Comments by **reviewer #1** are reproduced in a black font below. Our responses follow each comment in a blue font. Text additions to the manuscript, for example, significantly modified sentences, appear in the revised manuscript in red color. Deletions from the manuscript are not explicitly shown but are described in the responses below. Minor editorial edits to the text are not explicitly shown to prevent a cluttered view.

We thank the reviewer for the comments, which we have addressed in a point by point fashion below.

Urban organic aerosol composition in Eastern China differs from North to South: Molecular insight from a liquid chromatography-Orbitrap mass spectrometry study Wang et al.

This paper describes the results from the analysis of organic aerosol collected at three Chinese cities during haze events using a high resolution method. The paper is within the scope of ACP and is well written and easy to follow. A very careful analysis of the data is presented and the methods applied for formula assignment are appropriate. I agree that the organic aerosol in the North is likely to be more influenced by coal combustion and the warmer cities in the South more affected by photochemistry. However, I don't think that the data in this paper is sufficient to draw those conclusions. Far too much weight is given to very small differences in O:C and DBE based on peak area only, without any discussion about the impact of structure on ionization efficiency or any estimate of the uncertainty in these values. For instance on page 11, line 335, is a difference of 0.11 between the DBE from Shanghai and Guangzhou a meaningful difference? Nitrophenol species can have vastly different ionisation efficiencies in ESI- depending on the position of the constituents on the ring (see Schmidt et al., 2006. https://onlinelibrary.wiley.com/doi/full/10.1002/rcm.2591). These nitrophenols are some of the dominant species detected in this study and thus their peak area will have a significant impact on the calculation of DBE and O:C. They also effect the calculation of Xc since they give incorrect values using p=0.5. The ionization efficiency of carboxylic acids also depends on structure and can vary by several orders of magnitude. Compounds with the same formula such as an unsaturated hydroxy-acids and a carbonyl-acid are likely to have very different ionisation efficiencies (Leito et al., 2008. https://onlinelibrary.wiley.com/doi/pdf/10.1002/rcm.3371, Kruve et al., 2014 https://pubs.acs.org/doi/full/10.1021/ac404066v). The data presented is interesting and shows there are differences in composition between the three locations. But I would not recommend publication in ACP without major changes to the way the average peak area weighted metrics are used to draw conclusions.

Response: We thank the reviewer for pointing out the uncertainties existing in the peak abundance weighted comparison caused by the different ionization efficiencies among different compounds. Actually, we mentioned these uncertainties in Page 7, Line 202-204 in the original manuscript as well as in the original SI. Because OA is highly complex and authentic standards are limited, the identification and quantification of OA components are a challenging analytical task and it is very difficult to avoid ionization efficiency related uncertainties. Since the conclusions drawn in this study are mainly based on the peak abundance weighted comparison, we now emphasize the uncertainties in the sections of Abstract (Page 2, Line 50-53) and Limitations (Page 18, Line 555-571) in the revised manuscript as follows:

Abstract: "…It should be noted that the conclusions drawn in this study are mainly based on comparison of molecular formulas weighted by peak abundance, and thus, are associated with inherent uncertainties due to different ionization efficiencies for different organic species."

Limitations: "In this study, we used the peak abundance-weighted method to illustrate the difference in chemical formulas assigned by Orbitrap mass spectrometry. This comparison was made based on the assumption that the measured organic compounds have same peak abundance response in the mass spectrometer. However, this assumption can bring some uncertainties because the ionization efficiencies vary between different compounds (Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Kruve et al., 2014). For example, the ionization efficiencies of nitrophenol species detected in negative ESI mode can vary by a large degree depending on the position of the substituents at the nitrobenzene ring (Schmidt et al., 2006; Kruve et al., 2014) and the ionization efficiencies of carboxylic acids can also vary by several orders of magnitude depending on the structures (Kruve et al., 2014). Nonetheless, it is a challenging analytical task to identify and quantify all compounds in ambient OA due to the high chemical complexity of OA and the limits in authentic standards of OA. Despite the inherent uncertainties, the peak abundance-weighted comparison of molecular formulas provides an overview of the difference in chemical composition of OA in these three representative Chinese cities. In particular, the chemical formulas assigned in this study can be validated in future studies by authentic standards and the difference in ionization efficiencies can be further evaluated."

Specific comments

Abstract: There needs to be a comment in the abstract about the uncertainties of using this approach.

Response: A statement about the uncertainties has been now added in the Abstract (Page 2, Line 50-53 in the revised manuscript) as follows:

"It should be noted that the conclusions drawn in this study are mainly based on comparison of molecular formulas weighted by peak abundance, and thus, are associated with inherent uncertainties due to different ionization efficiencies for different organic species."

Chromatography: This paper uses UPLC to separate the species and where isomers are found, they are recombined to produce the reconstructed mass spectra and various figures. It seems a waste to have so much isomeric speciation and then not use any of it. For instance, how many isomers were found on average per molecular formula? A similar analysis could have been achieved by direct injection into the source. While using chromatography may minimise matrix effects, the lack of information on whether structure effects ionisation efficiency counteracts its usefulness.

