The authors thank the reviewer for taking the time to review this manuscript and for the constructive criticism.
This document includes authors' responses to anonymous referee #2 (RC1). Reviewer's comments are in black text while the authors' responses are in blue, with amended text quoted from the manuscript in quotation marks. Page numbers and lines refer to the revised version unless explicitly stated otherwise.

Anonymous Referee #2 (RC1)

General comments:

This paper characterized the elemental composition of polar organic compounds in PM2.5 from Beijing during wintertime and summertime. 918-1586 organic compounds were assigned molecular formulae by direct infusion negative nano-electrospray ionization ultrahigh resolution mass spectrometer. Then the differences of the chemical composition under different pollution conditions, and their potential primary and secondary sources were discussed. The overall strength of this study is acquisition of a detailed dataset of polar organic compounds that spanned summertime and wintertime, low and high pollution conditions. The topic of the paper is well suited for ACP, and the data itself are interesting. On the whole, the language requires improvement throughout the manuscript. Many sentences are not clearly written, leaving the reader puzzling about their meaning. In addition, the overall weakness is the data interpretation. Much more effort needs to be put into presentation of the results. I have some points where more information is needed or where I disagree. I use the abstract to illustrate my main concerns of this paper. The authors state in the abstract: . . .. . .There were strong differences in aerosol particle composition between the seasons. . …which were strongly enhanced in winter, likely due to increased fossil fuel and biomass burning for heating. . .. . .the contribution of sulfur-containing organic compounds strongly enhanced under high pollution conditions. . .. . ..The highlighted results above are not really exciting. In fact, many researches have reported these differences already. For the advantage of using the ultrahigh resolution mass spectrometer, I suggest the authors to focus on the new findings of this study.
We recognise that not all results presented here are absolutely new but we strongly believe that they are worth reporting as they clearly illustrate the organic compositional differences in Beijing between seasons and pollution levels.

Specific comments:

1. Introduction: The characterization and source identification of organic compounds in PM in Beijing have been extensively studied. I would suggest authors to improve the introduction by summarizing these previous studies and providing some results in line with the major conclusion of this study.
This part of the introduction section has been expanded and we added additional references (page 2, line 27-page 3, line 2).

2. Page 2, Line 10-12: "As a central of the project,. . .. . ." It makes no senses for your paper since the information on sampling has been provided in the Section Materials and Method.
This paper is part of the APHH campaign, which is a central piece of information for this paper. Thus, we believe it is appropriate to mention this at the very start of the paper (very shortly; 1.5 lines), as well as more detailed in the methods section.

3. Page 3: Maybe the meteorological conditions (e.g. temperature, RH, wind speed, wind direction, mixing layer height, etc.) play an important role on the organic components. I would suggest the authors to give a general characteristics of gas and PM pollutants and meteorological conditions during low and high pollution conditions (WH, WL, SH, SL), respectively, since the authors focus on the

comparison between the characteristics of organic groups under different pollution conditions, in the Supplementary Information, for instance?
The available information regarding gas-phase pollutants and meteorological conditions (RH, T) has been added to the supplementary information in table S2 and the following sentence has been added on page 10, line 9:
"In addition to ozone, the concentrations of other gas pollutants as well as temperature and humidity data for the different samples can be found in the supplement in Tab. S2."
The information one could get from wind direction regarding the particle sources is very similar as discussed in the back trajectory section. Boundary layer heights during this campaign are unfortunately currently not available to us.

4. Page 4, Line 16: What does "0.3âL' ¸eH/CâL' ˘g2.5" mean?
These symbols are displayed properly in the PDF we downloaded. We will make sure that they are displayed correctly in the final version.

5. Page 4, Line 21: Here x, y and z are the number of carbon, hydrogen, nitrogen atoms. However, in Page 12, Line 7, C, N, H and O are the number of carbon, nitrogen,
hydrogen and oxygen. I suggest the authors keep consistent in the nomination to avoid
the confusion.
The formula for calculation of the double bond equivalent was using different nomination since it is also valid for other elements with the same valence. That section has now been reworded to clarify this (p. 4, Line 31):
"with $I_yII_nIII_zIV_x$, where I=monovalent elements; II=bivalent elements; III=trivalent elements and IV=tetravalent elements. Sulfur was assumed to be bivalent and nitrogen trivalent for this calculation."

6. Page 5, Lines 17-20: It makes no senses since the air masses have been discussed in your paper.
Unlike the data shown in this manuscript, the referenced paper also covers time periods outside the duration of the APHH campaign. The sentence has been changed as following to state this more explicitly (p. 5, Line 27):
"More in-depth information about the origin of different air masses in Beijing, including time periods not covered by the APHH campaign, can be found in Panagi et al. (2020)."

