Anonymous Referee #1

Received and published: 10 November 2020

General Comments:

In this manuscript, the authors report chemical characteristics of $PM_{2.5}$ under the impact of biomass burning (BB) in the North China Plain. A unique episode with extreme biomass burning impact, with daily concentrations of levoglucosan as high as 4.37 μg m^{-3} was captured. The formation process and chemical characteristics of this severe biomass burning pollution episode were also reported. This field measurement was interesting and the data in this study was valuable. This study matches the definition of Measurement Report quite well, presenting substantial new results from field measurements of atmospheric properties and processes. The manuscript is well organized and concisely written, and minor revisions indicated below are needed before publication.

Our reply: We thank the reviewer for the pertinent comments. We have prepared the point-by-point responses to address the reviewer's comments as shown below. The blue color text shows the amended sections in the manuscript. The line numbers correspond to those in the revised version of the manuscript.

Major comments:

(1) LOD (limit of detection) of the water-soluble inorganic ion analysis also suggested described in the experimental section.

Our reply: According to the referee's comment, LOD (limit of detection) of the water-soluble inorganic ion analysis is described in the experimental section.

"The quartz filter samples were also analyzed for water-soluble inorganic ions by a Dionex ICS-5000+ ion chromatograph, including SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Ca^{2+}, Na^+, K^+ and Mg^{2+}. The method detection limits for the individual ionic species were 0.18 μg L^{-1}, 0.15 μg L^{-1}, 0.03 μg L^{-1}, 0.048 μg L^{-1}, 0.08 μg L^{-1}, 0.01 μg L^{-1}, 0.01 μg L^{-1}, 0.008 μg L^{-1}, respectively." (See Lines 115-118)

(2) Experimental section should include more detailed information regarding statistical analysis conducted.

<u>Our reply:</u> According to the referee's comment, we added the description of statistical methods applied to our data in the revised manuscript.

"Statistical analysis of data, i.e., the correlation analysis between the concentrations of levoglucosan, mannosan and K^+ at Gucheng site during the sampling period were conducted with the linear fitting method." (See Lines 151-154)

(3) "Concentration" in table 1 should be changed to "Average concentration".

<u>Our reply:</u> According to the referee's comment, we changed "Concentration" to "Average concentration" in Table 1 in the revised paper.

(4) The meteorological factors (temperature (T), relative humidity (RH), wind speed (WS) and rainfall) in Figure 1 were together expressed in one figure, difficult to distinguish. It is suggested to separate these meteorological factors to two figures and add the time-series variation of PBL as well.

<u>Our reply:</u> We thank the anonymous referee for this valuable comment. We added the time-series variation of PBL and separated the meteorological factors into two figures, i.e., Figure 1f and Figure 1g.

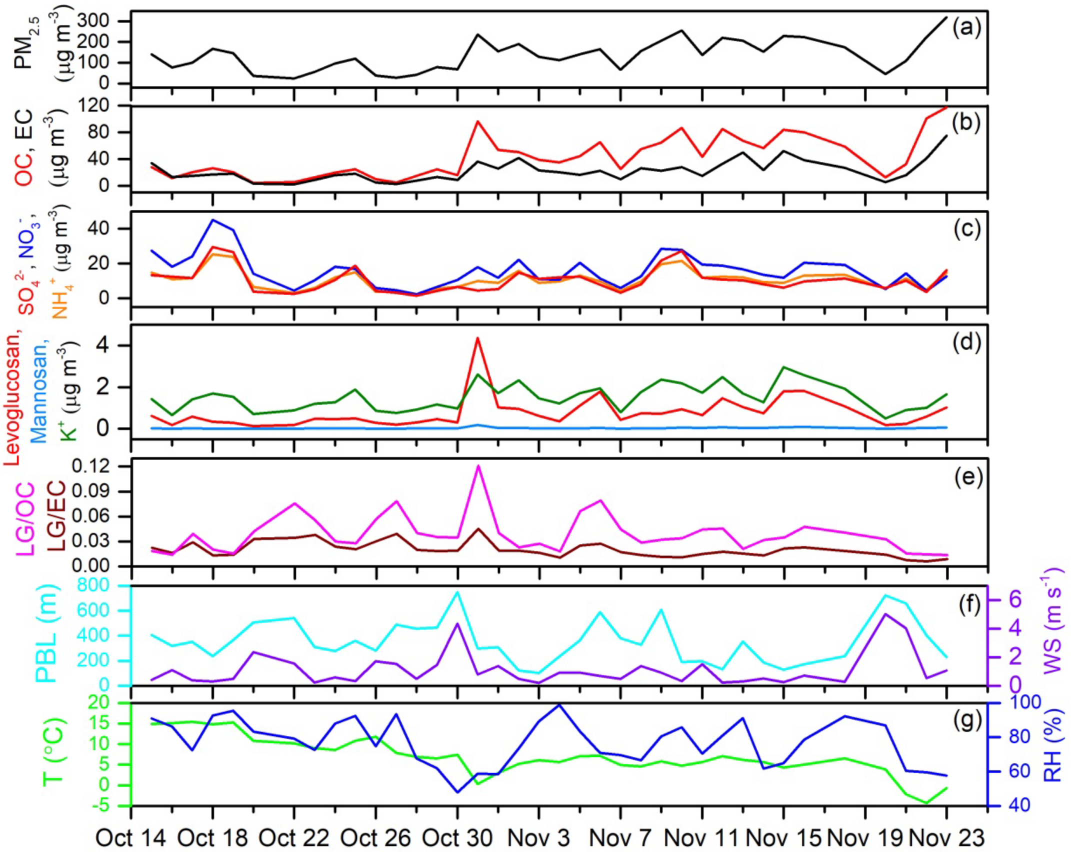

Figure 1. Time-series variation obtained for $PM_{2.5\text{-cal}}$ and its major components, biomass burning tracers as well as meteorological factors at the GC site during the sampling period from 15 Oct to 23 Nov 2016 (a) $PM_{2.5\text{-cal}}$, (b) OC and EC, (c) secondary inorganic aerosols, i.e., SO_4^{2-}, NO_3^- and NH_4^+, (d) levoglucosan, mannosan and K^+, (e) ratios of levoglucosan to OC (LG/OC) and levoglucosan to EC (LG/EC), (f) PBL and wind speed (WS), (g) temperature (T) and relative humidity (RH).

(5) The English grammar and usage should be polished by some English native speakers.

Our reply: According to the referee's comment, we have improved the English writing in the revised paper.

(6) The abbreviation such as LG and MN is not generally used in literatures. These abbreviations are not easy to be remembered and make the manuscript difficult to understand. I suggest that the authors using the origin names or abbreviations more easily to be remembered.

Our reply: According to reviewer's suggestion, the abbreviations of LG and MN were changed to the original names, i.e., levoglucosan and mannosan in the revised manuscript.

(7) Discussion of the possible degradation of levoglucosan should be included in the Day and night distributions.

Our reply: According to the referee's comment, we added a remark that the chemical degradation of levoglucosan may occur due to photochemical reaction in the ambient aerosols during daytime in the revised paper, extending the discussion of day-night distribution results.

"Moreover, besides the influence from variations of the PBL height, the chemical degradation of levoglucosan may occur due to photochemical reaction in the ambient aerosols during daytime, further enlarging the gap of levoglucosan levels between daytime and nighttime (Sang et al., 2016; Gensch et al., 2018). Consequently, the contribution of levoglucosan to $PM_{2.5\text{-cal}}$ during nighttime (0.64%) was observed to be higher than that during daytime (0.37%) (Figure 3)." (See Lines 201-206)

(8) More time series of diagnostic ratio such as levoglucosan to OC ratios should be presented to illustrate the impact of BB

Our reply: We thank the referee for this valuable comment. We added the time series of levoglucosan to OC ratios as Figure 1e, illustrating the impact of biomass burning. Meanwhile, the discussion of the influence of biomass burning emission on organic aerosol was also updated in the revised paper.

"The levoglucosan/OC ratio was utilized to estimate the effect of biomass burning on ambient organic aerosols. Accordingly, levoglucosan/OC ratios sharply increased to 0.045 during period II, which was noticeably higher than during other periods in this study. Moreover, this level is also higher than most of the published field observations, i.e., at urban sites (Zhang et al., 2008; Cheng et al., 2013; Zhang et al., 2014), rural sites (Sang et al., 2013; Ho et al., 2014; Pietrogrande et al., 2015; Mkoma et al., 2013) and agricultural sites (Ho et al., 2014; Jung et al., 2014), yet lower than at an urban site in northern Italy during wintertime (in the range of 0.01 to 0.13) (Pietrogrande et al., 2015). This illustrates that biomass combustion played an important role in organic aerosol pollution during the intensive BB episode II. However, due to other emissions of OC enhanced during the major BB episode (period III) and heating season (period IV), i.e., combustion of coal and biofuel for heating, OC increased to an even higher level (55.2 ± 17.1 μgC m^{-3} and 69.4 ± 24.6 μgC m^{-3}, respectively). Due to the abundance of organic aerosols, the contribution from biomass burning emission was thereby reduced and the levoglucosan/OC ratios during periods III and IV decreased to 0.016 ± 0.005 and 0.014 ± 0.006, respectively, even lower than those observed in the minor BB period I (0.025 ± 0.008)." (See Lines 254-268)

Anonymous Referee #2

Received and published: 18 November 2020

This study reports a measurement research on the characteristics of the chemical components of $PM_{2.5}$ during 15 October to 30 November at the agricultural site of the NCP. The authors linked their results to the BB emission and claimed the importance of softwood burning to the air quality in NCP during the heating season. Overall, this is a nice piece of paper with clear objectives and methods and will provide valuable results. Before considering publication in ACP, major revisions should be made. Some comments and suggestions are listed as follows:

Our reply: We appreciate the valuable comments of the anonymous referee. We have prepared the point-by-point responses to address the reviewer's comments as shown below. The blue color text shows the amended sections in the manuscript. The line numbers correspond to those in the revised version of the manuscript.

General comment:

(1) Although it is a measurement report, which should present substantial new results from measurements of atmospheric properties and processes, the scientific goal should be improved well through focusing on the innovation in measurement or data analysis methods. The current results are no longer new compared with that reported in 2013 of Beijing by Cheng et al. (2013). What is the current data in this rural site of NCP may bring us to a new knowledge of chemical characteristics, especially in atmospheric

properties and processes? Is there any difference between this study with that reported previously, e.g., a faster conversion rate, a new emission type due to the emission control by the government, etc.

Our reply: In fact, the topic of our paper is different from Cheng et al. (2013). Cheng et al. (2013) focused on investigating the relationships between levoglucosan and other biomass burning tracers (i.e., water soluble potassium and mannosan) based on both ambient samples collected in Beijing and pure biomass burning source samples. And they concluded that there are representative ranges of the levoglucosan to K^+ and levoglucosan to mannosan ratios for different kinds of biomass, and they compared the results from the ambient samples collected in Beijing. In section 3.4 we apply their results to our study, i.e., representative ranges of the levoglucosan to K^+ and the levoglucosan to mannosan ratios for different kinds of biomass, to discuss the sources for the severe biomass burning event at the rural site in North China. Although, the phenomenon observed in our study on biomass sources identification (section 3.4) is partly similar to those ambient observation results from Beijing during wintertime (Cheng et al., 2013), the discussion of potential influence factors on the biomass burning tracer ratios is different and extended to, e.g., combustion conditions (smoldering and flaming burns), back trajectory analysis, fire activity data and synoptic condition discussion, which were included in our study but not mentioned in Cheng et al. (2013). Moreover, our manuscript also includes the discussion on day-night variations in the patterns of $PM_{2.5}$ chemical components as well as the influence of different levels of biomass combustion pollution on $PM_{2.5}$ chemical characteristics.

Overall, the most notable merits of our manuscript include：

① To the best of our knowledge, this study is the first one to characterize the biomass burning pollution status at a heavily polluted rural site in Hebei province during the autumn-winter transition season, following the corn harvest. The results can provide valuable information about the biomass burning activities in the entire North China region. Moreover, we captured a unique episode with extreme biomass burning pollution, with concentrations of levoglucosan as high as 4.37 μg m^{-3}. Based on the multi-analysis of biomass burning molecular tracers, back trajectory analysis, fire activity data and synoptic condition, the formation process and chemical character of this severe biomass burning pollution episode were discussed in detail.

② Combined with other chemical components analysis, our study revealed the different levels of biomass combustion pollution impacting the different types of chemical components in ambient aerosol, which have rarely been reported by previous work.

③ From our observations and those reported in literature, we highlight that both biomass types and combustion conditions (flaming versus smoldering) exert non-negligible impact on the formation mechanisms of biomass burning tracers in the ambient aerosols.

(2) Besides, the logicality of this paper should be improved. For example, "the LG/MN ratios from crop residue burning, i.e., rice straw, wheat straw, and other straws, were similar and characterized by high values, yet overlapped with those from hard wood and leaf burning (>10.0), while soft wood characterized by relatively lower LG/MN ratios (< 5.0)". The ratio of LG/MN in this study is around 20, which the authors claim that the air quality was influenced by softwood emission. This conclusion is obviously inconsistent with their previous analysis.

Our reply: Indeed, the levoglucosan/mannosan ratios from hard wood, leaf as well as pure crop residues burning, i.e., rice straw, wheat straw, and other straws, were characterized by high values (>10.0), while pure soft wood is characterized by relatively lower levoglucosan/mannosan ratios (<5.0). The levoglucosan/mannosan ratios during minor, intense, major biomass burning pollution and heating season periods in this study were observed at high values, i.e., 24.9, 24.1, 24.8 and 18.3, respectively. However, compared to the levoglucosan/mannosan ratios during the former three episodes (24.1-24.9, averaged at 24.6), the ratio observed during the heating season period (18.3) decreased by 25.6%. We speculate this decline trend of levoglucosan/mannosan ratios was partly influenced by the raised proportion of softwood combustion for heating, which is characterized by relatively lower levoglucosan/mannosan ratios. In fact, biomass, especially of crop residues (e.g., wheat and corn straw) is more commonly used as biofuel for cooking in the rural areas in North China. However, due to the burning of crop residues or leaves typically being subject to quick flaming combustion under high temperature burning condition, such fuels are not suitable for extended heating during the cold season. According to the local habits, softwoods are also commonly used as biofuels for stove heating in North China during wintertime, especially during periods when the use of coal is restricted in the NCP.

