# Measurement Report:~~concentrations and composition profiles~~ Characterization of sugars and amino acids in atmospheric fine particulates: identify local primary sources ~~characteristics~~

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**Abstract.** Sugars and amino acids are major classes of organic components in atmospheric fine particles and play important roles in atmospheric processes. However, the identification of their sources in different regions is less explored. To characterize local primary sources (biomass burning, plant and soil sources) and evaluate their contributions to the total sugar compounds and amino acids (AAs)~~AAs~~ pool in different regions, fine particulate matter samples were collected from the urban, rural and forest areas in Nanchang, China~~locations~~. The concentrations and compositions of sugar compounds (anhydrosugars, primary sugars and sugar alcohols), free amino acids (FAAs) and combined amino acids (CAAs) were analyzed by gas chromatography–mass spectrometry (GC-MS) after silylation derivatization. Urban area had significantly higher average $\Sigma$sugars concentration ($317\pm139$ ng m$^{-3}$) than that of the rural ($181\pm72$ ng m$^{-3}$) and forest ($275\pm154$ ng m$^{-3}$) areas ($p < 0.05$). Overall, the distribution pattern of sugar compounds and CAAs in PM$_{2.5}$ was generally similar ~~among the urban, rural and forest locations~~ in three areas. Levoglucosan accounted for 24.4%, 22.0% and 21.7%, respectively of the total sugars pool in the urban, rural and forest areas. ~~Moreover, the average contribution of sugar compounds and CAAs reflecting BB, plant and soil sources to the total sugar and CAA pool were consistent in all sampling locations.~~ These suggest besides biomass burning (BB)~~BB~~, plant and soil sources ~~all~~ have important contributions to aerosol sugars and CAAs in three areas. In the urban area, the concentrations of anhydrosugars showed a positive correlation with combined Gly concentrations, but no correlation was found between these two compounds in the rural and forest areas, indicating that the urban area is mainly affected by local combustion sources~~.~~. This conclusion was also supported by the positive correlation between levoglucosan and non-sea-salt potassium only observed in the urban area (Lev = 0.07 K$^+$+37.7, r=0.6, p<0.05). ~~while the rural and forest areas may be more influenced by long-transport BB source.~~ In addition, the average levoglucosan and mannosan (L/M) ratio in the urban location (59.9) was much higher than those in the rural (6.9) and forest locations (7.2), implying BB aerosols collected in the urban location originated from lignite burning while the type of biofuels used in the rural and forest locations is mainly softwood. The concentrations of sugar alcohols in the rural and forest locations were positively correlated

with that of CAAs, which are abundant in the topsoil (r = 0.53 ~ 0.62, *p* < 0.05), suggesting that the contribution of local topsoil sources is large in these two locations. In the rural area, the concentrations of primary sugars were positively correlated with that of ~~combined CAA species abundant in local dominant vegetation.~~ ~~combined aspartic acid (a CAA specie abundant in grass, the dominant vegetation in the rural area), while in the forest area, primary sugars had good correlations with combined citrulline, lysine, ornithine, glutamic acid and serine (CAA species abundant in pine, dominant vegetation in the forest area), indicating that combining primary sugars with major CAA species in local dominant vegetations may identify local vegetation types. Furthermore, the nitrogen isotope of combined Gly and PMF model results demonstrated that the average contribution of combustion processes to total sugar compounds and CAAs pool in the urban and rural locations was higher than that in the forest location while primary biogenic sources showed a higher average contribution in the forest location than those in rural and urban locations.~~ Our findings suggest that combining specific sugar tracers and chemical profiles CAAs in local emission sources can provide insight to primary sources characteristics including the types of biofuels burned, the contribution of topsoil sources and local vegetation types.

## 1 Introduction

Organic aerosols (OAs), are recently highlighted because they account for a significant fraction (20%–90%) of fine aerosols (Verma et al., 2021; Wu et al., 2018; Xu et al., 2020a). Furthermore, they may influence the global climate as condensation nuclei (CCN) and ice nuclei (IN) (Ng et al., 2010; Steinfeld, 1998), contribute a large amount of terrestrial organic carbon to the remote oceans (Zhu et al., 2015), and cause human health problems (Nel, 2005; Fu et al., 2008). Thus, a profound understanding of the abundance, composition and sources of OAs in fine aerosols is of great significance to reduce the adverse effects of OAs on the atmospheric environments and human being health (Fan et al., 2020).

As the vital fraction of water-soluble organic compounds (WSOC), sugars and AAs are ubiquitous in the atmosphere from different geographical locations, including urban (Wang et al., 2019), forests (Mace et al., 2003), mountains (Barbaro et al., 2020; Fu et al., 2008), marine (Fu et al., 2013; Matsumoto and Uematsu, 2005) and polar regions (Feltracco et al., 2020; Feltracco et al., 2019). Moreover, chemical fingerprints of these two major classes of organic components in atmospheric particles have been used to elucidate relative contribution of different sources to aerosols (Jia et al., 2010; Matos et al., 2016; Yan et al., 2019). Specifically, levoglucosan and related anhydrosugar isomers (mannosan and galactosan), produced from pyrolysis of cellulose and hemicellulose at temperatures higher than 300°C and ranking as the most abundant compounds in biomass burning emissions, have been recognized as specific molecular markers for biomass burning (BB) sources (Simoneit, 2002). Although there is still lack of knowledge about BB and amino acids, the potential correlation between the free glycine (Gly) concentrations and BB aerosols has been suggested in past studies (Zhu et al., 2020a; Samy et al., 2013; Violaki and Mihalopoulos, 2010). ~~Besides that, BB can elevate the D/L-Ala ratio of atmospheric particles (Zangrando et al., 2016; Barbaro et al., 2019).~~

Primary sugars and sugar alcohols are frequently utilized in tracking and estimating the contribution of soil and associated biogenic aerosols, including fungi, viruses, bacteria, pollen, and plant and animal debris (Liang et al., 2016). For instance, plant-debris-derived aerosol organic carbon was estimated based

on the relationship of glucose and plant debris (Fan et al., 2020). Sucrose have been widely employed to indicate airborne pollen grains (Wang et al., 2021; Fu et al., 2012; Yan et al., 2019). The sugar alcohols arabitol and mannitol, are found to be produced by fungi, lichens, soil biota, and algae to overcome environmental stress (Medeiros et al., 2006). These sugar alcohols have been recently proposed as molecular tracers for fungal spores (Elbert et al., 2007). In addition, algae and higher plants are also proved to be an important source of mannitol (Feltracco et al., 2020). Similarly, the level of combined amino acids (CAAs) in aerosols has been used as marker for primary biological aerosol particles (PABPs) and its composition can distinguish different types PABPs based on chemical composition of CAAs in corresponding biological sources (Axelrod et al., 2021; Abe et al., 2016).

Obviously, sugars and AAs in aerosols may share similar source to some extent. However, the concentrations, compositions and source apportionment of sugars and AAs in aerosols have been studied separately in previous studies. Till now, few studies have focused on sugars and amino acids in aerosols simultaneously, and the concentration and composition profiles of sugar compounds and AAs in different areas impacted by different local primary sources is still poorly understood (Barbaro et al., 2019; Ruiz-Jimenez et al., 2021). It is expected that coupling source specific sugars with most abundant AA species in local primary sources may provide insight into more source signatures.

In recent years, we investigated the source and possible atmospheric transformation process of amino acids and proteinaceous material in different size-segregated particles collected from the forest, rural, suburban and urban sites under different ambient oxidation levels (Zhu et al., 2020a; Zhu et al., 2020b; Zhu et al., 2021b; Zhu et al., 2021a; Wen et al., 2022). The nitrogen isotope composition of free glycine ($\delta^{15}N_{F-Gly}$) in potentially emission sources were analysed and $\delta^{15}N_{F-Gly}$ values released by BB sources are significantly higher than those from natural primary sources (Zhu et al., 2020a). In the study of Zhu et al. (2020b), the origin of FAAs and CAAs and their atmospheric transformation processes in $PM_{2.5}$ were explored by analysing the concentrations of FAAs and CAAs, and $\delta^{15}N$ values of free and combined Gly in $PM_{2.5}$ and main primary emission sources (plant, soil, and aerosol from BB). Combined compound-specific $\delta^{15}N$ patterns of hydrolyzed amino acids (HAAs)HAAs, degradation index with the variance within trophic HAAs in fine and coarse particles, we demonstrated that AAs in coarse particles have advanced bacterial degradation states compared to fine particles (Zhu et al., 2021b). Correlations between the concentrations of FAAs, CAAs and oxidants under different ambient $NO_2$ and $O_3$ levels were discussed to elucidate the mechanism of FAAs formation from the protein degradation in relation to ambient $NO_2$ and $O_3$ concentrations (Zhu et al., 2021a). Although primary sources are proved to be important sources of AAs in the atmosphere in our previous study, further information of local primary sources characteristics including the type of biofuels burned, local vegetation types and the contribution of topsoil sources are missing.

To further clarify local primary source information in different locations, Tthe concentration and composition of sugars, FAAs and CAAs in $PM_{2.5}$ samples collected from the urban, rural and forest areas in Nanchang, China were analysed. In order to obtain a sufficient sample size for analysis of sugar compounds (anhydrosugars, primary sugars and sugar alcohols), FAAs and CAAs in one sample simultaneously, in this study different filter samples were collected during the same sampling period as our previous study (Zhu et al., 2020b). The concentration and composition of sugars, FAAs and CAAs

in PM~~2.5~~ samples collected from the urban, rural and forest areas in Nanchang, China were analysed. Given the documented roles of specific sugars as tracers for BB and PBAPs sources and the distribution of CAAs in primary sources, the variation pattern of the concentration and composition of specific CAAs species predominant in local primary source and the corresponding sugar tracers were compared. The correlations of source specific sugars with free amino acids (FAAs) and with major CAA species in local primary sources were evaluated (1) to character the concentration and composition profiles of sugar compounds, FAAs and CAAs in urban, rural and forest areas, (2) to obtain the information of the type of biofuels, local vegetation types and the contribution of topsoil sources in different sampling areas ~~(3) to quantify the contribution of each identified source to total aerosol sugars and CAAs based on positive matrix factorization (PMF).~~

## 2 Materials and Methods

### 2.1 Sample Collection

PM$_{2.5}$ samples were collected at three different locations (urban, rural and forest) in Nanchang, China from April 30, 2019 to May 13, 2019 (Figure S1). More details of sampling locations are available in supplement material (Table S1). Forty-two~~42~~ Filter samples were collected daily with a duration of 23.5 h on prebaked quartz fiber filters (450 °C, 10h) using high volume air samplers (KC-1000, Qingdao Laoshan Electronic Instrument company, China) at a flow rate of $1.05 \pm 0.03$ m$^3$ min$^{-1}$. Sampling was performed on the roof of buildings (15 m height) at each site. After the sampling the filter was recovered into a pre-combusted glass jar with a Teflon-lined screw cap, immediately placed in the freezer (the temperature is set to -20°C) and then transported to the laboratory within 1 hour and stored at -20°C before analysis, ~~then transported to the laboratory and stored at  20°C before analysis,~~ to prevent loss of semi-volatile/volatile organic compounds from the samples.

The field blank samples were collected by using a modified version of (Chow et al., 2010). After treated at 450 °C for 10 hours, field blank filters were loaded into filter holders and accompany the sampled filters to each sampling site. Field blanks accompanied sample shipments and were placed in the high-volume air samplers along with the sampled filters. The passive period for field blank filters was consistent with the samples. The only difference between samples and field blanks is that air is not drawn through field blanks. After the sampling, field blank filters were also recovered into filter holders and accompanied with the samples back to the laboratory. Three field blank samples were collected in this study, accounting for 7% of total sample number.

