

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 #3 (RC2). 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 #3 (RC2)**

#### *General comments:*

This study reports the analysis of organic aerosol composition in central Beijing during winter and summer months using orbitrap mass spectrometry coupled with a nanoelectrospray ionisation source. A main finding is that the number of S-containing organic species increased with inorganic sulfate concentration. This work provides new information on organic aerosol chemistry in northern China with a scope that fits well within ACP. But there are some issues on data analysis and interpretation, which may require major revisions to resolve. It is important that the authors discuss the limitations with negative ESI MS analysis, such as its low ionization efficiency towards, or inability to detect, certain types of C1 compounds.

Compounds with only one C atom usually have very high volatilities and thus are not expected to be present in the particle phase. We therefore do not discuss C1 compounds here.

A general comment on the ionisation efficiency of ESI was added on p. 6, line 9. A specific discussion of ionisation efficiency for N- and S-containing compounds has been added in the respective section (p. 17, line 10 & p. 19, line 27).

The calculation of aromaticity equivalent  $X_c$  is based on assumptions of elements' valences which may not always hold for atmospheric organics. The authors excluded S-containing species in their calculations of  $X_c$ , but nevertheless calculated the  $X_c$  for N-containing compounds, in which the valence of N can be either 3 or 5. In addition, the O valence in peroxides is 1 rather than 2 and it is known that organic peroxides can account for a significant fraction of the molecules. The authors should discuss how these issues affect their results and conclusions.

The relevant metric for the calculation of the aromaticity equivalent is not the valency but whether oxygen or sulfur atoms are present as  $\pi$ -bond structures in a particular compound, since the contribution of those structures is supposed to be removed when calculating the degree of unsaturation. For our calculations, we chose  $m=0.5$ , meaning that half of the oxygens in each functional group are present as  $\pi$ -bond structures, which is the case e.g. in carboxylic acids, which are likely dominant components in the sample. Peroxides, just like alcohols, only contribute  $\sigma$ -bond, so for them  $m=0$ . In the presence of many peroxide functions our assumption would lead to an underestimation of the degree of saturation. The same is true for organonitrates and peracids, since here only one in three O-atoms participates in a  $\pi$ -bond, rather than one in two as assumed with  $m=0$ . This is now discussed on page 14, line 11.

Additionally, some discussions on the technical aspects a bit vague and need clarification. See below for specific comments.

#### *Specific comments:*

This study only compares winter and summer compositional differences, thus is an overstatement to have a title of "Seasonal Differences . . ."

We have changed the title to "Differences in the Composition of Organic Aerosols between Winter and Summer in Beijing: a Study by Direct Infusion Ultrahigh Resolution Mass Spectrometry"

Page 2, how was sampling from Birmingham UK decided to be representative of a typical European urban background site?

The site is not a “representative background station”, which would require a huge effort by comparing the aerosol composition at many different sites. A comparison with this site was chosen because it is one of the only urban background sites in Europe where the aerosol composition was characterized with the same method as used here assuring direct comparability with the current study. We have removed the word “typical” to avoid any misunderstandings.

Page 3, What’s the sampling duration for the filters?

The sampling duration was 23 hours for each filter, as stated on page 3, line 9.

Page 3, Line 19, is the concentration corresponding to PM mass or OA mass? How was it known?

The concentration refers to PM mass, which was determined gravimetrically. Particle mass was used since OA mass was not known at the point of the mass spectrometric measurements. “total mass” has been changed to “total particle mass” to make this clearer.

Page 4: Line 1-2, what’s the mass accuracy of the instrument?

The mass accuracy of the instrument was below 1.5 ppm. This has now been clarified in the methods section (p. 4, line 7):

“The mass accuracy of the instrument was below 1.5 ppm, which was regularly checked before the analysis.”

Line 7 – 9, this sentence is vague. More information is needed to clarify how this was done.

This section has been changed as follows (p. 4, line 15):

“The three repeat measurements of the blank filters for both high and low mass range were manually merged to yield four final blank files: low mass range winter, high mass range winter, low mass range summer and high mass range summer. Each of these merged blank files contains all masses from the three repeat measurements as separate data points.”

I hope this makes it clearer. The consequence of this is that if the threshold for blank subtraction for a specific mass was met for any of the three repeat measurements, the peak was removed, i.e. a conservative approach.

Line 11, be specific about the threshold to remove signals and define how noises are determined.

The noise levels differ for each sample and are based on fitting a normal distribution to a histogram of intensities. The sentence has been changed to (p. 4, line 19):

“In the first instance, all ions below the noise level, which was estimated based on fitting a normal distribution to a histogram of intensities, were removed from the spectrum.” to clarify this. Further details about the procedure and the reasoning behind it can be found in the cited paper by Zielinski et al. (2018) cited on p. 4, line 19.

Line 12, “blank subtraction” usually means that all ions were subjected to blank subtraction, but this sentence suggests only the ions less than 10 times of the blank level are removed. This is confusing.

In direct infusion ESI, signal intensities cannot be correlated directly to concentrations. Thus, we have a very conservative approach where we delete peaks from the mass spectrum when we identify a peak with the same exact mass in the blank with 10% or more intensity compared to the sample spectrum. Much more details are given in Zielinski et al. (2018).

Line 20 -21, the formula for DBE calculation has limitations due to the assumptions about element valences. This issue should be clearly stated and the implications on the reported results should be discussed.