Nonetheless, in order to make the description more clearly and also addressing the comments from third reviewer, the discussion on the influence of different types of biomass on the tracer ratios has been modified in the revised manuscript as shown below:

"Levoglucosan and mannosan showed a good relationship during the entire sampling period (Figure 7a, $r = 0.97$, $p < 0.01$). The levoglucosan/mannosan ratios during minor, intense, major biomass pollution and heating season periods were observed at high values, i.e., 24.9, 24.1, 24.8 and 18.3 respectively (Table 2, Figure 7). Compared to the former three episodes (24.1 to 24.9, averaged at 24.6), the levoglucosan/mannosan ratios during heating season period (18.3) decreased by 25.6%. Based on source emission studies, the levoglucosan/mannosan ratios from crop residue burning, i.e., rice straw, wheat straw, and corn straw, are similar and are characterized by high values (averaged at 29, in the range of 12 to 55) (Zhang et al., 2007; Engling et al., 2009; Cheng et al., 2013; Jung et al., 2014), yet overlapping with those from hard wood (averaged at 28, in the range of 11 to 146) (Bari et al., 2009; Jung et al., 2014) and grass burning (18.2 ± 10.2) (Sullivan et al., 2008), while softwood is characterized by relatively lower levoglucosan/mannosan ratios (averaged at 4.3, in the range of 2.5 to 4.7) (Engling et al., 2006; Cheng et al., 2013; Jung et al., 2014). Subsequently, this declining trend in the levoglucosan/mannosan ratios during the heating season period was partly caused by the higher proportion of softwood combustion, which is characterized by relatively lower levoglucosan/mannosan ratios. According to the local habits, softwoods, e.g. China fir and pine are also commonly used as biofuels for stove heating in North China, since they allow sustained heating duration." (See Lines 315-332)

Specific comments:

(1) P4, L107. The abbreviation LG and MN should be spelled out first time. Similar with that in P7, L189, "Elemental carbon and primary organic components", which has been used as EC or POC before. The abbreviation through out the manuscript should be checked carefully to unified.

Our reply: According to the referee's comment, we checked the manuscript and confirmed that the acronyms were all defined when mentioned for the first time in the text. Considering the other reviewer's suggestion, the abbreviations of LG and MN were changed to the original names, i.e., levoglucosan and mannosan in the revised manuscript.

(2) P8, L202. "Moreover, such an enhancement in secondary transformations during daytime is more evident in terms of the mass contributions of secondary inorganic ions to PM2.5-cal, that the contributions of SO_4^{2-}, NO_3^- and NH_4^+ to $PM_{2.5\text{-cal}}$ decreased from daytime (9.9%, 14.5% and 10.0%) to nighttime (6.5%, 9.6% and 7.1%) (Figure 3)." The conversion rate of SOR, NOR should be useful here.

Our reply: We thank the referee for this valuable comment. We calculated the conversion rate of SOR and NOR in the revised manuscript, and extended the supplement for the evidence of secondary inorganic aerosol transformations enhanced during daytime.

"The mass contributions of secondary inorganic ions to $PM_{2.5\text{-cal}}$, that is the contributions of SO_4^{2-}, NO_3^- and NH_4^+ to $PM_{2.5\text{-cal}}$, decreased from daytime (9.9%, 14.5% and 10.0%) to nighttime (6.5%, 9.6% and 7.1%) (Figure 3). Such an enhancement in secondary transformations during daytime is more evident in terms of the sulfur and nitrogen oxidation ratios (SOR and NOR, molar ratio of sulfate or nitrate to the sum of sulfate and SO_2 or nitrate and NO_2), which have been used previously as indicators of secondary transformations (Sun et al., 2013; Zheng et al., 2015). Both SOR and NOR during daytime were higher than those during nighttime (Figure S3), further confirming the elevated secondary formations of sulfate and nitrate during daytime." (See Lines 209-216)

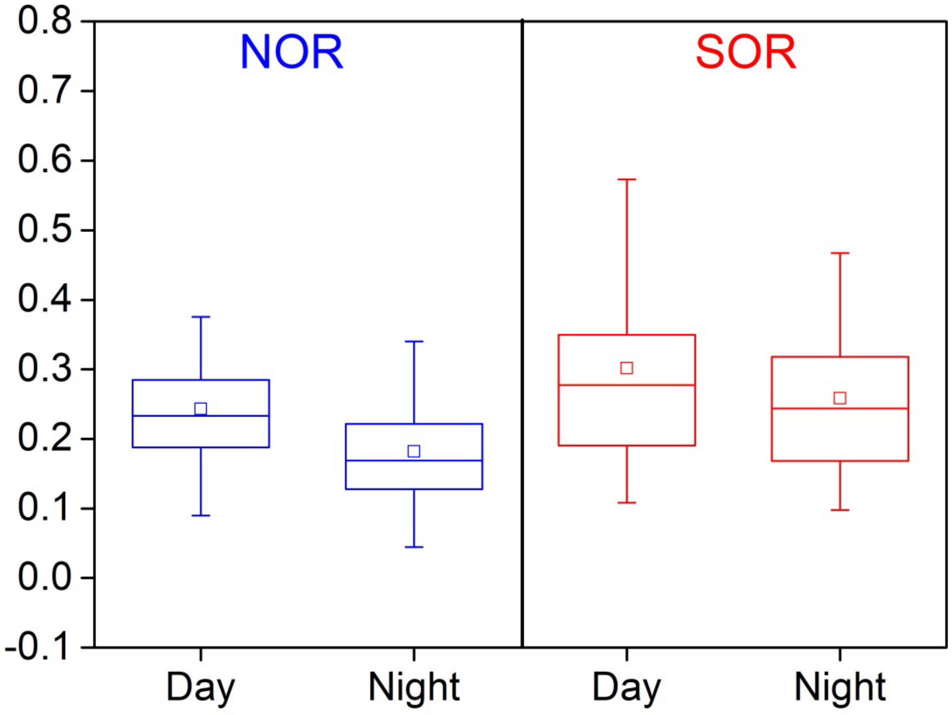

Figure S3. Variation of NOR and SOR during daytime and nighttime, respectively. In the box-whisker plots, the boxes and whiskers indicate the 95th, 75th, 50th (median), 25th and 5th percentiles, respectively. □ indicates the mean value.

(3) P8, L214. The BB episodes section. The detailed description of this episode 31 Oct is helpful to readers for understanding, such as the meteorological conditions, wind rose plot. Besides, the PMF or model simulation should be made to conclude how much the BB contribute to the $PM_{2.5}$.

Our reply: According to the referee's comment, the meteorological conditions during intense biomass burning episode on 31 October was described in detail in the revised manuscript.

As for the contributions of biomass burning to carbonaceous aerosol and $PM_{2.5}$, we quantified them by the molecular tracer approach and discussed the results in a companion paper, as it would render this paper too long otherwise. Nonetheless, we thank the referee for this valuable comment and have revised the corresponding text as follows.

"Meanwhile, there was significant change in the meteorological conditions, i.e., the wind direction changed from southwesterly to northerly winds (Figure S4). Northerly winds advected cold and dry air masses, with the lowest hourly temperature observed at -5.3 °C (Figure S5). This notable temperature decline before the commencing of the operation of the central heating systems should have caused intense combustion activities for heating purposes at the rural site. Moreover, the synoptic situation on 31 October, 2016 was under weaker turbulence with low PBL height and small wind speeds (Figure 1f). These worsened meteorological conditions would further enhance aerosol accumulation.” (See Lines 229-236)

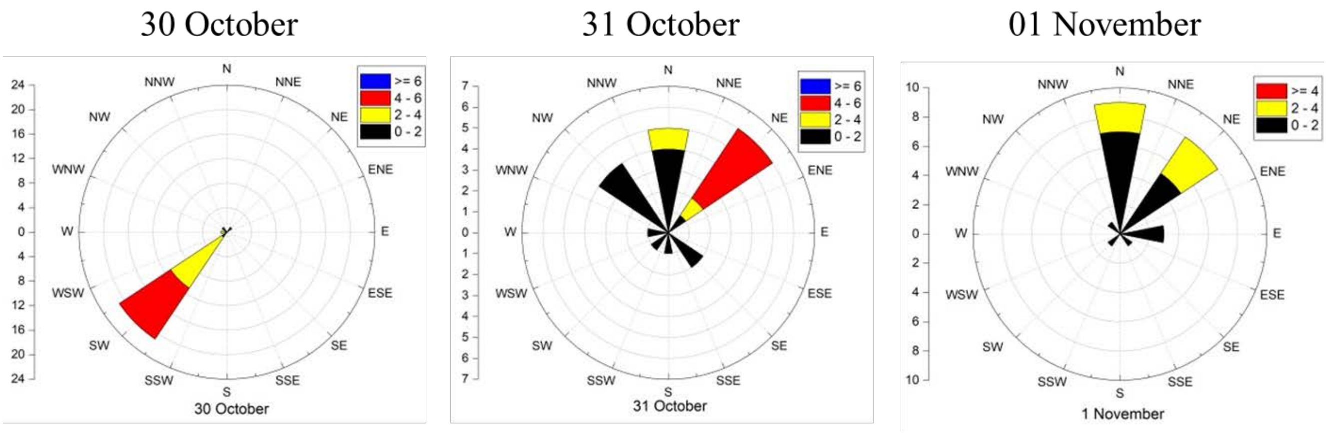

Figure S4. Wind-rose diagram of hourly wind direction at the GC site during 30 October, 31 October and 1 November 2016, respectively.

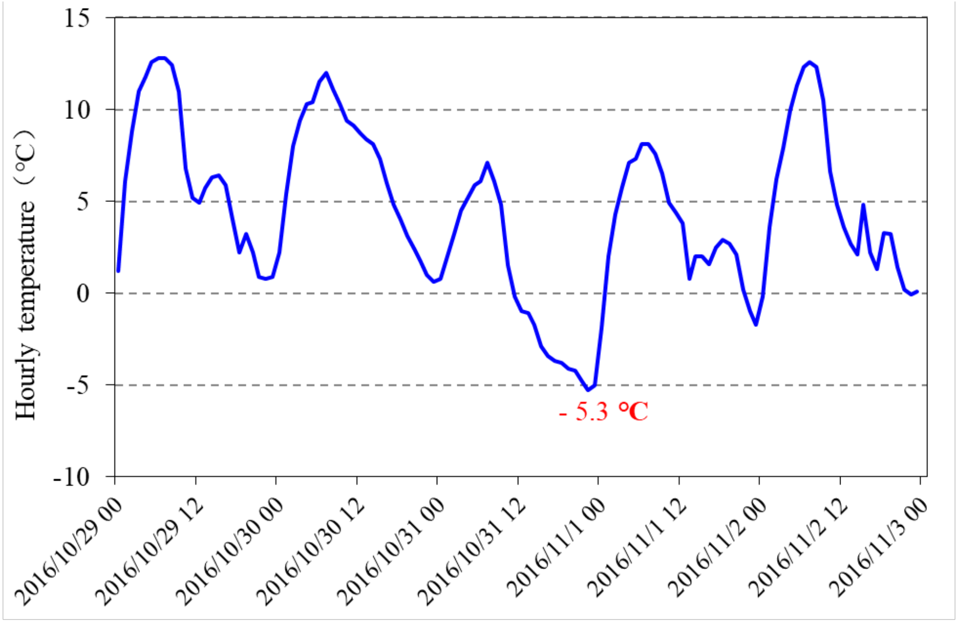

Figure S5. Hourly temperature from 00:00 on 29th October to 00:00 on 3rd November 2016 at the GC site.

(4) P9, L230. “The central heating systems in North China cities were operated during period IV, and the ambient level of LG was observed at 0.96 ± 0.63 μg m^{-3}, which was slightly higher than that in period III.” Is this statement telling us the central heating systems

used in NCP will emitted more LG. As we know, the heating system was changed since 2016 over NCP from coal to gas at least in the main cities of NCP. The rest area of NCP are substituted by the electric power system such as air conditioner. Does that means the LG may originated from gas or other fuels?

Our reply: Generally speaking, levoglucosan is a unique molecular tracer for biomass burning, formed during pyrolysis of cellulose, and has been the most common molecular tracers for biomass burning emissions, adopted in numerous laboratory and field studies (Simoneit, 1999;Simoneit, 2002;Engling et al., 2009;Gensch et al., 2018;Chantara et al., 2019;Fortenberry et al., 2018). Thus, there should be no levoglucosan emitted from natural gas combustion. Actually, the ambient level of levoglucosan was likely impacted by various factors, such as emission source characteristics, including biomass categories and combustion conditions, as well as meteorological conditions, e.g., wind speed and direction, the development of the boundary layer, etc. Therefore, the difference in levoglucosan concentrations between the major biomass burning period and central heating period was impacted by all environmental factors, including source emissions and meteorological conditions. However, in order to make the study focus more on data reporting, we removed the speculations regarding the cause for those similar ambient levoglucosan levels during major biomass burning period and central heating period. Nonetheless, we thank the referee for this valuable comment. To make the description more rigorous, we have modified the corresponding text as follow.

"The central heating systems in North China cities were operated during period IV, and the ambient level of levoglucosan was observed at 0.96 ± 0.63 μg m^{-3}, which was similar to that observed in period III." (See Lines 249-251)

(5) Conclusion section. The local soft wood contributed to high concentrations of $PM_{2.5}$ in NCP during heating season should be more considered.

Our reply: According to the referee's suggestion, we modified the description of this conclusion, to make the revised paper focus more on the reported data.

"Compared to the other biomass burning episodes, the levoglucosan/mannosan ratios during the heating season period slightly decreased, while levoglucosan/K^+ ratios during the intensive BB period were unusually higher than those in the other three biomass burning periods.” (See Lines 365-368)

(6) Language improvement should be made by a native speaker.

Our reply: According to the referee’s comment, we have improved the English language in the revised paper.

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.

Chantara, S., Thepnuan, D., Wiriya, W., Prawan, S., and Tsai, Y. I.: Emissions of pollutant gases, fine particulate matters and their significant tracers from biomass burning in an open-system combustion chamber, Chemosphere, 224, 407-416, 10.1016/j.chemosphere.2019.02.153, 2019.

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 Science and Technology, 43, 662-672, 10.1080/02786820902825113, 2009.

Fortenberry, C. F., Walker, M. J., Zhang, Y., Mitroo, D., Brune, W. H., and Williams, B. J.: Bulk and molecular-level characterization of laboratory-aged biomass burning organic aerosol from oak leaf and heartwood fuels, Atmospheric Chemistry and Physics, 18, 2199-2224, 10.5194/acp-18-2199-2018, 2018.

Gensch, I., Sang-Arlt, X. F., Laumer, W., Chan, C. Y., Engling, G., Rudolph, J., and Kiendler-Scharr, A.: Using delta(13)C of Levoglucosan As a Chemical Clock, Environ Sci Technol, 52, 11094-11101, 10.1021/acs.est.8b03054, 2018.

Simoneit, B. R. T.: Biomass burning — a review of organic tracers for smoke from incomplete combustion, Applied Geochemistry, 129-162, 2002.

