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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Urban organic aerosol composition in Eastern China differs from North to South: Molecular insight from a liquid chromatography-Orbitrap mass spectrometry study" *by* Kai Wang et al.

Anonymous Referee #1

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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 ionisation 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 ionisation 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.

Specific comments

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

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.

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.

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.

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.

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?

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?

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.

Minor comments

Page 3, line 64: Change "comprehended" 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.

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

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

Page 15, line 461: this should say "mononitrate organosulfate"

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

Page 7, line 190: change to "detected"

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