

Dear Editors and Reviewers:

Thank you for your letter and for the reviewers' comments concerning our manuscript entitled "Measurement Report: concentrations and composition profiles of sugars and amino acids in atmospheric fine particulates: identify local primary sources characteristics" Those comments are all valuable and very helpful improving our paper. We would also thank the editor for providing an opportunity to revise of this manuscript. We have revised the manuscript according to the referee's points as follows.

Reviewer 2

Zhu et al. investigated the concentrations and compositions profiles of sugars and amino acids in atmospheric fine particles to identify the source contributions at the urban, rural and forest sites in Nanchang, China. Sugars including anhydrosugars, primary sugars, alcohol-sugar were studied here as some tracers of sources. Together with the results of combined and free amino acids, the sources were identified using correlation analysis and a receptor model of PMF. It is a nice presentation on field measurement of organic tracers to suggest the possible local sources. My concerns are show as follows. I hope they could help improve the quality of this manuscript.

I do not think that PMF is suitable for the source apportionment in this study. We should be aware that there are only 14 samples at every site. It may cause large uncertainties on the outcome of source apportionment. The lack of secondary reaction tracers would easily underestimate the contribution of secondary processes. The results in Figure 8 also clearly show that the source profiles are very different even they are attributed to a certain source. The results shown in Figure 9 may not be reliable due to the highly possible uncertainties. It is not recommended to keep PMF source apportionment in this manuscript.

Answer: Thank you for your suggestion. The section of PMF source apportionment in this manuscript has been deleted and a new part of discussing biomass burning identification was added.

I found that the temporal variations of the organic tracers are quite different at the three sites e.g. total sugars and amino acids in Figure 1. The variations have not been clearly presented and discussed in the text. The difference may point to the contribution of sources along the sampling period.

Answer: Thank you for your suggestion. The difference in the temporal variations in the organic tracers among the three sites was further discussed in the revised manuscript. A new section of "Temporal variation of ambient sugars tracers and AAs" was added in the manuscript.

"The temporal variations of sugar and AA compounds in the PM_{2.5} 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 contrast, 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.”

Based the conclusions and discussions as well as the associated studies, biomass burning is expected and suggested as one of the major sources. I think there more efforts should be put on the identification of this specific source. A separate section is suggested. By the way, the discussion on sources of lignite combustion and road dust seem vague and should be improved.

Answer: Thank you for your suggestion. A new section of “identify classes of combustion sources” has been added in the manuscript. The sources of lignite combustion have been discussed further in the revised manuscript. The discussion on sources of road dust in urban area was added in the section 3.1.2.

“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 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 and Kawamura, 2014). However, previous studies also indicated that soil dust could be another source of water-soluble Nss-K⁺ in aerosols (Urban et al., 2012; Urban et al., 2014; Wang et al., 2021). Nss-K⁺ concentrations averaged 633.1 ng m⁻³ in the urban area which is 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 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 areas (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 and anhydrosugars and between combined Gly and anhydrosugars were observed in the urban area compared to rural and forest areas. Most positive $\delta^{15}\text{N}_{\text{C-Gly}}$ 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 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, this 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). 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 location. 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 (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.

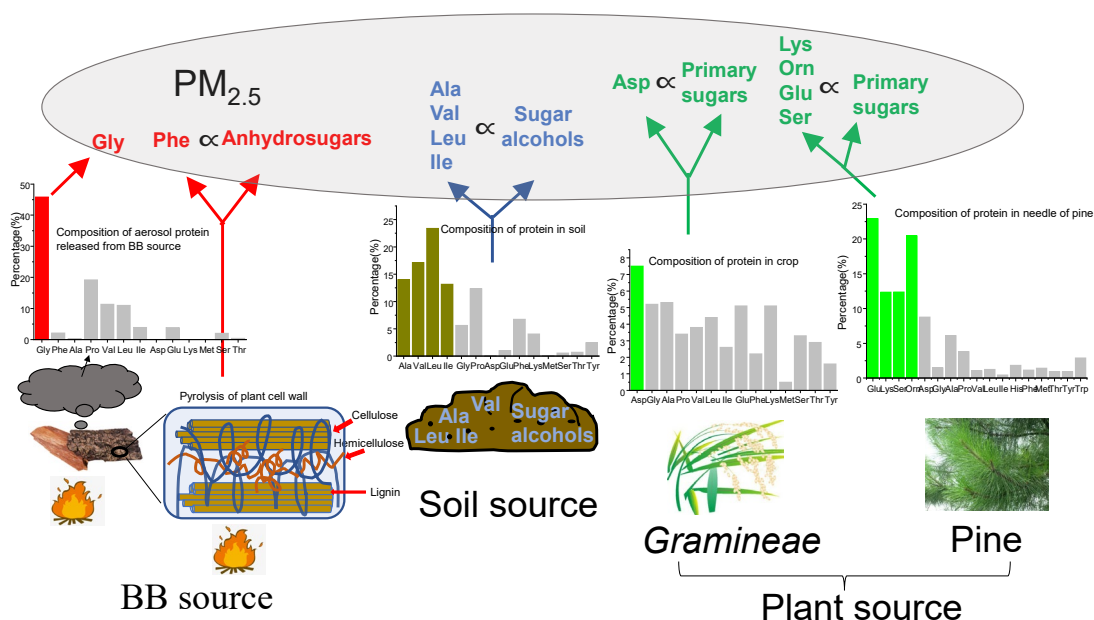
Levoglucosan/mannosan (L/M) ratios have been employed to identify specific burning substrates in numerous studies (Fabbri et al., 2009; Fan et al., 2020; Zhu et al., 2015). L/M ratios for smoke particles from the burning of crop residues (~40 to 55.7) were high, while L/M ratios for the burning of hardwood (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 locations were investigated. 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. 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//zbfj/front/tjjnnew/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).”