Simoneit, J. J. S., C.G. Nolte, D.R. Oros, V.O. Elias, M.P. Fraser, W.F. Rogge, G.R. Cass☐: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmospheric Environment, 173-182, 1999.

Anonymous Referee #3

Received and published: 9 December 2020

This is a well-written and structured manuscript to discuss the biomass burning pollution status in rural atmosphere of North China by presenting the biomass burning tracers and secondary inorganic ions in $PM_{2.5}$ during a transition heating season. It is interesting that an episode with extreme biomass burning tracer levels was identified to present the severity of biomass burning pollutions. Biomass burning tracer ratios were also introduced to discuss the biomass source types and burning process. I agree with the data discussion and to publish on ACP. There are some minor errors are necessary to be revised before publishing.

Our reply: We thank the reviewer for his/her valuable comments. We have prepared the point-by-point responses to address the reviewer's comments as shown below. The blue color texts indicate the amended sections in the manuscript. The line numbers correspond to those in the revised version of the manuscript.

Specific comments:

(1) Line 103: Are the "6 whole-day samples" are used in the data analysis? Please make a note for the "Whole period, N=37" in table 1 to explain sample categories in the data analysis.

Our reply: According to the referee's comment, we have added a note for "Whole period, N=37" in table 1, explaining sample categories in the data analysis.

"Six whole-day samples were included in the data analysis of the "Whole period". (See Line 649)

(2) Line 153: Why $PM_{2.5}$ measured (measured with High volume sampler) data was not used instead of $PM_{2.5\text{-cal}}$?

Our reply: $PM_{2.5}$ samples were collected using a high-volume sampler (Thermo Scientific, MA, USA; the flow rate was 1.13 m^3 min^{-1}). Quartz fiber filters (8×10 inch, 2500 QAT-UP; Pall Corporation, NY, USA) taken from the same lot were used for the entire sampling campaign.

It is difficult to weigh those big filters with typical laboratory balances; thus, there were no measured $PM_{2.5}$ concentration obtained in this study. Actually, the reconstituted $PM_{2.5\text{-cal}}$ mass concentration method has been commonly applied by other filed observations, to demonstrate the variation of ambient $PM_{2.5}$ pollution level (Turpin and Lim, 2001;Kanakidou et al., 2005;Cheng et al., 2015).

(3) Line 163: Organic matter (OM) appears first time in the paper to show the OM contribution to $PM_{2.5\text{-cal}}$. I suggest to explain that how OM was calculated.

Our reply: We thank the referee for this valuable comment. We added the definition of OM in the revised manuscript.

"Organic matter (OM), calculated by multiplying OC values with a coefficient of 1.6, was the most abundant PM component, the daily average value of which was 70.4 ± 49.6 μg m^{-3}, …" (See Lines 167-169)

(4) Line 170: Please show the data range in these references during summer and winter seasons to give a better understanding how high levels the anhydrosugars were.

Our reply: According to the referee's suggestion, we added the data range of levoglucosan during summer and winter season observed in Beijing in the reference.

"The ambient concentrations of levoglucosan in this study were higher than those observed in the city of Beijing during the summer (averaged at 0.23 ± 0.37 μg m^{-3}, in the range of 0.06 to 2.30 μg m^{-3}) and winter (averaged at 0.59 ± 0.42 μg m^{-3}, in the range of 0.06 to 1.94 μg m^{-3}) of 2010-2011 (Cheng et al., 2013)." (See Lines 173-176)

(5) Line 199: The contribution of LG to $PM_{2.5\text{-cal}}$ during daytime in Figure 3 was 0.45%. Please check the data.

Our reply: We thank the referee for this valuable comment. We checked the data and confirmed that the contribution of levoglucosan to $PM_{2.5\text{-cal}}$ during daytime was 0.45% and corrected it in the revised manuscript.

"Consequently, the contribution of levoglucosan to $PM_{2.5\text{-cal}}$ during daytime (0.45%) was observed to be considerably lower than that during nighttime (0.64%) (Figure 3)." (See Lines 204-206)

(6) Line 202: Please insert references for the photochemical formation of secondary inorganic species.

Our reply: According to the referee's suggestion, we added the related references for the photochemical formation of secondary inorganic species in the revised manuscript.

"Thus, the secondary inorganic species (SO_4^{2-}, NO_3^- and NH_4^+) were enhanced during daytime due to photochemical formation (Sun et al., 2013; Zheng et al., 2015; Wu et al., 2018)." (See Lines 207-209)

(7) Line 234: In Table 2, the OC contribution during intensive BB period II was 96.3, but not 59.9. Please check the data.

Our reply: We thank the referee for this valuable comment. We checked the data and confirmed that the OC concentration during the intensive BB period II was 96.3 μg m^{-3}, and corrected it in the revised manuscript.

"The concentrations of OC and EC were also observed to be strongly elevated in period II (Table 2), and especially OC levels increased to 96.3 μg m^{-3} during the intensive BB episode II, nearly 6 times of those during the minor BB period (16.2 ± 7.52 μg m^{-3})." (See Lines 252-254)

(8) Line 276: Please insert the increasing range of OC fraction.

Our reply: According to the referee's comment, we added the increasing range of the OC fraction in the revised paper.

"…, while the OC fraction increased significantly from 34.0% during the minor BB period I to 65.4% during the intense BB period II." (See Lines 299-300)

(9) Line 286: Check the data in Figure 6, the SO_4^{2-} and NO_3- contributions during the intense BB episode were 1.93 and 7.67%.

Our reply: We thank the referee for this comment. We checked the data and confirmed that the contributions of SO_4^{2-} and NO_3^- to $PM_{2.5\text{-cal}}$ during the intense BB episode were 1.93% and 7.67%, respectively, and corrected them in the revised manuscript.

"The contributions of SO_4^{2-}, NO_3^- and NH_4^+ to $PM_{2.5\text{-cal}}$ during the minor BB episode (11.6%, 20.5% and 12.5%) substantially declined during the intense BB episode (1.93%, 7.67% and 4.24%)." (See Lines 308-310)

(10) Line 295: The range of LG/MN ratios from crop residue burning in source emission studies is helpful to understand the biomass types.

Our reply: According to the referee's comment, we added the findings regarding levoglucosan/mannosan ratios from different biomass burning source emission studies in the revised paper.

"Based on source emission studies, the levoglucosan/mannosan ratios from crop residue burning, i.e., rice straw, wheat straw and corn straw, are similar and are characterized by high values (averaged at 29, in the range of 12 to 55) (Zhang et al., 2007; Engling et al., 2009; Cheng et al., 2013; Jung et al., 2014), yet overlapping with those from hardwood (averaged at 28, in the range of 11 to 146) (Bari et al., 2009; Jung et al., 2014) and grass burning (18.2 ± 10.2) (Sullivan et al., 2008), while softwood is characterized by relatively lower levoglucosan/mannosan ratios (averaged at 4.3, in the range of 2.5 to 4.7) (Engling et al., 2006; Cheng et al., 2013; Jung et al., 2014)." (See Lines 320-327)

(11) Line 304: The LG/K^+ ratio during III in Table 2 was 0.51, please check the data.

Our reply: We thank the referee for this comment. We checked the data and confirmed that the levoglucosan/K^+ ratio during episode III was 0.51, and corrected it in the revised manuscript.

"The levoglucosan/K^+ ratios during periods III and IV (0.51 and 0.53) were similar to those during a BB episode at an urban site in Beijing during wintertime (levoglucosan/K^+ = 0.51) (Cheng et al., 2013)." (See Lines 335-337)

Reference:

Cheng, Y., He, K.-b., Du, Z.-y., Zheng, M., Duan, F.-k., and Ma, Y.-l.: Humidity plays an important role in the PM2.5 pollution in Beijing, Environmental Pollution, 197, 68-75, 10.1016/j.envpol.2014.11.028, 2015.

Kanakidou, M., Seinfeld, J., Pandis, S., Barnes, I., Dentener, F., Facchini, M., Dingenen, R. V., Ervens, B., Nenes, A., and Nielsen, C.: Organic aerosol and global climate modelling: a review, Atmospheric Chemistry and Physics, 5, 1053-1123, 2005.

Turpin, B. J., and Lim, H.-J.: Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass, Aerosol Science and Technology, 35, 602-610, 10.1080/02786820119445, 2001.

Measurement report: Chemical characteristics of PM$_{2.5}$ during typical biomass burning season at an agricultural site of the North China Plain

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Abstract:

Biomass burning activities are ubiquitous in China, especially in North China, where there is an enormous rural population and winter heating custom. Biomass burning tracers (i.e., levoglucosan ~~(LG)~~, mannosan ~~(MN)~~ and potassium (K$^+$)), as well as other chemical components were quantified at a rural site (Gucheng, GC) in North China from 15 October to 30 November, during a transition heating season, when the field burning of agricultural residues was becoming intense. The measured daily average concentrations of ~~LG~~levoglucosan, mannosan~~MN~~ and K$^+$ in PM$_{2.5}$ during this study were 0.79 ± 0.75 μg m^{-3}, 0.03 ± 0.03 μg m^{-3} and 1.52 ± 0.62 μg m^{-3}, respectively. Carbonaceous components and biomass burning tracers showed higher levels at nighttime than daytime, while secondary inorganic ions were enhanced during daytime. An episode with high levels of biomass burning tracers was encountered at the end of October, 2016, with high ~~LG~~levoglucosan at 4.37 μg m^{-3}. Based on the comparison of chemical components during different biomass burning pollution periods, it appeared that biomass combustion can obviously elevate carbonaceous components levels, whereas no essentially effect on secondary inorganic aerosols in the ambient air. Moreover, the levoglucosan~~LG~~/mannosan~~MN~~ ratios during different biomass burning pollution periods remained at high values (in the range of 18.3 - 24.9), however, the levoglucosan~~LG~~/K$^+$ ratio was significantly elevated during the intensive biomass burning pollution

period (1.67) when air temperatures decreasing, substantially higher than in other biomass burning periods (averaged at 0.47).

Keywords**:** Biomass burning; Organic tracers; Levoglucosan; Mannosan; Potassium

1. Introduction

Particulate air pollution is attracting more and more concerns in China because of their obvious adverse impact on visibility reduction, as well as health implication and regional or global climate change (Kanakidou et al., 2009; Pope and Dockery, 2006; Cheng et al., 2016). Carbonaceous species, i.e., organic carbon (OC) and elemental carbon (EC), and water-soluble inorganic ions, e.g., SO_4^{2-}, NO_3^- and NH_4^+ are the major components of ambient aerosols (Liang et al., 2017; Du et al., 2014; Zheng et al., 2015; Tan et al., 2016). Biomass burning (BB) emissions constitute a large source of ambient particulate pollution, especially for carbonaceous components, i.e., primary organic carbon (POC) and black carbon (BC) on global scale (Bond et al., 2004; Tang et al., 2018; Salma et al., 2017; Titos et al., 2017). As an important aerosol component, black carbon from industrial and combustion emissions contributes to the enhanced $PM_{2.5}$ (particulate matter with aerodynamic diameters less than 2.5 μm) mass concentrations and influences regional radiative forcing (Chen et al., 2017). Fresh biomass burning aerosol was found to be mainly comprised of carbonaceous species which typically constitutes 50-60% of the total particle mass (Hallquist et al., 2009). Yao et al. (2016) identified approximately half of carbonaceous aerosols being contributed by biomass burning at Yucheng, a rural site in the North China Plain.

Biomass burning emissions also represent a potentially large source of secondary organic aerosol (SOA). The precursors and formation pathways of SOA from biomass burning emissions were investigated by extensive field observations (e.g., Zhu et al., 2015; 2017; Adler et al., 2011; Zhang et al., 2010; 2015). Based on morphological particle analysis, Yao et al. (2016) investigated the smoke emitted from biomass burning impacting SOA production. Sun et al. (2010) found that phenolic compounds, which were emitted in large amounts from wood combustion, can form SOA at high yields in aqueous-phase reactions. In addition, smoke from biomass burning can be transported thousands of kilometers downwind from the source areas. Biomass burning aerosol from Southeast Asia can be transported to China, Singapore and even further to North America (Liang et al., 2017; Hertwig et al., 2015; Peltier et al., 2008). Based on molecular tracer measurements, synoptic data as well as air mass back trajectory analysis, a fire episode was captured at a background site of East China with smoke advected from Southeast Asia (Liang et al., 2017).

The North China Plain (NCP) is one of the most polluted regions in China. Severe haze–fog of longer duration and more extensive coverage has occurred frequently in the NCP area, especially during the seasons of autumn and winter. NCP covers one quarter of China's cultivated land and yields 35% of the agricultural products in China (Boreddy et al., 2017). The rural population in NCP is also large and dense, and biomass burning activities are common in this region in form of cooking and heating. Intense fire activity typically occurs in October after the corn harvest. Abundant smoke is emitted from agricultural burning, i.e., residential biofuel combustion, open field burns, etc. Various field observations have investigated different aspects of biomass burning, e.g., seasonal variations, chemical and physical properties of smoke particles, spatial distribution, sources, transport, etc., in the NCP region (Cheng et al., 2013; Shen et al., 2018; Sun et al., 2013; 2016; Boreddy et al., 2017; Xu et al., 2019). However, these field investigations of the contribution of biomass burning to ambient aerosols in the NCP region were concentrated on the city of Beijing (Cheng et al., 2013; Zheng et al., 2015; Duan et al., 2004). Little field research about biomass burning was reported for rural areas in the NCP. In fact, biomass burning activities are common in the rural areas of the NCP region, and the resulting smoke aerosol can be transported to urban areas, e.g., the city of Beijing, resulting in haze episodic events. Meanwhile, biomass burning studies at rural sites can provide valuable source information of the biomass burning pollution in the North China region.

The objective of this study is to gain insights about the abundance of smoke during the typical biomass burning season, i.e., autumn-winter transition season, following the corn harvest. In this paper, we focus on quantifying multiple biomass burning tracers, i.e., levoglucosan~~LG~~, mannosan~~MN~~ and K^+ as well as other chemical species in $PM_{2.5}$ in the rural areas of the NCP region during the typical biomass burning season. The results of this study demonstrated the biomass burning pollution status, as well as chemical properties of ambient aerosols under different biomass burning pollution levels in the rural atmosphere of North China.

