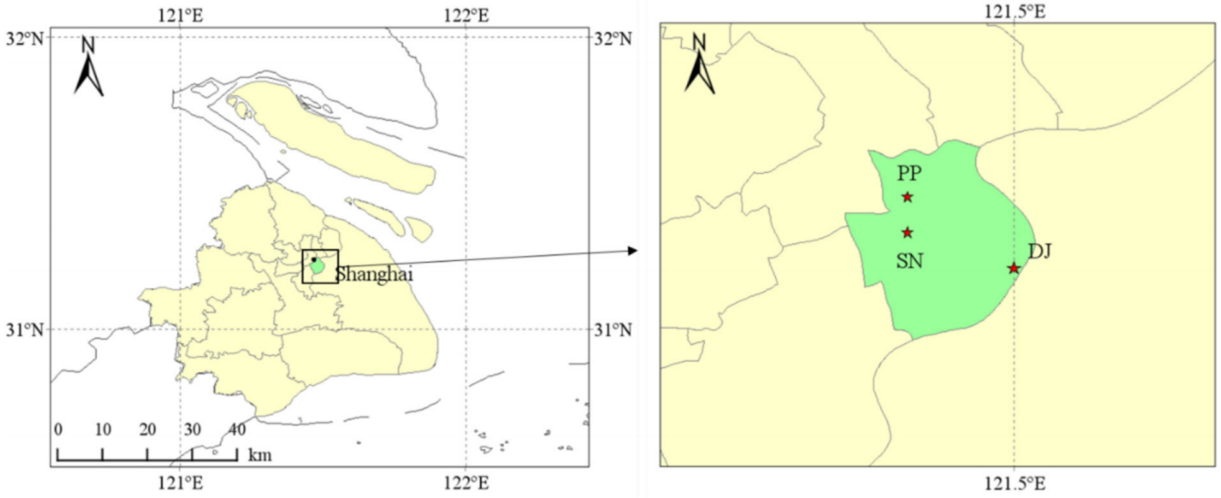

Fig. 1. The detailed sampling sites in central Shanghai, China.

Table 1
Mass concentrations and variations of $PM_{2.5}$ (μg/m^3) and polar organic compound (ng/m^3) in Shanghai.

	Aut	Win	Spr	Sum	Year
PM2.5	**38.2(18.3–69.6)**	**94.6(35.2–176.8)**	**50.0(26.1–121.1)**	**34.4(12.6–72.4)**	**55.6(12.6–176.8)**
Anhydrosugar					
Levoglucosan, Lev	47.2(6.7–203.4)	194.6(31.8–469.9)	57.4(0.3–181.9)	26.2(1.8–56.1)	80.9(0.3–469.9)
Galactosan, Gal	2.2(0.4–9.8)	8.9(1.2–23.0)	2.2(0.0–6.2)	1.0(0.1–2.6)	3.5(0.0–23.0)
Mannosan, Man	3.8(0.5–13.4)	15.3(1.7–33.0)	3.9(0.1–10.3)	2.3(0.0–5.3)	6.3(0.0–33.0)
Total anhydrosugar	**53.2(7.6–226.6)**	**218.7(34.6–525.9)**	**102.7(0.4–525.9)**	**31.9(2.1–122.7)**	**100.6(0.4–525.9)**
Primary sugar					
Xylose	1.6(0.4–4.4)	4.2(1.1–8.7)	1.7(0.1–4.9)	0.8(0.1–2.1)	2.1(0.1–8.7)
Mannose	1.9(0.2–5.5)	2.1(0.2–4.5)	2.0(0.1–7.2)	2.1(0.2–5.4)	2.0(0.1–7.2)
Fructose	15.3(4.8–73.8)	15.2(2.5–27.4)	28.3(0.3–120.3)	19.6(1.4–76.8)	19.4(0.3–120.3)
Glucose	4.8(0.4–18.4)	3.6(0.6–9.3)	3.4(0.3–8.1)	2.8(0.5–6.7)	3.7(0.3–18.4)
Sucrose	15.0(1.0–158.9)	4.7(0.5–15.7)	18.5(0.9–136.1)	29.8(2.2–191.9)	17.0(0.5–191.9)
Maltose	1.0(0.1–6.3)	1.6(0.1–6.0)	1.3(0.1–9.1)	1.6(0.5–5.8)	1.4(0.1–9.1)
Trehalose	2.4(0.3–14.1)	2.0(0.2–5.4)	2.4(0.1–8.1)	3.5(0.9–8.8)	2.6(0.1–14.1)
Total primary sugar	**42.1(8.6–260.2)**	**33.4(7.7–65.0)**	**57.6(6.6–286.5)**	**60.2(10.5–256.0)**	**48.1(6.6–286.5)**
Sugar alcohol					
Glycerol	13.6(7.9–20.7)	22.3(5.5–48.4)	12.3(0.0–24.0)	11.2(3.3–29.2)	14.8(0.0–48.4)
Erythritol	1.3(0.4–2.9)	2.6(0.5–5.2)	1.2(0.1–2.7)	2.1(0.4–4.8)	1.8(0.1–5.2)
Xylitol	0.2(0.0–0.9)	0.3(0.0–0.9)	0.2(0.0–1.0)	0.2(0.0–0.8)	0.2(0.0–1.0)
Arabitol	3.9(0.7–10.0)	5.1(0.7–15.2)	2.9(0.1–7.1)	4.0(1.5–6.5)	4.0(0.1–15.2)
Mannitol	15.7(2.6–59.3)	11.2(0.9–28.4)	8.5(0.3–26.3)	18.1(5.0–36.9)	13.5(0.3–59.3)
Sorbitol	0.6(0.1–1.5)	0.7(0.2–1.4)	0.6(0.1–1.4)	0.7(0.2–1.5)	0.6(0.1–1.5)
Cholesterol	1.1(0.2–2.6)	1.8(0.2–4.5)	0.6(0.0–2.2)	1.2(0.0–5.8)	1.2(0.0–5.8)
Total sugar alcohol	**36.5(14.7–79.6)**	**43.9(13.3–93.7)**	**26.2(6.0–61.1)**	**37.5(14.9–71.1)**	**36.1(6.0–93.7)**
Total saccharides[a]	**131.7(54.0–413.3)**	**296.0(55.7–668.5)**	**186.4(15.3–873.4)**	**129.6(31.4–398.8)**	**184.9(15.3–873.4)**
n–Dicarboxylic acid, DCAs					
Succinic, C4	17.3(6.1–61.4)	27.5(5.8–76.8)	22.6(0.1–95.2)	15.5(1.7–55.2)	20.6(0.1–95.2)
Glutaric, C5	4.2(1.4–12.7)	8.9(2.2–22.0)	6.0(0.1–23.9)	4.0(0.5–14.2)	5.7(0.1–23.9)
Adipic, C6	2.5(1.1–5.5)	5.4(1.4–10.3)	3.2(0.1–11.1)	2.4(0.5–7.8)	3.4(0.1–11.1)
Pimelic, C7	1.3(0.6–3.1)	2.4(0.8–4.8)	1.1(0.1–3.2)	1.0(0.1–2.4)	1.4(0.1–4.8)
Suberic, C8	3.5(2.0–6.6)	5.1(1.3–8.6)	2.7(0.2–5.6)	2.9(1.0–6.6)	3.5(0.2–8.6)
Azelaic, C9	22.1(10.7–41.2)	22.7(6.2–36.4)	15.3(1.9–34.7)	15.1(6.0–30.7)	18.9(1.9–41.2)
Total DCAs	**50.8(24.6–107.9)**	**72.0(25.0–149.4)**	**51.0(2.6–158.4)**	**40.9(10.5–111.9)**	**53.6(2.6–158.4)**
Aromatic acid					
3–hydroxybenzoic, 3–OHBA	0.6(0.2–1.7)	2.0(0.5–3.8)	0.5(0.0–1.1)	0.3(0.1–0.8)	0.8(0.0–3.8)
4–hydroxybenzoic, 4–OHBA	1.2(0.4–5.1)	6.8(1.1–15.7)	1.6(0.0–5.9)	0.4(0.1–1.1)	2.5(0.0–15.7)
Phthalic, Ph	9.3(2.4–36.8)	23.3(5.1–61.7)	7.9(0.1–41.1)	7.0(1.4–17.9)	11.9(0.1–61.7)
Isophthalic, iPh	1.0(0.4–2.6)	3.3(0.5–7.8)	1.0(0.0–3.3)	0.7(0.1–2.0)	1.5(0.0–7.8)
Vanillic	0.2(0.0–1.4)	1.5(0.2–2.8)	0.3(0.1–0.7)	0.1(0.0–0.2)	0.5(0.0–2.8)
Syringic	0.1(0.0–0.7)	0.9(0.1–1.8)	0.2(0.0–0.4)	0.1(0.0–0.2)	0.3(0.0–1.8)
1,2,4–benzenetricarboxylic, 1,2,4–BTCA	5.2(0.9–14.5)	16.0(0.4–54.2)	4.2(0.0–14.0)	3.5(0.1–13.2)	7.2(0.0–54.2)
1,3,5–benzenetricarboxylic, 1,3,5–BTCA	0.2(0.0–0.6)	0.5(0.0–1.5)	0.2(0.0–0.8)	0.1(0.0–0.9)	0.3(0.0–1.5)
Total aromatic acid	**17.9(5.7–49.7)**	**54.2(14.1–132.7)**	**15.9(0.3–64.3)**	**12.2(2.0–36.1)**	**25.0(0.3–132.7)**
Oxycarboxylic acids, OCAs					
Glyoxylic, ωC2	4.8(1.6–12.8)	10.0(2.3–20.8)	5.1(1.7–19.5)	5.6(1.8–18.7)	6.4(1.6–20.8)
α–Ketoglutaric	3.4(0.8–11.4)	4.0(0.8–9.0)	3.7(1.0–16.8)	3.2(0.8–6.8)	3.6(0.8–16.8)
Glyceric	21.2(6.5–63.3)	41.4(8.9–102.3)	23.0(0.1–76.8)	14.9(0.6–56.7)	25.0(0.1–102.3)
Malic, hC4	10.5(2.2–29.6)	7.9(0.7–28.0)	5.6(0.0–38.2)	9.7(0.2–38.9)	8.5(0.0–38.9)
Tartaric	0.4(0.1–2.6)	0.3(0.1–1.6)	0.2(0.0–1.4)	0.8(0.0–2.9)	0.4(0.0–2.9)
Total OCAs	**40.2(17.9–106.6)**	**63.6(15.8–157.5)**	**37.5(4.9–140.3)**	**34.2(3.8–120.4)**	**43.9(3.8–157.5)**
Total carboxylic acids,TACs[b]	**108.9(48.5–243.5)**	**189.8(54.9–439.6)**	**104.4(7.8–314.0)**	**87.2(20.6–268.4)**	**122.5(7.8–439.6)**