### 2.2 Analysis of sugar concentrations

For sugars analysis, samples were prepared using a modified version of (Fu et al., 2008). In brief, a filter aliquot (~160 m$^3$ of air) of each aerosol sample was extracted three times with dichloromethane/methanol (2:1; v/v) under ultrasonication for 10 min. The solvent extract was filtered through quartz wool packed in a Pasteur pipette and then dried with pure nitrogen gas. The dried extracts were reacted with 50 ml of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride (Sigma-Aldrich, St Louis, MO, USA) and 10 µl of pyridine (Sigma-Aldrich, St Louis, MO, USA) at 70°C for 3

h. After the reaction, derivatives were diluted by the addition of 140 μl of n-hexane containing the internal standard (C13 n-alkane, 1.43 ng μl$^{-1}$) prior to analysis by gas chromatography-mass spectrometry (GC-MS).

GC-MS analyses were performed on a Thermo Scientific TRACE GC (Thermo Scientific, Bremen, Germany) connected into a Thermo Scientific ISQ QD single quadrupole MS. The GC separation was achieved on a DB-5MS fused silica capillary column (30m × 0.25mm i.d., 0.25 μm film thickness) with the same GC oven temperature program: temperature hold at 90℃ for 1 min, increase from 90 to 120℃ at a rate of 12℃ min$^{-1}$, then further increase from 120 to 285℃ at a rate of 6℃ min$^{-1}$ with a final isotherm hold at 285℃ for 18 min. Helium was used as the carrier gas at a constant flow rate of 1.2 ml min$^{-1}$. The temperatures of GC injector and MS ion source were 280 ℃ and 250 ℃, respectively. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV and scanned from 50 to 650 Da. The individual compounds (TMS derivatives) were identified by comparing mass spectra with those reported in the literature and library data and authentic standards (Medeiros and Simoneit, 2007). Compounds were quantified using total ion current (TIC) peak area of each authentic standard relative to that of internal standard (C13 n-alkane), and converted to compound mass using calibration curves of internal standards. ~~In general, the obtained calibration curves show good linearity (R²>0.95) in the exploited range (Table S2). Field blanks were analyzed by the procedure used for the real samples. The data reported here were corrected for the field blanks. In total sixteen sugar compounds, including three anhydrosugars (levoglucosan, galactosan, mannosan), nine primary sugars (sucrose, glucose, fructose, ribose, trehalose, galactose, turanose, lactulose and maltose), and four sugar alcohols (arabitol, mannitol, pinitol and inositol), were detected in the Nanchang aerosols. The detailed method validation was provided in supporting information Table S2. Recoveries for sugars were better than 89% as obtained for the standards spiked onto the precombusted blank filters and treated as a real sample. The reproducibility of the analytical procedure was assessed through the relative standard deviation (RSD) of the replicate measurements. The RSD values ranged from 1.7 to 11.6%. The detection limits of sugars correspond to ambient concentrations of 0.2-0.9 ng μL⁻¹, which corresponds to ambient concentrations of 0.2-1.1 ng m⁻³ under a typical sampling volume of 1320m³.~~ In general, the obtained calibration curves show good linearity (R$^2$>0.99) in the exploited range (Table S2). The field blank filters were also analyzed by the procedure mentioned above in this section and then were run in parallel with the samples for all analyses in order to monitor significant background interferences (Urban et al., 2012). No signal different than that of the base line was obtained for any of the studied sugars. The concentrations of sugar reported here are corrected for the field blanks. The detailed method validation was provided in supporting information.

## 2.2 Analysis of FAAs and CAAs concentrations

The concentrations of FAAs and CAAs were prepared following the method described by our previous study and analyzed by gas chromatograph-mass spectrometer (Thermo Scientific, Bremen, Germany) (Zhu et al., 2020b). For more details of their concentrations analysis method are provided in the supplementary information~~analyses refer to our previous publication (Zhu et al., 2020b)~~.

### 2.3 Analysis of water-soluble ions

Water-soluble ions ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO^{3-}$ and $SO_4^{2-}$) were measured by ion chromatography (Dionex Aquion (AQ)™, Thermo Scientific™, USA) (Guo et al., 2020). Briefly, one eighth quartz filters were cut into pieces and transferred to a Nalgene tube. After added 50 mL Milli-Q water, the tube was ultrasonic vibration (30min), shaking (30min), and centrifugation (10min). Then, the supernatant was filtered by using pinhole filter with a 0.22μm microporous membrane. The extract was stored in a refrigerator at -20°C for analyses. The anions ($Cl^-$, $NO^{3-}$ and $SO_4^{2-}$) were determined by the ion chromatography system with an AS23 $4 \times 250$ mm analytical column, while the cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) were determined using the same IC system with a CS12A $4 \times 250$ mm column. A sample volume was 100 μL for both anion and cation analyses. Strict quality control was performed to avoid any possible contamination of the samples. In order to ensure the reliability of data, standard samples were re-measured every twenty samples. The standard solutions were bought from Merck, Germany. More details on quality assurance and control of water-soluble ions are available in the supporting information.

The detection limit of them were 0.001 μg L⁻¹, 1.21 μg L⁻¹, 1.77 μg L⁻¹, 2.47 μg L⁻¹, 0.09 μg L⁻¹, 5.1μg L⁻¹, 21.6 μg L⁻¹ and 11.5 μg L⁻¹, respectively. The relative standard deviation of the reproducibility test was less than 5% (Guo et al., 2020; Wen et al., 2022). The mass concentrations of non-sea salt $K^+$ (nss-$K^+$) and non-sea salt $Ca^+$ (nss-$Ca^+$) non-sea salt $SO_4^{2-}$ (nss-$SO_4^{2-}$) were calculated based on the measured $Na^+$ was assumed to be derived from sea salt as follows Ren et al. (2018) and Zhang et al. (2018)(Ren et al., 2018):

nss-$K^+$= $K^+$ -$Na^+ \times 0.037$

nss-$Ca^+$= $Ca^+$ -$Na^+ \times 0.0385$

nss-$SO_4^{2-}$= $SO_4^{2-}$ -$Na^+ \times 0.252$

### 2.4 Statistical Analyses

Statistical analysis and graphs were mainly was conducted by R (version 4.0.2) and Origin 2018 (OriginLab Corporation, USA). Normality tests of Shapiro-Wilk were performed. The concentrations sugar compounds (anhydrosugars, primary sugars and sugar alcohols), FAAs and CAAs are normally distributed. Pearson's correlations were conducted to examine the relationship between target sugar category and TFAA, between target sugar category and TCAA, between specific sugar tracers and individual CAA and between specific sugar tracers and individual FAA. Significant differences in the sugars concentration among three sampling sites were tested using the one-way analysis of variance (ANOVA) procedure, and compared using the LSD test; differences were considered significant at the level of $p < 0.05$.

## 3 Results and discussion

### 3.1 Sugars in the urban, rural and forest locations

### 3.1.1 Sugars concentrations in $PM_{2.5}$

The temporal variations of total sugars concentrations in $PM_{2.5}$ measured at the urban, rural and forest locations during the sampling campaign were shown in Figure 1. The total sixteen sugars ($\Sigma$sugars) were quantified in the atmospheric fine particulates. Average $\Sigma$sugars concentration measured in the urban, rural and forest location was 317±139, 181±72, 275±154 ng m$^{-3}$, respectively. Urban location had significantly higher average $\Sigma$sugars concentration than that observed in the rural location ($p < 0.05$), but the differences in average $\Sigma$sugars concentration between rural and forest locations are not significant ($p > 0.05$) (Figure S2).

Three target sugar categories (anhydrosugars, primary sugars, alcohol-sugar) were compared between the three sampling locations. The average concentrations of anhydrosugars in the urban location (88 ± 56 ng m$^{-3}$) was higher than those in the rural (44 ± 20 ng m$^{-3}$) and forest locations (62 ± 31 ng m$^{-3}$) (Figure S2). Similarly, the highest average concentration of levoglucosan, a good tracer of BB (Sheesley et al., 2003), was found in the urban location (83 ± 53 ng m$^{-3}$), followed by that in the rural (37 ± 16 ng m$^{-3}$) and forest locations (54 ± 27 ng m$^{-3}$) (Figure 2), indicating enhanced biomass burning activities in the urban location.

Nine primary sugars (fructose, glucose, xylose, sucrose, and trehalose) were measured in this study. The average concentration of total primary sugars measured in $PM_{2.5}$ was comparable in the urban, rural and forest location, with the averaged value of 120 ± 69, 71 ± 47 and 120 ± 82 ng m$^{-3}$, respectively (Figure 3). It is interesting to note that the average concentration of trehalose was higher in the urban location (28±66 ng m$^{-3}$) than those in the rural (2±4 ng m$^{-3}$) and forest locations (7±14 ng m$^{-3}$) ($p < 0.05$) (Figure S3). Trehalose has been reported to be the most abundant sugar in soils and be used as a tracer for the resuspension of surface soil and unpaved road dust (Fu et al., 2012; Medeiros et al., 2006). Thus, high levels of trehalose observed in the urban location indicates that soil resuspension and unpaved road dust are important sources in the urban location.

We also determined four sugar alcohols, consisting of mannitol, arabitol, pinitol and inositol. The concentrations of total sugar alcohols averaged 110 ± 50, 66 ± 28 and 93 ± 54 ng m$^{-3}$ in the urban, rural and forest locations, respectively (Figure 4). Average of the sum of mannitol and arabitol concentrations measured in the three sampling locations (75 ng m$^{-3}$) were higher than those reported in megacity Beijing (21 ng m$^{-3}$) (Kang et al., 2018) and rural site at Lincang, China (21.5 ng m$^{-3}$) (Wang et al., 2021). Since these sugar polyols are reported to be abundant in fungi, trees, branches, and leaves (Wang et al., 2021; Fu et al., 2008), the high abundance of mannitol and arabitol found in this study can be attributed to large amount of biological origin.

The average $\Sigma$sugars concentration measured in the three sampling locations were comparable to several previous studies, including those measured at urban Beijing, China (average: 200 ± 100 ng m$^{-3}$) (Yan et al., 2019), the urban HongKong, China (292 ng m$^{-3}$) (Wan and Yu, 2007) and Mangshan National Forest Park, China (325 ng m$^{-3}$) (Verma et al., 2021), lower than those observed at rural Linchang, China (638 ng m$^{-3}$) (Wang et al., 2021), rural Wangdu, China (487 ± 567 ng m$^{-3}$) (Yan et al., 2019), but much higher

compared to those measured in a natural forest area in India (156 ng m$^{-3}$) (Fu et al., 2010b) and Arctic
aerosol (0.6 ±0.5 ng m$^{-3}$) (Feltracco et al., 2020). In summary, the concentrations of aerosol sugars span
a large range in variety regions by different research groups, which may be caused by many factors,
including PM$_{2.5}$ concentration, the fraction of organic carbon in PM$_{2.5}$, vegetation and BB activities, and
anthropogenic activities (Jia et al., 2010; Verma et al., 2021). To further elucidate the differences in sugar
levels in aerosols collected from different regions, source apportionment is necessary.