2. Site description and experimental Methods

2.1 Site description and sampling

Samples were collected at a rural site, Gucheng (GC, 39°09'N, 115°44'E; 15.2 m a.s.l), located on a platform at the China Meteorological Administration farm in the town of Gucheng (GC site), approximately 110 km southwest of Beijing and 35 km north of the city of Baoding (population of about 5 million) in Hebei province, as shown in Figure S1. The station is surrounded by agricultural fields, with major crop species being corn and wheat. The dominant wind direction at GC is southwest and northeast during the study period. This site is upwind of Beijing, when the wind blows from the south or southwest, where heavily polluted cities and regions of Hebei province, i.e., Baoding, Shijiazhuang, Xingtai, Handan, are located. Thus, it is an appropriate station for representing the air pollution situation in the NCP region (Sheng et al., 2018; Chi et al., 2018; Xu et al., 2019; 2020; Kuang et al., 2020).

Daytime and nighttime $PM_{2.5}$ samples were collected from 15 October, 2016 to 23 November, 2016, by using $PM_{2.5}$ High-volume (Hi-Vol) sampler (GUV-15HBL1, Thermo Fisher Scientific CO., LTD), at the nominal flow rate of 1.13 m^3 min^{-1}. The daytime samples were collected from 07:00 to 19:00, while nighttime samples were collected from 19:00 to 07:00 local time of the next day. All $PM_{2.5}$ samples were collected on quartz fiber filters, prebaked at 850 °C for at least 5 h to remove carbonaceous material. A total of 33 couples of daytime/nighttime samples and 6 whole-day samples as well as 4 field blank samples were collected during the sampling period. The filters were stored at -20 °C after sample collection.

2.2 Experimental Methods

2.2.1 Anhydrosugar and water-soluble inorganic ion analysis

The quartz filter samples were analyzed for biomass burning anhydrosugar tracers, i.e., levoglucosan and mannosan~~LG and MN,~~ using an improved high-performance anion-exchange chromatography (HPAEC) method with pulsed amperometric detection (PAD) on a Dionex ICS-5000+ system. Levoglucosan~~LG~~ and mannosan~~MN~~ were separated by a Dionex Carbopac MA1 analytical column and guard column with an aqueous sodium hydroxide (NaOH, 480 mM) eluent at a flow rate of 0.4 mL min^{-1}. The detection limit of levoglucosan~~LG~~ and mannosan~~MN~~ was 0.002

mg L^{-1} and 0.005 mg L^{-1}, respectively. More details about the HPAEC-PAD method can be found elsewhere (Iinuma et al., 2009).

The quartz filter samples were also analyzed for water-soluble inorganic ions by a Dionex ICS-5000+ ion chromatograph, including SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Ca^{2+}, Na^+, K^+ and Mg^{2+}, and the method detection limits for the individual ionic species were 0.18 μg L^{-1}, 0.15 μg L^{-1}, 0.03 μg L^{-1}, 0.048 μg L^{-1}, 0.08 μg L^{-1}, 0.01 μg L^{-1}, 0.01 μg L^{-1}, 0.008 μg L^{-1}, respectively. The cations were separated on an Ionpac CS12 analytical column and CG12 guard column with a 20 mM methanesulfouic acid as eluent at a flow rate of 1.0 mL min^{-1}, while the anions were separated on an Ionpac AS11-HC column and AG11-HC guard column with 21.5 mM KOH eluent at a flow rate of 1.0 mL min^{-1}. The water-soluble inorganic ion data were corrected by field blanks.

2.2.2 Organic carbon/elemental carbon analysis

OC and EC were measured on a punch (0.526 cm^2) of each quartz sample by a thermal/optical carbon analyzer (DRI Model 2001, Desert Research Institute, USA), using the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol with reflectance charring correction. The analytical error of OC was within 10%, and one sample of every 10 samples was selected at random for duplicate analysis. The detection limit of OC was 0.82 μgC cm^{-2} (Liang et al., 2017).

2.2.3 Gas online monitoring (i.e., NO, NO_2, SO_2, O_3, CO and NH_3)

During this campaign, commercial instruments from Thermo Fisher Scientific Co., LTD were used to measure O_3 (TE 49C), NO/NO_2/Nox (Model 42CTL), CO (TE 48CTL), and SO_2 (TE43CTL), while NH_3 was measured by an ammonia analyzer (DLT-100, Los Gatos Research, USA) at GC station. All measurement data quality was controlled according to standard gases (Xu et al., 2019; Lin et al., 2011; Meng et al., 2018; Ge et al., 2018).

2.2.4 Meteorological parameters

The meteorological parameters, including air temperature, relative humidity (RH) and wind speed at a 24-h resolution at the GC site are presented in Figure 1. During this campaign, the daily average RH value was observed at 77 ± 13%, with a range from 48% to 99%, while the daily wind speed was observed with an average value of 1.07 ± 1.14 m s^{-1}, exhibiting moist and stable synoptic conditions at this rural site during the autumn-winter transition season. Moreover, there was rare precipitation during the sampling period at the GC site, except for two days, i.e., 20 and 27 October, 2016 (Figure 1).

2.2.5 Back trajectory and fire spot analysis

To characterize the transport pathways of the aerosol at the Gucheng site, back-trajectories were calculated with the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php).

To investigate the influence of biomass burning activities in surrounding areas, fire hot spot counts were obtained from the Fire Information for Resource Management System (FIRMS) (available at https://firms.modaps.eosdis.nasa.gov/download/).

2.2.6 –Statistical analysis

Statistical analysis of data, i.e., the correlation analysis between the concentrations of levoglucosan, mannosan and K^+ at the Gucheng site during the sampling period were conducted with the linear fitting method.

3. Results and discussion

3.1 Characteristics of chemical components in $PM_{2.5}$

In this study, the mass concentration of $PM_{2.5\text{-cal}}$ was reconstituted by the sum of carbonaceous components (1.6×OC + EC) and inorganic ions (SO_4^{2-} + NH_4^+ + NO_3^- + Cl^- + Ca^{2+} + Na^+ + K^+ + Mg^{2+}). Figure 1 describes the time-series variation obtained for daily $PM_{2.5\text{-cal}}$, and its major components (OC, EC, SO_4^{2-}, NO_3^- and NH_4^+), biomass burning tracers (levoglucosan~~LG~~, mannosan~~MN~~ and K^+), ratios of levoglucosan/OC and meteorological factors (temperature~~ (T)~~, ~~relative humidity (~~RH~~)~~, wind speed ~~(WS)~~ and planetary boundary layer (PBL) height~~ rainfall~~) during the sampling period. The average daily $PM_{2.5\text{-cal}}$ mass concentration in the autumn-winter transition season at GC reached 137 ± 72.4 μg m^{-3}, ranging from 23.3 μg m^{-3} to 319 μg m^{-3} (Table 1, Figure 1a), which is higher than during the severe winter haze in January, 2013 at an urban site in Beijing (121 μg m^{-3}) (Zheng et al., 2015). The mass concentrations of these chemical species during the day are distributed as follows (from highest to lowest): OC > EC > NO_3^- > SO_4^{2-} > NH_4^+ > Cl^- > Ca^{2+} > K^+ > Na^+ > Mg^{2+}. Organic matter (OM), calculated by multiplying OC values with a coefficient of 1.6, was the most abundant PM component, the daily average value of which was 70.4 ± 49.6 μg m^{-3}, accounting for nearly half (46.7%) of PM$_{2.5\text{-cal}}$ mass, indicating obvious organic pollution at the rural site in the North China Plain during the sampling season.

The measured daily average concentrations of biomass burning tracers, i.e., levoglucosan ~~LG~~, mannosan~~MN~~ and K$^+$ in PM$_{2.5}$ during our study were 0.79 ± 0.75 μg m^{-3}, 0.03 ± 0.03 μg m^{-3} and 1.52 ± 0.62 μg m^{-3}, respectively (Table 1). The ~~anhydrosugar~~ ambient concentrations of levoglucosan ~~levels (levoglucosanLG and mannosanMN)~~ in this study were higher than those observed in the city of Beijing during the summer (averaged at 0.23 ± 0.37 μg m^{-3}, in the range of 0.06 to 2.30 μg m^{-3}) and winter (averaged at 0.59 ± 0.42 μg m^{-3}, in the range of 0.06 to 1.94 μg m^{-3}) of 2010-2011 (Cheng et al., 2013). The highest concentrations of levoglucosan ~~LG~~ in GC were observed on 31 October, 2016 with 4.37 μg m^{-3}, which is a sharp increase (over 30 times) of the minimum concentration (0.14 μg m^{-3}) during that period (Figure 1c). Accordingly, the PM$_{2.5\text{-cal}}$ concentration during that period was also elevated (as high as 236 μg m^{-3}) (Figure 1a). Secondary inorganic aerosol (sulfate, SO$_4^{2-}$; nitrate, NO$_3^-$ and ammonium, NH$_4^+$, SNA) species, were the major water soluble ions, accounting for 82.8% of total water soluble ions, the daily average values of which were 10.5 ± 6.87 μg m^{-3}, 15.9 ± 9.29 μg m^{-3} and 10.9 ± 5.51 μg m^{-3}, respectively (Table 1). SNA species exhibited a synchronous temporal trend (Figure 1c), while the NO$_3^-$ concentrations exceeded those of SO$_4^{2-}$ at the GC site, in contrast to the results of previous studies, e.g., Tan et al. (2016), who found SO$_4^{2-}$ to be the dominant species in PM$_{2.5}$ during winter in 2006 in Beijing. Similarly, Chi et al., (2018) also found NO$_3^-$ concentrations exceeded those of SO$_4^{2-}$ at both Beijing and GC sites during the winter in 2016, although they observed that NH$_4^+$ was the dominant component of SNA (the concentrations of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were 14.0 μg m^{-3}, 14.2 μg m^{-3}, and 24.2 μg m^{-3}, respectively).

3.2 Day-night variations in the characteristics of PM$_{2.5}$ chemical components

Carbonaceous components and biomass burning tracers exhibited higher levels during nighttime than daytime, while secondary inorganic ions showed the opposite pattern, i.e., higher concentrations during daytime than nighttime (Figure 2 and Figure S2). Besides, the gap of carbonaceous components and anhydrosugars between daytime and nighttime (two-fold) was more significant than for secondary inorganic ions. EC and ~~primary organic components~~POC are not subject to significant differences in chemical reactions in ambient air between daytime and nighttime, and they will be mainly influenced by the variations of the ~~planetary boundary layer~~ ~~(~~PBL~~)~~ height. In the night, the PBL height decreases, compressing air pollutants into a shallow layer, and subsequently resulting in faster accumulation and higher concentrations of pollutants (Zheng et al., 2015; Zhong et al., 2018; 2019). The contributions of OM and EC to $PM_{2.5\text{-cal}}$ were observed to be higher at nighttime (53.9% and 16.6%) than daytime (43.8% and 13.7%) as well (Figure 3).

Besides the influence from variations of the PBL height, the chemical degradation of levoglucosan may occur due to photochemical reaction in the ambient aerosols during day-time, further enlarging the gap of levoglucosan levels ~~in~~ between daytime and nighttime (Sang et al., 2016; Gensch et al., 2018). Consequently, ~~T~~the contribution of levoglucosan to $PM_{2.5\text{-cal}}$ during daytime (~~0.37~~0.45%) was observed to be considerably lower than that during nighttime (0.64%) (Figure 3). However, secondary inorganic ions have an important formation pathway, i.e., photochemical processing, during daytime. Thus, the secondary inorganic species (SO_4^{2-}, NO_3^- and NH_4^+) were enhanced during daytime due to photochemical formation (Sun et al., 2013; Zheng et al., 2015; Wu et al., 2018). The mass contributions of SO_4^{2-}, NO_3^- and NH_4^+ to $PM_{2.5\text{-cal}}$ were decreased from daytime (9.9%, 14.5% and 10.0%) to nighttime (6.5%, 9.6% and 7.1%) (Figure 3). Such an enhancement in secondary transformations during daytime is more evident in terms of the sulfur and nitrogen oxidation ratios (SOR and NOR, molar ratio of sulfate or nitrate to the sum of sulfate and SO_2 or nitrate and NO_2), which have been used previously as indicators of secondary transformations (Sun et al., 2013; Zheng et al., 2015). Both SOR and NOR during daytime were higher than those during nighttime (Figure S3), further confirming the elevated secondary formations of sulfate and nitrate during daytime.

In addition, the concentrations of other water-soluble inorganic ions, i.e., K^+ and Cl^- during nighttime (1.78 ± 0.95 μg m^{-3} and 6.08 ± 4.00 μg m^{-3}) were higher than those in daytime (1.43 ± 0.54 μg m^{-3} and 4.33 ± 2.30 μg m^{-3}), while their contributions to $PM_{2.5\text{-cal}}$ were reversed, due to the significant accumulation and higher concentrations of pollutants during nighttime. As Ca^{2+}, Mg^{2+} and Na^+, mainly emitted from primary natural sources, such as dust, soil resuspension and sea salt, are subject to more activity during the daytime and also influenced by the airflow dynamics, the contribution of those species in nighttime were lower than those during daytime, especially for Ca^{2+}, decreasing from 2.2% in daytime to 0.9% at nighttime (Figure 3).

3.3 Biomass burning episodes and the impacts on chemical PM$_{2.5}$ characteristics

An episode with high biomass burning tracer levels was encountered on 31 October, 2016. The concentrations of levoglucosan~~LG~~ in PM$_{2.5}$ during this one-day episode (4.37 μg m^{-3}) were significantly higher than those during typical transition season at the GC site (0.69 ± 0.47 μg m^{-3}) (Figure 1d). Meanwhile, there was significant change in the meteorological conditions, i.e., the wind direction changed from southwesterly to northerly winds (Figure S4). Northerly winds advected cold and dry air masses, with the lowest hourly temperature observed at -5.3 °C (Figure S5). This notable temperature decline before the commencing of the operation of the central heating systems should have caused intense combustion activities for heating purposes at the rural site. Moreover, the synoptic situation on 31 October, 2016 was under weaker turbulence with low PBL height and small wind speeds (Figure 1f). These worsened meteorological conditions would further enhance aerosol accumulation.

Here, we mainly distinguish four sub-periods based on daily ~~—~~levoglucosan~~LG~~ concentrations during the time frame from 15 October to 23 November, 2016. The four periods were separated 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), 15-23 November (Period IV: Heating season). Table 2 compares the concentrations of PM$_{2.5\text{-cal}}$ mass, chemical components and gases at the GC site during these four periods, as well as the ratios between the intensive, major BB periods and heating season to minor BB period. The level of levoglucosan ~~LG~~ during the intensive BB episode II was about 12 times of that during the minor BB period I. K$^+$ and Cl$^-$, the common biomass burning tracers utilized in many studies (Duan et al., 2004; Cheng et al., 2013), were also observed with increased abundance during intensive BB episode II. When entering into November, the weather was becoming cold, and thus combustion activities for heating in the rural areas commenced, resulting in the ambient levels of levoglucosan~~LG~~ to increase to 0.92 ± 0.47 μg m^{-3} during period III, about 3 times of those in Period I. The central heating systems in North China cities were operated during period IV, and the ambient level of levoglucosan~~LG~~ was observed at 0.96 ± 0.63 μg m^{-3}, which was similar to that observed in period III.