Response: The important advantage of the application of UPLC in this study is that compounds are separated by the LC-column before they enter the ionization source, minimizing the matrix effects. Meanwhile, the compounds are concentrated in the LC-column, which can increase the sensitivity of the measurement. In addition, it can provide separation of some compounds and information of retention time of the compounds, which is useful for the identification of the compounds and the separation of isomers. This statement is now added in Page 5, Line 142-147 (also see it below). Since the numbers of isomer vary a lot depending molecular formulas, we have added the term named isomer number fraction (meaning the percentage of formula numbers that have isomers among all assigned formulas) in the revised Table 1. It shows that 31-34% and 30-56% of formulas have isomers in negative mode and positive mode, respectively. In addition, we now define the common formulas observed in all samples as the formulas that have the same molecular formulas and the same retention time (retention time difference ≤ 0.1 min).

"Compared to the direct infusion method applied in other UHRMS studies (Lin et al., 2012a; Lin et al., 2012b; Rincón et al., 2012; Kourtchev et al., 2016; Fleming et al., 2018), the UHPLC technique was used in this study, which could separate and concentrate the compounds before they entered the ion source, reducing the ionization suppression and increasing the sensitive of the measurement. In addition, it can provide separation of some compounds and information of retention time of the compounds, which is useful for the identification of the compounds and the separation of isomers."

Page 6, line 162: When first reading this I struggled to understand how the values for p and q were derived. I found the information in the SI, but this needs to be included in the main paper, alongsidea discussion of the uncertainties and issues using this approach.

Response: The detailed description of the aromaticity equivalent (Xc) and the values of p and q in the equation is now stated in Page 6, line 171-185 in the main paper as follows:

"The aromaticity equivalent (X_C) as a modified index for aromatic compounds was obtained using the equation: $Xc = [3(DBE - (p \times o + q \times n)) - 2] / [DBE - (p \times o + q \times n)]$, where p and q, respectively, refer to the fraction of oxygen and sulfur atoms involved in the π-bond structure of a compound. As such the values of p and q vary between compound categories (Yassine et al., 2014). For example, carboxylic acids and esters are characterized using p = q = 0.5, while p = q = 1 and p = q = 0 are used for carbonyl and hydroxyl, respectively. Since it is impossible to identify the structurers of the hundreds of formulas observed in this study, we cannot know the exact values of p and q in an individual compound. Therefore, in this study, p = q = 0.5 was applied for compounds detected in ESI− as carboxylic compounds are preferably ionized in negative mode. However, because of the high complexity of the mass spectra in ESI+, p = q = 1 was used in ESI+ to avoid an overestimation of the amount of aromatics. Moreover, for DBE $\leq (p \times o + q \times n)$ or $X_C \leq 0$, X_C was defined as zero. Furthermore, in ESI–, for odd numbers of $(p \times o + q \times n)$, the value of $(p \times o + q \times n)$ was rounded down to the lower integer. Xc ⩾ 2.50 and Xc ⩾ 2.71 have been suggested as unambiguous minimum criteria for the presence of monoaromatics and polyaromatics, respectively (Yassine et al., 2014)."

Page 7, line 189-200: The authors need to be careful with the use of the word significant here. It is impossible to tell if the values are significantly different without an estimate of the uncertainty in the values. An H:C of 1.03 does not seem "significantly lower" than a value of H:C = 1.05. What is the spread in the values between the three replicates? Again, this whole section assumes that peak area = abundance and that the differences in OC are driven by oxidation and not different sources.

Response: The word 'significant' is now carefully used and the sentences related to 'significant difference' is now rephrased throughout the manuscript. The effect of OA sources on the chemical composition (e.g., the different O/C ratio) is now added in the discussion throughout the revised manuscript (also see it below).

Page 2, Lines 44-47: "Moreover, the ESI− analysis showed higher H/C and O/C ratios for organic compounds in Shanghai and Guangzhou compared to samples from Changchun, indicating that OA undergoes more intense photochemical oxidation processes in lower latitude regions of China and/or is affected to a larger degree by biogenic sources."

Page 8, Lines 235-240: "The different chemical composition of the samples is probably caused by… or by different biogenic/anthropogenic precursors."

Page 10, Lines 307-309: "Altogether, these results indicate that CHO− compounds in urban OA from East and Southeast China experienced more intense oxidation and aging processes and/or were affected to a larger degree by biogenic sources."

Page 10-11, Lines 313-315: "Again, these average formulas show that CHO− in Shanghai− and Guangzhou− experienced more intense oxidation processes and/or were affected to a larger degree by biogenic precursors, indicated by the larger abundance-weighted MM_{avg} with a higher degree of oxygenation."

Page 8, line 230: In the reconstructed mass spectra in figure 1, the ESI+ spectra from Shanghai and Guangzhou seem to be dominated by a single ion. What is this ion and how does this affect the calculation of the % abundance of CHN+? Page 8, line 250: Are the 52 common formulas the same chromatographic peak, or is it just the formula that is common? Page 9, line 258: The Van Krevelen plots in S1 look fairly similar for compounds of high O:C, I don't really see any substantial difference. Page 9, line 266. I don't agree that these average abundance weighted formulas can be used to state that the Shanghai and Guangzhou OA experienced "more intense oxidation". Certainly the MF have a higher amount of O and a lower amount of C but this could also be related to the sources of the OA, with more biogenic/aliphatic material in the south.

