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Reply on RC1

Ren-Guo Zhu et al.

Author comment on "Measurement report: Characterization of sugars and amino acids in atmospheric fine particulates and their relationship to local primary sources" by Ren-Guo Zhu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-269-AC1>, 2022

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 #1 Evaluations:

In this manuscript, sugars (anhydrosugars, primary sugars and sugar alcohols) and amino acids (free and combined) were determined in atmospheric fine aerosol particles (PM 2.5) collected from urban, rural and forest locations. The multiple trends observed for the different compounds and locations and their potential correlations were widely discussed. In addition, positive matrix factorization was used for the identification of local primary sources.

It is well known that organic aerosols (OA) have a clear impact on the climate. In this way, the determination of water-soluble compounds such as sugars and amino acids in OA collected from different geographical locations might be considered of great relevance to elucidate potential emission sources. Different statistical techniques such as Pearson correlation or positive matrix factorization were used to establish the potential differences between the samples collected at different locations, identify the potential emission sources and quantify their contribution to the total aerosols. In general terms, results achieved in this research are promising and they could be of great interest for the atmospheric chemistry and physics researchers. However, there are some points related with the manuscript structure and the use of the different statistical tools that might be improved and/or clarified.

On one side materials and methods section includes a whole subsection devoted to sugar analysis. Almost no information (3 lines) has been included about the analysis of free and combined amino acids. It could be interesting provide a reliable summary of the analytical methods on the main text. Detailed information might be provided as reference or in the supplementary information section. On the other side, it could be difficult for the potential

readers a detailed evaluation of the results showed in results and discussion section. Most of the results achieved for the analysis of the sugars on the samples has been included as supplementary information. However, the results achieved for amino acids has been included as figures in the main text. This could be a bit confusing even if some of the results obtained for the sugars are also shown in these figures.

Furthermore, it should be clarified if data distribution has been evaluated by the authors. Normal data distribution is required for most of the used algorithms and no-information is provided in the text.

Finally, the use of certain terms as "good correlation" or "highly correlated" is not clear and it should be reconsidered.

Therefore, this manuscript is not deserved for its publication in Atmospheric Chemistry and Physics in the present form, but it could be published after clarification of the following points:

Answer: Thank you for your suggestion. We have carefully revised our manuscript. A reliable summary of the analytical methods of FAAs and CAAs have been added in the supplementary information section. Moreover, combined with your subsequent suggestion about the number of figures being pretty large, two figures in the manuscript have been deleted. The number of figures in the revised manuscript is eight now.

The result of Normality test has been provided in the section of statistical analysis. "Normality tests of Shapiro–Wilk were performed. The concentrations sugar compounds (anhydrosugars, primary sugars and sugar alcohols), FAAs and CAAs are normally distributed."

Furthermore, the use of certain terms as "good correlation" or "highly correlated" were avoided in the revised manuscript.

Abstract

This section is pretty large and it should be condensed. However, quantitative results are mostly missing in the abstract.

Answer: Thank you for your suggestion. The abstract section has been condensed and important quantitative results are added.

Line 18. Sampling locations should be specified in the text.

Answer: Sorry for our unclear description. Sampling locations were specified in the revised manuscript.

"fine particulate matter samples were collected from the urban, rural and forest areas in Nanchang, China."

Line 20. Analytical technique used for the determination of the compounds might be clarified in the text

Answer: Sorry for our unclear description. Analytical technique used for the determination of the compounds has been defined in the text.

"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.”

Line 28. This abbreviation (L/M) should be defined in the text before it first use.

Answer: Thank you for your suggestion. The abbreviation (L/M) has been defined in the text. Line 30-31.

“the average ratio between levoglucosan and mannosan (L/M)”

Line 32. R2 and p-values should be included in this section for correlations.

Answer: Sorry for our unclear description. Pearson Correlation Coefficient (r) and p-values have been added. Line 35.

“The concentrations of sugar alcohols in the rural and forest areas were positively correlated with that of CAAs, which are abundant in the topsoil ($r = 0.53 \sim 0.62$, $p < 0.05$)”

Introduction

Lines 66-67. Not a clear link with the previous sentences.

Answer: Thank you for your suggestion. This sentence was deleted in the revised manuscript.