The concentrations of OC and EC were also observed to be strongly elevated in period II (Table

2), and especially OC levels increased to ~~59.9~~96.3~~ ± 25.3~~ μg m^{-3} during the intensive BB episode II, nearly 6 times of ~~that~~ those during the minor BB period (16.2 ± 7.52 μg m^{-3}). The levoglucosan/OC ratio was utilized to estimate the effect of biomass burning to ambient organic aerosols. Accordingly, levoglucosan~~LG~~/OC ratios sharply increased to 0.045 during period II, which ~~is~~ was ~~obvious~~noticeably higher than during other periods in this study (Figure 1e). Moreover, this level is also higher than most of the published field observations, i.e., at urban sites (Zhang et al., 2008; Cheng et al., 2013; Zhang et al., 2014), rural sites (Sang et al., 2013; Ho et al., 2014; Pietrogrande et al., 2015; Mkoma et al., 2013) and agricultural sites (Ho et al., 2014; Jung et al., 2014), yet lower than at an urban site in northern Italy during winter time (in the range of 0.01 to 0.13) (Pietrogrande et al., 2015). This illustrates that biomass combustion played an important role in organic aerosol pollution during the intensive BB episode II. However, ~~During the major BB (period III) and heating season (period IV),~~ due to other emissions of OC enhanced during the major BB episode (period III) and heating season (period IV), i.e., combustion of coal and biofuel for heating, OC increased to a higher level (55.2 ± 17.1 μgC m^{-3} and 69.4 ± 24.6 μgC m^{-3}, respectively). Due to the abundance of organic aerosols, the contribution from biomass burning emission was thereby reduced and the levoglucosan~~LG~~/OC ratios during periods III and IV decreased to 0.016 ± 0.005 and 0.014 ± 0.006, respectively, even lower than those observed in the minor BB period I (0.025 ± 0.008).

Compared to the carbonaceous components, the concentrations of secondary inorganic aerosol species (SO_4^{2-}, NO_3^-, NH_4^+) exhibited a different pattern, i.e., showing no obvious differences between minor BB period I and other three periods. The ratios of SO_4^{2-}, NO_3^-, NH_4^+ during periods II, III and IV to period I were all around 1.0 (Table 2), with no increasing trend. Moreover, the relationships between levoglucosan~~ LG~~ and OC (and EC) were better than those between levoglucosan~~LG~~ and SNA during daytime and nighttime (Figure S3). The precursor gases of SNA, i.e., SO_2, NO, NO_2 and NH_3, were observed to have an increasing trend when biomass burning was prevalent during periods III and IV, with the ratios to period I arranged from 1.13 to 1.90 (Table 2). The time-series variations of the gases (SO_2, NO_x, NH_3, CO and O_3) and PBL during the sampling period are shown in Figure S4. The primary emission gases were exhibited negative relationships with PBL, while O_3 exhibited obvious positive relationship with PBL (Figure S5). Combustion from different fossil fuels (coal, gasoline, diesel, etc.) and biomasses (straws, woods, leaves, etc.) can all emit CO into the atmosphere (Streets et al., 2003; Chantara et al., 2019; Merico et al., 2020). Due to the more abundant combustion in the colder weather, the concentrations of CO also increased to 1.65 ± 0.53 ppm and 1.18 ± 0.83 ppm during the major biomass burning period III and the heating season period IV, respectively.

The combustion of biomass, especially of agricultural residues (e.g., wheat and corn straw) is very common in the rural areas in North China during the autumn-winter transition period. During the autumn harvest season in North China, wheat and corn straw burning is common practice, resulting in more abundant fire spots when entering into November than period I (Figure 4). The intense biomass burning event on 31 October, 2016 was also supported by air mass back trajectory analysis (Figure 5), performed with the TrajStat software. Based on the 48 h back trajectories at the GC site at 00:00 (UTC time) on 1 November, 2016, the air mass at the GC site was restricted in the region of Bejing-Tianjing-Hebei, the polluted area where fire spots were numerous. However, on the previous and following day of this episode, i.e., 31 October and 2 November onward, the air masses arriving at GC were advected from the northwest of Mongolia, where mostly desert areas are present, with less farm land and rare biomass burning activities (Figure 5).

Mean percentiles of major components in $PM_{2.5}$ with respect to different BB pollution periods at GC site during the sampling time are shown in Figure 6. With the variation of BB pollution periods, the EC fraction seems to exhibit no obvious change during periods I, II and III, but slightly increased during the heating season (period IV), while the OC fraction increased significantly from 34.0% during the minor BB period I elevated to 65.4% during the intense BB period II. The contributions of sulfate, nitrate and ammonium to $PM_{2.5\text{-cal}}$ all decreased sharply from the minor BB period to the intense period (Figure 6). This suggests that organic aerosol species become more important during BB pollution periods, concerning their contribution to the $PM_{2.5\text{-cal}}$, while EC has no such character. The OM percentage during intense BB period II was 65.4%, about double of that during the minor biomass burning period (34.0%), indicating that there was a large fraction of OM in $PM_{2.5\text{-cal}}$ originating from BB at the GC site during intensive BB period II. Opposite to OM, contributions of secondary inorganic ions to $PM_{2.5\text{-cal}}$ significantly decreased with the BB pollution becoming more severe. The contributions of SO_4^{2-}, NO_3^- and NH_4^+ to $PM_{2.5\text{-cal}}$ during the minor BB episode (11.6%, 20.5% and 12.5%) obviously declined during the intense BB episode (1.~~73~~93%, 7.~~73~~67% and 4.24%).

3.4 Relationships among tracers during different biomass burning pollution periods

In addition to pollution level information of biomass burning molecular tracers, the ratios between them could also be used to identify the different biomass types or indicate the burning formation processes of atmospheric aerosols. Levoglucosan and mannosan showed a good relationship during the entire sampling period (Figure 7a, r = 0.97, p < 0.01). The levoglucosan~~LG~~/mannosan~~MN~~ ratios during minor, intense, major biomass pollution and heating season periods were observed at high values, i.e., 24.9, 24.1, 24.8 and 18.3 respectively (Table 2, Figure 7). ~~LG and MN in the four periods showed a good relationship (Figure 7a, R^2 = 0.94).~~Compared to the former three episodes (24.1 to 24.9, averaged at 24.6), the levoglucosan/mannosan ration during the heating season period (18.3) decreased by 25.6%. Based on source emission studies, the levoglucosan~~LG~~/mannosan~~MN~~ ratios from crop residue burning, i.e., rice straw, wheat straw and corn straw, are similar and are characterized by high values (averaged at 29, in the range of 12 to 55) (Zhang et al., 2007; Engling et al., 2009; Cheng et al., 2013; Jung et al., 2014), yet ~~overlapped~~ overlapping with those from hardwood (averaged at 28, in the range of 11 to 146) (Bari et al., 2009; Jung et al., 2014) and grass burning (18.2 ± 10.2~~>10.0~~) (Sullivan et al., 2008), while softwood is characterized by relatively lower levoglucosan~~LG~~/mannosan~~MN~~ ratios (averaged at 4.3, in the range of 2.5 to 4.7~~< 5.0~~) (Engling et al., 2006; Cheng et al., 2013; Jung et al., 2014). Subsequently, this declining trend ~~of~~in the levoglucosan/mannosan ratios during the heating season period was partly caused~~contributed~~ by the higher~~raised~~ proportion of softwood combustion, which is characterized by relatively lower levoglucosan/mannosan ratios. According to the local habits, soft woods, e.g. China fir and pine are also commonly used as biofuels for stove heating in North China, since they allow sustained~~long-time~~ heating duration.

The concentrations of levoglucosan~~LG~~ and K$^+$ during minor, major BB episode and heating season were correlated well (Figure 7b, r = 0.84, p < 0.01), while the red dot of period II being off from the fitted regression line. The levoglucosan~~LG~~/K$^+$ ratios during periods III and IV (~~0.52~~0.51

and 0.53) were similar to those during a BB episode at an urban site in Beijing during winter time (levoglucosan~~LG~~/K^+ = 0.51) (Cheng et al., 2013). However, the levoglucosan~~LG~~/K^+ ratio during the intense BB period II increased to 1.67, which was significantly higher than that in typical straw combustion (< 1.0). Correspondingly, there was a significant drop in temperatures at the GC site during period II, with the average daily temperature sharply decreasing from 7.5 °C on 30 Oct to 0.31 °C on 31 October, 2016, and the average temperature at night of 31 October even decreased to -3.4 °C (Figure 1g). Hence, the combustion activities were apparently intense around the sampling site for heating purposes. Compared to K^+, there is a large enrichment of levoglucosan~~LG~~ in wood burning emissions, based on the results from previous biomass source combustion studies (Engling et al., 2006; Chantara et al., 2019). The influence of softwood and/or other materials from softwood, which are commonly used as biofuels for stove heating in North China (Cheng et al., 2013; Zhou et al., 2017), should be larger during this low temperature period. Moreover, levoglucosan~~LG~~/K^+ ratios also can be influenced by combustion conditions, i.e., smoldering versus flaming burns. Biofuels are typically subject to smoldering combustion condition in residential stoves for heating purposes in the rural areas in North China, which was reflected in relatively higher levoglucosan~~LG~~/K^+ ratios than during flaming combustion (Schkolnik et al., 2005; Lee et al., 2010).

4. Summary and conclusion

Anhydrosugars, including levoglucosan and mannosan, and water-soluble potassium ion were employed as molecular tracers to investigate the characteristics of biomass burning activities as well as chemical properties of ambient aerosols under different biomass burning pollution levels. The measured daily average concentrations of levoglucosan~~LG~~, mannosan~~MN~~ and K^+ in $PM_{2.5}$ during a typical biomass burning season from 15 October to 30 November, 2016 were 0.79 ± 0.75 μg m^{-3}, 0.03 ± 0.03 μg m^{-3} and 1.52 ± 0.62 μg m^{-3}, respectively. The concentrations of carbonaceous components and biomass burning tracers were observed higher at nighttime than daytime, while the patterns of secondary inorganic ions (SO_4^{2-}, NO_3^- and NH_4^+) were opposite, since they were enhanced by photochemical formation during daytime. An episode with extreme biomass burning tracer levels was encountered on 31 October, 2016, with concentrations of levoglucosan~~LG~~ as high as 4.37 μg m^{-3}. Comparing the chemical compositions between different biomass burning periods, it was apparent that biomass burning can considerably elevate the levels of organic components, while not showing a significant effect on the production of secondary inorganic ions. Compared to the other biomass burning episodes, the levoglucosan/mannosan ratios during the heating season period slightly decreased, ~~Moreover, due to more local soft wood and smoldering combustion taking place for heating under the low temperatures, the~~ while levoglucosan~~LG~~/K^+ ratio during the intensive BB period was unusually higher than those in the other three biomass burning periods.

Data availability. The data used in this study can be obtained from this open link: https://pan.baidu.com/s/11bKUZff1KJbzNVxS3VsLaA code: jvqx. It is also available from the corresponding author upon request (lianglinlin@cma.gov.cn).

Author contributions. LL designed conducted all observations and drafted the paper. GE revised the paper and improved the English writing. XL drew the Figure 4 and Figure 5. CL, WX, YC, ZD, GZ, JS and XZ interpreted the data and discussed the results. All authors approved the final version for publication.

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References:

Bari, M. A., Baumbach, G., Kuch, B., and Scheffknecht, G.: Wood smoke as a source of particle-phase organic compounds in residential areas, Atmos. Environ., 43, 4722-4732, https://doi.org/10.1016/j.atmosenv.2008.09.006, 2009.

Boreddy, S. K. R., Kawamura, K., Okuzawa, K., Kanaya, Y., and Wang, Z.: Temporal and diurnal variations of carbonaceous aerosols and major ions in biomass burning influenced aerosols over Mt. Tai in the North China Plain during MTX2006, Atmos. Environ., 154, 106-117, http://dx.doi.org/10.1016/j.atmosenv.2017.01.042, 2017.

Caseiro, A., Bauer, H., Schmidl, C., Pio, C. A., and Puxbaum, H.: Wood burning impact on PM_{10} in three Austrian regions, Atmos. Environ., 43, 2186-2195, https://doi.org/10.1016/j.atmosenv.2009.01.012, 2009.

Chantara, S., Thepnuan, D., Wiriya, W., Prawan, S., and Tsai, Y.I.: Emissions of pollutant gases, fine particulate matters and their significant tracers from biomass burning in an open-system combustion chamber, Chemos. 224, 407-416, https://doi.org/10.1016/j.chemosphere.2019.02.153, 2019.

Cheng, Y., He, K.B., Du, Z.Y., Engling, G., Liu, J.M., Ma, Y.L., Zheng, M., Weber, R.J.: The characteristics of brown carbon aerosol during winter in Beijing, Atmos. Environ., 127, 355–364, https://doi.org/10.1016/j.atmosenv.2015.12.035, 2016.

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.

Chi, X., He, P., Jiang, Z., Yu, X., Yue, F., Wang, L., Li, B., Kang, H., Liu, C., and Xie, Z.: Acidity of aerosols during winter heavy haze events in Beijing and Gucheng, China, J. Meteorol. Res., 32, 14-25, https://doi.org/10.1007/s13351-018-7063-4, 2018.

Drewnick, F., Hings, S. S., Curtius, J., Eerdekens, G., and Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany, Atmos. Environ., 40, 4316-4327, https://doi.org/10.1016/j.atmosenv.2006.03.040, 2006.

Du, Z.Y., He, K.B., Cheng, Y., Duan, F.K., Ma, Y. L., Liu, J.M., Zhang, X.L., Zheng, M., and Weber, R.: A yearlong study of water-soluble organic carbon in Beijing I: Sources and its primary vs. secondary nature, Atmos. Environ., 92, 514-521, https://doi.org/10.1016/j.atmosenv.2014.04.060, 2014.

Duan, F., Liu, X., Yu, T., and Cachier, H.: Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing, Atmos. Environ., 38, 1275-1282, https://doi.org/10.1016/j.atmosenv.2003.11.037, 2004.

Engling, G., Carrico, C.M., Kreidenweis, S.M., Collett Jr, J.L., Day, D.E., Malm, W.C., Lincoln, L., Hao, W.M., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, Atmos. Environ., 40, S299-S311, https://doi.org/10.1016/j.atmosenv.2005.12.069, 2006.

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.

Ge, B.Z., Wang, Z.F., Lin, W.L., Xu, X.B., Li, J., Ji, D.S., and Ma, Z.Q.: Air pollution over the north china plain and its implication of regional transport: a new sight from the observed evidences, Environ. Pollut., 166, 29-38, https://doi.org/10.1016/j.envpol.2017.10.084, 2017.

