

Title: “Chemical characteristics of PM_{2.5}: Impact of biomass burning at an agricultural site of the North China Plain during a season of transition”

Anonymous Referee #2

Received and published: 16 April 2020

In this manuscript, the authors report chemical characteristics of PM_{2.5} under the impact of biomass burning (BB) in the North China Plain. Several BB markers, including levoglucosan, mannosan and water-soluble potassium are measured in daytime and nighttime samples. The authors find large differences in chemical characteristics in different BB periods. They also claim that there might be other sources of potassium.

My major concerns are:

(1) The authors compare chemical characteristics of PM_{2.5} in three periods, named minor BB, intensive BB and major BB. The major BB period is from 1-23, November. As I know, the central heating system in Beijing usually starts from the middle of November. There should be large increase in the fuel consumption, including biofuel and coal due to residential heating. I suggest to exclude the heating period from the major BB. The authors can also compare chemical compositions in the heating period with other three episodes.

Our reply: According to the referee’s suggestion, we separated the observation periods into four sub-periods, as follows: 15-30 October (Period I: Minor biomass burning), 31 October (Period II: Intensive biomass burning), 1-14 November (Period III: Major biomass burning), and 15-23 November (Period IV: Heating season).

Accordingly, Table 2, Figure 6, Figure 7 and the discussion in **section 3.3 and section 3.4** were also updated in the revised paper. (See Lines 255-402).

Table 2. Concentrations of chemical components in PM_{2.5} aerosols and gaseous species collected at the GC site during the four biomass burning periods from 15 Oct to 23 Nov 2016.

Species	Period I (15-30 Oct) Minor BB	Period II (31 Oct) Intensive BB		Period III (1 -14, Nov) Major BB		Period IV (15 -23, Nov) Heating period	
	Concentration	Concentration	Ratio*	Concentration	Ratio*	Concentration	Ratio*
PM _{2.5}	81.0 ± 44.5	235	2.91	163 ± 46.7	2.01	189 ± 83.0	2.33
Levogluconan	0.36 ± 0.14	4.37	12.1	0.90 ± 0.37	2.50	0.96 ± 0.63	2.67
Mannosan	0.015 ± 0.005	0.18	12.0	0.038 ± 0.015	2.53	0.050 ± 0.026	3.33
OC	16.2 ± 7.52	96.3	5.93	55.2 ± 17.1	3.41	69.4 ± 24.6	4.28
EC	12.2 ± 5.85	36.0	2.96	25.5 ± 10.1	2.09	36.4 ± 21.5	2.98
TC	28.4 ± 13.1	132	4.66	80.9 ± 34.6	2.85	106 ± 55.3	3.73
SO ₄ ²⁻	10.3 ± 8.96	4.56	0.44	11.8 ± 6.02	1.15	9.08 ± 3.87	0.88
NO ₃ ⁻	16.6 ± 12.9	18.1	1.09	16.5 ± 6.42	0.99	12.6 ± 5.76	0.76
NH ₄ ⁺	10.1 ± 7.40	10.0	0.99	12.0 ± 4.35	1.19	10.3 ± 3.62	1.02
K ⁺	1.16 ± 0.36	2.61	2.25	1.76 ± 0.46	1.52	1.65 ± 0.84	1.42
Cl ⁻	3.46 ± 1.97	7.49	2.16	5.58 ± 2.16	1.61	6.27 ± 2.58	1.81
OC/EC	1.53 ± 0.35	2.67	1.75	2.31 ± 0.59	1.51	2.04 ± 0.31	1.33
NO ₃ ⁻ /SO ₄ ²⁻	1.74 ± 0.60	3.96	2.28	1.50 ± 0.35	0.86	1.42 ± 0.47	0.82
LG/OC	0.025 ± 0.008	0.045	1.80	0.016 ± 0.005	0.64	0.014 ± 0.006	0.56
LG/EC	0.039 ± 0.019	0.121	3.10	0.038 ± 0.017	0.97	0.028 ± 0.013	0.72
LG/MN	24.9 ± 4.44	24.1	0.97	24.8 ± 6.46	1.00	18.3 ± 4.27	0.73
LG/K ⁺	0.36 ± 0.081	1.67	4.64	0.51 ± 0.16	1.42	0.53 ± 0.15	1.47
NO (ppb)	21.7 ± 12.5	21.7	1.00	39.6 ± 15.4	1.82	39.3 ± 23.6	1.81
NO ₂ (ppb)	21.8 ± 4.95	26.5	1.22	32.7 ± 7.27	1.50	24.6 ± 10.2	1.13
NO _x (ppb)	43.6 ± 16.3	48.2	1.11	72.4 ± 17.8	1.66	64.0 ± 33.4	1.47
SO ₂ (ppb)	5.83 ± 2.46	8.04	1.38	11.1 ± 4.10	1.90	9.75 ± 3.31	1.67
CO (ppm)	0.44 ± 0.33	0.70	1.59	1.65 ± 0.53	3.75	1.18 ± 0.83	2.68
O ₃ (ppb)	9.79 ± 4.88	23.2	2.37	7.51 ± 3.87	0.77	9.59 ± 7.55	0.98
NH ₃ (ppb)	14.3 ± 6.12	11.1	0.78	18.6 ± 8.03	1.30	21.2 ± 14.2	1.48