7. Page 5, Lines 22-25: Here these sentences make no sense for the paper.
These sentences were removed as suggested by the reviewer.

8. Page 5: Here DBE was calculated based on the number of C, H, N atoms. I am not sure whether DBE should be calculated with the relative abundance weight since the relative abundance of each molecule in the mass spectrum is different. The same consideration also applies for the other parameters such as H/C, O/C, Xc and so on.
While a weighting calculation based on signal intensity would be possible for averaged metrics such as O/C and H/C ratio, we have come to the conclusion that it would not be more appropriate than the current method since signal abundance cannot be directly linked to compound concentrations due to matrix effects and variation in ionisation efficiency.

9. Page 6, Line 5: A reference would be helpful.
The text has been changed to (p. 6, line 11):
A trend that can be seen in the detected formulae is the presence of significantly more CHON formulae in summer compared to winter. The opposite trend was observed in Shanghai by Wang et al. (2017a), who found higher numbers and relative contribution of CHON in winter. Further information would be needed to explain this discrepancy.

10. Page 6: I suggest the authors add the number of four different groups identified in different pollution conditions in Figure 1.

We have now added the absolute numbers of detected formulae for the different groups for each sample in figure 2 (formerly figure 1). No other changes were made to the content of the figure, although we have changed the order of the samples to bring it in line with the other figures.

11. Pages 6-8: The chemical composition and some ratios (i.e., O/C, H/C) of organic compounds have been characterized by ultrahigh resolution mass spectrometer in some cities such as Beijing and Shanghai, and some typical emission sources (i.e., coal combustion, biomass burning). I suggest the authors compare their result with those reported in literature.
While there are several studies looking at chemical composition of organic compounds in PM in Chinese megacities, results are often difficult to compare, especially quantitatively, due to differences in methodology. The extraction solvent can for example strongly influence the chemical composition (see e.g. the Song et al. reference suggested by the reviewer), with many studies using other solvents than methanol, which we used in our study. In addition, some of the available studies use HPLC or UPLC instead of direct infusion, which due to the separation of isomers will lead to different results for the detected number of formulae, O/C etc.
It is therefore mostly only possible to compare general trends. In addition to the UPLC-MS measurements by Wang et al. (2018 & 2019), which are referenced on page 14, line 31, page 18, line 15 and page 19, line 20, we have now added references to results from Jiang et al. (2016) (p. 6, line 19).

12. Page 7, Line 14: You are right, here a reference would be helpful.
References were added and the sentence was changed to (p. 9, Line 11):
"Aromatic compounds are predominantly produced from anthropogenic sources such as traffic, industry and heating (Baek et al., 1991; Hamilton and Lewis, 2003) whereas aliphatic compounds can be of both anthropogenic and biogenic origin, the latter of which makes a larger contribution to organic particle mass in the summer (Gelencsér et al., 2007; Hu et al., 2017; Kleindienst et al., 2007)."

13. Page 7, Line 15: What does "high and low H/C particulate matter" mean?
The sentence has been reworded (p. 9, line 13):
"One type of source that will be present in both seasons and which contributes compounds of both high and low H/C to particulate matter is vehicle emissions, as these are usually a mix of low carbon number (<24) PAHs and single-ring aromatics with low H/C and alkenes and cyclic, branched and straight-chain alkanes with high H/C (Gentner et al., 2012, 2017; Huang et al., 2015; May et al., 2014; Worton et al., 2014) ."

14. Page 8, Lines 1-2: The SH showed high H/C ratio. The authors suggest that is due to a large proportion of biogenic organic aerosol from plant sources. It might be good here to give more evidences. Is there any assigned formula which could be used as markers for biomass burning or biogenic organic aerosol? For example, nitrophenols, nitrocatechols? They show higher number fraction and/or relative abundance in SH samples?
A reference for increased concentration of biogenic aliphatic compounds from plant waxes during summer in Beijing has been added (Feng, 2005).
Direct infusion high resolution MS does not allow for structural identification of compounds. Thus, we do not speculate about specific markers.
Nitrophenols and nitrocatechols have low H/C of typically below 1 and not high H/C near 2, as discussed here.

15. Page 8, Line 9: It might be better to give the ozone concentrations for the WH, WL, SH, SL samples.
We have now added the average ozone concentrations for the different samples, so that the text now reads (p. 10, line 8):
" The average ozone concentrations at the IAP site during sample collection were 13 ppb (WL), 6 ppb (WH), 39 ppb (SL) and 63 ppb (SH)."

16. Page 9: The VK plots show the aromaticity of CHO and CHON is quite different in winter and summer. Please speculate more in depth on the difference.
Differences in aromaticity between the winter and summer sample are discussed in depth in the following section, 3.2.