**3.1.2 The composition of sugars in PM$_{2.5}$**

The distribution pattern of sugar compounds in PM$_{2.5}$ was generally similar among the urban, rural and
forest locations (Figure 5). The average contribution of anhydrosugars to total measured sugars in the
urban, rural and forest locations was 25.8%, 25.9% and 25.0%, respectively (Figure 5). Levoglucosan
was the most dominant species among anhydrosugars in all sampling locations (Figure S4), accounting
for 24.4%, 22.0% and 21.7% of the total sugars pool in PM$_{2.5}$ in the urban, rural and forest locations,
respectively, indicating biomass burning is common in all locations. However, the average contribution
of levoglucosan to the total measured sugars in all locations were lower than those of the aerosol samples
sampled from other regions in China, such as Mountain Tai (46.1 ± 20.4% of total sugars in daytime
versus 39.0 ± 18.0% in nighttime) and fourteen cities in China (around 90%) (Fu et al., 2008; Wang et
al., 2006). This suggests that besides BB sources, other sources are also important sources for sugar
compounds in PM$_{2.5}$ in this study.

The contribution of primary sugars to total measured sugars measured at urban (40.1%) and forest
locations (41.2%), were slightly higher than that in the rural location (36.9%) (Figure 5). Fructose,
glucose and sucrose were the dominant primary sugar species in the three sampling locations (Figure S5).
It is noted that PM$_{2.5}$ sampled from the urban location had a larger contribution from trehalose (an average
6.5% of the total sugars) compared to those sampled from the rural (0.2%) and forest (0.8%) locations
(Figure 5). ~~This result also supports that PM$_{2.5}$ collected in the urban location may be more impacted by
road dust outflow than those in the rural and forest locations.~~ Since trehalose is proved to be the most
abundant saccharide in soils, the higher fraction of trehalose in total sugars pool in the urban location
than those in the rural and forest locations may indicate PM$_{2.5}$ collected in the urban location may be
more impacted by resuspension of surface soil or road dust outflow than the rural and forest locations
(Simoneit et al., 2004; Medeiros et al., 2006; Rogge et al., 2007; Fu et al., 2012). This is further supported
by the significantly higher average concentration of nss-Ca$^{2+}$ observed in urban site (1834.3 ng m$^{-3}$) than
that of rural (1027.8 ng m$^{-3}$) and forest (1130.7 ng m$^{-3}$). nss-Ca$^{2+}$ is reported to be mainly derived from
resuspended dust/soil in the ambient air (Barbaro et al., 2019; Rathnayake et al., 2016).

The average contribution of sugar alcohols to the total sugars pool in PM$_{2.5}$ was also close in the urban
(34.1%), rural (37.2%) and forest (33.8%) locations (Figure 5). Mannitol was the major sugar alcohol
specie in PM$_{2.5}$ (Figure S6), with an average contribution of 26.7%, 26.1% and 24.4% to the total sugars
pool in the urban, rural and forest locations, respectively. Primary sugars and sugar alcohols are reported
to be generally abundant in several animals, vegetative debris, microorganisms, fungal spores and pollen
(Jaenicke, 2005; Jia et al., 2010). The large proportion of primary sugars and sugar alcohols observed in

PM$_{2.5}$ collected from the three locations, further implying ambient sugars in this study were greatly influenced by primary biological sources.

### 3.1.3 Temporal variation of ambient sugars

305 Figure S7 presents the overall temporal variations of three classes of sugar compounds (anhydrosugars, primary sugars and sugar alcohols) in PM$_{2.5}$ collected at the three sampling locations. The temporal patterns of biomass burning tracers (anhydrosugars), primary bioaerosols tracers (primary saccharides) and surface soil and associated biotas tracer (sugar alcohols) are similar in the forest location. In the rural location, the temporal variation of primary saccharides is similar to that of sugar alcohols, but it is not

310 consistent with that of anhydrosugars. In contracts, anhydrosugars, primary sugars and sugar alcohols showed different trends in the urban location, indicating that sugar compounds in PM$_{2.5}$ collected in the urban location might be more influenced by combustion sources whereas ambient sugars in the forest are more influenced by primary biogenic sources.

### 3.2 AAs in the urban, rural and forest locations

315 ### 3.2.1 Concentration of specific CAAs

The temporal variations of source-specific sugars and amino acids concentrations in PM$_{2.5}$ were compared in this study. As exhibited in Figure 1, the temporal variation pattern of ambient total free amino acids (TFAA) was different from that of Σsugar concentrations in all locations. Therefore, the concentration and composition of FAAs will not be compared with sugar compounds in the following

320 sections. In contrast, the temporal variation pattern of Σsugar concentrations was consistent with that of TCAA measured in the three locations during the sampling period (Figure 1). Furthermore, the temporal variations in the concentrations of source-specific sugars (including anhydrosugars, primary sugars and sugar alcohols) were compared with those of some specific CAA species in PM$_{2.5}$. CAA species were initially grouped by their correlation with source-specific sugars at three sampling sites (Figure 6) and

325 their abundance in local primary biological sources (Figure S7).
there were similar time variation patterns in the concentrations of anhydrosugars, combined Gly and Phe (Figure 2), indicating anhydrosugars, combined Gly and Phe may be influenced by the identical source. The temporal variation pattern of primary sugars concentrations was similar to those of the Asp and the sum of combined Cit, Lys, Orn, Gly and Ser (Figure 3), implying primary sugars may share the similar

330 source with combined Asp, Cit, Lys, Orn, Gly and Ser. Additionally, the time variation pattern of sugar alcohols concentrations was consistent with that of the sum of Ala, Val, Leu and Ile concentrations (Figure 4), suggesting sugar alcohols and combined Ala, Val, Leu and Ile may be derived from the same sources.

In our previous study, the composition profiles of CAAs in the biomass burning (honeycomb briquette,

335 pine, and straw burning), soil, and plant sources (pine and straw) were investigated. Gly was found to be the predominant CAA in the aerosol from biomass burning sources, hydrophobic species (Ala, Val, Leu, and Ile) were the major CAA species in soil sources, and hydrophilic species (Glu, Lys, and Asp) were the abundant CAA species in plant sources (Zhu et al., 2020b). Based on these, temporal variation pattern between source specific sugar marker and CAA species abundant in this specific primary biological

source were compared. It is interesting to note that there were similar time variation patterns in the concentrations of anhydrosugars, combined Gly and Phe (Figure 2), indicating anhydrosugars, combined Gly and Phe may be influenced by the identical source. The temporal variation pattern of primary sugars concentrations was similar to those of the Asp and the sum of combined Cit, Lys, Orn, Gly and Ser (Figure 3), implying primary sugars may share the similar source with combined Asp, Cit, Lys, Orn, Gly and Ser. Additionally, the time variation pattern of sugar alcohols concentrations was consistent with that of the sum of Ala, Val, Leu and Ile concentrations (Figure 4), suggesting sugar alcohols and combined Ala, Val, Leu and Ile may be derived from the same sources.

Finally, according to the positive correlation between source-specific sugar markers and specific CAA species, and CAAs species predominant in each local primary biological source, as well as the similar temporal variation patterns between source-specific sugars and specific CAA species (Figure S8), Therefore, based on the specific CAAs species predominant in each emission source and temporal variations pattern of source-specific sugars and CAA species, ambient CAAs were finally divided into 4 groups: the first group includes Gly and Phe, which are may be closely related to the BB source; the second group includes Ala, Val, Leu, and Ile, which are greatly impacted by soil source; the third group including Asp, Cit, Lys, Orn, Glu, Ser, which is close with plant sources, and the other CAAs are classified into the fourth group (Figure 5).

The sum of Phe and Gly concentrations (group 1) in $PM_{2.5}$ averaged $58 \pm 46$ ng m$^{-3}$, $55 \pm 33$ ng m$^{-3}$ and $57 \pm 38$ ng m$^{-3}$ in the urban, rural and forest locations, respectively (Figure 2). Average concentration of the sum of Ala, Val, Leu, and Ile (group 2) in urban, rural and forested mosses were $110 \pm 75$ ng m$^{-3}$, $85 \pm 40$ ng m$^{-3}$ and $79 \pm 45$ ng m$^{-3}$, respectively, and average concentration of the sum of Asp, Cit, Lys, Orn, Glu, Ser (group 3) were $123 \pm 135$ ng m$^{-3}$, $78 \pm 53$ ng m$^{-3}$ and $93 \pm 68$ ng m$^{-3}$, respectively (Figure 3 and Figure 4). By comparing the concentration of CAAs in different groups, it can be found that the average of the sum of CAAs concentrations in group 2 and group 3 is higher than that in group 1. This suggested that similar to sugar compounds, CAAs in $PM_{2.5}$ collected from the three sampling locations were greatly impacted by plant and soil sources in addition to biomass burning source.

**3.2.2 Composition profiles of specific CAAs at the three sampling sites**

To better understand the influence of primary sources on the composition profiles of sugar compounds and CAAs, the percentage of CAA species abundant in specific primary sources was compared with that of the corresponding sugar molecular markers. As discussed above, combined Gly and Phe are the predominant CAA species in the aerosols from BB sources and they exhibited similar time variation patterns with molecular markers for BB sources (anhydrosugars). Therefore, their percentage were compared with the contribution of BB molecular marker to the total sugar compounds in three sampling sites. These two CAAsCombined Gly and Phe together accounted for an average of 19.7%, 23.9% and 20.4%, respectively, of the TCAAs pool in $PM_{2.5}$ collected from the urban, rural and forest locations. It is interesting to note that the percentage of Gly and Phe (abundant in BB source) in CAAs pool was generally similar to the percentage of the anhydrosugars in total sugar compounds in $PM_{2.5}$. Ala, Val, Leu, and Ile (abundant in soil source) together contributed an average of 35.0%, 33.3% and 31.1%, respectively, to the TCAAs pool in the urban, rural and forest locations, which was also similar to the

contribution of sugar alcohols to the total sugar compounds in the three locations. Furthermore, the
average contribution of the combined CAA species in groups 3 and 4 to the TCAA pool was similar to
the percentage of primary sugars to total sugar compounds in the three sampling locations (Figure 5). It
is likely that composition profiles of sugar compounds and CAAs in $PM_{2.5}$ are mainly controlled by their
primary sources.

### 3.3 Temporal variation of ambient sugars

The temporal variations of sugar and AA compounds in the PM2.5 samples collected during the sampling
periods are quite different at the three sites (Figure 1). In the urban area, the total sugar concentrations
showed two major peaks, one during 4-6 May and the other during 10-12 May. Anhydrosugars, the
marker of BB source, showed similar trend with the highest concentration occurred during 4-6 May and
10-12 May, suggesting urban sites may be more influenced by BB sources. In the rural area, the temporal
variations of the total sugar concentrations showed different patterns, with two major peaks on 3 May
and 6 May. On these two days, sugar alcohols and primary sugars exhibited the highest concentration,
indicating a significant contribution from primary biogenic sources in the rural location. In the forest
area, total sugars showed its concentration maximum on 2 May and 5 May. The concentrations of sugar
alcohols and primary sugars in the forest area showed similar trends to total sugars, with the highest
concentration occurring on 2 May and 5 May, implying that this area may be greatly influenced by
primary biological sources.

Figure S8 presents the overall temporal variations of three classes of sugar compounds (anhydrosugars,
primary sugars and sugar alcohols) in $PM_{2.5}$ collected at the three sampling sites. The temporal patterns
of biomass burning tracers (anhydrosugars), primary bioaerosols tracers (primary saccharides) and
surface soil and associated biotas tracer (sugar alcohols) are similar in the forest area. In the rural area,
the temporal variation of primary saccharides is similar to that of sugar alcohols, but it is not consistent
with that of anhydrosugars. In contracts, anhydrosugars, primary sugars and sugar alcohols showed
different trends in the urban area. This further supported that the difference in the temporal variations of
sugar compounds in $PM_{2.5}$ may point to the contribution of sources along the sampling period. The sugar
compounds in $PM_{2.5}$ collected in the urban area might be more influenced by combustion sources whereas
ambient sugars in the forest area are more influenced by primary biogenic sources.