[a] Sum of all studied saccharides

[b] Sum of all studied carboxylic acids

statistical significance of pollutant concentrations between different sampling sites and different seasons were conducted by One-Way Analysis of Variance (ANOVA) test. Statistical significance was defined as a *p*-value < .01. Principle component analysis (PCA) was applied in order to visualize the overall differences. Additionally, multiple linear regression (MLR) was applied following PCA to determine the percent contribution of different sources to those polar organic compounds. The relevant formula of MLR is displayed in the supporting materials.

3. Results and discussion

3.1. $PM_{2.5}$ mass concentrations

The annual average mass concentrations, seasonal mass concentrations, and the concentration range of $PM_{2.5}$ and $PM_{2.5}$-bound saccharides and carboxylic acids are listed in Table 1. The detailed data for each sampling site are reported in the supplementary material (Table S1, S2, and S3). As shown in Table 1, the annual average values of the $PM_{2.5}$ mass concentrations were 60.5, 55.8, and 51.6 μg/m^3 for sites SN, PP, and DJ, respectively. A one-way ANOVA showed no statistical difference in the $PM_{2.5}$ mass concentrations between the three sampling sites ($p > .05$). Therefore, all samples were combined and analyzed as a whole. The annual average $PM_{2.5}$ concentration was thus 55.6 μg/m^3, which is lower than the Chinese pollution standard of 75 μg/m^3. We found 84.3% of the total 108 daily samples to be lower than the pollution standard. $PM_{2.5}$ mass concentrations showed seasonal variability; seasonal average $PM_{2.5}$ concentrations decreased in the order of winter > spring > autumn > summer with values of