17. Page 10: Here the authors give some data on polyaromatic compounds. How about the single-ring aromatics? I think they contribute more to the aromatic compounds.
The relative dominance of monocyclic vs. polycyclic aromatics in the different samples is discussed in more depth on page 12, line 21 to 23 of the original manuscript. We have added some absolute numbers for comparison, so that this section now reads (p. 14, line 25):
"The SL sample is particularly low in aromatic formulae (132 aromatic formulae vs. 801 in total), especially regarding polycyclic aromatics (26 formulae). In contrast, there are a reasonable number of polycyclic (85) and monocyclic (159) aromatics in SH. The two winter samples both show high contributions of aromatic formulae (76% in WH vs. 77% in WL of all detected formulae in these samples). However, the WH sample is strongly dominated by polycyclic aromatics with 403 polycyclic vs. 260 monocyclic aromatic formulae, while monocyclic and polycyclic aromatics are present in nearly equal numbers in the WL sample (320 monocyclic and 297 polycyclic aromatic formulae)."

18. Page 12: The authors spend too many words to discuss the aromaticity equivalent (Xc). I suggest the authors focus on the new finding which cannot be deduced from the H/C and O/C ratios.
Excluding the introduction of the concept, the discussion of the aromaticity equivalent on page 14 is largely focused on the presence of monocyclic vs. polycyclic aromatics, which cannot be deduced from H/C and O/C ratios.

19. Page 13, Line 21: A reference regarding the heating source would be helpful.
We have added the following sentence (p. 15, line 29):
"This link between higher-ring number polyaromatics and residential heating is supported by studies showing a sharp increase in the concentration of higher-ring-number PAHs at the start of the heating season in Beijing (Zhang et al., 2017) and increased emissions of higher-ring-number PAHs for coal combustion compared to gasoline and diesel (Huang et al., 2014).

20. Page 16, Line1: The authors state that sulfate concentrations are usually higher in summer than in winter in Beijing. Are you sure? Please give the concentrations of sulfate and nitrate in WH, WL, SH, and SL samples in a Table, for instance, in the Supplementary Information. And in Line 25, you state the lower sulfate concentrations in summer. It is significantly contradictory.
The average concentration of sulfur in fine PM in Beijing are indeed usually higher in summer, as shown in the four cited papers. This is often explained by the increase in photooxidation during summer. During our sampling campaign the average sulfate concentration was however slightly higher in winter (8.5 ug/m3) than in summer (6.9 ug/m3). This might be due to the fact that our campaign only covered early summer, whereas the very high sulfate levels found in the cited papers were all measured later in summer than ours. This is now explained in the paper to resolve this apparent contradiction (p. 18, line 7).
In addition, sulfate concentrations also increase during haze events, of which there were several very strong ones during our winter measurement campaign. For our study, samples were chosen at clean vs. polluted conditions. This explains the very high sulfur levels we see in winter since the extreme pollution events in winter lead to higher maximum sulfate concentrations. We agree that the sentence in line 25 is confusing in the original text. The wording has been changed to (p. 19, line 14):
"The sulphate data did not correlate as well for summer (Fig. 8b), which might be explained by the lower maximum concentrations of SO_4^{2-} and the on average slightly lower SO_4^{2-} concentrations during our summer campaign, where particle-phase formation reactions of S-containing organics might become less important."

We hope that this, in combination with the abovementioned explanation about the sulfate concentration during our sampling campaign vs. other summer measurements has clarified the issue.

21. Page16: It is a good idea to discuss the relationship between sulfate and nitrate with the number of CHOS and CHON compounds, but I recommend the authors to provide in-depth insights into this discussion. In addition to the secondary formation, Song et al. (EST 2019, 53, 13607-13617; 52, 2575-2585) reported that S-containing compounds account for 36% of the total number of compounds identified, making up the largest component in coal smoke, and N-containing compounds show high abundance in biomass burning. The primary sources of S- and N-containing compounds should also be considered.
The discussion of the formation of S- and N-containing compounds has been expanded (p. 18, line 12 & 28).

22. Page 16: The authors state that the particles in winter are sampled before they can undergo atmospheric ageing processes, for example reacting with OH radicals and ozone in Page 8, Lines 6-7. It seems inconsistent with the good positive correlation between sulfate and CHOS compounds.
As stated previously, the sulfate concentration depends not only on oxidation but also on SO_2 emissions, which are usually much higher during winter.

Technical corrections:

1. Page 5, Lines 27-28: What does “Fehler! Verweisquelle konnte nicht gefunden warden” mean? Mistype?
This has been corrected.

2. Page 5, Line 30: “off” should be “of”.
This has been corrected