The covariation of TCAA concentration with total sugar concentration was found in the three sampling
areas. On the contrary, the temporal variations of TFAA concentrations showed different patterns from
total sugar concentrations. These suggest that CAA may have similar sources and atmospheric processes
to sugar compounds in $PM_{2.5}$, whereas FAA may have different sources and atmospheric processes from
them, which will be discussed further in the following section.

### 3.3 4 Comparative behaviour of sugars and AAs in aerosols

### 3.34.1 Implications of formation pathways and atmospheric processes of ambient sugars and AAs

Pearson's correlation coefficients were performed based on sugar and AAs concentrations in $PM_{2.5}$
samples aggregated by sampling sites, and the results are shown in the Figure 67. It is interesting to note
that no correlation was observed between total free amino acids (TFAA) and the other individual

measured sugar and total sugars in the three sampling locations (Figure ~~6a~~7a, yellow shadow). This could be explained by the formation pathways and atmospheric processes of aerosol FAAs and sugars. The fact

420 that secondary processes ~~involved in the photochemical oxidation of atmospheric proteinaceous matter~~ is an important formation pathway of FAAs in the atmosphere has been corroborated by many studies (Wang et al., 2019; Xu et al., 2020b). Both laboratory simulations and field measurements demonstrated that~~Laboratory simulation experiments observed that~~ the oxidation of proteins and peptides with hydroxyl radicals (·OH) and $O_3$ can release of FAAs ~~upon in aqueous phase~~ (Liu et al., 2017b; Mcgregor and Anastasio, 2001; Song et al., 2017). ~~Song et al. (2017) also demonstrated that $O_3$ can also induce~~

425 ~~more proteinaceous matter to release FAAs in the atmosphere.~~ On the other hand, sugar compounds are suggested as atmospheric primary organic aerosol, which directly emitted from sources such as plant material, soil dust, microorganisms and BB, and then aerosolized ~~by active release from biological~~ ~~organisms, wind suspension, droplet impaction or human activities such as agricultural activities~~ (Fröhlich-Nowoisky et al., 2016; Joung et al., 2017). Moreover, compared to FAAs, sugars are not

430 derived from secondary photochemical processes in the atmosphere.

To further investigate the correlation between ambient Σsugar concentrations and FAAs, Pearson's correlation coefficients were calculated based on total sugar concentrations and individual FAA concentrations in $PM_{2.5}$ aggregated by sampling locations, which are exhibited in Figure S9~~8~~. Generally, no correlation was recorded at the three sampling sits (Figure S9~~8~~). Only Gln, Cit, Phe and Thr were

435 weakly correlated with the concentration of total sugar concentrations in the forest location, and Glu exhibited a weak correlation with total sugar compounds in the rural location. These individual FAAs are known to be relatively high reactive with short half-lives in the atmosphere (Mcgregor and Anastasio, 2001). It is likely that these individual reactive FAAs are directly emitted from biological sources rather than secondary processes. Accordingly, we infer that there are differences in the formation pathways and

440 atmospheric processes of sugars and FAAs in fine particles.

On the contrary, significant correlations at 95% confidence level were found~~good correlations~~ between total combined amino acids (TCAA) and total sugars (r=0.56~0.57, $p < 0.05$, n=14) ~~were obtained~~ at ~~three~~ each sampling ~~sites~~ site in this study (Figure ~~6a~~7a). Although the relationship between CAAs and sugars in the atmosphere has not been directly analysed, their sources have been explored in previous

445 studies. For instance, Feltracco et al. (2019) investigated the possible sources of AAs in Artic aerosol and proved FAAs and CAAs in aerosols might have different sources. They suggest that similar to aerosol sugars, ambient CAA derive from PBAPs, including viruses, algae, fungi, bacteria, protozoa, spores and pollen, fragments of plants and insects, and epithelial cells of animals and humans. Previous studies also demonstrated that unlike FAAs greatly influenced by atmospheric processes, composition profiles of

450 aerosol CAAs are highly depended on the origin of CAAs and it has been used to trace emission sources including primary biological sources and BB sources (Abe et al., 2016; Zhu et al., 2020b). Thus, significant ~~good~~ correlations between TCAA and total sugars in aerosols found in this study further corroborate that they may have common sources and are less impacted by atmospheric photochemical processes.

**3.~~2~~4.2 Evaluate the contribution of primary emission sources in different locations.**

Sugars in the atmosphere have been demonstrated to be derived from numerous sources. Three target sugar categories (anhydrosugars, primary sugars and sugar alcohols) can be used as tracers for specific source information (Simoneit, 2002; Simoneit et al., 2004). Anhydrosugars (including levoglucosan, mannosan and galactosan), generated by the thermal decomposition of cellulose and hemicellulose, are regarded as the specific markers for BB in the atmosphere (Simoneit et al., 2004; Zangrando et al., 2016). In this study, TCAA was found to be highly correlated with anhydrosugars at the urban and rural locations whereas no correlation between TCAA and anhydrosugars was observed in the forest location (Figure ~~6a~~7a, red shadow), indicating the urban and rural areas were more influenced by BB sources compared to the forest area. These conclusions were also corroborated by the $\delta^{15}N$ signatures of combined Gly ($\delta^{15}N_{C\text{-}Gly}$) in $PM_{2.5}$ measured at these three sites. Our previous study found that more positive $\delta^{15}N_{C\text{-}Gly}$ values were observed in $PM_{2.5}$ at the urban (average = +8.2 ± 5.4‰) and the rural (average = +5.9 ± 3.2‰) site than the forest site (average = +3.3 ± 6.2‰) (Zhu et al., 2020b) (Figure 6b). According to the $\delta^{15}N$ inventories of emission sources of atmospheric combined Gly, the urban location was highly influenced by combustion sources, followed by the rural location, while the forest location was more affected by natural sources.

Primary sugars are reported to be derived from microorganisms, plants, animals, lichens, and bacteria and have been considered to be good tracers for PBAPs (Fu et al., 2013; Zangrando et al., 2016). Particularly, sucrose and fructose are predominantly produced from plant fragments (e.g., bark, pollen grain, flowers buds, fruit and leaves) and soil dust (Fu et al., 2012; Xu et al., 2020a). In this study, TCAA only exhibited positive correlation with primary sugars (fructose and sucrose) in the forest location (Figure ~~6a~~7a, purple shadow), pointing to aerosols in the forest area were mainly influenced by intensive biological activities and vegetation growth during sampling period. Previous studies mentioned that increased biological activities and active vegetation such as developing flower buds in the spring can emit abundant primary sugars into the air (Jia et al., 2010). Hence, the sampling period (spring) of this study and intensive biological sources in the forest location may explain the positive correlation between TCAA and primary sugars in the forest area.

Sugar alcohols primarily come from fungal spores, bacteria, plants, algae and detritus of mature leaves (Bauer et al., 2008; Feltracco et al., 2020). Xu et al. (2020a) suggest that in spring mannitol and arabitol may be closely related to the activities of the terrestrial biosphere. When comparing the correlation results of sugars classes between sites, it is important to note that the correlation of primary sugars with sugar alcohols varied degrees at different sampling sites (Figure ~~6a~~7a, green shadow). More species of primary sugars and sugar alcohols in $PM_{2.5}$ positively correlated at the rural and forest sites ($p < 0.05$) compared to the urban site. Moreover, the stronger correlation between primary sugars with sugar alcohols were observed for $PM_{2.5}$ samples collected from the rural and forest sites than that at the urban site. This may imply that the impact from local biogenic sources at the rural and forest sites was greater than that of the urban site, which is also supported by the temporal patterns of anhydrosugars, primary sugars and alcohol-sugar at the three sites (Figure S7). We can thus conclude that the influence of primary biogenic and BB sources on aerosols in different locations can be evaluated by the correlations between TCAA and source specific sugar tracers (anhydrosugars, primary sugars and sugar alcohols).

**3.24.3 Identify burning tissues, local vegetation classes and soil-related biological sources**

A Pearson's correlation test was also calculated for the dataset containing ambient concentrations of sugar compounds and individual CAAs in $PM_{2.5}$ collected at three sites, which are exhibited in Figure 76. In the urban location, the concentrations of anhydrosugars showed a positive correlation with that of combined Gly, but no correlation was found between these two compounds in the other two locations. As we discussed above, combined Gly is major CAA specie in the honeycomb briquette, pine, and straw burning aerosols. Therefore, anhydrosugars and combined Gly both are closely related to biomass burning sources. A possible explanation for the positive correlation found between these two BB tracers is that the urban region is mainly affected by local combustion sources, while rural and forest regions may be more influenced by BB source from long-transport.

Significant positive correlations of anhydrosugars with Phe were observed simultaneously in the urban (r=0.68, *p*<0.05), rural (r=0.65, *p*<0.05) and forest (r=0.57, *p*<0.05) locations, serving as statistical support for a common source for the combined Phe and anhydrosugars in aerosols (Figure 76). Previous Recent studies indicate that the amino acid Phe is not only used as vital constituent of proteins but also a critical metabolic node that plays an essential role in lignin biosynthesis in vascular plants (Bonawitz and Chapple, 2010; Wallace and Fry, 1994). It is estimated that nearly 30–45% of photosynthetically fixed carbon is channelled through Phe for the biosynthesis of lignin during wood formation (Pascual et al., 2016). In addition, the vascular plant cell wall is a heterogeneous natural nanocomposite of cellulose, hemicelluloses and lignin (Agarwal, 2006; Jin et al., 2017). The lignin, the second most abundant polymer in plants, deposited in the secondary wall in which cross-linked to the structural polysugars, such as hemicelluloses and cellulose found there (Bonawitz and Chapple, 2010; Wallace and Fry, 1994). During the combustion processes of plant cell wall, the thermal breakdown of lignin takes place along with cellulose/hemicellulose. Therefore, the combustion of plant cell wall may explain the observed concentration coupling between combined Phe and anhydrosugars.

In this study, primary sugars were found to be highly correlated with combined Asp in $PM_{2.5}$ samples collected in the rural location, but primary sugars were correlated with combine Glu, Lys, Orn, Cit and Ser in the forest location (Figure 76, blue shadow), which is consistent with the temporal variation pattern of primary sugars and these CAA species (Figure 3). This may be attributed to the difference vegetation types in these two regions. The rural site is a typical agricultural area where grasses and crops are the main vegetation classes. Asp is reported to be the most abundant free and combined amino acids in Gramineae (Barnett and Naylor, 1966) (Burkholder et al., 1959; Wilson and Tilley, 1965). On the other hands, conifers dominate ecosystems at the forest site. In particular, hydrophilic species (Glu, Lys, Orn, Cit and Ser) have been shown to be the predominant CAA species in pine needles (Zhu et al., 2020b). Hence, the correlation between primary sugars (primary bioaerosols tracers) and specific CAAs may be used to track the predominant local vegetation types.