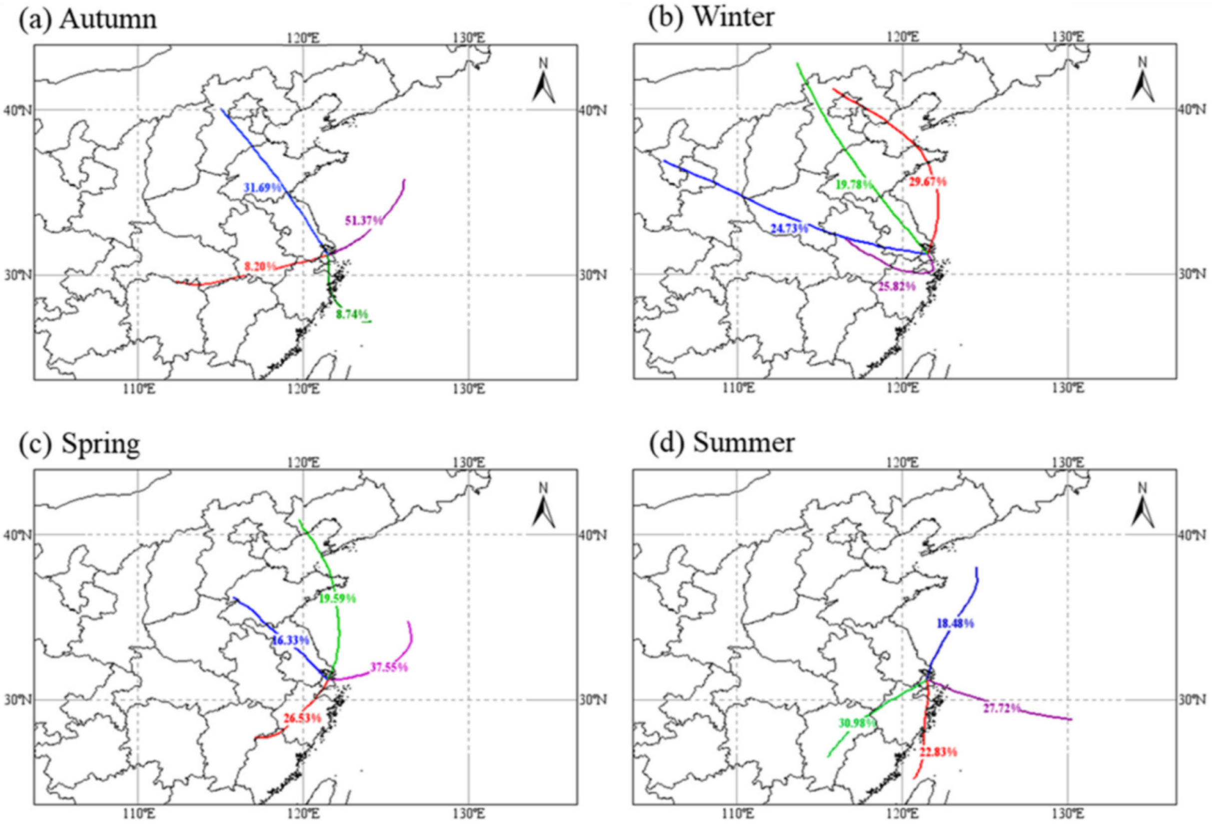

Fig. 2. Cluster analysis of 48-h backward trajectories arriving at Shanghai at a height of 500 m during (a) autumn, (b) winter, (c) spring, and (d) summer in Sep 2015-Aug 2016. The percentage represents the ratio of the number of back trajectories in each cluster to the total number of back trajectories.

94.6 ng/m^3, 50.0 ng/m^3, 38.2 ng/m^3, and 34.4 ng/m^3, respectively. Seasonal variability in concentration is predominantly caused by seasonal changes in meteorological conditions and the dominant sources of $PM_{2.5}$ in a particular season. For example, processed backward trajectories calculated by the Hybrid Single-Particle Lagrangian Integrated Trajectory model inferred higher dilution of local air pollutants during Shanghai summers due to the influence of clean oceanic winds from the summer monsoons (Nan, 2019; Wang et al., 2009), whereas prevailing winds from the northern continent brought aged and polluted air to Shanghai in winter (Fig. 2). Moreover, the removal of air pollutants may be enhanced in spring and summer due to higher precipitation (Ye et al., 2003). Particulate pollution in China (particularly during haze events) is largely driven by secondary aerosol formation (Liu et al., 2019c). In this study, a strong linear correlation was observed between the concentrations of $PM_{2.5}$ and polar organic compounds (POCs) (r = 0.73) in the Shanghai samples (Fig.S1), indicating a higher contribution of polar organic compounds to particulate pollution in this region.

3.2. Characteristics of $PM_{2.5}$-bound saccharides

Saccharides are an important part of organic compounds and contribute 13–26% of the total mass of compounds identified in continental aerosols (Simoneit et al., 2004b). In our study, 17 sugars (alcohols) were quantified, including 3 anhydrosugars, 7 primary sugars, and 7 sugar alcohols. The annual average concentration of the total saccharides in $PM_{2.5}$ was 184.9 ng/m^3, and all of the samples ranged between 15.3 and 873.4 ng/m^3 (Table 1). Anhydrosugar was the most abundant saccharide in the samples with an average contribution of 54% to the total sugar concentration, followed by primary sugars with an average contribution of 26%. Sugar alcohols had the lowest concentration with an average contribution of 20%. The contributions of the individual sugar groups to the total sugar concentration varied seasonally, with higher percentages of anhydrosugars and sugar alcohols during winter and higher percentages of primary sugars during spring and summer.

3.2.1. Anhydrosugar

Three anhydrosugars were detected in this study: levoglucosan (Lev), mannosan (Man), and galactosan (Gal). Lev was the most abundant of the three. The annual average concentration of Lev in $PM_{2.5}$ was 75.1 ng/m^3 for SN, 86.5 ng/m^3 for PP, and 78.2 ng/m^3 for DJ. We observed no significant differences in Lev concentrations between the three sampling sites likely due to their close proximity. This observations also suggests a similar source of Lev in the three sites, likely from biomass burning via long-range transport from the northern mainland (Fraser and Lakshmanan, 2000). Lev is a superior tracer of biomass/biofuel burning (BB) due to its source-specific generation and atmospheric stability (Fraser and Lakshmanan, 2000; Simoneit et al., 1999). Atmospheric Lev concentrations have been reported worldwide, including in China (Table S4). The Lev concentrations in Shanghai were generally lower than the reported global values, including in urban sites in Beijing (Liang et al., 2016), Xi'an (Wang et al., 2018), Guangzhou (Ma et al., 2009), Thessaloniki (Balla et al., 2018), in agro-industrial regions in São Paulo State (Urban et al., 2014), and in urban background and suburban sites (winter) in Norway (Yttri et al., 2007). However, Lev concentrations in this study were higher than reported values in the Amazon basin in Brazil (Graham et al., 2003) and rural background locations in Norway (Yttri et al., 2007) (Table S4). These comparisons indicate that biomass burning has a lower impact on aerosol composition in Shanghai relative to other cities around the world. Seasonal Lev concentrations were 57.4 ng/m^3 in spring, 26.2 ng/m^3 in summer, 47.2 ng/m^3 in autumn, and 194.6 ng/m^3 in winter. Winter Lev concentrations were therefore significantly higher than the other three seasons, with lowest concentrations in summer. In general, higher mass concentrations of anhydrous saccharides are typically observed in autumn and winter due to the combustion of agricultural waste and wood burning for heating. However, our results infer higher Lev mass concentrations in spring relative to autumn. Backward trajectory clustering analysis (Fig. 2) shows that some of the air masses over Shanghai in spring were transported from northern China. High concentrations of Lev during spring could be ascribed to the following process: high particulate matter from biomass burning is deposited and frozen in soil in winter and becomes released to the atmosphere in spring when the soil dries and loosens in response to warming temperatures. Lev from the soil is therefore released into atmospheric aerosols via dust and other suspension and is transported by wind. Similar results have also been reported by Shen et al. (2018).

Man and Gal were much lower in concentration relative to Lev but showed similar seasonal and spatial variability. A strong positive correlation was observed between the three studied anhydrosugars ($r > 0.95$, Fig. S2) potentially inferring similar sources. The annual average $PM_{2.5}$ concentrations of Man and Gal in all samples was 6.2 ng/m^3 and 3.5 ng/m^3, respectively. We assessed the concentration ratios of the different anhydrosugars (Lev/Man and Man/Gal) to identify possible biomass burning categories and contributions of biomass burning smoke in ambient aerosols (Sang et al., 2013). Table S5 shows the anhydrosugar ratios (Lev/Man and Man/Gal) of crop residues and soft and hardwood reported from various regions of the world. We compared these global ratios with the average seasonal ratios in each site of this study in a scatter plot (Fig. 3). According to Fig. 3, the dominant types of biomass burning emissions in Shanghai are hardwood and crop residue smoke.

