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

Anonymous Referee #2

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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.

<u>Our reply:</u> 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.

<u>Our reply:</u> 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)

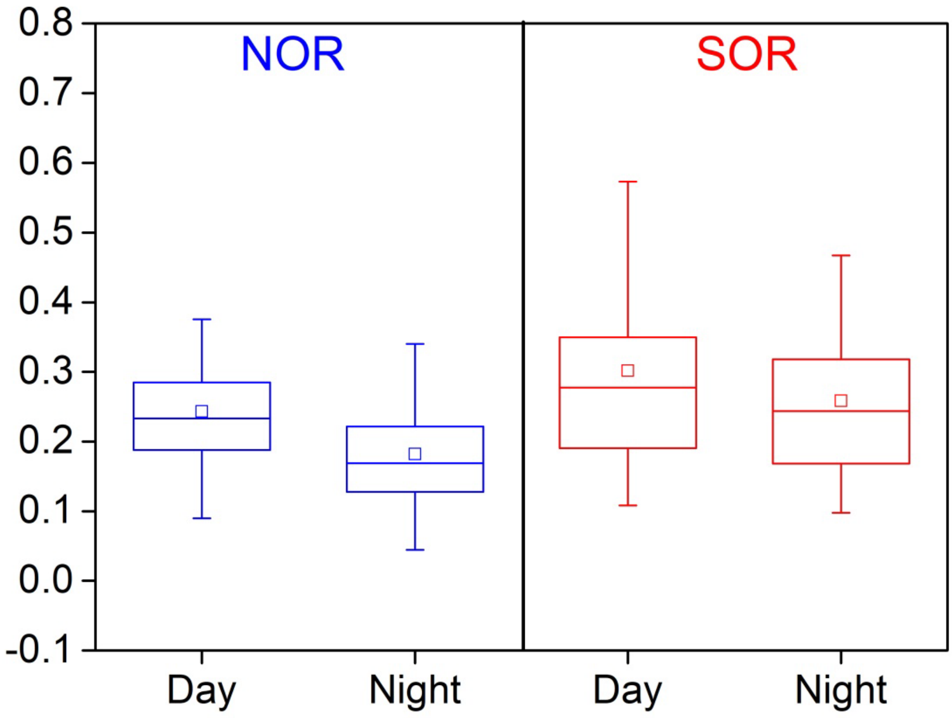

Figure S3. Variation of NOR and SOR during daytime and nighttime, respectively. In the box-whisker plots, the boxes and whiskers indicate the 95th, 75th, 50th (median), 25th and 5th percentiles, respectively. □ indicates the mean value.

(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 $PM_{2.5}$.

<u>Our reply:</u> 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)

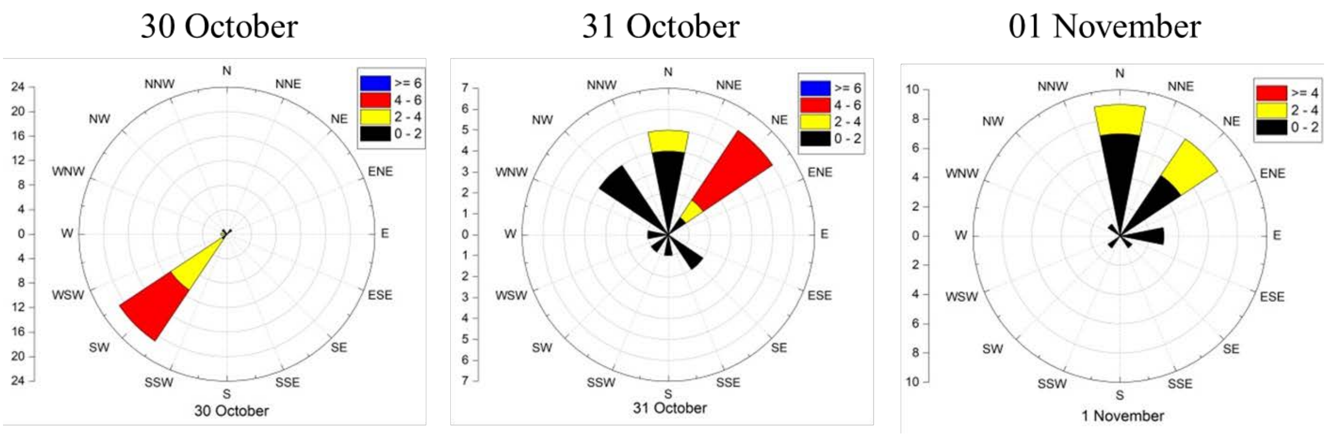

Figure S4. Wind-rose diagram of hourly wind direction at the GC site during 30 October, 31 October and 1 November 2016, respectively.

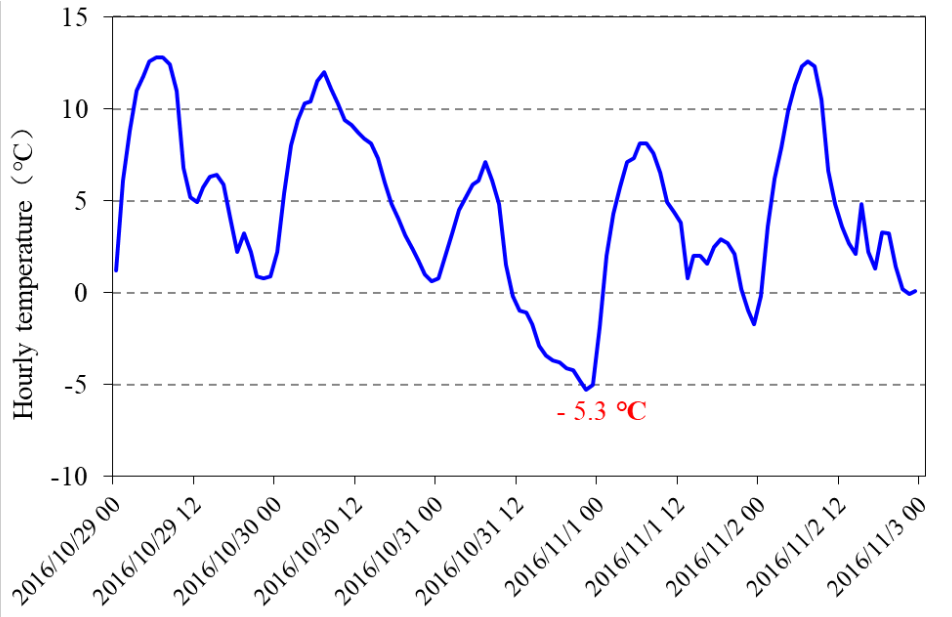

Figure S5. Hourly temperature from 00:00 on 29th October to 00:00 on 3rd November 2016 at the GC site.

(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.

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