Response:

1. In Shanghai and Guangzhou samples, the ion with molecular formula of $C_{10}H_{14}N_2$ is dominant among all CHN+ compounds, which is probably due to its high concentration and/or high ionization efficiency in ESI+. This ion accounts for 63% and 52% in terms of peak abundance in Shanghai and Guangzhou CHN+ compounds, respectively. The discussion about this ion is now added to Page 14, line 438-442 in the revised manuscript, as follows:

"Remarkably, as can be seen in Fig. 6, the abundance of CHN+ compounds in Changchun+ distribute evenly among different individual CHN+ compounds, while in Shanghai+ and Guangzhou+ they are dominated by the formula of $C_{10}H_{14}N_2$ (the biggest purple circle in Fig. 6) with DBE value of 5, which probably has high concentration and/or high ionization efficiency in the positive ESI mode."

2. In the original manuscript, the common formulas just refer to the same formula and do not refer to the same chromatographic peaks. Now, in the revised manuscript we define the common formulas observed in all samples as the formulas that have both the same molecular formulas and the same retention time (retention time difference ≤ 0.1 min).). It shows that most of compounds with the same molecular formulas have similar retention time. And the Figure 2 about the new definition of common formulas is now redrawn in the revised manuscript (please see the revised Figure 2 below).

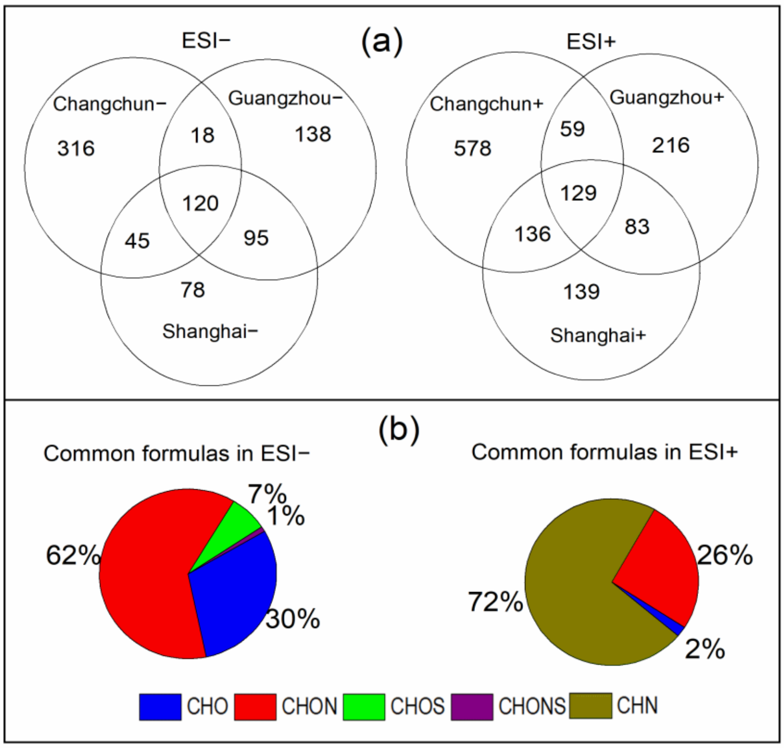

Figure 2. (a) Venn diagrams showing the number distribution of all molecular formulas detected in ESI− and ESI+ for all sample locations. The overlapping molecular formulas refer to the compounds detected in each city with the same molecular formulas and with the same retention times (retention time difference ≤ 0.1 min). (b) Peak abundance contribution of each elemental formula category to the total common formulas.

3. Since the Van Krevelen diagram is plotted by the O/C and H/C, it hides the compounds with different formulas but with the same O/C and H/C and is not the best tool to present the difference of compounds with high O/C in these three samples. Therefore, we have calculated the relative peak abundance fraction of CHO- compounds with O/C ≥ 0.6 (which are considered as highly oxidized compounds, please see the reference ‘Tu et al., 2016, Analytical Chemistry’) in all samples measured in the negative mode. It shows that 14% of compounds in terms of peak abundance in Changchun− have O/C ratio larger than 0.6, while they are relatively higher in Shanghai− and Guangzhou− samples, accounting for 34% in Shanghai and 45% in Guangzhou. The Figure S1 in Supporting Information is now removed and the following discussion is now added in Page 10, line 304-307 in the revised manuscript.

“Furthermore, the relative peak abundance fraction of CHO− compounds with O/C ≥ 0.6, which are considered as highly oxidized compounds (Tu et al., 2016), is 14% in Changchun and somewhat higher in Shanghai– (34%) and Guangzhou– (45%).”

Tu, P., Hall, W. A. t., and Johnston, M. V.: Characterization of Highly Oxidized Molecules in Fresh and Aged Biogenic Secondary Organic Aerosol, Anal. Chem., 88, 4495-4501, 10.1021/acs.analchem.6b00378, 2016

4. Yes, we agree that the sources of SOA may also affect the chemical composition of aerosols. Therefore, the conclusion is now modified in Page 10, line 313-315 in the revised manuscript as follows:

"these average formulas show that CHO− compounds in Shanghai− and Guangzhou− experienced more intense oxidation processes and/or were affected to a larger degree by biogenic sources, indicated by the larger abundance-weighted MM_{avg} with a higher degree of oxygenation."

Page 10, line 289: When discussing "individual" compounds, do you mean peaks? For these formulas, how many peaks were observed? For these species discussed, i.e. C8H8O3, why have you chosen these specific oxidation products of estragole? Surely this could also be biomass burning emissions such as vanillin?