3.2.2. Primary sugars

Seven primary sugars were detected in $PM_{2.5}$ in this study, including xylose, mannose, fructose, glucose, sucrose, maltose, and trehalose. Total concentrations of primary sugars ranged from 6.7 to 286.5 ng/m^3 with an average of 48.1 ng/m^3. Primary sugars accounted for 26% (6%–78%) of the total saccharide concentration. The proportion of primary sugars to the total saccharides varied in the order of summer (40%) > spring (35%) > autumn (30%) > winter (13%). Summer ratios were approximately 4 times that of winter, likely due to biogenic influences. Primary sugars in aerosols are predominantly derived from plant debris, pollen, and fungi, but minor fractions can also be derived from biomass burning (Fu et al., 2012; Medeiros and Simoneit, 2008). Higher concentrations of primary sugars are therefore expected in the warm season under higher rates of microbial metabolic activities and plant growth. The annual average mass concentrations of primary sugars were significantly higher in PP (79.1 ng/m^3) relative to SN (29.2 ng/m^3) and DJ (33.7 ng/m^3); PP concentrations were more than twice the value of SN and DJ, likely due to the higher microbial metabolic activities and vegetation density in People's Park. Fructose and sucrose were the most abundant of the primary sugars accounting for 40% and 35% of the total, respectively. Sucrose is an important sugar in developing flower buds (Bieleski, 1995) and pollen grains (Pacini, 2000) and can also be found in some fungi and spores (Feofilova et al., 2012). Fructose is derived from vegetation constituents (e.g., pollen, fruits) and their detritus (Pacini, 2000; Rutledge and Adeli, 2007). The seasonal trends of xylose had differed significantly from the other primary sugars in this study, where winter concentrations were higher than summer. Xylose was highly correlated with levoglucosan ($r = 0.91$), indicating biomass burning to be its predominant source.

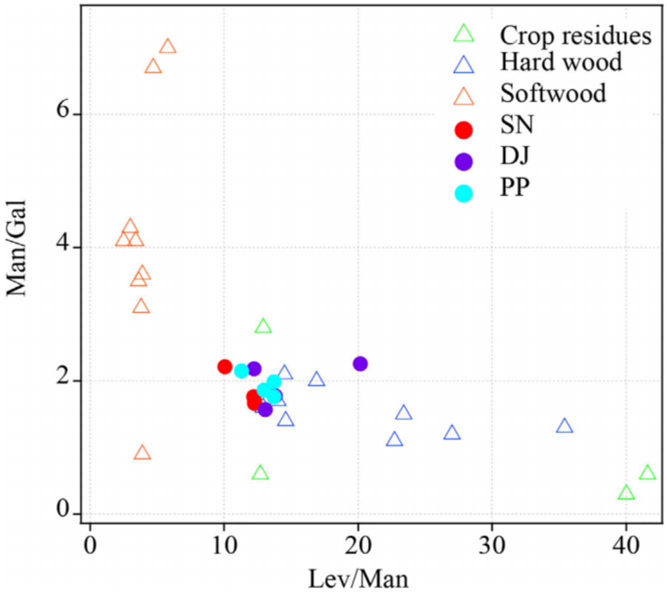

Fig. 3. Scatter plot of LG/MN and MN/GA ratios from source emissions (literature values) and ambient aerosols at the three sampling sites (this study).

3.2.3. Sugar alcohols

Seven sugar alcohol compounds were detected in our study, including glycerol, erythritol, xylitol, arabitol, mannitol, sorbitol, and cholesterol. The average annual concentration of total sugar alcohols was 36.1 ng/m^3, contributing 20% to the total saccharide concentration. Glycerol and mannitol were the most abundant compounds, accounting for nearly 80% of the total sugar alcohols. Different compounds of sugar alcohols dominated in different seasons, where glycerol concentrations were highest in winter and mannitol concentrations were highest in summer.

As shown in Table 1, highest glycerol content in winter is linked to an increase in biomass burning, indicating that biomass burning is a dominant source of glycerol (Liang et al., 2016; Wang et al., 2011). This finding is further confirmed by the significant positive correlation between glycerol and levoglucosan ($r = 0.72$). The annual average mass concentrations of glycerol was highest in PP (19.7 ng/m^3), followed by DJ (13.7 ng/m^3) and SN (10.5 ng/m^3); this spatial variability is expected, as glycerol in ambient aerosols are predominantly derived from biological sources such as fungal metabolism in soils (Simoneit et al., 2004a).

Mannitol and arabitol are produced in a number of fungal species and are commonly used as tracers for fungal spores (Bauer et al., 2008). Although mannitol and arabitol in the three sites were significantly correlated ($r = 0.75$), we observed obvious differences in the seasonal variability of the two sugar alcohols. The lowest concentrations of both compounds were observed in spring, but the highest concentrations of mannitol and arabitol were observed in summer and winter, respectively. Mannitol is the most abundant saccharide polyol in nature and is typically sourced from marine aerosols (Chen et al., 2013). As Shanghai is affected by summer monsoons, high concentrations in summer may be due to the transport of mannitol from oceanic winds. We observed a low correlation between arabitol and levoglucosan ($r = 0.54$), which implies that fungal spores may be emitted from biomass burning (Yang et al., 2012). Biomass burning may therefore be the cause for higher arabitol concentrations in winter.

The presence of cholesterol in aerosol samples may be attributed to the cooking of meat (Rogge et al., 1991a). The annual average concentrations of cholesterol between the three sites were SN (1.5 ng/m^3) ≈ PP (1.1 ng/m^3) ≈ DJ (1.1 ng/m^3). The concentration levels of the three sites were therefore similar. Higher cholesterol concentrations were observed in winter, but concentrations remained relatively constant throughout the rest of the year.

3.2.4. Source identification of saccharides by PCA

In this study, we performed a principal component analysis (PCA) with orthogonal distribution and varimax rotation using SPSS (IBM, version 23.0) to categorize the possible sources of saccharides in the Shanghai $PM_{2.5}$ aerosols. The contribution of each factor was determined by the multiple linear regression (MLR) model following the PCA. Four factors were extracted as principal components (eigenvalue > 1), which explained 78.7% of the variance in the data (Table S6). Factor 1 explained 33.6% of the total variance, with Lev, Man, and Gal loadings as high as 0.9 representing biomass burning emissions. Factor 2 explained 18.3% of the total variance, with high loadings from primary sugars such as fructose, sucrose, and maltose representing emissions from biological sources from plant emissions. Factor 3 explained 18.2% of the total variance, with high loadings from mannitol, arabitol, and trehalose representing biological sources from fungal emissions. Factor 4 explained 8.6% of the total variance and was only characterized by glucose. Glucose in aerosol can be sourced from vascular plants (Cowie and Hedges, 1984), soil microbial metabolism (Paul and Clark, 1996), and biomass burning (Paul and Clark, 1996), and thus factor 4 represents a mixed source.