Gensch, I, Sang-Arlt, X,F, Laumer, W, Chan, C,Y, Engling, G, Rudolph, J., and Kiendler-Scharr, A.: Using δ13C of levoglucosan as a chemical clock, Environ. Sci. Tech. https://pubs.acs.org/doi/10.1021/acs.est.8b03054, 2018.

He, K.B., Zhao, Q., Ma, Y.L., Duan, F.K., Yang, F.M., Shi, Z.B., and Chen, G.: Spatial and seasonal variability of PM2.5 acidity at two Chinese megacities: insights into the formation of secondary inorganic aerosols, Atmos. Chem. Phys., 12, 1377-1395, https://doi.org/10.5194/acp-12-1377-

2012, 2012.

Hertwig, D., Burgin, L., Gan, C., Hort, M., Jones, A., Shaw, F., Witham, C., and Zhang, K.: Development and demonstration of a Lagrangian dispersion modeling system for real-time prediction of smoke haze pollution from biomass burning in Southeast Asia, J. Geophys. Res.: Atmos., 120, 12605-12630, https://doi.org/10.1002/2015JD023422, 2015.

Ho, K.F., Engling, G., Sai Hang Ho, S., Huang, R., Lai, S., Cao, J., and Lee, S.C.: Seasonal variations of anhydrosugars in PM2.5 in the Pearl River Delta Region, China, Tellus B, 66, 22577, https://doi.org/10.3402/tellusb.v66.22577, 2014.

Jung, J., Lee, S., Kim, H., Kim, D., Lee, H., and Oh, S.: Quantitative determination of the biomass-burning contribution to atmospheric carbonaceous aerosols in Daejeon, Korea, during the rice-harvest period, Atmos. Environ., 89, 642-650, https://doi.org/10.1016/j.atmosenv.2014.03.010, 2014.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, https://doi.org/10.5194/acp-5-1053-2005, 2005.

Klejnowski, K., Janoszka, K., and Czaplicka, M.: Characterization and seasonal variations of organic and elemental carbon and levoglucosan in PM_{10} in Krynica Zdroj, Poland, Atmos., 8(10), 190. https://doi.org/10.3390/atmos8100190, 2017.

Kuang, Y., Xu, W.Y., Lin, W.L., Meng, Z.Y., Zhao, H. R., Ren, S.X. Zhang, G., Liang, L. L., and Xu, X. B.: Explosive morning growth phenomena of NH_3 on the North China Plain: Causes and potential impacts on aerosol formation, Environ. Pollut., https://doi.org/10.1016/j.envpol.2019.113621, in press, 2020.

Lee, T., Sullivan, A.P., Mack, L., Jimenez, J.L., Kreidenweis, S.M., Onasch, T.B., Worsnop, D.R., Malm, W., Wold, C.E., Hao, W.M., and Collett Jr., J.L.: Chemical smoke marker emissions during flaming and smoldering phases of laboratory open burning of wildland fuels, Aerosol Science and Technology 44. http://dx.doi.org/10.1080/02786826.2010.499884, 2010.

Lin, W.L., Xu, X.B., Sun, J.Y., Liu, X.W., and Wang, Y.: Background concentrations of reactive gases and the impacts of long-range transport at the jinsha regional atmospheric background station, Science China (Earth Sciences), 54, 1604-1613, 2011.

Liu, L., Liu, Y., Wen, W., Liang, L., Ma, X., Jiao, J., and Guo, K.: Source Identification of Trace Elements in PM2.5 at a Rural Site in the North China Plain, Atmos., 11(2), 179, https://doi.org/10.3390/atmos11020179, 2020.

Meng, Z.Y., Xu, X.B., Lin, W. L., Ge, B.Z., Xie, Y.L., Song, B., Jia, S.H., Zhang, R., Peng, W., Wang, Y., Cheng, H.B., Yang, W., and Zhao, H.R.: Role of ambient ammonia in particulate ammonium formation at a rural site in the North China Plain, Atmos. Chem. Phys., 18, 167–184, https://doi.org/10.5194/acp-18-167-2018, 2018.

Merico, E., Grasso, F.M., Cesari, D., Decesari, S., Belosi, F., Manarini, F., De Nuntiis, P., Rinaldi, M., Gambaro, A., Morabito, E., and Contini, D.: Characterisation of atmospheric pollution near an industrial site with a biogas production and combustion plant in southern Italy, https://doi.org/10.1016/j.scitotenv.2020.137220, Sci. Tot. Environ., 717, 137220, 2020.

Mkoma, S. L., Kawamura, K., and Fu, P. Q.: Contributions of biomass/biofuel burning to organic aerosols and particulate matter in Tanzania, East Africa, based on analyses of ionic species, organic and elemental carbon, levoglucosan and mannosan, Atmos. Chem. Phys., 13, 10325–10338, https://doi.org/10.5194/acp-13-10325-2013, 2013.

Peltier, R. E., Hecobian, A. H., Weber, R. J., Stohl, A., Atlas, E. L., Riemer, D. D., Blake, D. R., Apel, E., Campos, T., and Karl, T.: Investigating the sources and atmospheric processing of fine particles from Asia and the Northwestern United States measured during INTEX B, Atmos.

Chem. Phys., 8, 1835-1853, https://doi.org/10.5194/acp-8-1835-2008, 2008.

Pietrogrande, M.C., Bacco, D., Ferrari, S., Kaipainen, J., Ricciardelli, I., Riekkola, M.-L., Trentini, A., and Visentin, M.: Characterization of atmospheric aerosols in the Po valley during the supersito campaigns — Part 3: Contribution of wood combustion to wintertime atmospheric aerosols in Emilia Romagna region (Northern Italy), Atmos. Environ., 122, 291-305, https://doi.org/10.1016/j.atmosenv.2015.09.059, 2015

Pope, C.A., and Dockery, D.W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manage., 56, 709-742, https://doi.org/10.1080/10473289.2006.10464485, 2006.

Sang, X.F., Zhang, Z.S., Chan, C.Y., and Engling, G.: Source categories and contribution of biomass smoke to organic aerosol over the southeastern Tibetan plateau, Atmos. Environ., 78, 113-123, https://doi.org/10.1016/j.atmosenv.2012.12.012, 2013.

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.

Schkolnik, G., Falkovich, A.H., Rudich, Y., Maenhaut, W., and Artaxo, P.: New analytical method for the determination of levoglucosan, polyhydroxy compounds, and 2-methylerythritol and its application to smoke and rainwater samples, Environ. Sci. Technol., 39, 2744-2752, https://doi.org/10.1021/es048363c, 2005.

Shen, X.J., Sun, J.Y., Zhang, X.Y., Zhang, Y.M., Wang, Y.Q., Tan, K.Y., Wang, P., Zhang, L., Qi, X.F., Che, H.Z., Zhang, Z., Zhong, J.T., Zhao, H.R., and Ren, S.X.: Comparison of submicron particles at a rural and an urban site in the North China Plain during the December 2016 heavy pollution episodes, J. Meteorol. Res., 32, 14-25, https://doi.org/10.1007/s13351-018-7060-7, 2018.

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.H., and Yarber, K.F.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, J. Geophys. Res., 108 (D21), 8809. http://dx.doi.org/10.1029/2002JD003093, 2003.

Sullivan, A.P., Holden, A.S., Patterson, L.A., McMeeking, G.R., Kreidenweis, S.M., Malm, W.C., Hao, W.M., Wold, C.E., and Collett Jr., J.L.: A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient $PM_{2.5}$ organic carbon, J. Geophys. Res., 113, D22302, https://doi.org/10.1029/2008JD010216, 2008.

Sun, K., Liu, X.G., Gu, J.W., Li, Y.P., Qu, Y., An, J.L., Wang, J.L., Zhang, Y.H., Hu, M., Zhang, F.: Chemical characterization of size-resolved aerosols in four seasons and hazy days in the megacity Beijing of China, J. Environ. Sci., 32, 155-167, https://doi.org/10.1016/j.jes.2014.12.020, 2015.

Sun, Y.L., Wang, Z.F., Fu, P.Q., Yang, T., Jiang, Q., Dong, H.B., Li, J., and Jia, J.J.: Aerosol composition, sources and processes during wintertime in Beijing, China, Atmos. Chem. Phys., 13, 4577-4592, https://doi.org/10.5194/acp-13-4577-2013, 2013.

Sun, Y.L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry, Atmos. Chem. Phys., 10, 4809-4822, https://doi.org/10.5194/acp-10-4809-2010, 2010.

Tan, J.H., Duan, J.C., Zhen, N.J., He, K.B., and Hao, J.M.: Chemical characteristics and source of size-fractionated atmospheric particle in haze episode in Beijing, Atmos. Res., 167, 24-33, https://doi.org/10.1016/j.atmosres.2015.06.015, 2016.

Tang, R., Wu, Z., Li, X., Wang, Y., Shang, D., Xiao, Y., Li, M., Zeng, L., Wu, Z., Hallquist, M., Hu, M., and Guo, S.: Primary and secondary organic aerosols in summer 2016 in Beijing, Atmos. Chem. Phys., 18, 4055-4068, https://doi.org/10.5194/acp-18-4055-2018, 2018.

Urban, R.C., Lima-Souza, M., Caetano-Silva, L., Queiroz, M.E.C., Nogueira, R.F.P., Allen, A.G., Cardoso, A.A., Held, G., and Campos, M.L. A.M.: Use of levoglucosan, potassium, and water-soluble organic carbon to characterize the origins of biomass-burning aerosols, Atmos. Environ., 61, 562-569, https://doi.org/10.1016/j.atmosenv.2012.07.082, 2012.

Wang, Z., Wang, T., Guo, J., Gao, R., Xue, L.K., Zhang, J.M., Zhou, Y., Zhou, X.H., Zhang, Q.Z., and Wang, W.X., 2012. Formation of secondary organic carbon and cloud impact on carbonaceous aerosols at Mount Tai, North China, Atmos, Environ., 46, 516-527, https://doi.org/10.1016/j.atmosenv.2011.08.019, 2012.

Wu, Y., Ge, X., Wang, J., Shen, Y., Ye, Z., Ge, S., Wu, Y., Yu, H., and Chen, M.: Responses of secondary aerosols to relative humidity and photochemical activities in an industrialized environment during late winter, Atmospheric Environment, 193, 66-78, 10.1016/j.atmosenv.2018.09.008, 2018.

Xu, W., Kuang, Y., Zhao, C., Tao, J., Zhao, G., Bian, Y., Yang, W., Yu, Y., Shen, C., Liang, L., Zhang, G., Lin, W., and Xu, X.: NH_3-promoted hydrolysis of NO_2 induces explosive growth in HONO, Atmos. Chem. Phys., 19, 10557-10570, https://doi.org/10.5194/acp-19-10557-2019, 2019

Xu, W., Kuang, Y., Liang, L., He, Y., Cheng, H., Bian, Y., Tao, J., Zhang, G., Zhao, P., Ma, N., Zhao, H., Zhou, G., Su, H., Cheng, Y., Xu, X., Shao, M., and Sun, Y.: Dust-Dominated Coarse Particles as a Medium for Rapid Secondary Organic and Inorganic Aerosol Formation in Highly Polluted Air, Environ Sci Technol, 54, 15710-15721, 10.1021/acs.est.0c07243, 2020.

Xu, X., Zhang, H., Lin, W., Wang, Y., Xu, W., and Jia, S.: First simultaneous measurements of peroxyacetyl nitrate (PAN) and ozone at Nam Co in the central Tibetan Plateau: impacts from the PBL evolution and transport processes, Atmos. Chem. Phys., 18, 5199–5217, https://doi.org/10.5194/acp-18-5199-2018, 2018.

Yang, F.M., Tan, J.H., Zhao, Q. Du, Z.Y., He, K.B., Ma, Y.L., Duan, F.K., Chen, G., and Zhao, Q.: Characteristics of $PM_{2.5}$ speciation in representative megacities and across China, Atmos. Chem. Phys., 11, 5207-5219, https://doi.org/10.5194/acp-11-5207-2011, 2011.

Yao, L., Yang, L.X., Chen, J.M., Wang, X.F., Xue, L.K., Li, W.J., Sui, X., Wen, L., Chi, J.W., Zhu, Y.H., Zhang, J.M., Xu, C.H., Zhu, T., and Wang, W.X.: Characteristics of carbonaceous aerosols: Impact of biomass burning and secondary formation in summertime in a rural area of the North China Plain, Sci. Tot. Environ., 557-558, https://doi.org/10.1016/j.scitotenv.2016.03.111, 2016.

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.

Zhang, T., Cao, J.J., Chow, J.C., Shen, Z.X., Ho, K.F., Ho, S.S.H., Liu, S.X., Han, Y.M., Watson, J.G., Wang, G.H., and Huang, R.J.: Characterization and seasonal variations of levoglucosan in fine particulate matter in Xi'an, China, J. Air Waste Manage., 64, 1317-1327, https://doi.org/10.1080/10962247.2014.944959, 2014.

Zhang, T., Claeys, M., Cachier, H., Dong, S.P., Wang, W., Maenhaut, W., and Liu, X.D.: Identification and estimation of the biomass burning contribution to Beijing aerosol using levoglucosan as a molecular marker, Atmos. Environ., 42, 7013-7021, https://doi.org/10.1016/j.atmosenv.2008.04.050, 2008.

Zhang, Z., Engling, G., Lin, C.-Y., Chou, C. C. K., Lung, S.-C. C., Chang, S.-Y., Fan, S., Chan, C.-Y., and Zhang, Y.-H.: Chemical speciation, transport and contribution of biomass burning smoke to ambient aerosol in Guangzhou, a mega city of China, Atmospheric Environment, 44, 3187-3195, 10.1016/j.atmosenv.2010.05.024, 2010.

Zhang, Z., Gao, J., Engling, G., Tao, J., Chai, F., Zhang, L., Zhang, R., Sang, X., Chan, C.Y., Lin, Z., and Cao, J.: Characteristics and applications of size-segregated biomass burning tracers in China's Pearl River Delta region, Atmos. Environ., 102, 290-301, https://doi.org/10.1016/j.atmosenv.2014.12.009, 2015.

Zheng, G.J., Duan, F.K., Su, H., Ma, Y.L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmos. Chem. Phys., 15, 2969-2983, https://doi.org/10.5194/acp-15-2969-2015, 2015.

Zheng, M., Salmon, L. G., Schauer, J. J., Zeng, L., Kiang, C. S., Zhang, Y., and Cass, G. R.: Seasonal trends in $PM_{2.5}$ source contributions in Beijing, China, Atmos. Environ., 39, 3967-3976, https://doi.org/10.1016/j.atmosenv.2005.03.036, 2005.