*: indicates that the ratios of the heating period, intense BB period or major biomass burning period were divided by those from the minor BB period.

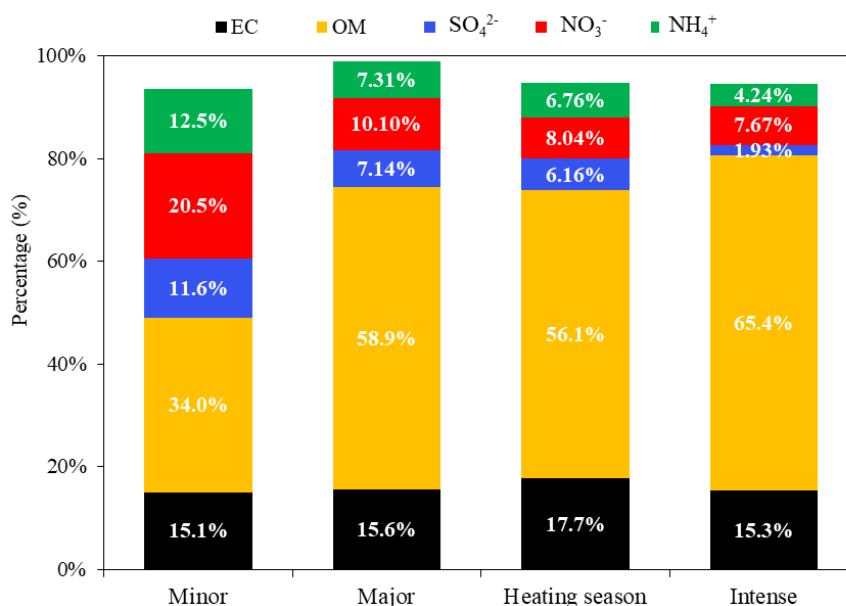


Fig. 6. Mean percentiles of major components in PM_{2.5} with respect to different biomass burning pollution periods at GC site during the sampling time.

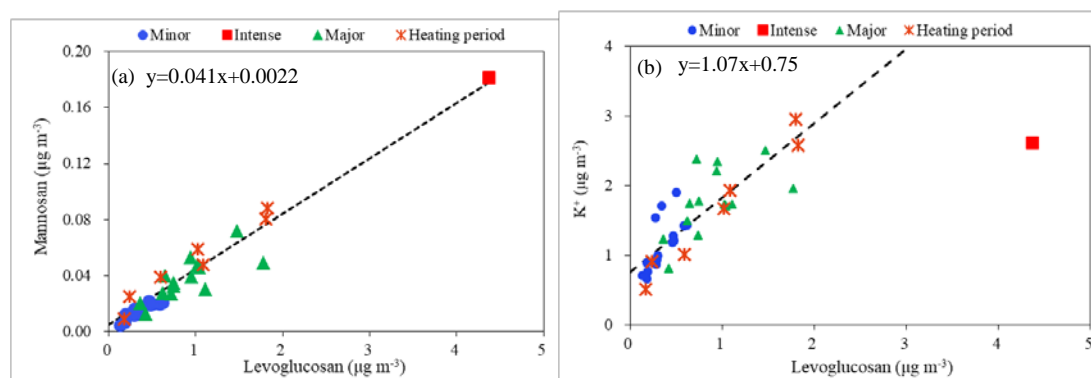


Fig. 7. Scatter plots of (a) levoglucosan versus mannosan, (b) levoglucosan versus K⁺

(2.1) The ratio of levoglucosan to mannosan (L/M) is wide used to distinguish different BB types. As Figure 7 showed, the L/M ratios are very stable during the whole campaign. However, the air masses are originated from different places (Figure 5) where should have different BB types. The authors should explain why the air masses passed through different BB areas have the similar L/M ratios.

