Comments by **reviewer #3** 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.

General comments:

This manuscript presents the application of UHPLC/Orbitrap MS to three sets of samples collected in urban locations in China. The observed molecular formula are classified according to the components (CHO, CHON, CHOS, etc.) and overall trends in the abundance and characteristics of these molecular formulas are compared between the three samples. The paper is well written and the results are clearly communicated. I appreciate the careful and detailed break down of trends by compound class. The largest gap that I see is a lack of discussion/consideration for the information provided by the chromatography itself. I recommend publication after the following concerns are addressed.

Response: We thank the reviewer for the comments. We have revised and improved the manuscript according to these comments.

Specific comments:

1. Throughout the manuscript, a comparison is made between overlapping molecular formula. However, no reference to the LC data set is provided. The separation should provide some information on whether the observed molecular formulas actually correspond to the same chemical structure.

Response: Compared to direct infusion in other studies, the UHPLC technique used in this study could separate and concentrate the compounds before they enter the ion source, reducing the ionization suppression and increasing the sensitive of the measurement. We have now added this description in the Sample Analysis section in Page 5, Line 142-147 in the revised manuscript (also see it below). Meanwhile, it can provide additional information of isomers that have the same molecular formulas but different retention time. In the revised manuscript, 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 the negative mode and positive mode, respectively.

"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.”

a. What fraction of the overlapping formulas in Figure 2 (and discussed throughout the document) have the same or very similar retention times in the column?

Response: It is true that compounds with the same molecular formulas may not have the same retention time. Therefore, the Figure 2 is now redrawn (please see the revised Figure 2 below) and the overlapping molecular formulas now refer to the compounds detected in each city with the same molecular formula as well as with 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. Therefore, the changes of the definition of overlapping molecular formulas do not change the main conclusions drawn in the manuscript. Furthermore, the values of the number and peak abundance of the overlapping molecular formulas according to the revised Figure 2 have been updated in the revised manuscript.

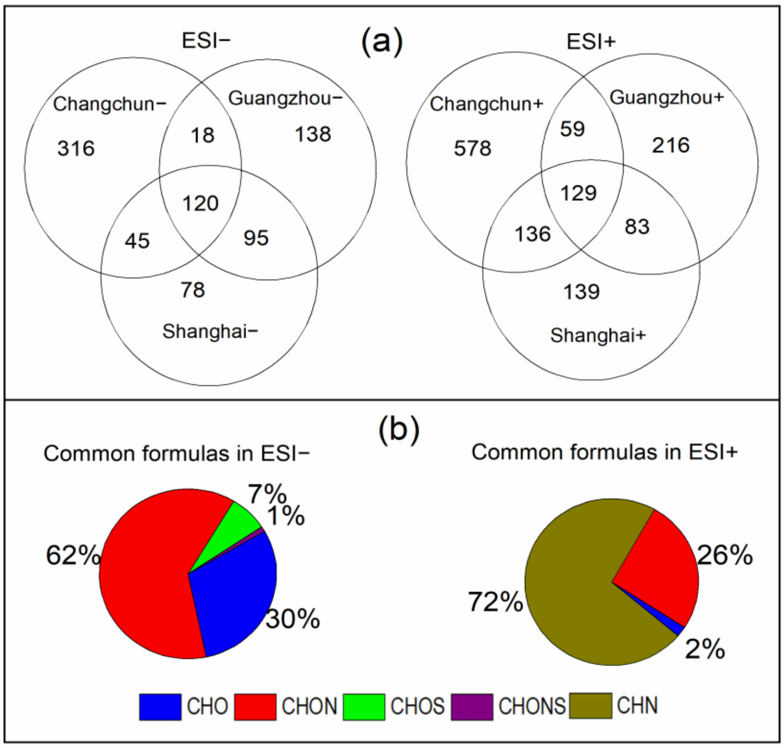

Figure 2. (a) Venn diagrams showing the number distribution of all molecular formulas detected in ESI− and ESI+ for all sample locations. The overlapping molecular formulas refer to the compounds detected in each

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.

b. Possible identities for some compounds are given (e.g. page 10 lines 289-330 and page 11 lines 342-355). How do the retention times of these compounds compare to standards run with the same column settings?

Response: In this study, the possible identities for these compounds are based on their molecular formulas and published data in the literatures. It will be very interesting to check/verify these compounds by adding some standards in future studies. Related discussion has been added in the section of Limitations on Page 18, Line 569-571 as follows:

"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."

2. How clean was the separation? Were multiple ions observed under each chromatography peak? Were there differences in this between the three sample locations? It looks like there are a lot more compounds in the Changchun samples as a whole. If there was more charge competition during ionization (especially in positive ion mode) in specific samples, it would be good to clarify this because you are using the signal to directly correlate to abundance.