Response: 1. They refer to individual formulas. For clarification, we have rephrased the sentence from "through mass spectrometric analysis of individual compounds" to "through the analysis of individual formulas". There are 3-4, 1-2, 1-4, 1-5, 2-8 peaks were observed for formulas of $C_8H_6O_4$, $C_7H_6O_2$, $C_7H_6O_3$, $C_8H_8O_2$, and $C_8H_8O_3$, respectively, in these three cities. 2. For the discussion about the source of these specific compounds, we checked these compounds in the aerosol-related literatures, in which these compounds were also observed. Yes, the compounds with formula of $C_8H_8O_3$ could also be suggested to vanillin emitted from biomass burning. We have now considered 'vanillin' as one possible compound of $C_8H_8O_3$ and the related discussion is now revised in Page 11, Line 343-345 as follows:

"$C_8H_8O_2$ is likely 4-hydroxy acetophenone, which could be derived from estragole (Pereira et al., 2014), while $C_8H_8O_3$ is suggested to be either 4-methoxybenzoic acid generated from estragole (Pereira et al., 2014) or vanillin emitted from biomass burning (Li et al., 2014)."

Page 25, figure 2: In the upper panel, the Venn diagrams need to be labelled as ESI+ and ESI-. Also, the Guangzhou circle in the Venn Diagram has 304 compounds but in the table there are 488 compounds. Why are they different?

Response: The label of ESI+ and ESI- is now added in the revised Venn diagram in Figure 2. The number in the Venn diagram refers to the number of the formulas. However, the number of compounds in Table 1 refer to the number of peaks, which is higher compared to the number of formulas due to the isomers. In addition, the information of formula numbers for each compound group is now added in the revised Table 1.

Page 26, Figure 3: Can you explain why the dots are scaled to the fourth root of the peak area? I assume it is to reduce the size of the largest peaks. However, this is not mentioned in the text and could be easily missed in the caption. This should be clearly stated in the text. I would also like to see these figures with the observed peak area for comparison in the SI.

Response: Yes, the purpose for the use of the fourth root of the peak area is to reduce the size difference of the dots related to different formulas, because the peak areas vary a lot between different formulas. For clarification, the following statement is now added in Page 10, line 284-288 in the revised manuscript (also see it below). Meanwhile, the figures with the size of dot related to the absolute peak area are now added in the SI (also see them below: Figure S2 of DBE vs. C-atom numbers for CHO-; Figure S6 of DBE vs. C-atom numbers for CHON-; Figure S8 of DBE vs. C-atom numbers for CHON+; Figure S10 of H/C vs. N/C for CHN+; Figure S11 of DBE vs. C-atom numbers for CHOS-).

“In addition, since peak abundances for the formula can vary by orders of magnitude, the area of the circles presented in the Figure 3 and Figures 5–7 is proportional to the fourth root of the peak abundance of each formula to reduce the size difference of the circles. For a more detailed comparison, figures with the circle size related to the absolute peak abundances are presented in the SI.”

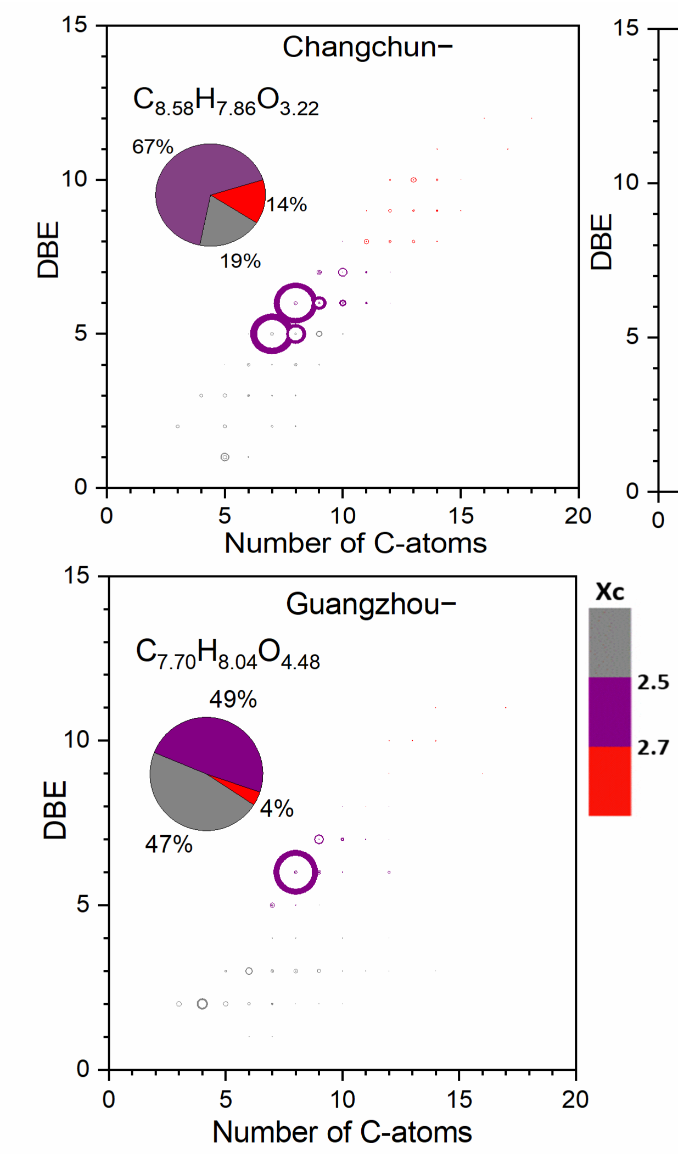

Figure S2. Double bond equivalent (DBE) versus carbon number for all CHO− compounds for all sample locations. The molecular formula represents the abundance-weighted average CHO− formula and the area of the circles is proportional to the absolute peak abundance of an individual compound. The color bar denotes the aromaticity equivalent (gray with Xc < 2.50, purple with 2.50 ≤ Xc < 2.70 and red with Xc ≥ 2.70). The pie charts show the percentage of each Xc category (i.e., gray color-coded compounds, purple color-coded compounds and red color-coded compounds) in each sample in terms of peak abundance.