Our reply: According to the referee's comment, we clustered 161 backward trajectories of the air masses arriving at GC during the whole sampling period from 15 Oct to 23 Nov, 2016, into four groups (see Fig. R1). Specifically, 50% of air masses originated from North China (group 1

and group 4), while another 32% of the air masses originated from Mongolia (group 2), having passed through North China, i.e., Inner Mongolia and Hebei provinces on their route to the GC site. A similar long and high air mass, transported from West China (group 2), across Xinjiang and Inner Mongolia provinces to the GC site, was observed during the sampling period (19%).

Straws are commonly burned in China; rice straw is popular in southern China, whereas wheat straw and corn straw prevail in northern and western China. Based on source burning studies, the LG/MN ratios from burning these crop residues were similar at a relatively high values (> 10.0), and also overlapped with those from hardwood and leaf burning (*Fig. R2*) (Engling et al., 2009; Cheng et al., 2013). Thus, the LG/MN ratios alone are insufficient to separate burning emissions from crop residuals, hardwoods or leaves. Although different straw types (rice, wheat or corn straw) are prevalent in different parts of China, the LG/MN ratios of all biofuel materials in China are characterized by relatively high values. The LG/MN ratios during minor, major and intense biomass pollution periods were observed at similar high values, i.e., 24.9, 24.1 and 24.8, respectively, which were all in the range of typical straw burning values in China.

We added the discussion of the potential reason for why the ratios of LG/MN are consistently high during periods I to III in the revised paper.

“Based on source emission studies, the LG/MN ratios from crop residue burning, i.e., rice straw, wheat straw, and other straws, were similar and characterized by high values (> 10.0), yet overlapped with those from hard wood and leaf burning (Engling et al., 2009; Cheng et al., 2013). The LG/MN ratios during minor, major and intense biomass pollution periods were observed at similar high values, i.e., 24.9, 24.1 and 24.8, respectively, which were all in the range of straw burning in China.” (See Lines 357-362).

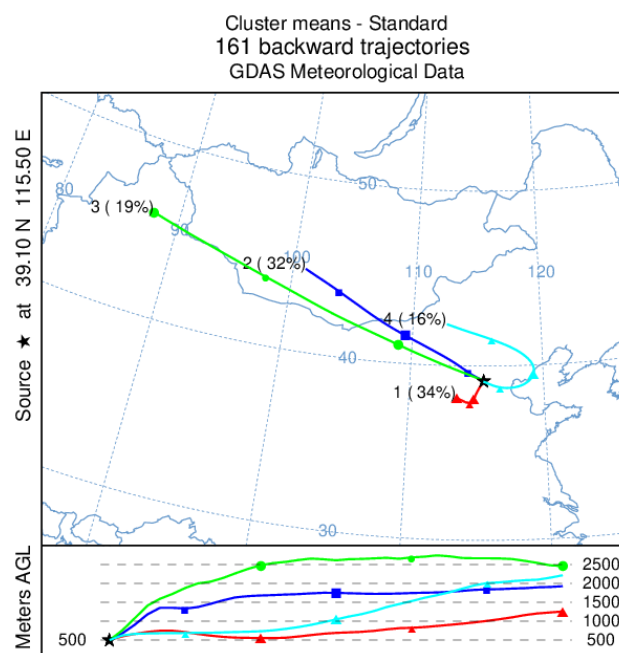


Figure R1. Variations of air mass origins to GC during the observation time from 15 Oct to 23 Nov, 2016, shown by clusters of 48 hours backward trajectories arriving at 500m aboveground level. The numbers in each panel indicate the percentages of daily trajectories in the sampling time with such origins.

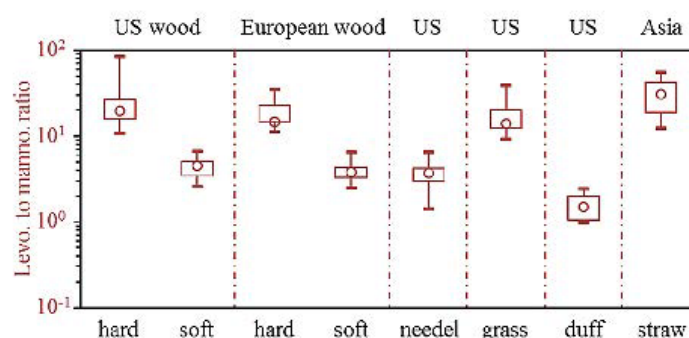


Figure R2. The ratios of LG/MN measured in source samples (Cheng et al., 2013)

(2.2) Moreover, recent studies have demonstrated that levoglucosan is not stable in the air and will be decomposed during atmospheric transport. How does the aging process affect the L/M ratio and its application in BB type identification?

