Responses to Reviewer #2

We are grateful to the reviewer for the thoughtful comments and suggestions, which greatly improved the quality of our manuscript. Below we make a point-by-point response to these comments. According to editor's requirement, the responses are structured in the following sequence: (1) comments from the referee is in black, (2) our responses are in blue.

Reviewer #2 (Formal Review for Author (shown to author)):

This paper identified and quantified the Molecular markers of biomass burning and primary biological aerosols. Atmospheric concentrations, seasonal variations and size distributions of anhydrosugars and sugar alcohols were investigated, the analysis and interpretation of the results are overall fair. The paper presents useful information about the organic aerosols. However, some additional information is still necessary for the readers to better understand this work.

Comments:

1. Three anhydrosugars, six primary saccharides and four sugar alcohols should be introduced clear in the section 1, such as the sources, property.

Response:

Thanks for the reviewer's suggestions. Before analysis, we have gave an introduction about all anhydrosugars, primary saccharides and sugar alcohols in Sections 3.1 and 3.2. Hence, we added the following sentences in the revised manuscript as a supplemental description in Section 1.

"Amongst sugar alcohols, mannitol and arabitol are the primary ones" (see Page 2, Line 20).

"Sparse data about erythritol and inositol can be found in the literature. Recently, these two species were reported as having similar sources as other sugar alcohols, such as arabitol and mannitol" (see Page 2, Line 23).

"On the basis of difference of burning materials (e.g. deciduous leafs, grass), BB is classified as open-field burning in forests, savannas, croplands and residential heating and cooking (Akagi et al., 2011; Yan et al., 2006)" (see Page 2, Line 25).

"Because levoglucosan is chemically stable in the air with no decay over 10 days" (see Page 3, Line 1).

"The levoglucosan to mannosan (L/M) ratio varies for aerosols generated by burning of hardwood, softwood and agricultural waste, with a ratio of 13–27, 2.5–5.8 and 25–55.7, respectively" (see Page 3, Line 2–3).

2. In the section 2.1, a brief introduction to the surrounding environment of sampling sites should be provided, and the details about the sampling time should be described, including start time, end time, and duration.

Response:

We have added the following paragraph in the revised manuscript (see Page 3, Line 18). "Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences locate on the north side of Beijing city, which is considered be a representative urban urea for a mixed district of teaching, residential and commercial areas. Urban aerosol samples collected here are influenced by anthropogenic (transport emissions, cooking operations etc.) and natural sources (soil dust, plant debris, microorganisms etc.)."

The details about the sampling time (start time, end time, and duration) were presented in Table S1.

3. There are only four cases (less than 10 days) in each season, more field measurement estimation could decrease the influence produced by accidental elements, making the results more convincing.

Response:

Thanks for the reviewer for pointing this deficiency. Offline experiments allow investigators to repeat the process under controlled conditions to analyze the emission process, influencing factors and mechanisms (Chen et al., 2012; Zhang et al., 2011). The concentrations of organic tracers, such as compounds analyzed in our study were measured offline using GC/MS and OC/EC were also determined offline using a thermal/optical carbon analyzer (model RT-4, Sunset Laboratory Inc., USA). While field measurement are preferable and realistic since the field studies can reflect the real process at random conditions (Roden et al., 2006). It is realized that more online studies are required in our study. During sampling, we documented basic information about meteorological data, such as relative humidity, wind scale and so on simultaneously (see Table S1). These field measurement do support our conclusion. For example, information about PM2.5 and PM10 defined the weather conditions precisely; higher relative humidity found in haze days do prefer hygroscopic growth, coagulation and/or condensation fine particle, resulting lager GMDs in the fine mode.

4. Lots of ratios of individual anhydrosugars were showed in section 3.1.2, the result were almost consistent with previous results, and the conclusion should be summarized and classified, so that the author can better understand.

Response:

Thanks for the reviewer's suggestion. We adjusted the order of the paragraphs and some sentences in Section 3.1.2 to arrange a clear and logical order. The first three paragraphs described the features of ratios of individual anhydrosugars and OC/EC, respectively. A new paragraph was added (the fourth paragraph) to give some comparison with other studies. The rest paragraphs were about ratios according to according to particle size.

The fourth paragraph is as followed:

"The L/M, L/OC and L/EC ratios calculated in this study were compared with those reported for other Asian cities in recent studies. The L/M ratios showed different seasonal and spatial distributions as city changed. Those reported in Nepal (16.3±5.96) were much higher than our study (Wan et al., 2019). Study in Okinawa found a L/M ratio of 10.7±6.1 and exhibited a similar seasonal trend to our study (Zhu et al., 2015a). Lower ratio of L/M suggested that more burning substrates were softwood in Beijing. While in previous studies in Beijing, lower ratios L/M in winter were observed (Cheng et al., 2013). Higher ratio of L/M in our study may ascribe to the reduced use of coal in recent years in Northern China. Coal combustion is also a source of levoglucosan, leading to a lower ratio of L/M (Yan et al., 2018). In comparison to annual mean L/OC ratios in Guangzhou and Zhaoqing in the PRD region (10.8×10-3 and 27.5×10-3, respectively) (Ho et al., 2014), the lower values of L/OC in Beijing were potentially associated with the less extensive burning activities under the prohibition of open agricultural residue burning. Though indicating a similar seasonal trend to Okinawa, the L/EC ratios in Beijing were much higher than those in Okinawa. Besides the more release of levoglucosan in Beijing, such result may also imply that EC was associated with other sources, such local transport emission and coal combustion, while EC in Okinawa might represent a regional background level (Zhu et al., 2015a)."