After determining the four factors from the PCA, we performed the MLR to determine the contribution rate of the different pollution sources (PCA factors) to the saccharides in $PM_{2.5}$. The dependent variable was the total concentration of the seventeen saccharides, and the independent variables were the factor scores. We applied a significance level of 0.05 for the entry variable and 0.10 for the deleted variable. The stepwise regression method was used for the multiple linear regression analysis. The results of the MLR infer that the contribution from factor 4 to the saccharides was negligible (significant level > 0.1). Fig. 4. shows biomass combustion to be the dominant source of saccharides in Shanghai accounting for 53%, followed by the contribution of fungal spores at 25% and plant emissions at 22%.

3.3. Characteristics of $PM_{2.5}$-bound carboxylic acids

The main carboxylic acids identified in this study were saturated n-dicarboxylic acids, aromatic organic acids, and oxycarboxylic acids. The sum of all carboxylic acids is referred to as the total acid concentrations (TACs). The annual average TACs (including all three sites) was 122.5 ng/m^3. On average, the abundance of TACs in winter was more than double that of summer, with mean concentrations of 189.8 ng/m^3 and 87.2 ng/m^3 in winter and summer, respectively. Higher concentrations in winter may be due to a number of meteorological differences, including higher humidity, lower precipitation, a decrease in the mixing height, and a lowering of the inversion layer. These conditions lead to increased atmospheric concentrations of pollutants as a result of poorer atmospheric diffusion rates and dilution factors (Bernd and Simonelt, 1993; Oliveira et al., 2007). High summer temperatures may also stimulate the conversion of organic compounds in aerosols from particulate phases to gaseous phases (Feng et al., 2006). In addition, the high correlation between TACs and levoglucosan (r = 0.66) infers a dominant contribution from biomass burning during winter.

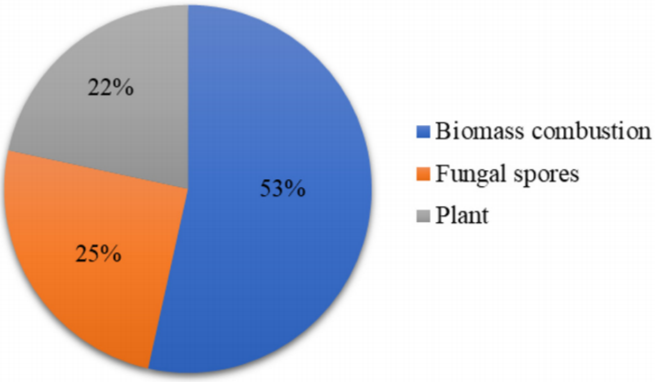

Fig. 4. Contribution of each source to saccharides in Shanghai.

3.4. N-dicarboxylic acids

In this study, we analyzed the aerosol samples for homologous series of n-dicarboxylic acids (DCAs, C4 to C9). As shown in Table 1, the annual average mass concentration of DCAs was 53.6 ng/m^3. On average, we observed the highest concentrations for succinic (C4) and azelaic acids (C9) (mean values: 20.6 ng/m^3 and 18.9 ng/m^3, respectively), which each account for > 30% of the total DCA concentration. Table S7 provides a summary of previously reported atmospheric DCA concentrations in China and other parts of the world. We compared the average concentrations between our data and the data from these studies. As shown in table S7, the concentration of C4 in Shanghai (20.6 ng/m^3) was higher than urban sites in Hong Kong (13.8 ng/m^3, (Ho et al., 2011)), Guangzhou (14.8 ng/m^3, (Ho et al., 2011)), Fairbanks (8.62 ng/m^3, (Deshmukh et al., 2018)), and Sapporo (17.1 ng/m^3, (Pavuluri et al., 2018)), but lower than urban sites in Seoul (135.6 ng/m^3, (Choi et al., 2016)), Beijing (41.9 ng/m^3, (Zhao et al., 2018)), Huangshi (48.0 ng/m^3, (Liu et al., 2019a)), and 14 Chinese cities (75.8 ng/m^3, (Ho et al., 2007)). C6 concentrations (3.4 ng/m^3) in Shanghai were lower than most other urban sites, except for Fairbanks (1.67 ng/m^3) and Sapporo (2.38 ng/m^3). The average concentration of C9 (18.9 ng/m^3) was comparable to levels in Hong Kong (17.0 ng/m^3), Guangzhou (15.5 ng/m^3), and Sapporo (13.8 ng/m^3) and was higher than the averages of China (30.3 ng/m^3), Seoul (74.1 ng/m^3), Huangshi (62.3 ng/m^3), and 14 Chinese cities. The C9 concentrations were also four times higher than those reported from Fairbanks (4.1 ng/m^3). DCAs are mainly derived from secondary oxidation. For example, C5 and C6 are predominantly produced by the photo-oxidation of cyclohexene and methylene cyclohexane in the atmosphere (Kawamura and Yasui, 2005; Müller et al., 2007; Wang et al., 2006). This is confirmed by the strong correlation observed between the concentrations of the two species (r = 0.96) in this study. However, C9 is predominantly formed by the oxidation of biogenic unsaturated fatty acids (UFAs) (e.g., oleic acid, C18:1) (Hung et al., 2005; Kawamura and Kaplan, 1987). Therefore, C6/C9 ratios can be used to identify the source contributions to the aerosol diacids from either anthropogenic or biogenic precursors (Kawamura and Yasui, 2005). The annual average value of C6/C9 in the Shanghai samples was 0.2 (0.1–0.6), suggesting that Shanghai aerosols are predominantly influenced by biogenic UFAs. As a megacity, central Shanghai does not suffer from high amounts of crop biomass burning. The observed higher C9 concentration may therefore be sourced from the oxidation of biogenic unsaturated fatty acids, either from plant emissions or domestic cooking (Rogge et al., 1991b).The C6/C9 ratios in this study were lower than those reported from other domestic and foreign cities such as the 14 cities in China (0.6), Beijing (0.5), and Huangshi (0.9). However, the Shanghai ratios are comparable to the ratios reported from urban areas in Sapporo (0.17) and Seoul (0.19).