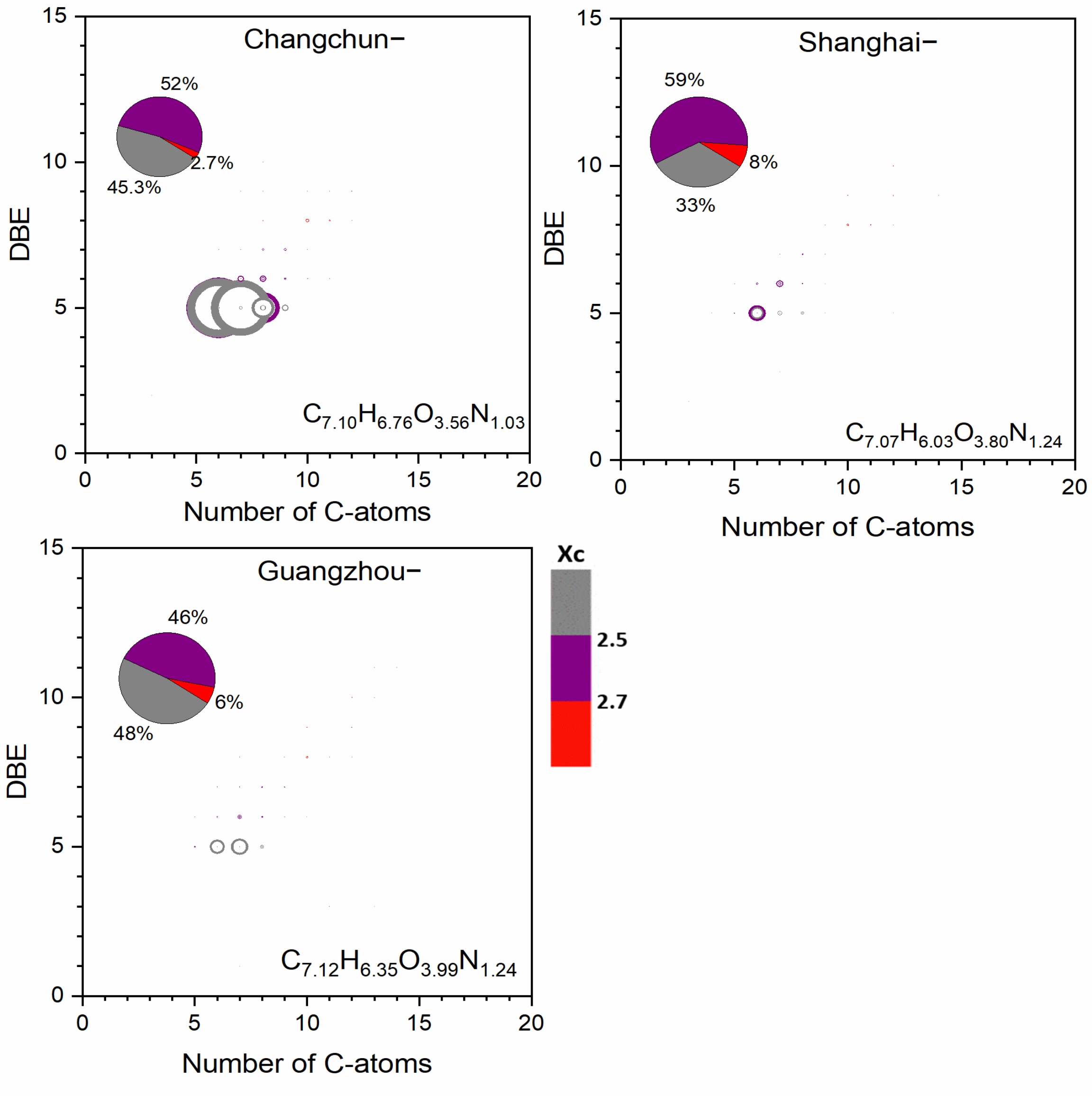

Figure S6. Double bond equivalent (DBE) versus carbon number for all CHON− compounds for all sample locations. The molecular formula represents the abundance-weighted average CHON- formula and the area of circles is proportional to the absolute peak abundance of an individual compound. The color bar denotes the aromaticity equivalent (gray with $Xc < 2.50$, purple with $2.50 \leq Xc < 2.70$ and red with $Xc \geq 2.70$). The pie charts show the percentage of each Xc category (i.e., gray color-coded compounds, purple color-coded compounds and red color-coded compounds) in each sample in terms of peak abundance.