Our reply: We admit that the chemical loss of biomass burning tracers, i.e., LG and MN, may occur in the ambient aerosols due to photochemical reaction during the aging process. Several studies have investigated the loss rate of levoglucosan in ambient air (e.g., Sang et al., 2016; Gensch et al., 2018). However, it is still not known whether mannosan will undergo similar

atmospheric reactions as levoglucosan, the concentrations of which are 1-2 orders of magnitude lower than levoglucosan in ambient aerosols. Therefore, although a change in the L/M ratio with aging process may occur in the ambient aerosols, potentially impacting the source apportionment, we still can't quantify the specific change of the L/M ratio in the real ambient environment at present. In any case, we added the discussion about the potential change of the L/M ratio during the aging process in the revised paper to make the results more rigorous and reasonable.

“In addition, atmospheric degradation of levoglucosan may occur due to photochemical reaction or other aging processes. However, it is still not known whether mannosan will undergo atmospheric reactions to a similar extent as levoglucosan, the concentrations of which are 1-2 orders of magnitudes lower than levoglucosan in ambient aerosols. Therefore, although a change in the LG/MN ratio with aging processes may occur in ambient aerosols, potentially impacting the source apportionment, assessing the specific effect on the LG/MN ratios in the real ambient environment is uncertain at present.” (See Lines 370-377)

(3) For the additional sources of potassium, previous studies have demonstrated that coal combustion is the major source of potassium in Beijing, especially during winter haze. Thus, the apparent difference in levoglucosan / potassium ratios between intensive BB and other periods (Figure 7b) could be largely due to the impact of regional coal combustion.

Our reply: We admit that coal combustion may impact the levoglucosan / potassium ratios in the typical heating season in winter. Yan et al. (2017) and Yu et al. (2018) demonstrated that coal combustion can also be an important source of LG and K^+ . However, there is no information about LG/ K^+ ratios from coal combustion reported from previous studies. We thank the referee for this valuable suggestion, and we added coal combustion as a potential impact factor for the variation of LG/MN ratios between the four periods in the revised paper.

“Moreover, it should be noted that coal combustion can also act as a potential source of LG and MN, with the relatively low LG/MN ratios (8.3) (Yan et al., 2018). Thus, the decreasing trend of LG/MN ratios in the typical heating season can partly be caused by extensive coal combustion. However, it is noteworthy that emissions from crop straws are still expected to be dominant burning materials during the heating season at the GC site, as evidenced by the low LG/ K^+ ratios

(0.53 ± 0.15), i.e., in the typical range for straw and hard wood burning (Cheng et al., 2013).” (See Lines 364-370)

References:

- 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, <https://doi.org/10.5194/acp-13-7765-2013>, 2013.
- Engling, G., Lee, J.J., Tsai, Y.W., Lung, S.C.C., Chou, C. C.K., and Chan, C.Y.: Size resolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw, *Aerosol Sci. Tech.*, 43, 662-672, <https://doi.org/10.1080/02786820902825113>, 2009.
- Gensch, I., Sang-Arlt, X.,F., Laumer, W., Chan, C.,Y., Engling, G., Rudolph, J., and Kiendler-Scharr, A.: Using $\delta^{13}\text{C}$ of levoglucosan as a chemical clock, *Environ. Sci. Technol.* <https://pubs.acs.org/doi/10.1021/acs.est.8b03054>, 2018..
- Sang, X.F., Gensch, I., Kammer, B., Khan, A., Kleist, E., Laumer, W., Schlag, P., Schmitt, S.H., Wildt, J., Zhao, R., Mungall, E.L., Abbatt, J.P.D., and Kiendler-Scharr, A.: Chemical stability of levoglucosan: An isotopic perspective, *J. Geophys. Res.*, 43, 5419-5424, <https://doi.org/10.1002/2016GL069179>, 2016.
- Yan, C.Q., Zheng, M., Sullivan, A.P., Shen, G.F., Chen, Y.J., Wang, S.X., Zhao, B., Cai, S.Y., Desyaterik, Y., Li, X.Y., Zhou, T., Gustafsson, Ö., and Collett, J.L.: Residential coal combustion as a source of levoglucosan in China, *Environ. Sci. Technol.*, 52(3), 1665-1674, <https://doi.org/10.1021/acs.est.7b05858>, 2017.
- Yu, J.T., Yan, C.Q., Liu, Y., Li, X.Y., Zhou, T., and Zheng, M.: Potassium: A Tracer for Biomass Burning in Beijing? *Aerosol Air Qual. Res.*, 18, 2447-2459, doi: 10.4209/aaqr.2017.11.0536, 2018.