Line 96. This abbreviation (HAAs) should be defined in the text before it first use.

Answer: Sorry for our unclear description. This abbreviation (HAAs) was defined in the text. Line 90.

“Combined compound-specific $\delta^{15}\text{N}$ patterns of hydrolyzed amino acids (HAAs)”

Lines 104-109. This paragraph is a bit confusing; it could be interesting to clarify the aims of the study and then the different methodological improvements.

Answer: Thank you for your suggestion. This paragraph was rewritten. The structure has been adjusted. The purpose of the research is first explained, and then the method improvement is further explained. Line 99-104.

“To further clarify local primary source information in different locations, the concentration and composition of sugars, FAAs and CAAs in $\text{PM}_{2.5}$ samples collected from the urban, rural and forest areas in Nanchang, China were analyzed. 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).”

Line 106. Reference should be included in the text.

Answer: Thank you for your suggestion. The reference was added in the revised manuscript.

“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).”

Materials and methods

Line 121. Avoid the use of numbers at the beginning of the sentences.

Answer: Special thanks for your careful checks. Sorry for our mistake. This sentence was rephrased.

"Forty-two samples were collected daily with a duration of 23.5 h on prebaked quartz fiber filters (450 °C, 10h)"

Line 125. The time between the sampling and the transport to the laboratory should be clarified in the text. In addition, storage temperature in this step should be clarified in the text.

Answer: Sorry for our unclear description. The time between the sampling and the transport to the laboratory and storage temperature in this step were defined in the revised manuscript.

"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, to prevent loss of semi-volatile/volatile organic compounds from the samples."

Line 130. Have the authors considered the adsorption of the target analytes on the quartz wool during the sample preparation.

Answer: Thank you for your suggestion. We have considered the adsorption of the target analytes on the quartz wool during the sample preparation. Recovery experiment of target analytes were performed. If large quantity of target analytes were adsorbed to the quartz wool, the recoveries of analytes will be very low. However, recoveries for sugar standards ranged from 89% to 108% (Table S2), which fall within the range of previous studies (Pietrogrande et al., 2013; Medeiros and Simoneit, 2007). Recoveries for AAs standards were provided in our previous study, which ranged from 83% to 102% (Zhu et al., 2020b).

Line 149. At least $R^2 > 0.99$ are required for quantitative purposes.

Answer: Thank you for your carefully review. The linearity of sugar compounds is established simultaneously with the sample measurement. It may be more accurate to use the standard curve created with the samples than to recreate the standard curve now because the current instrument and environment conditions may be different from when the samples were measured. In order to solve this problem, we narrowed the linear range of some sugar compounds according to the actual concentration of the aerosol samples. For some sugar compound, their R^2 of the calibration curves is above 0.99 in a narrow concentration range.

"In general, the obtained calibration curves show good linearity ($R^2 > 0.99$) in the exploited range (Table S2)."

Line 150. Preparation of field blanks should be clarified at some point (text or supplementary information)

Answer: Sorry for our unclear description. Preparation of field blanks was added in the revised manuscript.

"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."

"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."

Line 155. Results should be avoided in the material and methods section. This information might be provided at results and discussion section.

Answer: Thank you for your suggestion. We have deleted the results of recoveries, reproducibility and the detection limits of sugars in the material and methods section. Considering the length of the results and discussion sections of the article, these results have been described in the supplementary information. A new section of "Analytical characteristics for sugar compounds " was added in supplement.

Line 166. Additional information about the selected methodology might be interesting for the potential readers.

Answer: Thank you for your suggestion. Additional information about the methodology of the water-soluble ions concentration determination was added in the revised manuscript. Line 164-181.

"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)TM, ICS-90, Thermo ScientificTM, 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 0.22 μm 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 × 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 × 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."

Lines 167-169. Results should be avoided in the material and method section.

Answer: Thank you for your suggestion. We move this section into the supplementary materials.