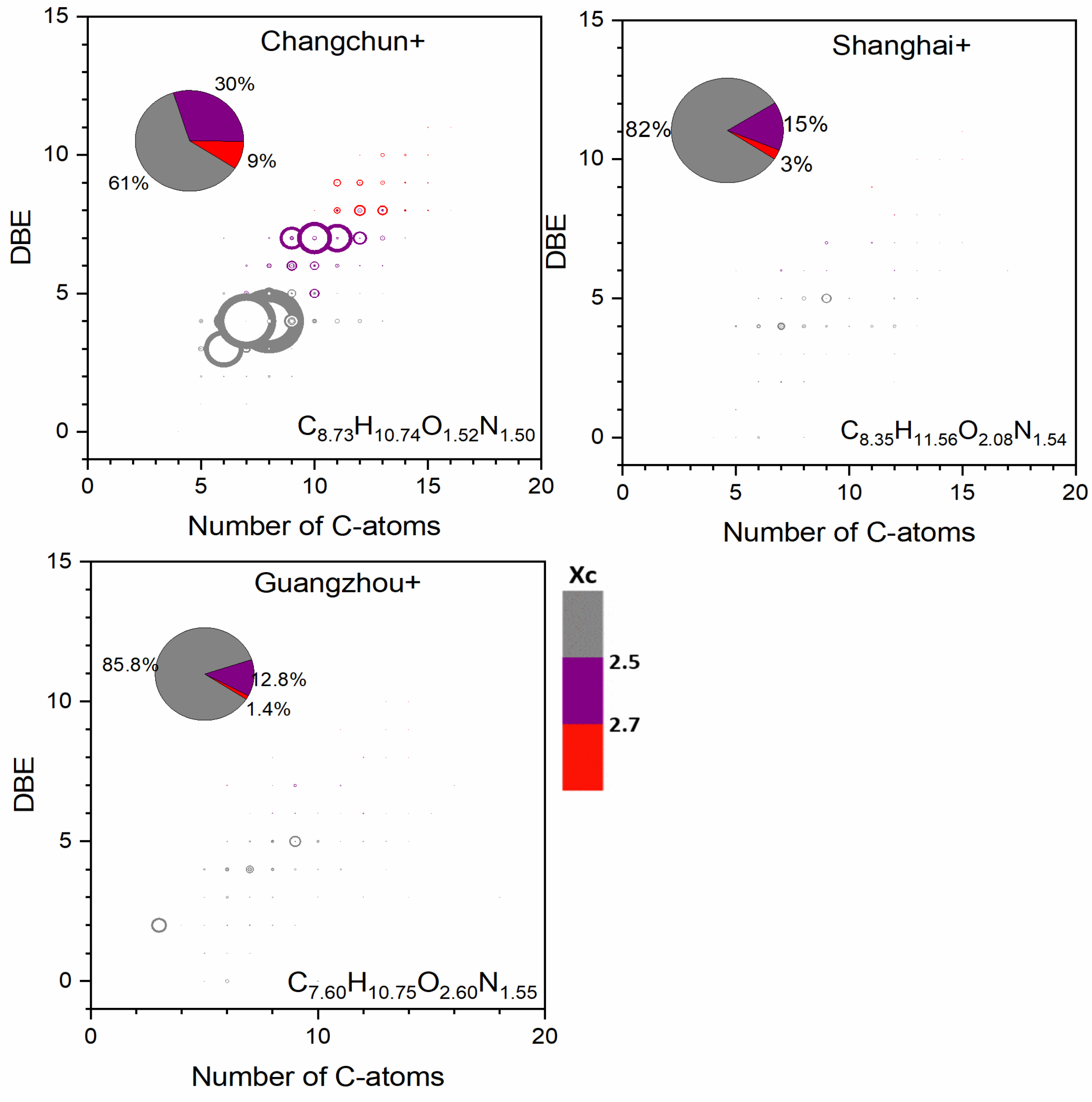

Figure S8. Double bond equivalent (DBE) vs C number for all CHON+ compounds of all samples. The molecular formula represents the abundance-weighted average CHON+ formula and the area of the circles is proportional to the absolute peak abundance of an individual compound. The color bar denotes the aromaticity equivalent (gray with Xc < 2.50, purple with 2.50 ≤ Xc < 2.70 and red with Xc ≥ 2.70). The pie charts show the percentage of each Xc category (i.e., gray color-coded compounds, purple color-coded compounds and red color-coded compounds) in each sample in terms of peak abundance.