3.4.1. Aromatic acids

A group of eight $PM_{2.5}$-bound aromatic organic acids were analyzed, including two phthalic acids (phthalic acid (pH) and isophthalic acid (iPh)), two benzene-tricarboxylic acids (BTCAs) (i.e., 1,2,4-BTCA, and 1,3,5-BTCA), and four phenolic acids (i.e., 3-hydroxy benzoic acid (3-OHBA), 4-hydroxy benzoic acid (4-OHBA), syringic acid, and vanillic acid). The annual average mass concentration of aromatic acids was 25.0 ng/m^3. Ph was the most abundant aromatic acid species in this study, followed by 1,2,4-BTCA, and 4-OHBA. The average Ph concentration (11.9 ng/m^3) in Shanghai was higher than Alaska (2.58 ng/m^3) and Sapporo (3.99 ng/m^3), but lower than those from other Chinese urban sites, such as Hong Kong (33.5 ng/m^3), Guangzhou (153 ng/m^3), Beijing (27.7 ng/m^3), the 14 Chinese cities, and the national average for China (90.1 ng/m^3) (see Table S7). According to field measurements, pH is mainly produced by secondary photochemical reactions of polycyclic aromatic hydrocarbons (PAHs) and is considered a tracer for naphthalene-derived SOA. In addition to C6/C9, Ph/C9 can also be used as an indicator to identify the relative contributions of anthropogenic and biogenic sources to the aerosol diacids. The annual average value of Ph/C9 in the aerosols of Shanghai was 0.6 (0.0–3.9), which is lower than the ratios reported for Hong Kong (1.96), Guangzhou (9.9), Huangshi (2.23), and Gosan (5.6), and is comparable to the ratio reported in Fairbanks (0.63) (Table S7). These comparisons suggest that aerosols in Shanghai are predominantly influenced by biogenic UFAs. The ratios of C6/C9 and Ph/C9 were highest in winter relative to the other three seasons, likely due to a reduction in the C9 concentration from biogenic sources in winter, and an increase in the flux anthropogenic pollutants to the city via the north and northwest air masses. The annual average concentration of 1,2,4-BTCA of the entire Shanghai dataset was 7.2 ng/m^3. A small number of studies have already reported the abundance of BTCA in our study region. Molecular simulation and field research have shown that substances containing aromatic rings with PAHs and black carbon can generate BTCA via the process of photochemical oxidation. The two BTCAs in this study were highly correlated with each other (r = 0.95) and with the concentrations of C4 , C5 , C6, and Ph (r: 0.72–0.81), inferring the dominance of secondary aerosol formation. Among the four phenolic acids, 3-OHBA, vanillic acid, and syringic acid were similar in value, with averages of 0.8, 0.5, and 0.3 ng/m^3, respectively, while the average 4-OHBA concentration was significantly higher at 2.5 ng/m^3. Similar concentration levels and homologue distributions were reported in a previous study in Southern China in which phenolic acids were highly correlated (R from 0.79–0.94). Phenolic acids were strongly correlated with levoglucosan (r > 0.9) in this study, which further confirms their origins from BB activities. Phenolic compounds such as 4-OHBA, vanillic acid, and syringic acid are major tracers of burning lignin (Bernd R. T. Simonelt, 1993; Simoneit, 2002). The high correlation between 3-OHBA and 4-OHBA strongly infers 3-OHBA to also be derived from BB. The mass ratio of syringic acid to vanillic acid (S/V) can also be used to identify the relative contributions of the different types of vegetation used in BB (Myers-Pigg et al., 2016). According to previous studies, the burning of both woody angiosperms (hardwood) and non-woody angiosperms results in aerosol S/V ratios of 0.1 to 2.44, while the burning of gymnosperms (softwood) results in much lower ratios of 0.01–0.24 (Myers-Pigg et al., 2016; Shakya et al., 2011). In this study, S/V ratios throughout the sampling period ranged from 0.1 to 6.8 with an average of 0.7, suggesting that hardwood and grass (including crop residue) were dominant sources of BB aerosols in Shanghai. This finding is further supported by the results derived from the anhydrosugar pyrolysis ratios (Lev/Man, Man/Gal) discussed in Sect. 3.2.1.

3.4.2. Oxycarboxylic acids

We identified five PM$_{2.5}$-bound oxycarboxylic acids, including three hydroxyl-carboxylic acids (malic acid (hC4), glyceric acid, and tartaric acid) and two carbonyl-carboxylic acids (glyoxylic acid (ωC2) and α-ketoglutaric acid). Glyceric acid was the dominant compound, followed by hC4 and ωC2, which together accounted for 88% (38%–98%) of the total oxycarboxylic acid concentration. Glyceric acid is predominantly derived from biological sources (Decesari et al., 2006). Glyceric acid is also derived from the atmospheric oxidation of 1,3-butadiene, which itself is sourced from automobile exhausts (as a combustion byproduct), gasoline evaporative emissions, biomass burning, and heated cooking oils (Jaoui et al., 2014). Malic acid (hC4) is a secondary photooxidation product of dicarboxylic acids and is also hypothesized to be photochemically generated from succinic acid (C4) via hydroxylation (Kawamura and Ikushima, 1993). The average hC4/C4 ratio in summer and autumn in this study were two times higher than spring and winter, which further supports this hypothesis. Similar observations have also been reported in urban Tokyo and Gosan (Kawamura and Ikushima, 1993; Kundu et al., 2010). Other than direct emissions, the concentrations of atmospheric ketoacids are predominantly controlled by photochemical processes, particularly for small ketoacids. In this study, ωC2 was well correlated with C4–C6 (r: 0.55–0.59), which is consistent with the atmospheric oxidation process proposed by Ho et al. (2006) (Ho et al., 2006).

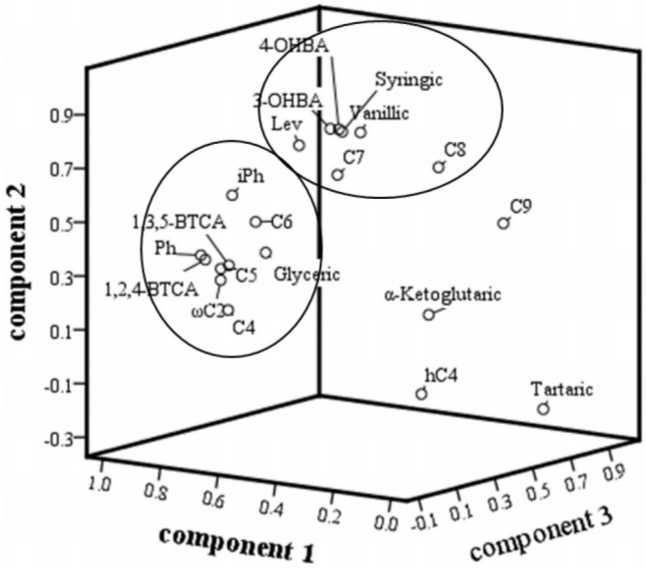

Fig. 5. Principal components plots.

3.4.3. Source identification of carboxylic acids by PCA

We performed PCA on the correlation matrix of the nineteen carboxylic acids and levoglucosan (Fig. 5 and Table S3–S4) to further investigate the sources of detected carboxylic acids. PCA identified three components that explain 36.6%, 32.6%, and 14.8% of the total variance (Table S8). The first factor was characterized by C4–C7, ωC2, pH, iPh, 1,2,4-BTCA, 1,3,5-BTCA, and glyceric acid, which represent pollutants mainly derived from secondary atmospheric oxidation. The second factor was characterized by 3-OHBA, 4-OHBA, vanillic acid, syringic acid, and Lev, which represent pollutants mainly derived from biomass burning emissions. The third factor was characterized by C9, hC4, and tartaric acid. C9 is primarily derived from the atmospheric photochemical oxidation of biogenic unsaturated fatty acids emitted from plants. Combined, factor 3 represents pollutants derived from plant emissions.