Zhong, J.T., Zhang, X.Y., and Wang, Y.Q.: Reflections on the threshold for $PM_{2.5}$ explosive growth in the cumulative stage of winter heavy aerosol pollution episodes (HPEs) in Beijing, Tellus B, 71, 1-7, https://doi.org/10.1080/16000889.2018.1528134, 2019.

Zhong, J.T., Zhang, X.Y., Wang, Y.Q., Liu, C., and Dong, Y.S.: Heavy aerosol pollution episodes in winter Beijing enhanced by radiative cooling effects of aerosols, Atmos. Res., 209, 59-64, https://doi.org/10.1016/j.atmosres.2018.03.011, 2018.

Zhou, Y., Xing, X., Lang, J., Chen, D., Cheng, S., Wei, L., Wei, X., and Liu, C.: A comprehensive biomass burning emission inventory with high spatial and temporal resolution in China, Atmos. Chem. Phys., 17, 2839-2864, 10.5194/acp-17-2839-2017, 2017.

Zhu, C., Kawamura, K., and 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, https://doi.org/10.5194/acp-15-1959-2015, 2015.

Zhu, Y.H., Yang, L.X., Kawamura, K., Chen, J.M., Ono, K., Wang, X.F., Xue, L.K., and Wang, W.X.: Contributions and source identification of biogenic and anthropogenic hydrocarbons to secondary organic aerosols at Mt. Tai in 2014, Environ. Pollut., 220, 863-872, https://doi.org/10.1016/j.envpol.2016.10.070, 2017.

Table 1. Average concentrations and the range of $PM_{2.5\text{-cal}}$ and its chemical components, biomass burning tracers (μg m^{-3}), gaseous species, ratios of OC/EC and levoglucosan ~~LG~~/OC, as well as meteorological data observed at GC site at daytime, nighttime and whole day, respectively, during the sampling period from 15 Oct to 23 Nov 2016.

Species	Daytime (N = 34)		Nighttime (N = 33)		Whole period (N = 37)*	
	Average c~~C~~oncentration	Range	Average concentration~~Concentration~~	Range	Average concentration~~Concentration~~	Range
$PM_{2.5\text{-cal}}$	117 ± 58.8	19.0 - 225	170 ± 116	21.1 - 465	137 ± 72.4	23.3 - 319
OC	26.8 ± 15.7	3.78 - 64.8	61.6 ± 49.5	2.88 - 175	44.0 ± 31.0	4.13 - 117
EC	13.4 ± 8.49	1.44 - 34.0	30.9 ± 28.5	2.21 - 129	21.7 ± 15.8	2.46 - 74.9
TC	49.3 ± 27.6	5.76 - 124	92.5 ± 73.6	5.10 - 289	65.8 ± 44.1	7.36 - 192
OC/EC	2.02 ± 1.26	1.09 - 3.31	2.25 ± 1.04	1.04 - 6.72	1.95 ± 0.60	0.83 - 3.10
SO_4^{2-}	12.1 ± 9.31	1.65 - 39.7	9.02 ± 6.22	1.55 - 23.2	10.5 ± 6.87	1.66 - 29.5
NO_3^-	16.9 ± 9.96	1.85 - 41.2	13.1 ± 8.52	1.56 - 38.0	15.9 ± 9.29	2.40 - 45.2
Cl^-	4.33 ± 2.30	0.82 - 9.46	6.08 ± 4.00	0.62 – 16.0	4.90 ± 2.46	0.93 - 9.37
NH_4^+	11.7 ± 6.76	1.84 - 26.0	10.0 ± 5.75	1.33 - 22.2	10.9 ± 5.51	1.99 - 25.4
K^+	1.43 ± 0.54	0.20 - 2.64	1.78 ± 0.95	0.22 - 4.19	1.52 ± 0.62	0.50 - 2.96
Mg^{2+}	0.26 ± 0.14	0.07-0.64	0.19 ± 0.09	0.06 - 0.38	0.14 ± 0.12	0.04 - 0.43
Ca^{2+}	2.24 ± 1.01	1.02-4.75	1.56 ± 0.08	0.77 - 3.56	1.54 ± 0.90	0.49 - 3.84
Na^+	0.44 ± 0.17	0.10 - 0.79	0.43 ± 0.24	0.10 - 1.31	0.42 ± 0.17	0.11 - 0.88
NO_3^- / SO_4^{2-}	1.67 ± 0.82	0.75 - 5.52	1.54 ± 0.57	0.74 - 3.50	1.65 ± 0.62	0.78 ± 3.96
Levoglucosan	0.57 ± 0.62	0.05 - 3.74	1.10 ± 0.99	0.05 - 4.82	0.79 ± 0.75	0.14 - 4.37
Mannosan	0.024 ± 0.023	0.00 - 0.14	0.05 ± 0.04	0.00 - 0.21	0.03 ± 0.03	0.00 - 0.18
levoglucosan~~LG~~/OC	0.018 ± 0.011	0.005 - 0.067	0.020 ± 0.010	0.004 - 0.047	0.020 ± 0.009	0.006 - 0.045
NO (ppb)	23.0 ± 14.7	2.07 - 56.0	45.9 ± 29.5	1.59 - 96.9	31.8 ± 18.3	1.81 - 68.5
NO_2 (ppb)	25.8 ± 10.4	8.18 - 51.6	29.3 ± 9.37	8.81 - 51.1	26.6 ± 8.74	8.62 - 51.4
SO_2 (ppb)	9.78 ± 4.96	3.11 - 22.5	9.63 ± 5.67	2.91 - 28.7	8.61 ± 4.04	3.37 - 20.4
CO (ppm)	0.96 ± 0.73	0.03 - 2.49	1.29 ± 1.04	0.02 - 3.26	1.05 ± 0.76	0.12 - 2.48
O_3 (ppb)	13.0 ± 9.10	1.42 - 41.84	5.00 ± 5.73	1.60 - 24.30	9.25 ± 5.78	1.67 - 24.0
NH_3 (ppb)	16.4 ± 11.3	1.68 - 46.2	18.3 ± 10.7	1.03 - 42.7	17.1 ± 9.88	1.46 - 44.4
Temperature (°C)	7.71 ± 4.01	- 2.07-15.9	3.30 ± 4.69	- 6.60 - 14.5	6.95 ± 4.58	- 4.33 - 15.4
Relative Humidity (%)	68 ± 17	31 - 98	85 ± 14	34 - 100	77 ± 13	48 - 99
Wind speed (m s^{-1})	1.43 ± 1.17	0.09 - 5.65	0.79 ± 1.55	0.03 - 7.19	1.07 ± 1.14	0.04 - 5.02

* Six whole-day samples were included ~~used~~ in the data analysis of the "Whole period".

Table 2. Concentrations of chemical components in PM$_{2.5}$ aerosols as well as their ratios and gaseous species collected at the GC site, during the four biomass burning periods (i.e., Minor, Intensive, Major and Heating period) 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	
	Average ~~C~~concentration	Average concentration~~Concentration~~	Ratio*	Average concentration ~~Concentration~~	Ratio*	Average concentration~~Concentration~~	Ratio*
PM$_{2.5\text{-cal}}$	81.0 ± 44.5	235	2.91	163 ± 46.7	2.01	189 ± 83.0	2.33
Levoglucosan	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
levoglucosan-~~LG~~/OC	0.025 ± 0.008	0.045	1.80	0.016 ± 0.005	0.64	0.014 ± 0.006	0.56
levoglucosan ~~LG~~/EC	0.039 ± 0.019	0.121	3.10	0.038 ± 0.017	0.97	0.028 ± 0.013	0.72
levoglucosan-~~LG~~/ mannosan~~MN~~	24.9 ± 4.44	24.1	0.97	24.8 ± 6.46	1.00	18.3 ± 4.27	0.73
levoglucosan~~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.

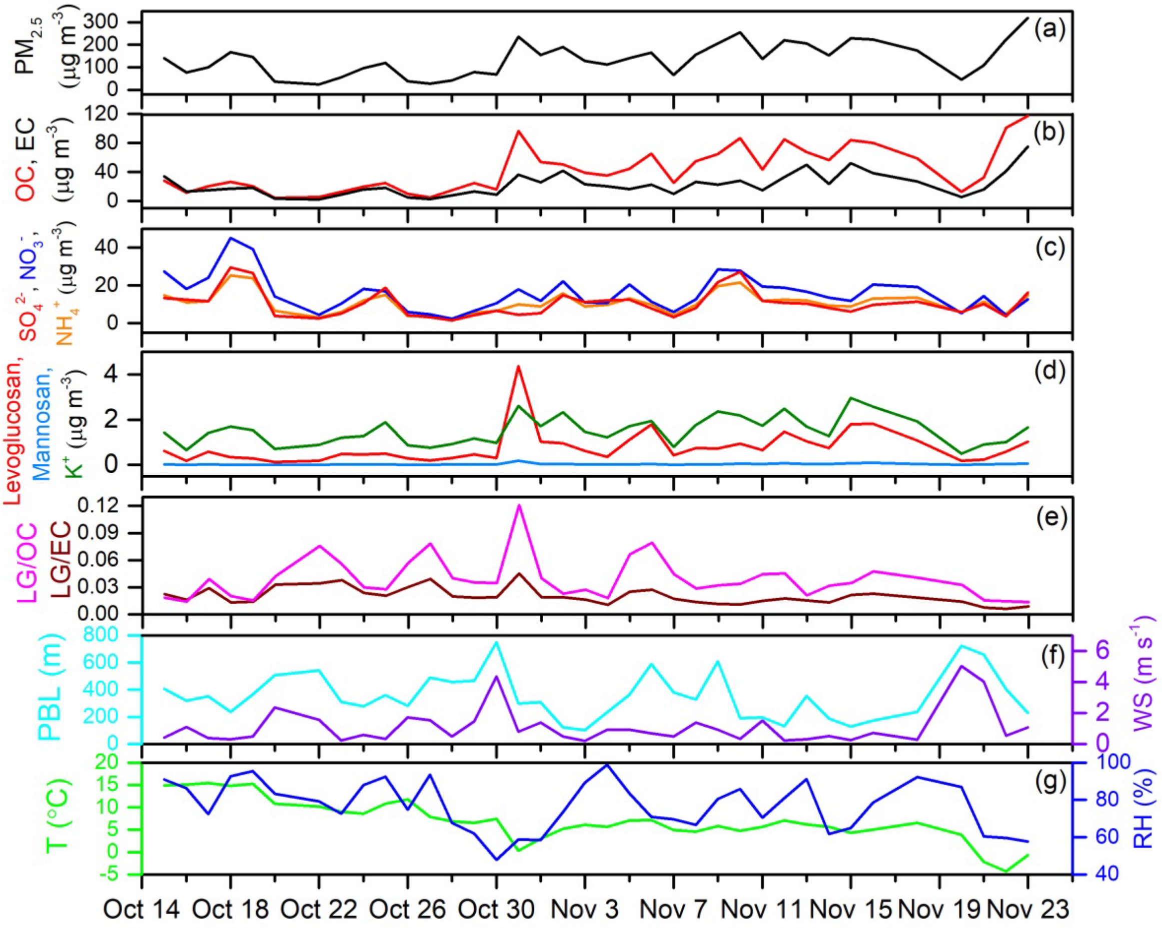

Figure 1. Time-series variation obtained for $PM_{2.5\text{-cal}}$ and its major components, biomass burning tracers as well as meteorological factors at the GC site during the sampling period from 15 Oct to 23 Nov 2016. (a) $PM_{2.5\text{-cal}}$~~, and its major components~~ (b) OC~~, ~~ and EC, (c) secondary inorganic aerosols, i.e., SO_4^{2-}, NO_3^- and NH_4^+, (d) ~~biomass burning tracers (~~levoglucosan~~LG~~, mannosan~~MN~~ and K^+~~)~~, (e) ratios of levoglucosan to OC (LG/OC) and levoglucosan to EC (LG/EC), ~~and meteorological factors ~~(f) PBL and wind speed (WS), (g) temperature (T) and~~,~~ relative humidity (RH)~~, wind speed (WS) and rainfall) at the GC site during the sampling period from 15 Oct to 23 Nov 2016~~.

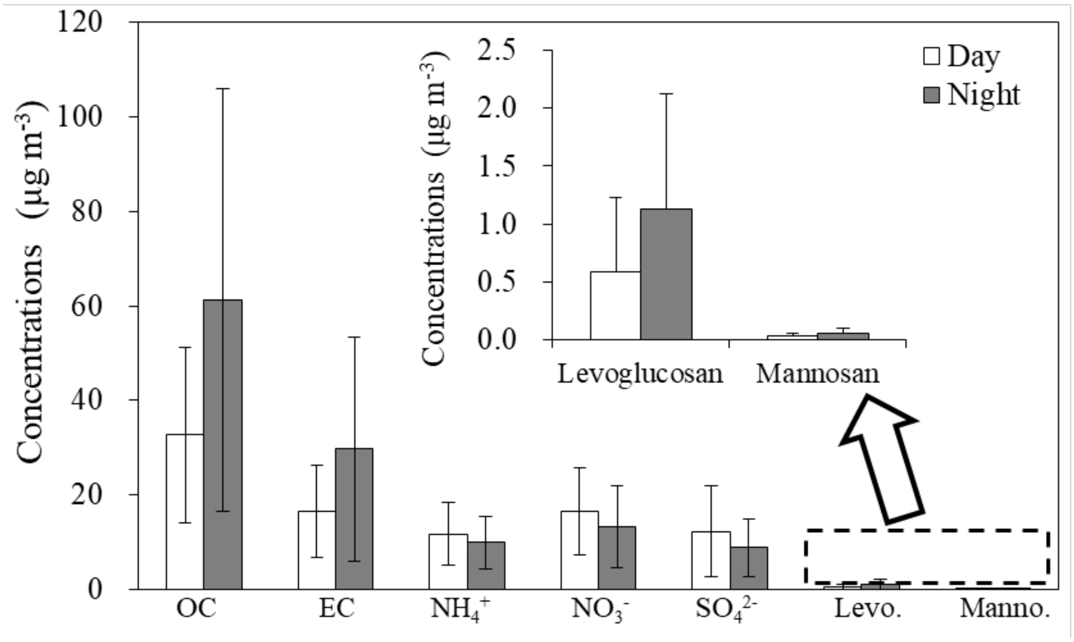

Figure 2. Day and night distributions of mean concentrations of main chemical components (OC, EC, SO_4^{2-}, NO_3^- and NH_4^+) and biomass burning tracers (levoglucosan ~~LG~~ and mannosan~~MN~~) in $PM_{2.5}$ observed at GC site during the sampling period.