The assumption of trivalence for nitrogen has now been explicitly stated (p. 4, line 32). The implications of the valence assumptions are now discussed in the results section (3.2 Aromatic compounds). In

short, the calculated DBE values represent a lower boundary on the DBE due to the assumptions about the valence state.

However, this lower limit is likely to be a better representation of the aromaticity of the compounds than one calculated with taking the higher valency into account since the additional double-bonds added by including the higher valencies are not contributing to aromaticity, ring formation or condensation.

Line 23 – 24, the sentence “If . . .” is confusing. Please be specific.

The sentence has been changed to (p. 5, line 1):

“If there was no peak with a matching composition containing only the lighter isotope or if the intensity ratio of heavier-to-lighter isotope was greater than the natural isotopic abundance, the formula with the next larger mass error was used instead.”

Further information about the process can be found in Zielinski et al. (2018).

Page 5: The Panagi et al. paper is not yet published and unavailable. It is not appropriate to cite it as a source of information used in this paper. Either provide the paper as supplementary or reiterate relevant key points.

This paper is now published and the proper citation has been added.

The meaning of “the residence time of the air masses (or the integrated concentration of theoretical air mass particles)” is not straightforward, needs clarification.

The model releases 1g/s of particles for 3 hours (so  $3600 \times 3 \text{ g} = 10800\text{g}$ ). Snap shots of the particle locations are taken every 15 minutes and then summed up to give the number of particles in each grid box during the past 72 hours so that for areas close to the station, if a particle doesn't move much it could be sighted  $72 \times 4$  times! So, when we say relative residence time, the color scale is denoting whether there are lots or few particles, on a logarithmic scale.

We have changed this sentence accordingly in the caption, which we hope is clearer (p. 9, line 2):

"The colors denote the relative residence time (on a logarithmic scale) of the air masses in each  $0.25^\circ \times 0.25^\circ$  grid box (up to 100m from the surface) during the last 72 hours before arriving at the monitoring station (the model calculates the concentration of theoretical air mass particles in a grid box integrated over time)."

Line 22-24 seems unnecessary, consider to remove.

We have removed these sentences.

There are strange characters shown at Line 27 – 28.

This has been corrected.

Change “off” to “of” on Line 30

Done

Page 7. Line 14. Ref?

The appropriate references have now been added.

Page 8: Line 1-2, waxy biogenic organic aerosol components likely have high H/C, but not all biogenic compounds have high H/C. It is more useful to define the cutoff value of "high H/C"

We agree that particles with biogenic sources do not necessarily have high H/C, we were here specifically referring to primary biogenic plant sources with high H/C. The sentence has been reworded as following to clarify this (p. 9, line 17):

“ The SL H/C ratio is particularly high which may be due to a larger proportion of primary biogenic organic aerosol components from plant sources with a high H/C, such as plant waxes, and a smaller influence of industrial sources or vehicle emissions which is more pronounced in the high pollution sample.”

line 14, what's the basis for claiming that compounds with  $H/C < 1$  and  $O/C < 0.5$  are aromatic? Citing a previous study here without proper context is not sufficient.

Non-alkylated (poly-)aromatic compounds have by definition an  $H/C < 1$ . The  $O/C$  ration is a softer limit but a mono-aromatic with  $> 3$  oxygen groups would be a rather exotic structure. The same applies for PAHs.

Page 10, specify the "low" and "high" values use in describing elemental ratios and discussing chemical meanings.

"High" and "low" are used here to compare the numbers in the table in a relative and qualitative way. The chemical meanings of the elemental ratios are described on p. 10, line 3:

"While the overall  $H/C$  ratio shows whether the sample is more aromatic or aliphatic, the  $O/C$  ratio gives an indication of how strongly oxidised a sample is."

Page 12, 1st paragraph, N also has two valences, so what's the validity of calculating  $X_c$  for N-containing compounds using the given formula?

As mentioned previously, the important factor is the fraction of oxygen atoms in each compound participating in  $\pi$ -bonds. With our current assumption, this number is 0.5 which is true for the nitro group. For organonitrates, this number would be lower, leading to an underestimate of unsaturation using the current assumptions. This would also be the case for reduced nitrogen compounds such as e.g. amines, although the reviewer notes correctly that these are unlikely to be detected in negative mode ESI.

Page 16, line 33, what's the reasoning behind this sentence – "This suggests . . ."? Why does the correlation suggest how the compounds are formed? The authors appear to imply that the N-containing ions detected in this study are representative of "N-containing organics" in aerosol, but this is misleading as negative mode ESI-MS generally biases against reduced nitrogen compounds. Such issues should be articulated throughout the manuscript.

As mentioned earlier, any mass spectrometry method is biased against the compound classes which ionise best with the particular ionisation technique used. ESI negative mode ionisation is specifically sensitive towards oxidised N-compounds, not reduced functional groups such as amines, which ionise very efficiently in positive mode. This has now been clarified at the beginning of section 3.3 (p. 17, line 10).

We agree that the mentioned paragraph might be misleading and have therefore changed this to (p. 19, line 27):

"As stated earlier, the detection mode we used is biased towards oxidised N-containing organics such as organic nitrates, which are known to form predominantly in the gas phase and and nitro compounds, which can be of either primary or secondary origin, with a strong contribution of gas-phase oxidation in the second case. A correlation with particle-phase nitrate is therefore not expected."