4. Conclusion

Total of thirty-six PM$_{2.5}$-bound polar organic compounds (nineteen dicarboxylic acids and seventeen saccharides) were quantitated from September 2015 to August 2016 in central of Shanghai, China. The concentration and the chemical composition of PM$_{2.5}$ in three sampling sites within central of Shanghai showed significant seasonal variation but no spatial variation. PM$_{2.5}$ mass and major PM$_{2.5}$-bound POC concentrations showed seasonal variations with significant higher concentrations in winter than in other three seasons. Higher concentrations in winter could be attributed to more aged and polluted air which was transported into the region by the prevailing wind from the northern continent, especially for POCs that is greatly affected by biomass burning. The content of levoglucosan was the most abundant among the saccharide compounds of PM$_{2.5}$, with the annual average concentration of 80.0 ng/m^3. The results of positive matrix factorization analysis suggested that saccharides compounds in atmospheric PM$_{2.5}$ in Shanghai could be derived from biomass burning, plant, fungal spore, as well as other mixed source emissions. The annual average concentration of total acids concentration is 122.1 ng/m^3 with C4, pH and glyceric acid were found as the most abundant saturated n-dicarboxylic acids, aromatic organic acids and oxycarboxylic acid in Shanghai PM$_{2.5}$, respectively. Ratios of C6/C9 and Ph/C9 in Shanghai were lower than other cities indicating that it had more influenced by biogenic UFAs. The PCA results showed that secondary aerosols(both from anthropogenic and biogenic sources)and biomass burning emissions were the most important sources of carboxylic acids in Shanghai.

Decalaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosres.2019.104817.

References

Balla, D., Voutsa, D., Samara, C., 2018. Study of polar organic compounds in airborne particulate matter of a coastal urban city. Environ. Sci. Pollut. Res. Int. 25, 12191–12205.

Bauer, H., et al., 2008. Arabitol and mannitol as tracers for the quantification of airborne fungal spores. Atmos. Environ. 42, 588–593.

Bernd, R.T., Simonelt, W.F.R., 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. Environ. Sel. Technol. 27, 2533–2541.

Bieleski, R.L., 1995. Onset of Phloem Export from Senescent Petals of Daylily. Plant Physiol. 109, 557–565.

Chen, J., Kawamura, K., Liu, C.-Q., Fu, P., 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.

Choi, N.R., Lee, S.P., Lee, J.Y., Jung, C.H., Kim, Y.P., 2016. Speciation and source identification of organic compounds in PM(1)(0) over Seoul, South Korea. Chemosphere 144, 1589–1596.

Cowie, G.L., Hedges, J.I., 1984. Carbohydrate sources in a coastal marine environment. Geochim. Cosmochim. Acta 48, 2075–2087.

Decesari, S., et al., 2006. Characterization of the organic composition of aerosols from Rondonia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds. Atmos. Chem. Phys. 6, 375–402.

Deshmukh, D.K., Mozammel Haque, M., Kawamura, K., Kim, Y., 2018. Dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in fine aerosols over Central Alaska: Implications for sources and atmospheric processes. Atmos. Res. 202, 128–139.

Feng, J., et al., 2006. Characteristics of organic matter in $PM_{2.5}$ in Shanghai. Chemosphere 64, 1393–1400.

Feofilova, E.P., Ivashechkin, A.A., Alekhin, A.I., 2012. Sergeeva Ia, E., [Fungal spores: dormancy, germination, chemical composition, and role in biotechnology (review)]. Prikl. Biokhim. Mikrobiol. 48, 5–17.

Fraser, M.P., Lakshmanan, K., 2000. Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. Environ. Sci Technol. 34, 4560–4564.

Fu, P.Q., Kawamura, K., Kobayashi, M., Simoneit, B.R.T., 2012. Seasonal variations of sugars in atmospheric particulate matter from Gosan, Jeju Island: significant contributions of airborne pollen and Asian dust in spring. Atmos. Environ. 55, 234–239.

Fu, P., Kawamura, K., Usukura, K., Miura, K., 2013. Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise. Mar. Chem. 148, 22–32.

Fu, P.Q., et al., 2016. Molecular markers of biomass burning, fungal spores and biogenic SOA in the Taklimakan desert aerosols. Atmos. Environ. 130, 64–73.

Graham, B., et al., 2003. Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography-mass spectrometry. J Geophys Res-Atmos 108 pp. n/a-n/a.

Hatakeyama, S., et al., 1985. Ozone-cyclohexene reaction in air: quantitative analysis of particulate products and the reaction mechanism. Environ. Sci. Technol. 19, 935–942.

Ho, K.F., et al., 2006. Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong. Atmos. Environ. 40, 3030–3040.

Ho, K.F., et al., 2007. Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China. J. Geophys. Res.-Atmos. 112.

Ho, K.F., et al., 2011. Summer and winter variations of dicarboxylic acids, fatty acids and benzoic acid in $PM_{2.5}$ in Pearl Delta River Region, China. Atmos. Chem. Phys. 11, 2197–2208.

Hung, H.M., Katrib, Y., Martin, S.T., 2005. Products and mechanisms of the reaction of oleic acid with ozone and nitrate radical. J. Phys. Chem. A 109, 4517–4530.

Jaoui, M., Lewandowski, M., Docherty, K., Offenberg, J.H., Kleindienst, T.E., 2014. Atmospheric oxidation of 1,3-butadiene: characterization of gas and aerosol reaction products and implications for $PM_{2.5}$. Atmos Chem. Phys. 14, 13681–13704.

Jia, Y., Fraser, M., 2011. Characterization of saccharides in size-fractionated ambient particulate matter and aerosol sources: the contribution of primary biological aerosol particles (PBAPs) and soil to ambient particulate matter. Environ. Sci. Technol. 45, 930–936.

Kawamura, K., Bikkina, S., 2016. A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation. Atmos. Res. 170, 140–160.

Kawamura, K., Ikushima, K., 1993. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. Environ. Sci. Technol. 27, 2227–2235.

Kawamura, K., Kaplan, I.R., 1987. Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. Environ. Sci. Technol. 21, 105–110.

Kawamura, K., Yasui, O., 2005. Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. Atmos. Environ. 39, 1945–1960.

Kawamura, K., Kasukabe, H., Barrie, L.A., 1996. Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations. Atmos. Environ. 30, 1709–1722.

Kumar, P.P., Broekhuizen, K., Abbatt, J.P.D., 2003. Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species. Atmos. Chem. Phys. 3, 509–520.

Kundu, S., Kawamura, K., Lee, M., 2010. Seasonal variations of diacids, ketoacids, and α-dicarbonyls in aerosols at Gosan, Jeju Island, South Korea: Implications for sources, formation, and degradation during long-range transport. J. Geophys. Res. Atmos. 115.

Li, M., Jing, Z.M., Feng JL, L., 2013. Concentrations and sources of Saccharides in $PM_{2.5}$ in Shanghai. In: Journal of Shanghai University (Natural Science).

Li, X., et al., 2017. Molecular composition of organic aerosol over an agricultural site in North China Plain: Contribution of biogenic sources to $PM_{2.5}$. Atmos. Environ. 164, 448–457.

Liang, L.L., et al., 2015. Composition and source apportionments of saccharides in atmospheric particulate matter in Beijing. Environ. Sci. 36, 3935–3942.

Liang, L., et al., 2016. Seasonal variations and source estimation of saccharides in atmospheric particulate matter in Beijing, China. Chemosphere 150, 365–377.