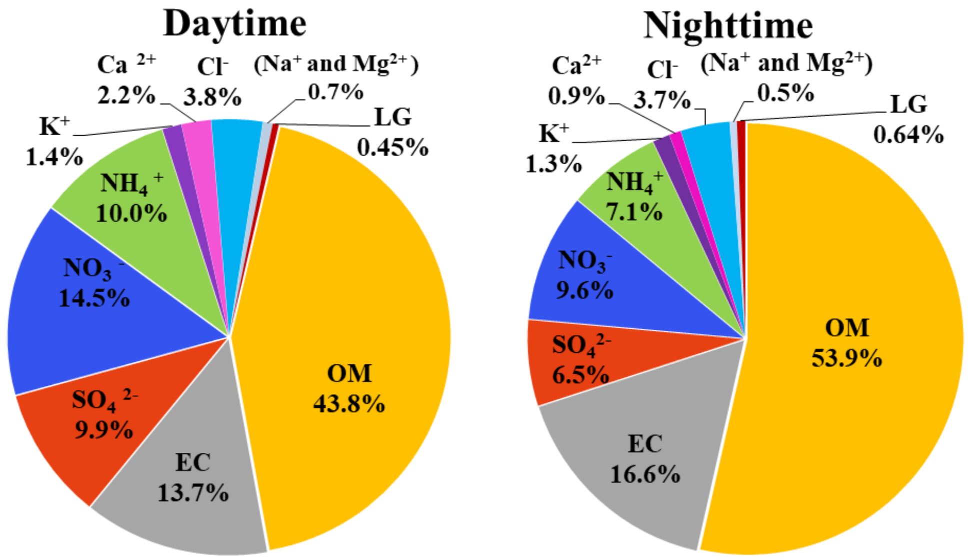

Figure 3. Percent contributions of individual component mass concentrations to total estimated $PM_{2.5\text{-}cal}$ mass in daytime and nighttime during the sampling period.

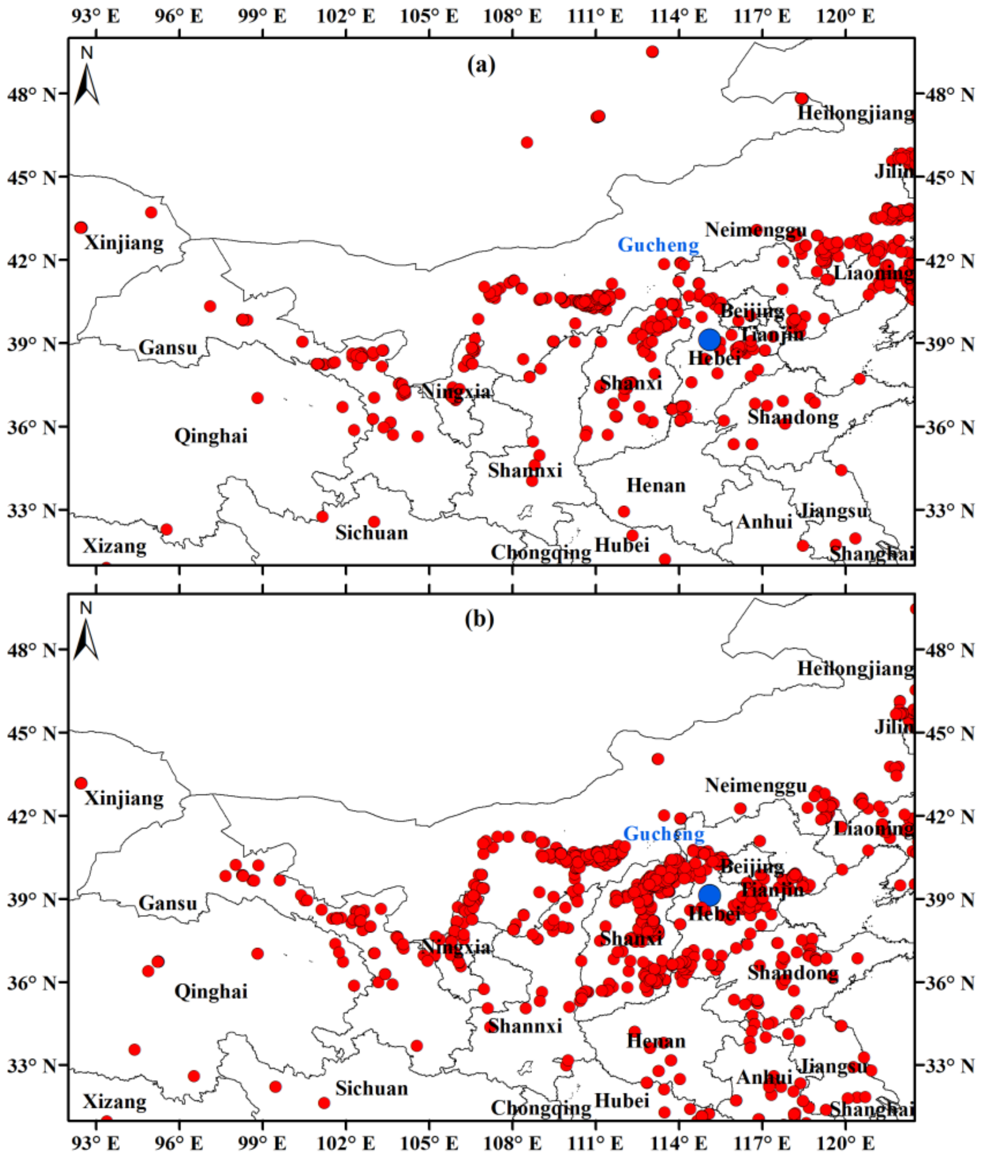

Figure 4. Fire spots at GC site and the surrounding provinces from (a) 15-30 October, 2016 and (b) 1 - 23, November, 2016, observed by MODIS Terra satellites (blue dot is GC station).

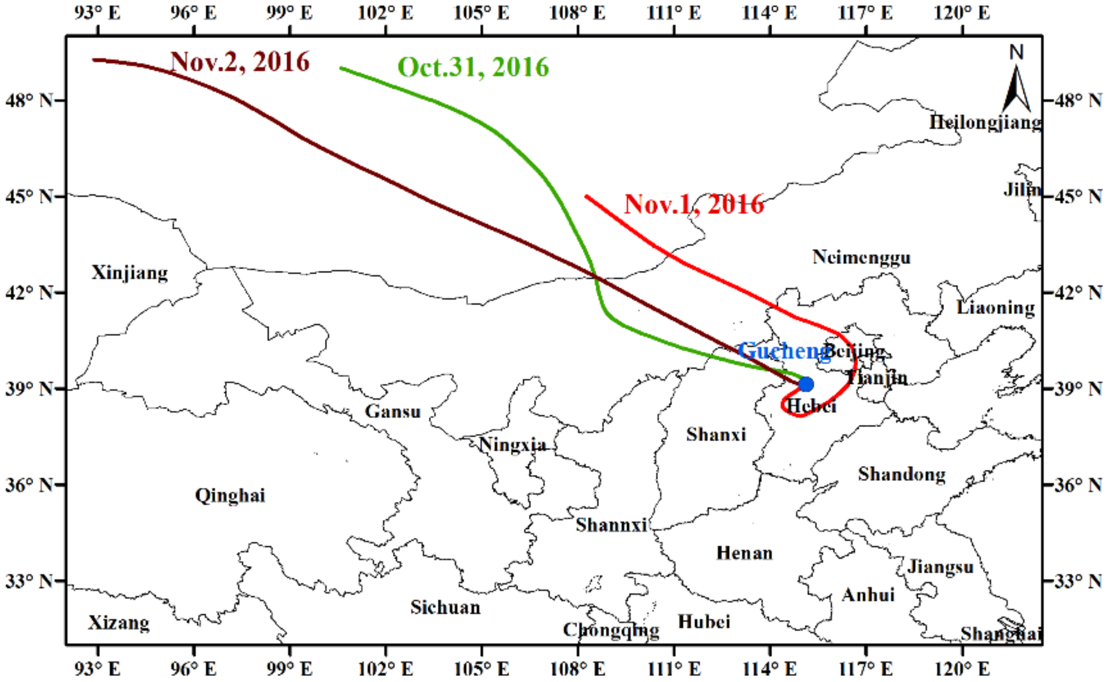

Figure 5. 48 h back trajectories at 500 m at GC site (39°09'N, 115°44'E) at 00:00 (UTC time) from 31 October to 2 November, 2016.

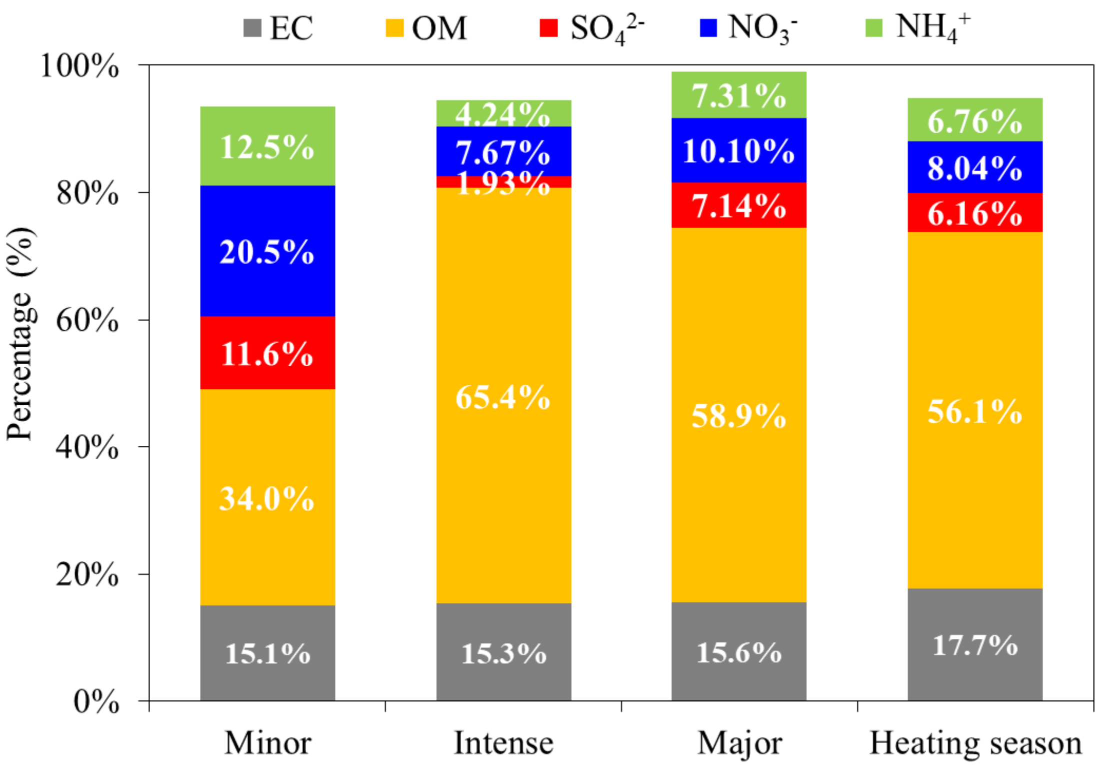

Figure 6. Mean percentiles of major components in $PM_{2.5}$ with respect to different biomass burning pollution periods at GC site during the sampling time.

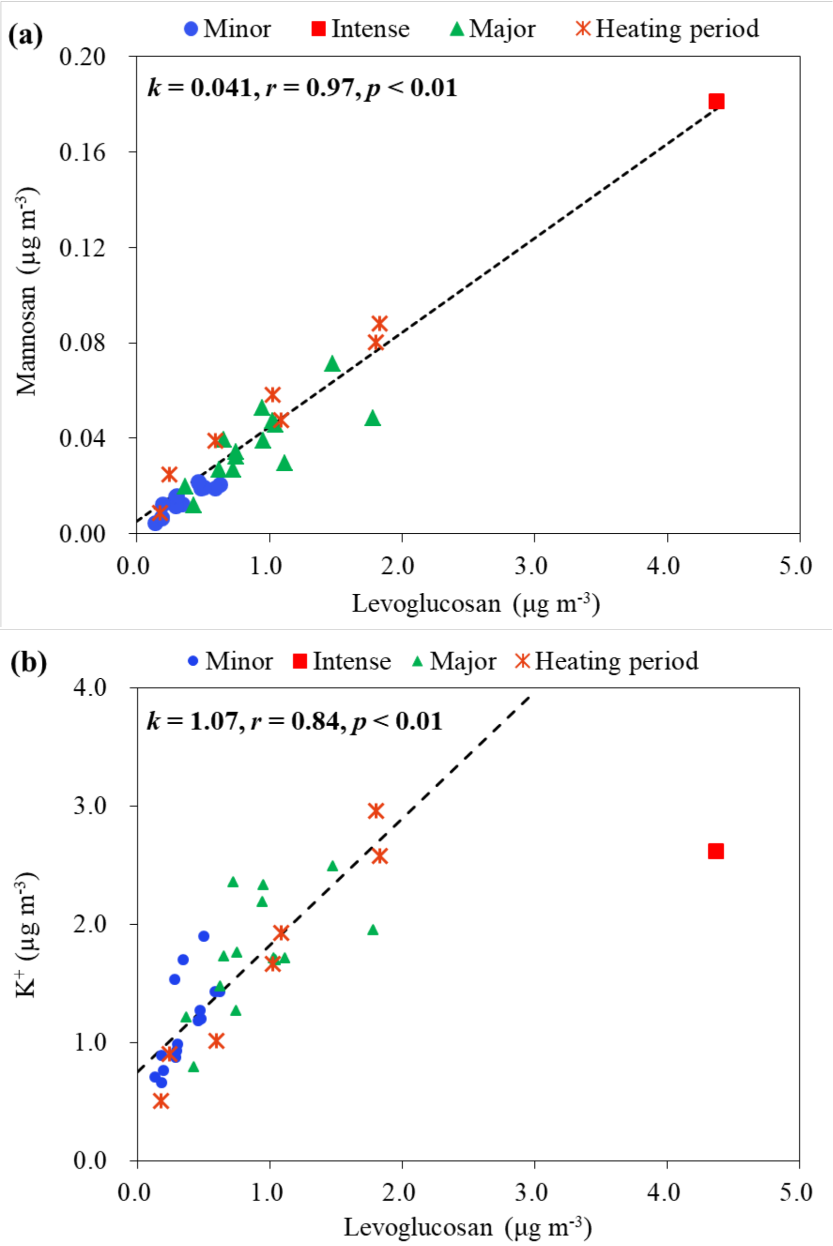

Figure 7. Scatter plots of (a) levoglucosan versus mannosan, (b) levoglucosan versus K$^+$. Statistical analysis of sampling data was conducted with the linear fitting method.