Consistent correlations were observed between sugar alcohols and combined Ala, Val and Leu at the rural and forest sites (Figure 76, green shadow), pointing to the significant contribution of biological sources associated with surface soil to aerosols at these two sites (Simoneit et al., 2004; Fu et al., 2013; Moura et al., 2013; Zhu et al., 2020b). As above mentioned, sugar alcohols indicate soil and associated biota contribute to ambient aerosols through resuspension by wind erosion or agricultural activities (Fu

535 et al., 2013; Fu et al., 2010a). Similarly, Friedel and Scheller (2002) showed that Ala, Val and Leu were the main hydrolysable amino acid species in soil organic matter and soil microbial biomass. Grass land environments are characterized by higher content of Ala, Asp and Leu (Moura et al., 2013). Our previous studies also demonstrated that hydrophobic Ala, Val, Leu, and Ile were the major CAA species in local crop soil (Zhu et al., 2020b). On the contrary, primary sugars and sugar alcohols exerted no correlation

540 with individual CAA at the urban site except for Phe, further supporting that aerosol at urban location are less influenced by biogenic source than combustion sources. Thus, it can be concluded that the correlations between individual CAAs and target category sugars can provide insight into various source characteristics such as plant tissues used for combustion, local vegetation classes (based on the correlation of primary sugars with specific CAAs dominant in local plants) and soil-related biological

545 sources vs combustion sources (based on the correlation of sugar alcohols with specific CAAs dominant in soil source).

### 3.~~3~~ 5 Identify classes of combustion sources~~Source identified by PMF~~

Levoglucosan has been tested and confirmed as an excellent tracer for biomass burning, which produces from the pyrolytic decomposition of cellulose and hemicellulose, or thermal stripping of sugar polyols

550 during the combustion processes (Jia et al., 2010; Kang et al., 2018; Simoneit, 2002), but it could not distinguish different classes biomass combustion sources. Detailed fingerprint tracers should be measured to get comprehensive information to identify different biomass burnings. To accurately qualify the BB source in different locations, Nss-$K^+$ have been also used as a typical tracer of BB in previous studies (Kunwar & Kawamura, 2014). However, previous studies also indicated that soil dust could be

555 another source of water-soluble Nss-$K^+$ in aerosols (Urban et al., 2014; Urban et al., 2012; Wang et al., 2021). Nss-$K^+$ concentrations averaged 633.1 ng $m^{-3}$ in the urban area which was higher than that observed in the rural (549.6 ng $m^{-3}$) and forest (590.2 ng $m^{-3}$) areas. Using levoglucosan as a representative BB tracer, the correlations between anhydrosugars and Nss-$K^+$ were further analyzed at three sampling sites to investigate the contribution of BB sources at each site (Table S3). Nss-$K^+$ showed

560 a statistically significant linear correlation with levoglucosan in the urban location (r=0.6, $p < 0.05$, n=14), whereas no correlation between levoglucosan and Nss-$K^+$ was observed in the rural and forest locations (Table S3). These may suggest the rural and forest areas were more impacted by the other sources of Nss-$K^+$, such as soil resuspension and fertilizers, while the urban area was more influenced by BB sources. This conclusion can also be confirmed by the fact that the stronger positive correlations between TCAA

565 and anhydrosugars and between combined Gly and anhydrosugars were observed in the urban area compared to rural and forest areas. Most positive $\delta^{15}N_{C-Gly}$ values observed in the urban location. In addition, different temporal variation pattern of anhydrosugars from that of primary sugars and sugar alcohols was only found in the urban area.

The average ratio of levoglucosan to potassium (lev/$K^+$) was 0.07 given by the slope of the linear

570 regression equation, which is close to the value of aerosols collected from a rural region of São Paulo State, Brazil (average = 0.08), where is strongly influenced by burning sugar cane (Urban et al., 2012). Furthermore, these ratios observed in this study were also comparable with the ratio found in Beijing, China during the typical summer period (0.05), which is greatly impacted by the combustion of crop

residuals (Cheng et al., 2013). However, this value was lower than those for aerosol samples collected in the Amazon (average = 1.01) and those in Austria (ranged 0.22 to 1.7), where are dominated by wood burning. 2013). The ratio of lev/K$^+$ was used to characterize the type of biomass burned (Wang et al., 2021) (Table S3). Cheng et al. (2013) found that that levoglucosan to K$^+$ ratios in emissions from the combustion of crop residuals were below 1.0, which is much lower than the ratio for hardwood burning (average = 25.69±9.11) and softwood burning (average = 105.58±102.60). Therefore, the contribution of wood burning was negligible for the biomass burning aerosol in the urban area. However, using lev/K$^+$ ratio to identify the type of combustion source is severely limited in the presence of potassium derived from non-biomass burning sources (Roberta Cerasi Urban et al., 2012). It is therefore that biomass combustion sources in the rural and forest locations cannot be distinguished by the lev/K$^+$ ratio.

L/M ratios have been employed to identify specific burning substrates in numerous studies (Fabbri et al., 2009; Fan et al., 2020; Zhu et al., 2015). L/M ratios for smoke particles from the burning of crop residues (~40 to 55.7) were high, while L/M ratios for the burning of hardwood (15-33) and softwood (3 to 10) were low (Engling et al., 2014; Engling et al., 2009; Sheesley et al., 2003; Wang et al., 2021). Besides that, recently studies demonstrate that levoglucosan is also present in lignite smoke particle matter (Rybicki et al., 2020a). Moreover, pyrolysis experiments confirm that lignite produce levoglucosan concentrations fully comparable to that of hardwoods and softwoods (Fabbri et al., 2009; Sheesley et al., 2003). Burning of lignite has been proved to be an additional input of levoglucosan to the atmosphere in regions where brown coal is utilized. Rybicki et al. (2020b) reported that the L/M ratios in lignites smoke (ranged from 31 to 189) were generally higher than those found for other fuel types because cellulose is more resistant to diagenetic (bio)degradation than hemicelluloses.

To better understand the different classes of combustion sources, the L/M ratio in the three areas were investigated. In this study, the ratios of L/M in the rural and forest areas ranged from 5.1 to 8.4 (average: 6.9) and from 4.3 to 9.8 (average: 7.2), respectively. According to Figure 8, the L/M ratios for rural and forest areas fall within the range for softwood burning. Thus, biomass burning aerosol in the rural and forest areas were mainly derived from softwood burning. However, the extremely high L/M ratios found in the urban area (ranged: 7.9 to 359.1; average: 59.9). These ratios were even higher than the values in the smoke particles released by the burning of crop residuals (>57) reported in the previous literature but fell within the range of lignite combustion, implying the urban area may be influenced by lignite combustion besides burning of crop residuals. Further support for this result was provided by the fact that a great quantity of lignite was used at the urban site (averaged 3803646 tons per year, the data are from the statistical yearbook of Nanchang city, http://tjj.nc.gov.cn//zbft/front/tjjnjnew/2020/mobile/index.html). Besides that, the average concentration of Cl$^-$ in the urban location (107.3±68.4 ng m$^{-3}$) was higher than those in the rural (99.9±71.3 ng m$^{-3}$) and forest (62.5±29.9 ng m$^{-3}$). Cl$^-$ has been reported to be a major chemical composition of coal combustion (Guo et al., 2020).

To investigate the source apportionment of sugars and TCAA in PM$_{2.5}$, positive matrix factorization (PMF) software version 5.0 (Environmental Protection Agency, USA) was used. The PMF analysis was performed for twenty-five tracer compounds, including anhydrosugars, primary sugars, sugar alcohols, water soluble ions, TFAA and TCAA. As discussed in section 3.2.1, the sources and atmospheric

photochemical processes of individual FAAs are different from sugar compounds and CAAs, thus individual FAAs were also excluded from the PMF. We adopted 15% of sugars and combined CAA concentration values as their measurement uncertainties (Fu et al., 2012; Xu et al., 2020b). The measurement uncertainties (10%) were used for the error estimates of the measured values of water-soluble ions. To maximize the quantity of data, half of the LOD was used for the values below the detection limit and 5/6 of the LOD was used for the corresponding error estimate (Wen et al., 2022).

The number of factors can be determined by the change of Q (robust) and Q (true). In this study, based on the possible sources of sugars and TCAA, four to six factor solutions were run in PMF model. In moving from four to six factors, the decrease of Q/Qexpected is illustrated from 4.7 to 3.2 in the urban location, from 3.8 to 2.9 in the rural location, and from 3.5 to 2.5 in the forest location. When the changes in Q values are small with the increase of factors, it can suggest that there may be too many factors being fit, indicating that four factors could be the appropriate factor number as to the probable origin of total sugars and TCAA at three sampling sites (Liu et al., 2017a). These four factor solutions were preferred based on minimum robust and true Q values (goodness of fit parameters) of the base runs, which observed 753.9 and 846.3, 669.6 and 684.8, 641.3 and 683.5, at the urban, rural and forest sites respectively. In each bootstrap run, the concentrations of tracers were close to those of base run results.

As shown in Figure 8, factor 1 is characterized by the high contribution of levoglucosan and nss $K^+$. Levoglucosan has been tested and confirmed as an excellent tracer for the biomass burning, which produce from the pyrolytic decomposition of cellulose and hemicellulose, or thermal stripping of sugar polyols during the combustion processes (Jia et al., 2010; Kang et al., 2018; Simoneit, 2002). nss $K^+$ is also reported to be a tracer of biomass burning (Kunwar and Kawamura, 2014). Besides that, it was noted that CAAs and TFAA also had a relatively important proportion in factor 1, particularly for combined Glu and Ser in the urban sites. Previous studies showed that the concentration of fungal material in $PM_{2.5}$ elevated during BB events and viable fungal spores have been identified in the smoke of biomass burning (Mims and Mims, 2004; Yang et al., 2012). Wei et al. (2019) attributed this result to turbulent air during the burning event can transport bacterial, fungal cells, various metabolism microbes and human or plant pathogens into atmosphere. Moreover, protein and AAs are widely distributed in these organisms (Dauwe et al., 1999). In urban site, anthropogenic origin and combustion-related elemental carbon are easily coated with a layer of peptides and protein (Filippo et al., 2014). Matsumoto et al. (2021) also suggest that combined Glu in fine particle was derived from biomass burning particles both from long transport and local sources. Thus, factor 1 can serve as an indicator of the influence of BB.

Factor 2 is dominated by high loading of levoglucosan, $Ca^{2+}$ and $Mg^{2+}$. In addition, mannitol and some saccharides contributed a high proportion to factor 2, especially in the urban and forest sites. Previous studies reported that mannitol and these primary saccharides were close related to biologically active surface soils and unpaved road dust (Wang et al., 2021; Rogge et al., 2007). Similarly, $Mg^{2+}$ and $Ca^{2+}$ are mainly derived from resuspended dust/soil in the ambient air (Barbaro et al., 2019; Rathnayake et al., 2016). Recently studies demonstrate that levoglucosan is also present in lignite smoke particle matter (Rybicki et al., 2020a). Moreover, pyrolysis experiments confirm that lignite produce levoglucosan concentrations fully comparable to that of hardwoods and softwoods (Fabbri et al., 2009; Sheesley et al., 2003). Burning of lignite has been proved to be an additional input of levoglucosan to the atmosphere in

regions where brown coal is utilized. Moreover, compared to factor1, factor2 shows high loadings of $Cl^-$. $Cl^-$ has been reported to be a major chemical composition of coal combustion. It is reasonable to assume that burning substrates associated with factor 1 and factor 2 might be different. In order to confirm this idea, we analyzed the concentration ratios of levoglucosan to mannosan (L/M) in the three sampling locations (Figure 10). L/M ratios have been employed to identify specific burning substrates in numerous studies (Fabbri et al., 2009; Fan et al., 2020; Zhu et al., 2015). For instance, high L/M ratios were reported for smoke particles from the burning of crop residues (~40 to 55.7), while those from softwood (3 to 10) and hardwood (15-33) combustion were characterized by low L/M ratios (Engling et al., 2014; Engling et al., 2009; Sheesley et al., 2003; Wang et al., 2021). However, even higher L/M ratios (>57) were observed at the urban sites (Figure 10). Rybicki et al. (2020b) showed that the levoglucosan/mannosan (L/M) ratios in lignites smoke (ranged from 31 to 189) are generally higher than those found for other fuel types because cellulose is more resistant to diagenetic (bio)degradation than hemicelluloses. These results may imply that factor 2 represents a mixture source of lignite combustion and resuspended dust/soil.

factor 3 is characterized by the high contribution of $NH_4^+$, nss $SO_4^{2-}$, $NO_3^-$, and TFAA. Both $NH_4^+$ and nss $SO_4^{2-}$ are reported to be the secondary particulate components that are converted from gas pollutants (Dai et al., 2013; Guo et al., 2020). Additionally, secondarily process is an important pathway of the formation of atmospheric FAAs (Xu et al., 2020b). Thus, Factor 3 can be identified as secondary processes.