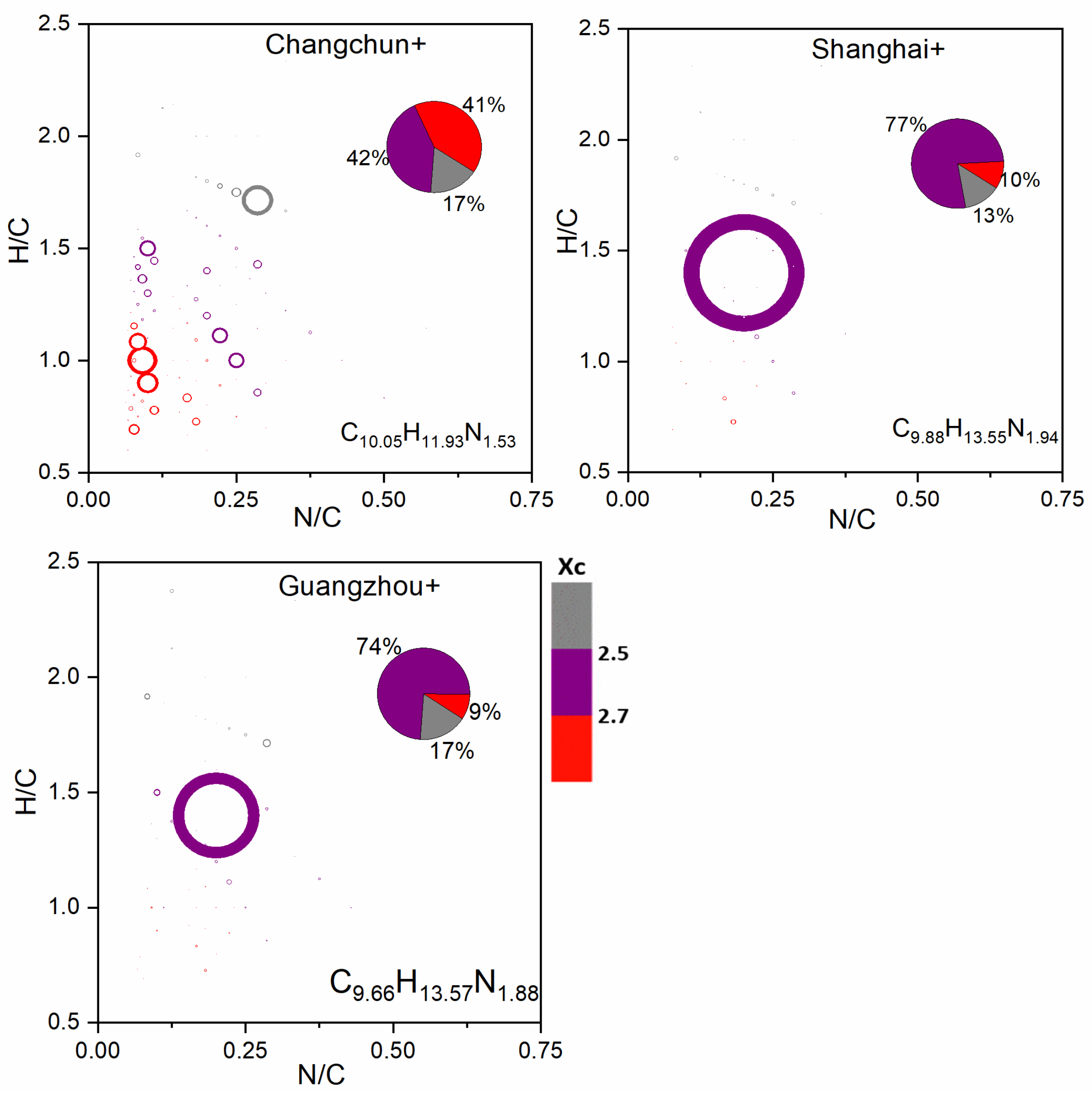

Figure S10. Van Krevelen diagrams for CHN+ compounds in Changchun, Shanghai and Guangzhou samples. The area of circles is proportional to the absolute peak abundance of an individual compound and the color bar denotes the aromaticity equivalent (gray with $X_c < 2.50$, purple with $2.50 \leq X_c < 2.70$ and red with $X_c \geq 2.70$). The pie charts show the percentage of each Xc category (i.e., gray color-coded compounds, purple color-coded compounds and red color-coded compounds) in each sample in terms of peak abundance.