Response: 1. Since there were hundreds of different compounds detected in each measurement, it was very difficult to completely separate all these compounds using one UHPLC method. However, as a high-resolution Orbitrap MS was applied in this study, these compounds can be efficiently distinguished by the m/z ratios, even though they had same/similar retention time. 2. Yes, the charge competition during ionization can be different for samples of different mass loadings and organic components. To reduce the uncertainties from charge competition, we set the particle mass concentration in the extract to 600 μg mL^{-1} for all samples (please see Page 5, Line 139-140 in the revised manuscript). In addition, we have now added a discussion about uncertainties caused by using the signal to directly correlate to abundance in Page 6-7, Line 186-193 in the revised manuscript as well as in the section of Limitations (Page 18, Line 555-571) as follows:

"Comparing the peak abundance has been used in UHRMS recent studies (Wang et al., 2017; Fleming et al., 2018; Song et al., 2018; Ning et al., 2019) to illustrate the relative importance of specific types of compounds. However, it should be noted that different organic compounds have different signal responses in the mass spectrometer due to the differences in ionization and transmission efficiencies (Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Kruve et al., 2014). Therefore, uncertainties may exist when comparing the peak areas among compounds. In this work, we assume that all organic compounds have the same peak abundance response in the mass spectrometer.”

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.”

3. The positive ion mode data for Guangzhou and Shanghai are interesting in that they appear to be dominated by (one?) very high abundance peak. The fact that amines can ionize very well in ESI+ is discussed in the manuscript. However, it would be helpful to provide more context/information on these samples. In particular, I suggest including (possibly in the supplemental) the reconstructed MS for Shanghai+ and Guangzhou+ with a zoom in on the lower abundance ions (indicate those CHN+ ions are off scale). I also recommend making comparisons in the CHN+ section both in terms of numbers of chemical formula and in terms of abundances (as is currently provided).

Response: Yes, the organic compounds detected in ESI+ in Guangzhou and Shanghai samples are dominated by several CHN+ compounds. This is probably because that these CHN+ have high concentrations and/or have high ionization efficiencies in the positive ESI mode. To display other ions (CHO+, CHON+, CHONS+ and other CHN+ with low intensity) more obviously, the positive mass spectra figures for Shanghai+ and Guangzhou+ has been modified by inserting a break in the Y-axis (please see the revised Figure 1 below). In addition, more information/discussion related to the chemical formula numbers has been now added in the CHN+ section in Page 13-14, Lines 406-442 in the revised manuscript (also see it below).

“696 CHN+ compounds were detected in Changchun+ samples in ESI+, which is higher than in Shanghai+ (253) and Guangzhou (205). These CHN+ compounds are likely assignable to amines according to previous studies (Rincón et al., 2012; Wang et al., 2017; Wang et al., 2018)”

“The number of CHN+ compounds accounts for 24%, 36% and 30% of the total organic compounds in Changchun+, Shanghai+ and Guangzhou+, respectively, whereas the peak abundance of these compounds accounts for 40%, 71% and 62%, respectively.”

“Moreover, the pie charts show that the majority (83−87% in terms of peak abundance and 72−90% in terms of peak numbers) of these CHN+ compounds can be assigned to mono- and polyaromatics with Xc ⩾ 2.5.”

“Polyaromatic compounds with Xc ⩾ 2.7 are displayed in the lower left corner of the van Krevelen diagram, accounting for 41% in terms of peak abundance (48% in terms of peak numbers) of CHN+ compounds detected in Changchun+, but merely for 9−10% in terms of peak abundance (27−31% in terms of peak numbers) in Shanghai+ and Guangzhou+.”