Liu, H., et al., 2019a. Dicarboxylic acids and related compounds in fine particulate matter aerosols in Huangshi, Central China. J. Air Waste Manag. Assoc. 69, 513–526.

Liu, N., Zhou, S., Liu, C., Guo, J., 2019b. Synoptic circulation pattern and boundary layer structure associated with $PM_{2.5}$ during wintertime haze pollution episodes in Shanghai. Atmos. Res. 228, 186–195.

Liu, Y., et al., 2019c. Secondary organic aerosols in Jinan, an urban site in North China: significant anthropogenic contributions to heavy pollution. J. Environ. Sci. (China) 80, 107–115.

Ma, S.X., Wang, Z.Z., Bi, X.H., Sheng, G.Y., Fu, J.M., 2009. Composition and source of saccharides in aerosols in Guangzhou, China. Chin. Sci. Bull. 54, 4500–4506.

Medeiros, P.M., Simoneit, B.R.T., 2008. Source Profiles of Organic Compounds Emitted upon Combustion of Green Vegetation from Temperate climate Forests. Environ. Sci. Technol. 42, 8310–8316.

Müller, C., Iinuma, Y., Böge, O., Herrmann, H., 2007. Applications of CE-ESI-MS/MS analysis to structural elucidation of methylenecyclohexane ozonolysis products in the particle phase. Electrophoresis 28, 1364–1370.

Myers-Pigg, A.N., et al., 2016. Signatures of Biomass burning Aerosols in the Plume of a Saltmarsh Wildfire in South Texas. Environ. Sci. Technol. 50, 9308–9314.

Nan, D.S., 2019. Transport Pathways and potential sources of $PM_{2.5}$ during the Winter in Zhengzhou. Environ. Sci. 40.

Oliveira, C., et al., 2007. Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the North and South of Europe. Atmos. Environ. 41, 5555–5570.

Pacini, E., 2000. From anther and pollen ripening to pollen presentation. In: Pollen and pollination. Springer, pp. 19–43.

Paul, E., Clark, F.J.S.M., 1996. Soil microbiology biochemistry. Academic Press, San Diego.

Pavuluri, C.M., Kawamura, K., Fu, P., 2018. Seasonal Distributions and Stable Carbon Isotope Ratios of Water-Soluble Diacids, Oxoacids, and α-Dicarbonyls in Aerosols from Sapporo: Influence of Biogenic Volatile Organic Compounds and Photochemical Aging. ACS Earth and Space Chem. 2, 1220–1230.

Peng, C., Chan, M.N., Chan, C.K., 2001. The hygroscopic properties of dicarboxylic and multifunctional acids: measurements and UNIFAC predictions. Environ. Sci. Technol. 35, 4495–4501.

Popovicheva, O., et al., 2014. Physicochemical characterization of smoke aerosol during large-scale wildfires: Extreme event of August 2010 in Moscow. Atmos. Environ. 96, 405–414.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1991a. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. Environ. Sci. Technol. 25, 1112–1125.

Rogge, W.F., et al., 1991b. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. Environ. Sci. Technol. 25, 1112–1125.

Rutledge, A.C., Adeli, K., 2007. Fructose and the metabolic syndrome: pathophysiology and molecular mechanisms. Nutr. Rev. 65, S13–S23.

Sang, X.F., Zhang, Z.S., Chan, C.Y., Engling, G., 2013. Source categories and contribution of biomass smoke to organic aerosol over the southeastern Tibetan Plateau. Atmos. Environ. 78, 113–123.

Saxena, P., Hildemann, L.M., 1996. Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. J. Atmos. Chem. 24, 57–109.

Shakya, K.M., Louchouarn, P., Griffin, R.J., 2011. Lignin-derived phenols in Houston aerosols: implications for natural background sources. Environ. Sci. Technol. 45, 8268–8275.

Shen, R., et al., 2018. Typical polar organic aerosol tracers in $PM_{2.5}$ over the North China Plain: Spatial distribution, seasonal variations, contribution and sources. Chemosphere 209, 758–766.

Simoneit, B.R.T., 2002. Biomass burning — a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 129–162.

Simoneit, B.R.T., et al., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos. Environ. 33, 173–182.

Simoneit, B.R., et al., 2004a. Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. J. Geophys. Res.: Atmos. 109.

Simoneit, B.R.T., et al., 2004b. Sugars - Dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. Environ. Sci. Technol. 38, 5939–5949.

Tedetti, M., et al., 2007. Hydroxyl radical-induced photochemical formation of dicarboxylic acids from unsaturated fatty acid (oleic acid) in aqueous solution. J. Photochem. Photobiol. a-Chem. 188, 135–139.

Urban, R.C., et al., 2014. Sugar markers in aerosol particles from an agro-industrial region in Brazil. Atmos. Environ. 90, 106–112.

Wang, H.B., Kawamura, K., Ho, K.F., Lee, S.C., 2006. Low molecular weight dicarboxylic acids, ketoacids, and dicarbonyls in the fine particles from a roadway tunnel: possible secondary production from the precursors. Environ. Sci. Technol. 40, 6255–6260.

Wang, Y.Q., Zhang, X.Y., Draxler, R.R., 2009. TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data. Environ. Model Softw. 24, 938–939.

Wang, G.H., et al., 2011. Molecular composition and size distribution of sugars, sugar-alcohols and carboxylic acids in airborne particles during a severe urban haze event caused by wheat straw burning. Atmos. Environ. 45, 2473–2479.

Wang, X., et al., 2018. Saccharides in summer and winter $PM_{2.5}$ over Xi'an, Northwestern China: sources, and yearly variations of biomass burning contribution to $PM_{2.5}$. Atmos. Res. 214, 410–417.

Yang, Y.H., et al., 2012. Observation of elevated fungal tracers due to biomass burning in the Sichuan Basin at Chengdu City, China. Sci. Total Environ. 431, 68–77.

Yang, F., et al., 2016. Anthropogenic and biogenic organic compounds in summertime fine aerosols ($PM_{2.5}$) in Beijing, China. Atmos. Environ. 124, 166–175.

Ye, B.M., et al., 2003. Concentration and chemical composition of $PM_{2.5}$ in Shanghai for a 1-year period. Atmos. Environ. 37, 499–510.

Yin, S., et al., 2018. Characteristics of inorganic aerosol formation over ammonia-poor and ammonia-rich areas in the Pearl River Delta region, China. Atmos. Environ. 177, 120–131.

Yttri, K.E., Dye, C., Kiss, G., 2007. Ambient aerosol concentrations of sugars and sugar-alcohols at four different sites in Norway. Atmos. Chem. Phys. 7, 4267–4279.

Zhang, Y.L., Kawamura, K., Cao, F., Lee, M., 2016. Stable carbon isotopic compositions of low-molecular-weight dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and fatty acids: Implications for atmospheric processing of organic aerosols. J. Geophys. Res.: Atmos. 121, 3707–3717.

Zhao, W., et al., 2018. Molecular distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids and < i > α < /i > -dicarbonyls in PM < sub > 2.5 < /sub > from Beijing, China. Atmos. Chem. Phys. 18, 2749–2767.