Factor 4 was loaded with CAAs and primary sugars. CAAs are the basic component of primary biological aerosol particles, including viruses, algae, fungi, bacteria, protozoa, spores and pollen, debris of plants and insects, and epithelial cells of animals and humans (Abe et al., 2016; Matos et al., 2016). Primary sugars are also reported to be generally more abundant in vegetation detritus, airborne pollen and microorganisms (Jia et al., 2010; Xu et al., 2020a). Thus, this factor represents the primary biogenic source.

Overall, the average contributions of each factor to total sugars were estimated by PMF analyses (Figure 9). The two factors associated with combustion processes (factor 1 and factor 2) contributed higher to total sugars in $PM_{2.5}$ at the urban and rural sites than the forest site. This result is consistent with $\delta^{15}N$ signatures of combined Gly in $PM_{2.5}$ and the correlation between anhydrosugars and TCAA in PM2.5 (Figure 6). More specifically, BB was found to account for 22.6%, 45.5% and 30.55% of total sugars at urban, rural and forest sites. On the contrary, coal combustion and road dust sources contribute a greater fraction to total sugars at urban site (53.9 %), compared with 18.6% at rural and 8.3% at forest site. This is supported by the L/M ratios. Higher L/M ratios were found in the urban location whereas lower ratios were observed in the rural and forest locations (Figure 10). In this study, the ratios of L/M in the rural and forest locations ranged from 5.1 to 8.4 (average: 6.9) and from 4.3 to 9.8 (average: 7.2), respectively, indicating major contribution from softwood burning at these two regions. The extremely high L/M ratios found in the urban location (ranged: 7.9 to 359.1; average: 59.9). These ratios were even higher than the values in the smoke particles released by the burning of crop residuals reported in the previous literature but fell in the range of lignite combustion, implying the urban site may be influenced by lignite combustion besides biomass burning. Further support for this result was provided by the fact that a great

695 ~~quantity of lignite was used at the urban site (averaged 3803646 tons per year, the data are from the statistical yearbook of Nanchang city, http://tjj.nc.gov.cn//zbft/front/tjjnjnew/2020/mobile/index.html). As mentioned above, factor2 is a mixture source of lignite combustion and resuspended dust/soil. Greater impact of resuspended dust/soil on total sugars in PM$_{2.5}$ at the urban site can be corroborated by higher concentration (Figure S3) and abundance of trehalose (Figure 5) measured in PM$_{2.5}$ in the urban location compared to those found in the rural and forest locations.~~

700 ~~In addition, primary biogenic sources (factor 4) had a larger contribution in the forest location (53.7%) than those in the rural (8.4%) and urban (8.3%) locations. The urban (15.2%), rural (27.5%), and forest (7.5%) sites exhibited relatively low secondary processes contributions (factor 3), paralleling the correlation result between the total sugars and TCAA (Figure 6a), which confirming that ambient sugars and CAAs are mainly derived from primary sources.~~

705 ~~We also analyzed the proportional contributions to the TCAA in PM$_{2.5}$ in the three sampling locations (Figure 9). The primary difference among the three locations lies in the contributions from BB and biogenic sources. Fractional contributions of aerosol TCAA from BB in the urban (41.9%) and rural (70.3%) locations were significantly higher than that in the forest location (12.1%), but TCAA from biogenic source in the urban (34.4%) and rural (15.2%) locations were significantly lower than that in~~
710 ~~the forest (42.4%) location. Similar to total sugars in PM$_{2.5}$, there are relatively low secondary processes contributions for TCAAs in the three sampling locations (lower than 20.2%).~~

**4 Conclusions**

Determining the presence and signatures of source specific sugars and AAs in aerosol samples can be of great value to estimate the contribution of primary biogenic and BB sources to aerosols at different
715 sampling locations. Anhydrosugar, a confirming BB tracer, highly correlated with combined Phe suggests the burning of plant cell wall. The correlations between primary sugars (primary bioaerosol tracer) and specific CAAs dominant in local plant classes can help to identify potential local plant classes. Combined sugar alcohols (soil and associated biota tracer) with specific CAAs species dominant in soil source can help to distinguish soil-related biological sources contribution. Previous work on aerosols
720 focused on using only sugars or AAs biomarker alone to trace the aerosol sources. To our knowledge, this is the first report combining source specific sugar tracers with amino acids species dominant in primary emission sources to trace primary sources signatures at different locations. Moreover, this paper clearly demonstrates combining these two molecular biomarkers in atmospheric particles may provide more source characteristics than using a single biomarker alone. Future work should be aimed at
725 comprehensively characterizing physical, chemical, and biological properties of sugars and amino acids in aerosols, assessing possible interaction mechanisms between them, and extensively addressing the distribution of these two compound classes in potential aerosol sources.

*Data availability.* The data for lignite consumption at the urban site were obtained from the statistical
730 yearbook of Nanchang city (http://tjj.nc.gov.cn/zbft/front/tjjnjnew/2020/mobile/index.html) (Nanchang Statistics Bureau, 2020). Raw data sets (Zhu, 2021) used in this manuscript were available at https://figshare.com/articles/dataset/Concentration_of_saccharides_in_PM2_5_xlsx/17158661.

*Supplement.* The supplement related to this article is available online.

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*Author contributions.* This research was designed RGZ and HYX. Laboratory measurements were performed by HXZ, LQC and YYG. The paper was prepared by RGZ, HYX and HWX.

*Competing interests.* The authors declare that they have no conflict of interest.

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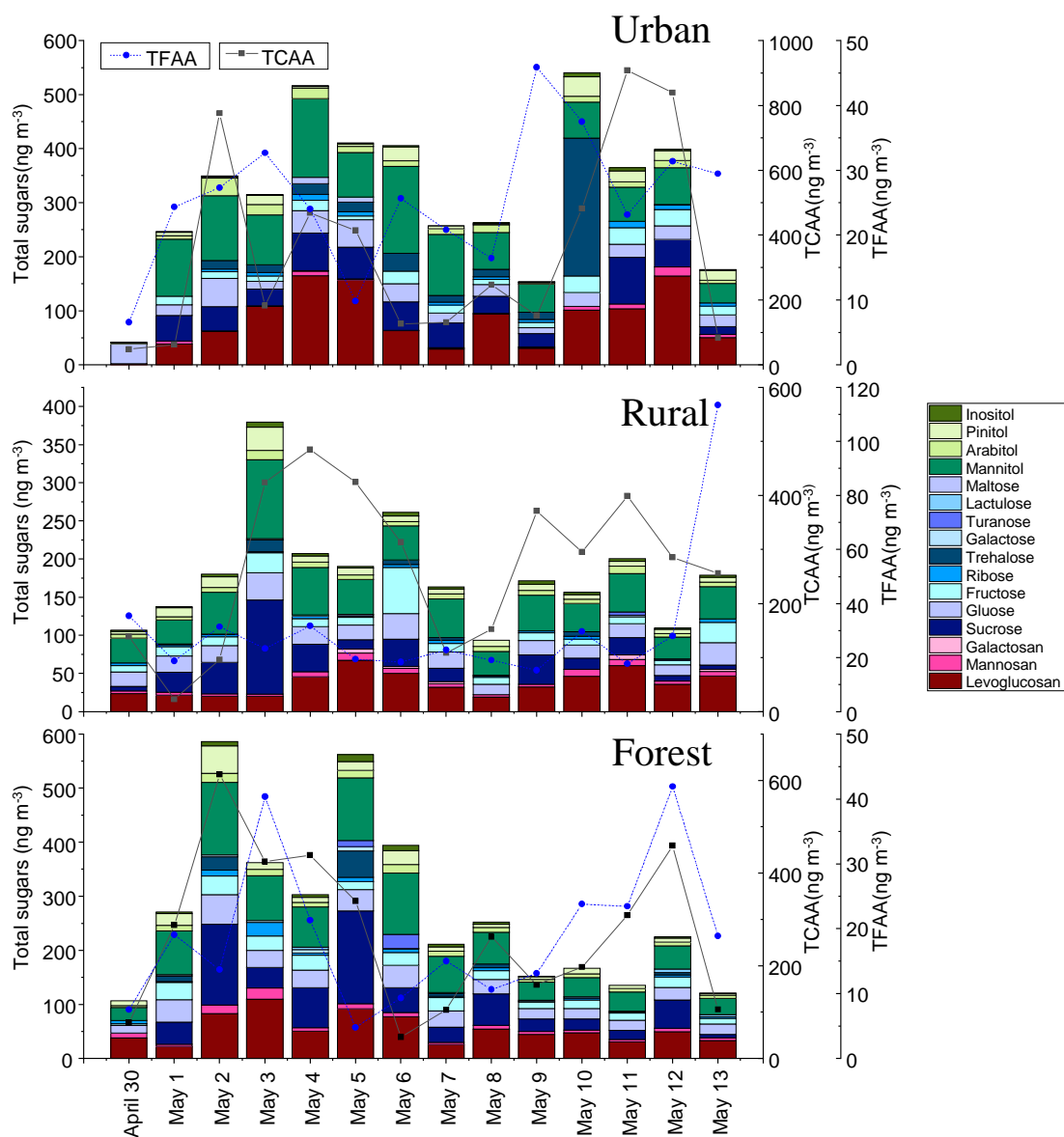
**Figure 1. Temporal variations in the concentrations of total sugars and total combined amino acids measured in PM2.5 samples collected at the urban, rural and forest sites in Nanchang, China.**