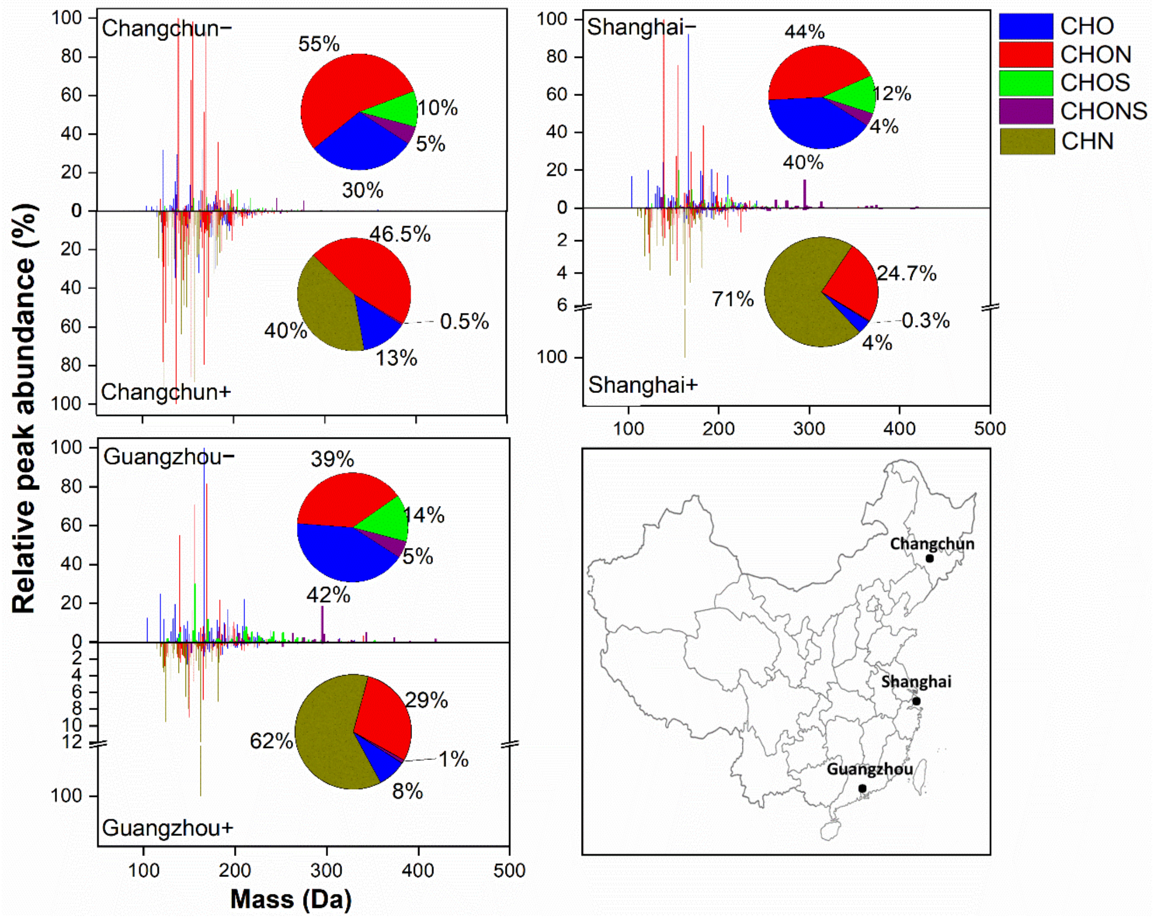

Figure 1. Mass spectra of detected organic compounds reconstructed from extracted ion chromatograms in ESI− and ESI+. The horizontal axis refers to the molecular mass (Da) of the identified species. The vertical axis refers to the relative peak abundance of each individual compound to the compound with the greatest peak abundance. The pie charts show the percentage of each organic compound subgroup (i.e. CHO, CHON, CHOS,

CHONS and CHN) in each sample in terms of peak abundance. The map in the lower right corner shows the locations of these three megacities in China.

4. The conclusion that there is more photochemical aging in the southern locations compared to the more northern location is made throughout the manuscript. However, I would argue that the differences could also be due to more fresh emissions being sampled in the northern location compared to the southern ones. This is supported by, for example, the data in Figure S1 which I think shows similar higher O/C numbers across all three, but more total lower O/C and aromatic compounds for Changchun. I recognize that van Krevelen diagrams can hide some depth (different molecular formulas with the same O/C and H/C). If this is the case here, that should be clarified in the text.

Response: This is a very good point. We have calculated the relative abundance of 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 negative mode. It shows that 31% 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 46% in Shanghai and 51% in Guangzhou. Therefore, we suggest that there is more photochemical aging process in the southern locations compared to the more northern location. This statement is now added in Page 8, line 233-235 in the revised manuscript as follows:

"Furthermore, the relative peak abundance of compounds with O/C ≥ 0.6, which are considered as highly oxidized compounds (Tu et al., 2016), is 31% in Changchun−, and higher in Shanghai– (46%) and Guangzhou– (51%)."

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

We also agree with the reviewer that more fresh emissions (e.g., coal combustion) were sampled in the northern location and this was stated in the Abstract section (Page 2, Line 41-43 in the revised manuscript) as "The degree of aromaticity and the number of polyaromatic compounds were substantially higher in samples from Changchun, which could be attributed to the large emissions from residential heating (i.e. coal combustion) during winter time in Northeast China."