"Analytical characteristics for water-soluble ions

Standard solutions of water-soluble ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-}) were used for making the external standard curve before the analysis of $\text{PM}_{2.5}$ samples. The correlation coefficients of the calibration curves were greater than 0.999. The detection limit of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} were $0.001 \mu\text{g L}^{-1}$, $1.21 \mu\text{g L}^{-1}$, $1.77 \mu\text{g L}^{-1}$, $2.47 \mu\text{g L}^{-1}$, $0.09 \mu\text{g L}^{-1}$, $5.1 \mu\text{g L}^{-1}$, $21.6 \mu\text{g L}^{-1}$ and $11.5 \mu\text{g L}^{-1}$, respectively. The relative standard deviation of the reproducibility test was less than 5% (Guo et al., 2020; Wen et al., 2022). ”

Results and discussion

Line 213. It could be interesting to clarify if reported results can be associated to pre- or post-pandemic samples.

Answer: Thank you for your suggestion. It is very regrettable that the results reported here cannot be linked with the samples pre and post the epidemic. $\text{PM}_{2.5}$ samples in this study were collected at Nanchang, China from April 30, 2019 to May 13, 2019. However, the first outbreak of COVID-19 in China occurred in Wuhan in December 2019. The sampling period in this study is 6 months before the outbreak of the COVID-19 pandemic, so it is very regrettable that our sampling period is not pre- or post- the epidemic.

Lines 276 and 278. The selection of these groups of amino acids for study might be clarified in the text.

Answer: Thank you for your suggestion. The selection of these groups of amino acids for study was clarified in the revised manuscript. Furthermore, the sequence of this section was adjusted.

“Furthermore, the temporal variations in the concentrations of source-specific sugars (including anhydrosugars, primary sugars and sugar alcohols) were compared with those of specific groupings of CAA species in $\text{PM}_{2.5}$. CAA species were initially grouped by their correlation with source-specific sugars at three sampling sites (Figure 6) and their abundance in potential emission sources (Figure S7).”

Line 300. The use of the combination of Gly and Phe for the evaluation of the results should be clarified in the text.

Answer: Thank you for your suggestion. The use of the combination of Gly and Phe for the evaluation of the results was clarified in the revised manuscript.

“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 CAAs together accounted for an average of 19.7%, 23.9% and 20.4%, respectively, of the TCAAs pool in $\text{PM}_{2.5}$ collected from the urban, rural and forest areas. It is interesting to note that the percentage of Gly and Phe in total CAAs pool was generally similar to the percentage of the anhydrosugars in total sugar compounds in $\text{PM}_{2.5}$. ”

Line 338. Not clear that this is a good correlation. A more appropriate term might

be correlation at 95%. In addition, the number of samples included in the model should be provided in the text.

Answer: Sorry for our unclear description. This sentence was rewritten. Line 379-381.

"On the contrary, significant correlations at 95% confidence level ($r=0.56\sim 0.57$, $p < 0.05$, $n=14$) were found between total combined amino acids (TCAA) and total sugars at each sampling site in this study (Figure 7a)."

Lines 405-406. These reference should not be considered as recent references.

Answer: Thank you for your suggestion. It has been changed to "Previous 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)." Line 444-445.

Line 428. References from previous studies should be included in the text.

Answer: Thank you for your suggestion. References from previous studies were added. Line 469-470.

"Consistent correlations were observed between sugar alcohols and combined Ala, Val and Leu at the rural and forest sites (Figure 7, green shadow), pointing to the significant contribution of biological sources associated with surface soil to aerosols at these two sites (Zhu et al., 2020; Moura et al., 2013; Fu et al., 2013; Simoneit et al., 2004)."

Lines 493-494. Results obtained for L/M should be expressed homogeneously.

Answer: Thank you for your suggestion. This section was rewritten.

"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."

Line 501. Please check the use of capital letters at the beginning of the sentences.

Answer: Thank you for your suggestion. Based on the comments provided by reviewer 2, source apportionment based on PMF mode was deleted in this manuscript because the outcome of source apportionment may have large uncertainties. This sentence was also deleted with the deletion of PMF model results. So, this problem doesn't exist now.

The number of figures is pretty large. Some figure should be summarized or moved into supplementary information.

Answer: Thank you for your suggestion. As we mentioned above, since the source apportionment based on PMF mode was deleted in this manuscript, Figure 8 and 9 were also deleted along with the deletion of this section. However, more efforts were put on the identification of biomass burning source. A separate section “Identify classes of combustion sources” has been added in the revised manuscript.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2022-269/acp-2022-269-AC1-supplement.pdf>