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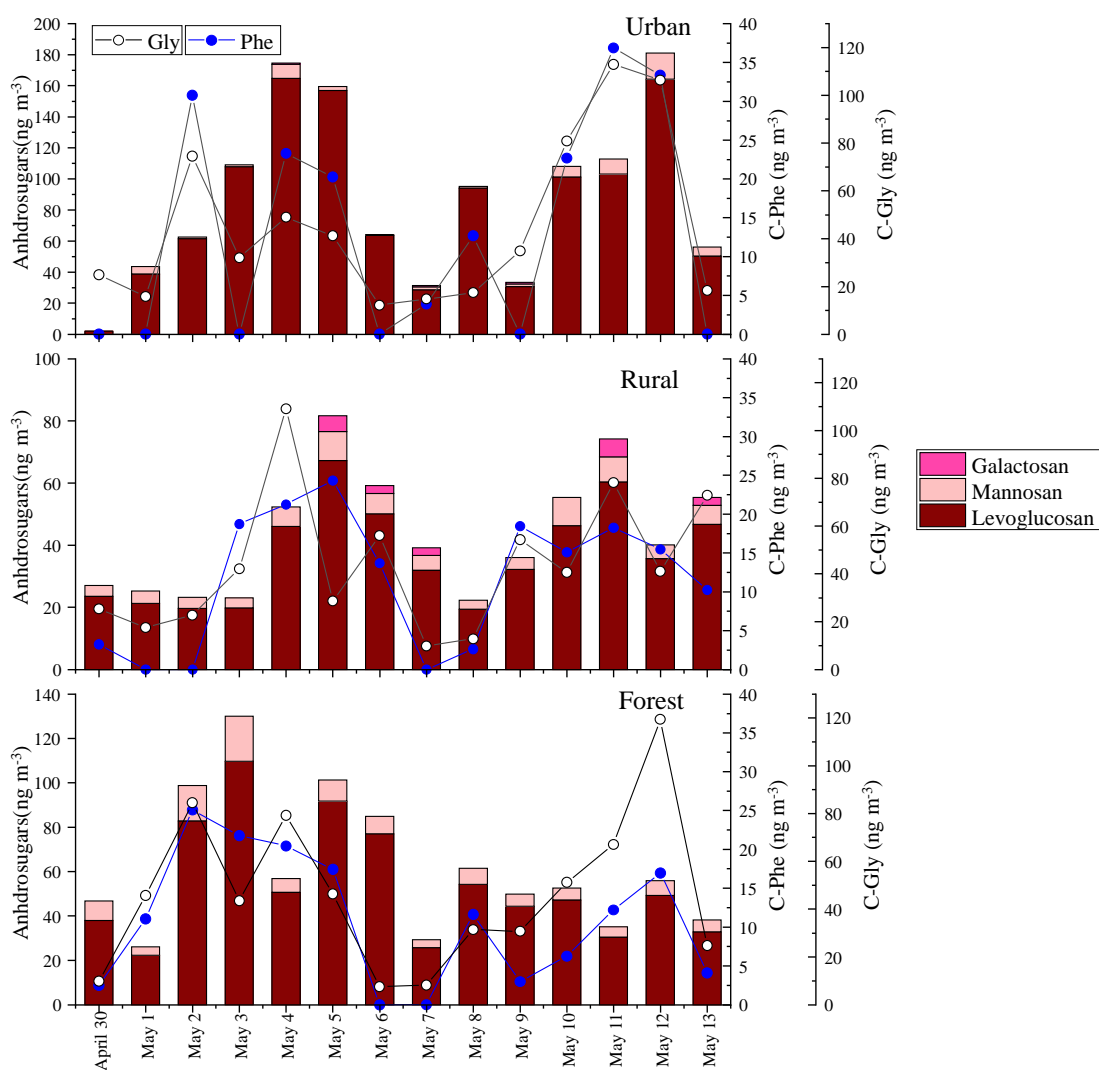
**Figure 2. Concentrations of anhydrosugars, combined Phe and Gly in urban, rural and forest. The**
1050 **concentrations of anhydrosugars and CAAs for each sample were normalized for the total volume of air**
**sampled.**
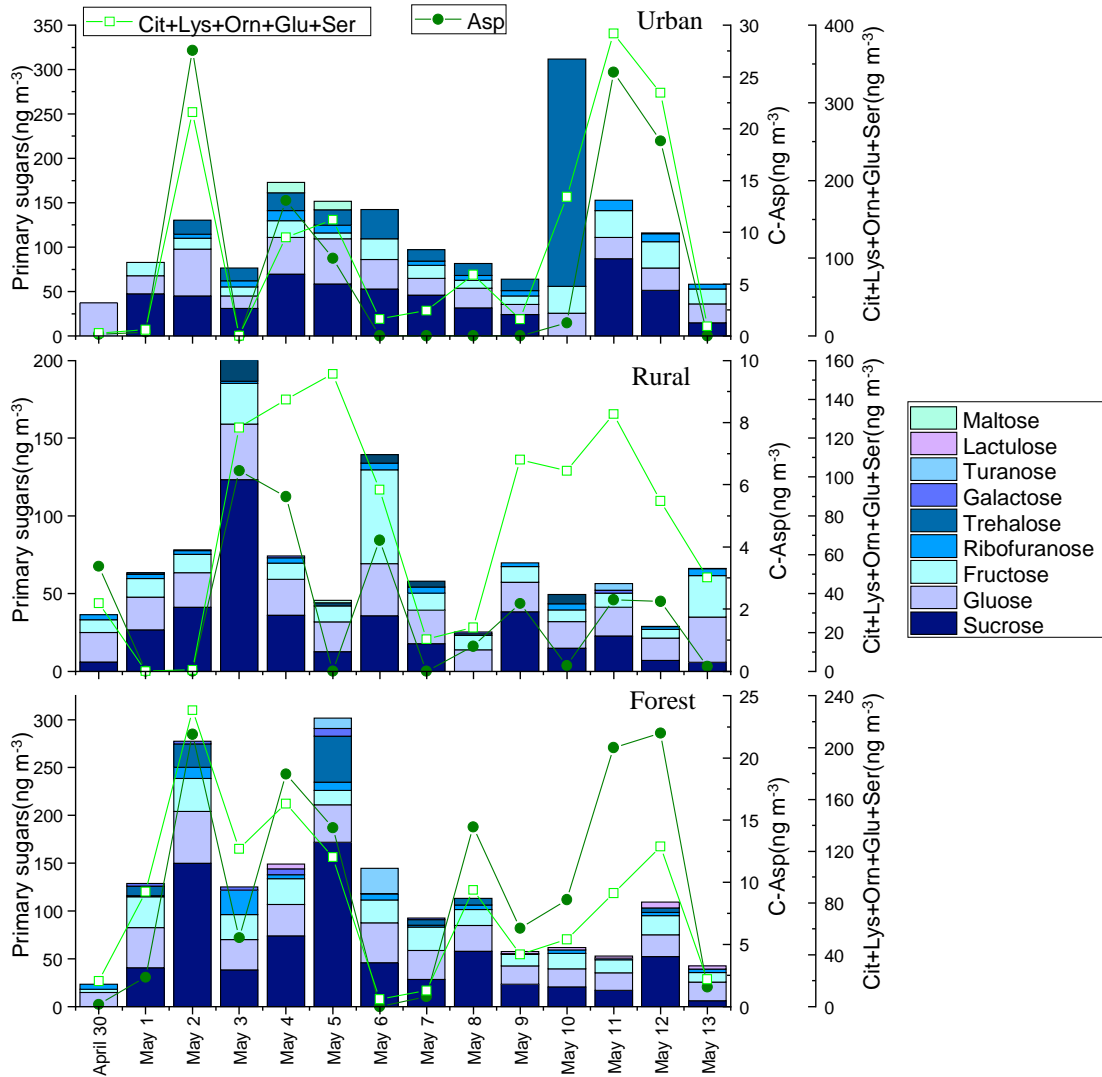
**Figure 3. Concentrations of primary saccharides, combined Asp and the sum of Cit, Lys, Orn, Glu and Ser in urban, rural and forest. The concentrations of primary saccharides and CAAs for each sample were normalized for the total volume of air sampled.**

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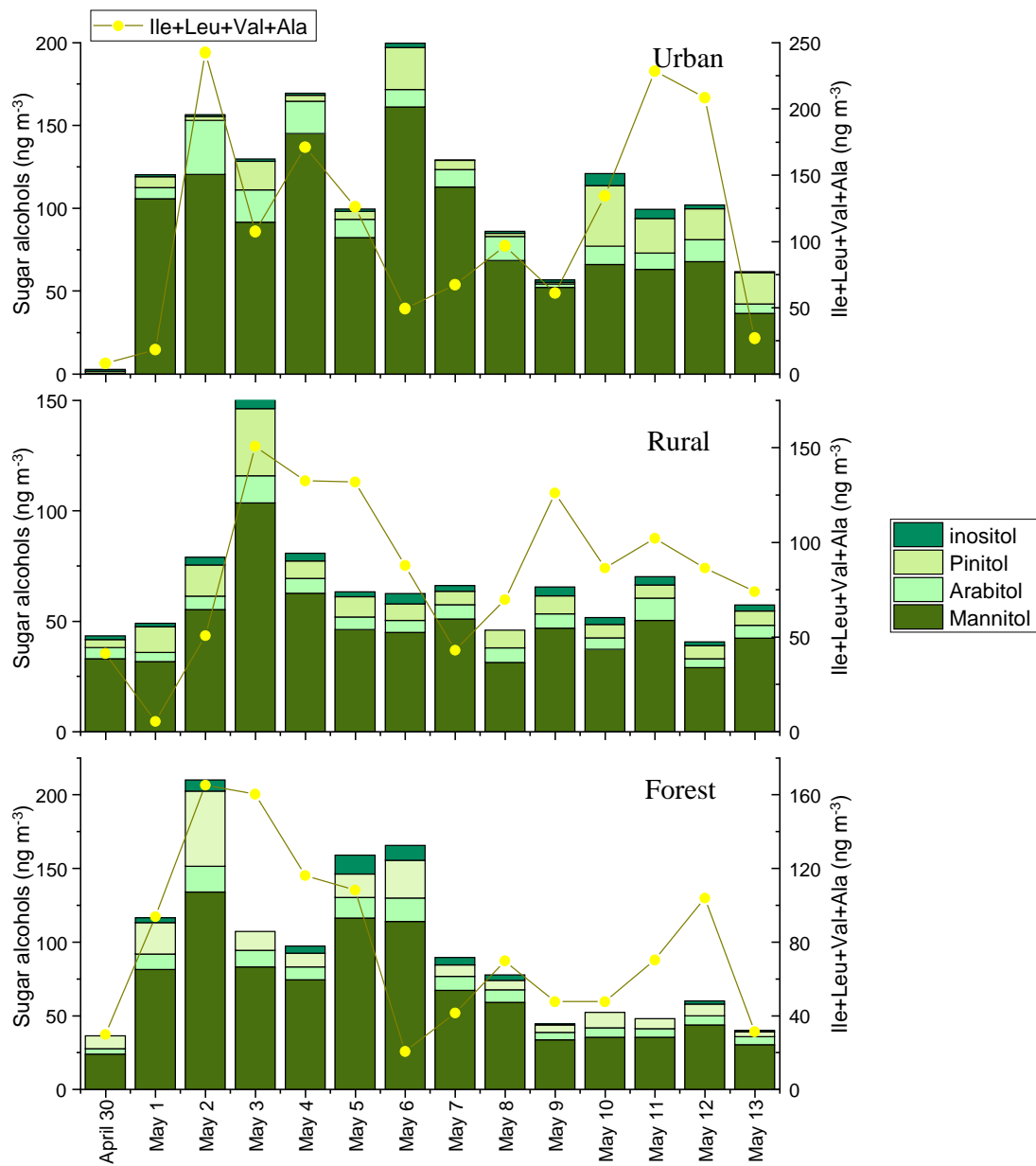
**Figure 4. Concentrations of sugar alcohols the sum of Ile, Leu, Val and Ala in urban, rural and forest. The concentrations of sugar alcohols for each sample were normalized for the total volume of air sampled.**
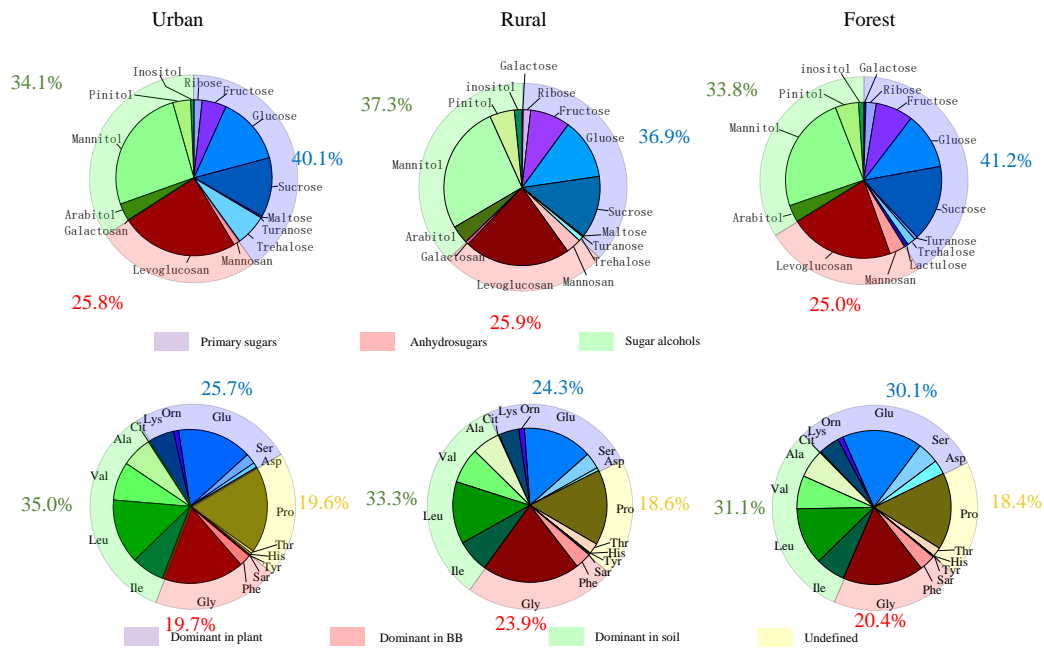
**Figure 5. Illustrations of the average contributions of individual species to total sugars and those of each CAA to total combined amino acids in urban, rural and forest sites.**
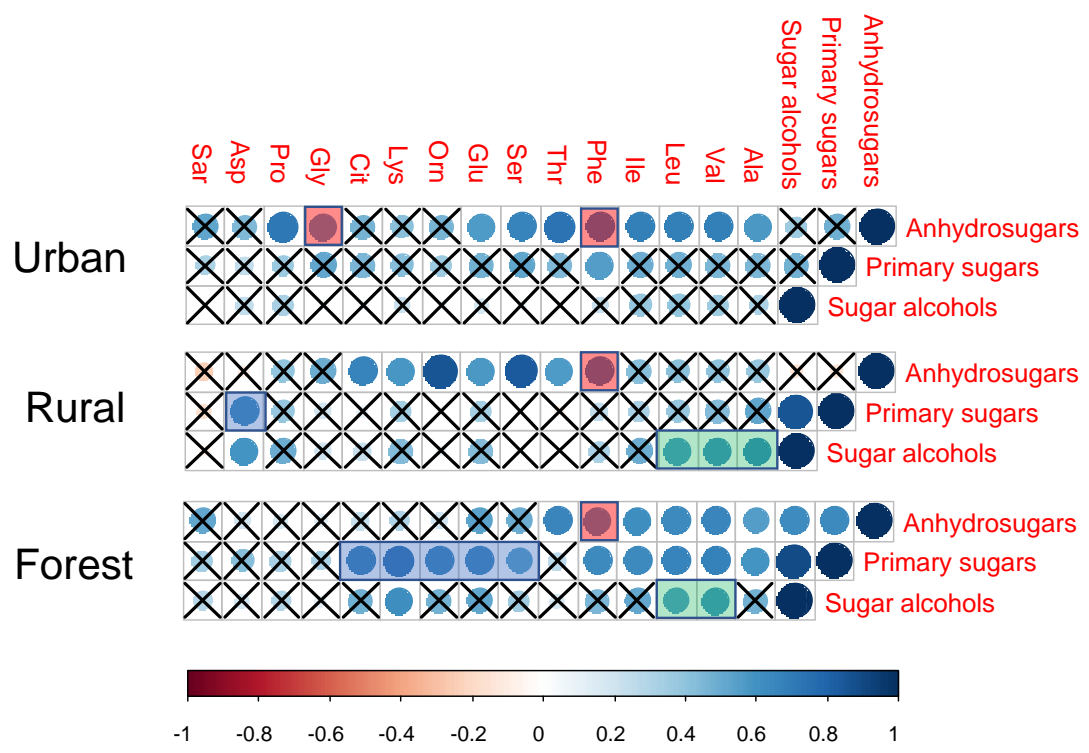
**Figure 6. Pearson correlations between three target sugars (anhydrosugars, primary sugars and sugar alcohos) and individual combined amino acids. The cross indicates a *p*-value higher than 0.05. The ball indicates a p-value less than 0.05. The larger a ball is, the more significant the correlation is.**