5. What was the photoactive radiation level at each site (were any of them cloudy)? Is there any information on the age of the air mass (back trajectories, wind speed, wind direction, etc.)? The other possible explanations for this trend should be addressed: different source types and different overall age of the OA material (i.e. longer transport for the southern locations).

   Response: The daily solar radiation values (J cm^{-2}) for each city during the sampling dates are now presented in the revised Table S1 in the SI, which were taken from the World Radiation Data Centre. It shows that the solar radiation in the two Southern Chinese cities (Shanghai and Guangzhou) is 994-1329 J cm^{-2}, which is higher compared to 485-841 J cm^{-2} in the Northern city (Changchun). The related discussion is now added in Page 8, line 235-240 in the revised manuscript as follows:

   "The different chemical composition of the samples is probably caused by the rather low ambient temperatures and decreased photochemical processing of organic compounds in Northeast China (indicated by the lower solar radiation in Northeast China, see Table S1), slowing down oxidation processes and leading to a larger number of PAHs, which are mainly emitted from coal burning (Huang et al., 2014; Song et al., 2018)."

   48 hours back trajectories of air arriving at the three cities (Changchun, Shanghai and Guangzhou) during the sampling time is now calculated using the NOAA HYSPLIT model and they are now presented in Figure S1 in the SI (please also see Figure S1 below). It shows that air masses from Northwest of Changchun and Shanghai may affect the aerosol samples in Changchun and Shanghai, respectively, while the air masses from Northeast or North of Guangzhou may affect the aerosol samples in Guangzhou. However, in our study it is difficult to say how much effect the long transport of air masses can make on the aerosol samples. The related discussion is now stated in Page 8, line 240-242 in the revised manuscript as follows:

   "In addition, long-range transport of air masses (see the 48 hours back trajectories in Fig. S1) may have a certain effect on the chemical properties of aerosol samples collected in the three cities."