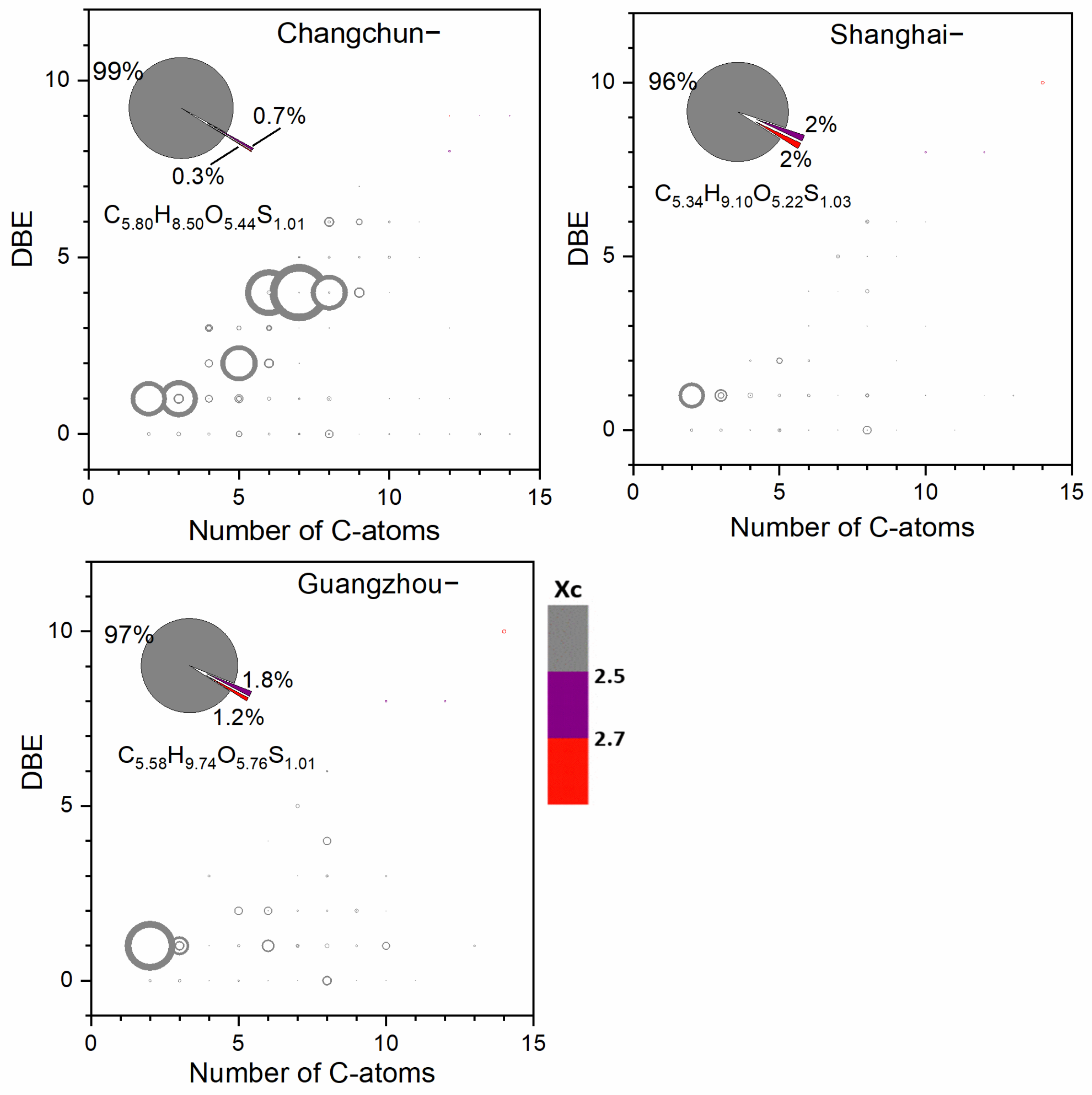

Figure S11. Double bond equivalent (DBE) versus carbon number for all CHOS− compounds for all sample locations. The molecular formula represents the abundance-weighted average CHOS− formula and the area of circles is proportional to the absolute peak abundance of an individual compound. The color bar denotes the aromaticity equivalent (gray with Xc < 2.50, purple with 2.50 ≤ Xc < 2.70 and red with Xc ≥ 2.70). The pie charts show the percentage of each Xc category (i.e., gray color-coded compounds, purple color-coded compounds and red color-coded compounds) in each sample in terms of peak abundance.

Minor comments

Page 3, line 64: Change “comprehended” to “understood”.

Response: “comprehended” is now changed to “understood”.

Page 4, line 104: I would help the reader to know a little bit more about the differences in industrial structure, energy etc.

Response: The city of Changchun is located in Northeast of China, which was used to be the center of heavy industry of China (Zhang, Chinese Geographical Science, 2008). The heavy industries like the coal chemistry industry and steelworks can produce a large amount of air pollutants (e.g., NOx and SO_2), which can affect the chemical composition of aerosols in this area. However, the cities of Shanghai and Guangzhou are located in the East Coast of China, where there are much less of heavy industries. Moreover, another important factor is that residential heating (i.e. coal combustion) is extensively used in wintertime in Northeast of China, which can make a large contribution to the $PM_{2.5}$ mass (Huang et al., Nature 2014; An et al., PNAS 2019). And, these statements are now added in Page 4, line106-111, in the revised manuscript as follows:

“In addition, the industrial structure, energy consumption and energy sources in these three cities are different, such as much more heavy industries (e.g., coal chemical industry and steelworks) in Northeast China (Zhang, 2008), which can cause difference in anthropogenic emissions, and can therefore influence the chemical composition of urban OA. Moreover, OA is strongly affected by residential coal combustion during winter in Northeast China (Huang et al., 2014; An et al., 2019).”

Zhang, P.: Revitalizing old industrial base of Northeast China: Process, policy and challenge, Chin. Geogra. Sci., 18, 109-118, 10.1007/s11769-008-0109-2, 2008

Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 10.1038/nature13774, 2014.

An, Z., Huang, R. J., Zhang, R., Tie, X., Li, G., Cao, J., Zhou, W., Shi, Z., Han, Y., Gu, Z., and Ji, Y.: Severe haze in northern China: A synergy of anthropogenic emissions and atmospheric processes, Proc Natl Acad Sci U S A, 116, 8657-8666, 10.1073/pnas.1900125116, 2019.

Page 11, line 317: I don’t understand this sentence. What data does the 59 % relate to?

Response: This sentence means that in terms of peak abundance, 59% of all CHON compounds detected in the negative mode in Guangzhou samples can be assigned with formulas with oxygen to nitrogen ratio higher than or equal to 4. And, this sentence is now clarified in Page 12, Line 369-371 as follows:

“In terms of the peak abundance, 59% of CHON− compounds observed in Guangzhou− exhibited formulas with O/N ratios ≥ 4, …”

Page 12, line 371: Is the 83 -87% the percentage of the peak area?

Response: Yes, the value of 83-87% refers to the percentage of the peak area. For clarification, we have added “in terms of peak abundance” right after the “83-87%”.

Page 15, line 461: this should say “mononitrate organosulfate”

Response: “pinanediol mononitrate” is now changed to “mononitrate organosulfate”.

Page 23, table 1: Does the “number of compounds” mean number of formulas or number of peaks?

Response: “number of compounds” in Table 1 refers to the number of peaks detected in this study. In addition, the number of formulas assigned fot these compounds is now added in the revised Table 1.

Page 7, line 190: change to “detected”

Response: It is now corrected.