**Figure 7<s>6</s>. (a) Pearson correlations between TFAA and sugar species, and between TCAA and sugar species in PM$_{2.5}$ collected in urban, rural and forest sites. The cross indicates a $p$-value higher than 0.05. The ball indicates a $p$-value less than 0.05. The larger a ball is, the more significant the correlation is; (b) The range of δ$^{15}$N for combined Gly in PM$_{2.5}$ and major emission sources. The data of combined Gly was cited from Zhu et al. (2020). Open circles represent the isotopic composition data of combined Gly.**
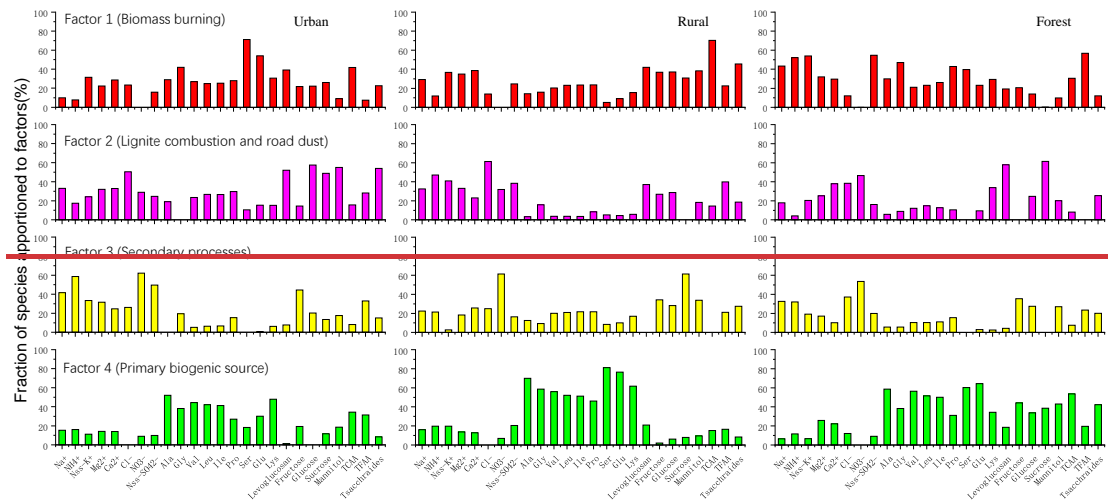
Figure 8. Profiles of four sources obtained with the PMF. Percentage contribution of each factor to the concentration of each species.

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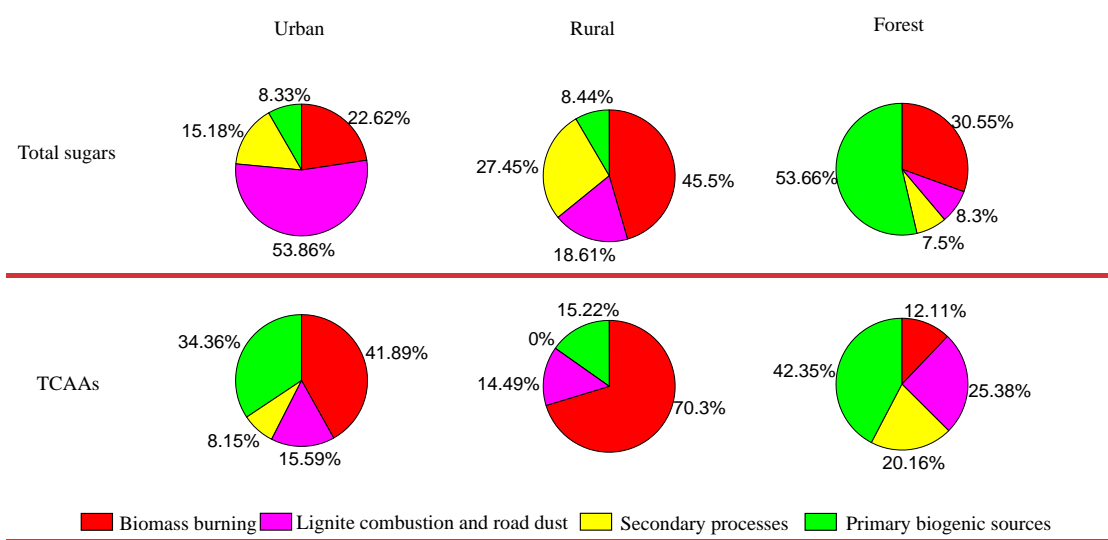
Figure 9. Illustrations of the percentage of factor contributions to the total sugars and CAAs in PM$_{2.5}$ obtained by PMF.

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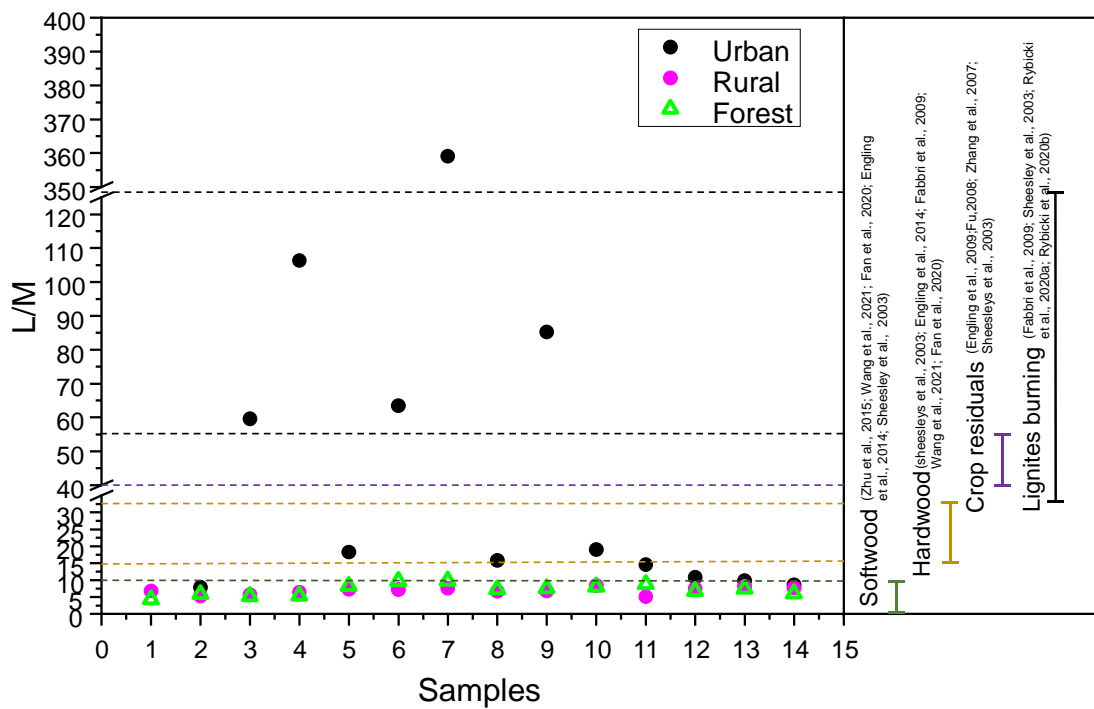
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**Figure 10Figure 8.** Ratios of levoglucosan to mannosan in PM₂.₅ and source test emissions from softwood, hardwood, crop residuals and lignites burning.