5. The size distribution of Anhydrosugars, Primary saccharides and Sugar alcohols was analyzed in Section 3.3, a size shift towards large particles and large GMDs in the fine fraction (<2.1 m) was detected during the hazy days. The author ascribes them to higher humidity, but did not analyze the impact of RH on size distribution. Please give more discussion.

Response:

Thanks. Herner et al (2006) found that the particle size can be modified by chemical reactions, condensation/evaporation, coagulation with other particles, and activation during high humidity, wet and dry deposition. Anhydrosugars, primary saccharides and sugar alcohols are important parts of atmospheric primary organic aerosols (POA), which are highly water-soluble compared with fossil fuel derived particles (Reid et al., 2005). Larger GMDs of primary carbon particles in the fine mode in haze days than in non-haze days have been observed in previous and our studies. One reason for that is enhanced hygroscopic growth of the airborne particles under relatively higher humidity. As exhibited in Table S1, haze days were characterized by higher relative humidity in our study. Wang et al (2011) found that all fine mode of WSOC showed a larger GMD in the hazy days. Kang et al (2016) also discovered that the fine mode GMDs of aliphatic hydrocarbons generally larger in haze samples due to higher relative humidity. In addition, the increase concentrations of airborne aerosols could increase the overall coagulation rate, resulting in faster rate of collisions between particles and formation of larger particles (Herner et al., 2006). Table 2 showed that the concentrations of anhydrosugars, primary saccharides and sugar alcohols were much higher in haze days, which responsible for the larger GMDs in the fine mode and a size shift towards large particles.

References:

Chen Y., Roden C., Bond T.: Characterizing biofuel combustion with patterns of real-time emission data (PaRTED), Environ. Sci. Technol., 46, 6110–6117, doi: 10.1021/es3003348, 2012.

Cheng, Y., Engling, G., He, K. B., Duan, F. K., Ma, Y. L., Du, Z. Y., Liu, J. M., Zheng, M., and Weber, R. J.: Biomass burning contribution to Beijing aerosol, Atmos. Chem. Phys., 13, 7765-7781, doi:10.5194/acp-13-7765-2013, 2013.

Herner, J. D., Ying, Q., Aw, J., Gao, O., Chang, D. P., Kleeman, M. J.: Dominant mechanisms that shape the airborne particle size and composition distribution in central California, Aerosol Sci. Technol., 40, 827-844, doi:10.1080/02786820600728668, 2006.

Kang M., Fu P., Aggarwal S., Size distributions of n-alkanes, fatty acids and fatty alcohols in springtime aerosols from New Delhi, India, Environ. Pollut., 219, 957-966, doi:10.1016/j.envpol.2016.09.077, 2016.

Reid, J.S., Koppmann, R., Eck, T.F., Eleuterio, D.P.:A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. Atmos. Chem. Phy. 5, 799–825, doi:10.5194/acp-5-799-2005, 2005.

Roden C., Bond T., Conway S., Pinel A.: Emission factors and real-time optical properties of particles emitted from traditional wood burning cookstoves, Environ. Sci. Technol., 40, 6750–6757,doi:10.1021/es052080i, 2006.

Wan, X., Kang, S., Rupakheti, M., Zhang, Q., Tripathee, L., Guo, J., Chen, P., Rupakheti, D., Panday, A. K., Lawrence, M. G., Kawamura, K., and Cong, Z.: Molecular characterization of organic aerosols in the Kathmandu Valley, Nepal: insights into primary and secondary sources, Atmos. Chem. Phys., 19, 2725–2747, doi:10.5194/acp-19-2725-2019, 2019.

Wang, G., Chen, C., Li, J., Zhou, B., Xie, M., Hu, S., Kawamura, K., and Chen, Y.: Molecular composition and size distribution of sugars, sugar-alcohols and carboxylic acids in airborne particles during a severe urban haze event caused by wheat straw burning, Atmos. Environ., 25 45, 2473-2479, doi:10.1016/j.atmosenv.2011.02.045, 2011.

Yan, C., Zheng, M., Sullivan, A.P., Shen, G., Chen, Y., Wang, S., Zhao, B., Cai, S., Desyaterik, Y., Li, X., Zhou, T., Gustafsson, O., Collett, J.L., Jr., 2018, Residential Coal Combustion as a Source of Levoglucosan in China, Environ. Sci. Technol., 52, 1665-1674, doi:10.1021/acs.est.7b05858, 2017.

Zhang H., Hu D., Chen J., Ye X., Wang S., Hao J., Wang L., Zheng R., An Z.: Particle size distribution and polycyclic aromatic hydrocarbons emissions from agricultural crop residue burning, Environ. Sci. Technol., 45, 5477–5482, doi:10.1021/es1037904, 2011.

Zhu, C., Kawamura, K., Kunwar, B.: Effect of biomass burning over the western North Pacific Rim: wintertime maxima of anhydrosugars in ambient aerosols from Okinawa, Atmos. Chem. Phys., 15, 1959–1973, doi:10.5194/acp-15-1959-2015, 2015a.