The authors claimed that some specific combined amino acids represent certain source contribution. For example, in Line 274, “anhydrosugars, combined Gly and Phe may be influenced by the identical source”. It is really not the case because CAA(s) are hydrolyzed products from certain proteins or peptides. One or two CAA(s) may not be released from a certain sources.

Answer: Sorry for our unclear description. There is an error in our description here. The concentration of some specific combined amino acids cannot represent certain source contribution. The revised manuscript grouping principle for CAAs was sufficiently described to clarify, and a graph for the grouping principle of CAAs was added (Figure S7). In this study, a hydrolysis method was used to measure CAAs in aerosol samples.

After complete hydrolysis, the peptide bonds in the protein are broken, so that the combined amino acids that constitute the protein are released as free amino acids. As your suggested, not only one or two specific CAA(s) are released from a certain source. However, previous studies found the protein CAA compositions differs in different primary biological emission sources. For example, Combine Gly, Ser, and Gln are demonstrated to be abundant CAA species in barley and cereals (Filippo et al., 2014). In our previous study, combined 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 local soil sources, and hydrophilic species (Glu, Lys, and Asp) were the abundant CAA species in local plant sources (Zhu et al., 2020b). (Abe et al., 2016; Miguel et al., 1999) suggested that the composition profiles of aerosol CAAs highly depended on the composition profiles of CAAs in major emission sources. If one primary biological emission source contributes significantly to the aerosols, the concentration and abundance of the CAA species predominant in this primary biological source will be higher than those of the other CAA species in PM_{2.5}. Furthermore, the CAA species predominant in this primary biological source may positively correlate with molecular marker of this emission source and exhibit a similar temporal variation pattern of the specific molecular marker. Therefore, the correlation and similar temporal variation pattern of the CAA species abundant in one primary biological emission source with the corresponding source specific molecular marker as well as the comparison of these CAA species with other CAA species in the aerosol may provide information on local primary biological emission source (Figure S7). The corresponding sections have been revised in the revised manuscript. Line 276-299.



Line 243-247: I do not understand why? Trehalose is not a specific tracers of road dust.

Answer: Sorry for our mistake. The impact of resuspension of surface soil is missing in the text. This sentence has been rewritten.

“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., 2004a,b; Medeiros et al., 2006b; Rogge et al., 2007)(Fu et al., 2012). This is further supported by the significantly higher average concentration of nss-Ca²⁺ 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-Ca²⁺ is reported to be mainly derived from resuspended dust/soil in the ambient air (Barbaro et al., 2019; Rathnayake et al., 2016). ”

Line 278: Why the sum of Ala, Val, Leu and Ile are calculated? As I mentioned above, they are dependent on the proteins and peptides in aerosol samples but we should have known nothing of them in this cause.

Answer: Ala, Val, Leu and Ile are found to the major CAA species in local crop soil (Zhu et al., 2020). Thus, the sum of Ala, Val, Leu and Ile were calculated and compared with sugar alcohols (surface soil and associated biotas tracer).

Line 284-289: Why they are separated into four groups? A reason is necessary.

Answer: Thank you for your suggestion. CAAs are grouped by the positive correlation between source-specific sugar markers and specific CAA species, and the similar temporal variation patterns between source-specific sugars and specific CAA species, as well as the predominant specific CAAs species predominant in each local primary biological source, ambient CAAs were finally divided into 4 groups.

The text in Line 312-325 presents some background information. It can be shortened.

Answer: Thank you for your suggestion. This part has been shortened in the revised manuscript.

“This could be explained by the formation pathways and atmospheric processes of aerosol FAAs and sugars. The fact that secondary processes 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 the oxidation of proteins and peptides with hydroxyl radicals ($\cdot\text{OH}$) and O₃ can release of FAAs (Liu et al., 2017b; Mcgregor and Anastasio, 2001; Song et al., 2017). 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 (Fröhlich-Nowoisky et al., 2016; Joung et al., 2017).”

Maybe the authors should rephrase the title. Make it clear and concise

Answer: Thank you for your suggestion. The new title is “Characterization of sugars and amino acids in atmospheric fine particulates: identify local primary sources.”

All changes were also highlighted in yellow color in the revised manuscript. Thank you very much again.

Yours sincerely,

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