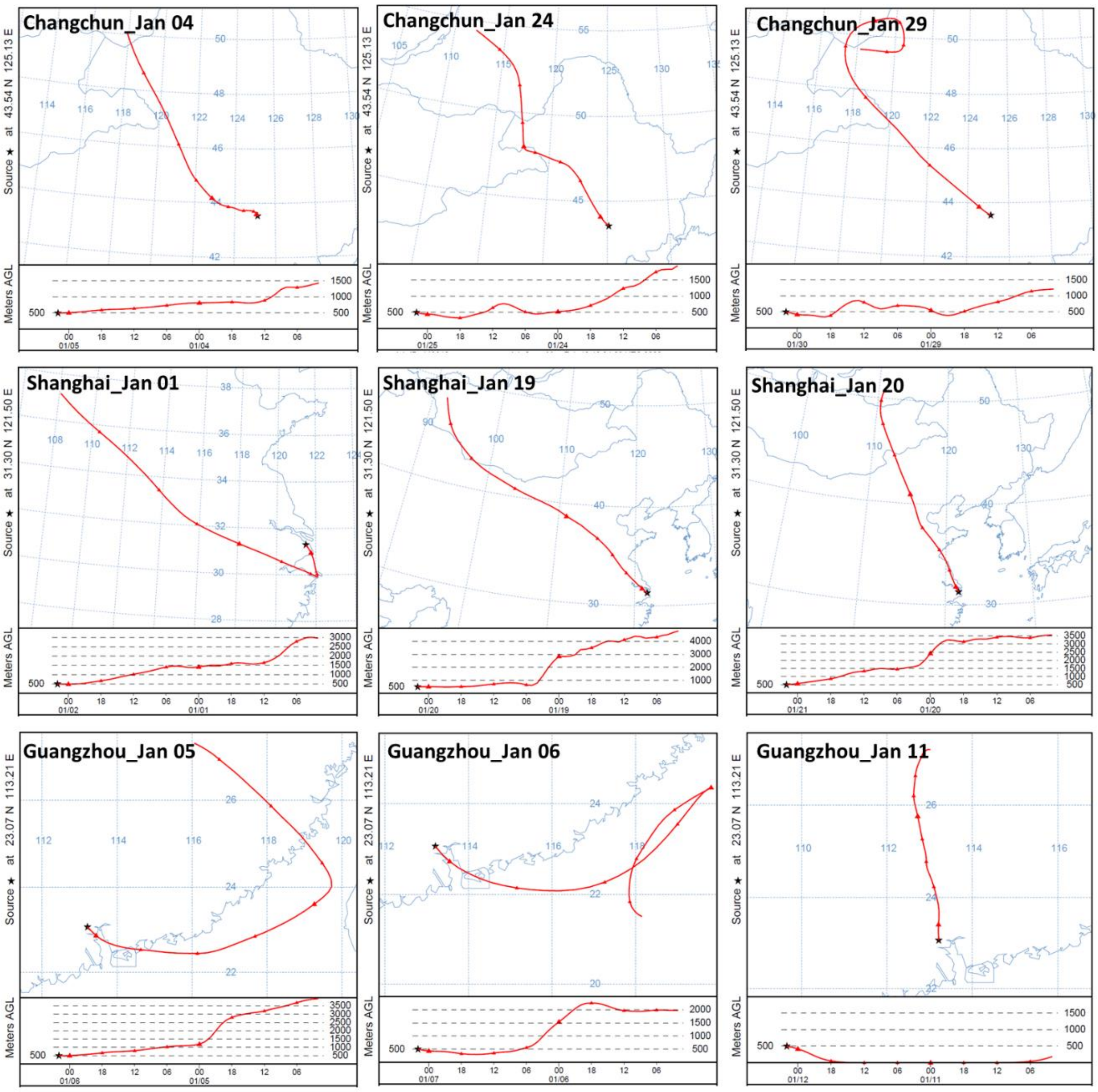

Figure S1. 48 hours back trajectories of air arriving at the three cities (Changchun, Shanghai and Guangzhou) during the sampling time calculated using the NOAA HYSPLIT model (Rolph et al., 2017).

6. For the CHON and CHN compounds, how many contained two or three nitrogen atoms? I can see evidence for a few of them in Figures 4 and S2 but it is hard to quantify. This may be a useful piece of information to include in the supplemental.

Response: In the negative ESI mode, 33-51 CHON- compounds, accounting for 1-17% of all CHON- compounds in terms of peak abundance, were assigned with formulas containing two or more than two nitrogen atoms in the three city samples (this information is now presented in Figure S4 in the SI, also see Figure S4 below). In the positive ESI mode, 140-662 CHON+ compounds (accounting for 42-46% of all CHON+ compounds in terms of peak abundance) and 164-405 CHN+ compounds (accounting for 49-93% of all CHON+ compounds in terms of peak abundance) were assigned with formulas containing two or more than two nitrogen atoms in the three city samples (this information is now presented in Figure S5 and S9 in the SI, also see Figure S5 and S9 below).

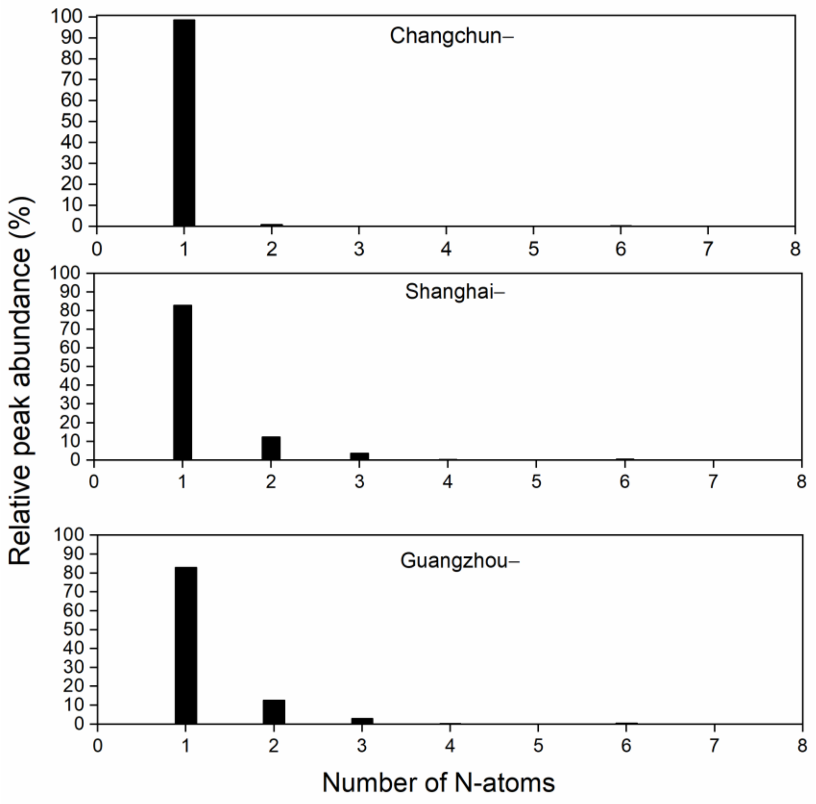

Figure S4. Classification of CHON− compounds into different subgroups according to nitrogen atoms number in their formulas. The y-axis indicates the relative contribution of each subgroup to the sum of peak abundance of all CHON− compounds.

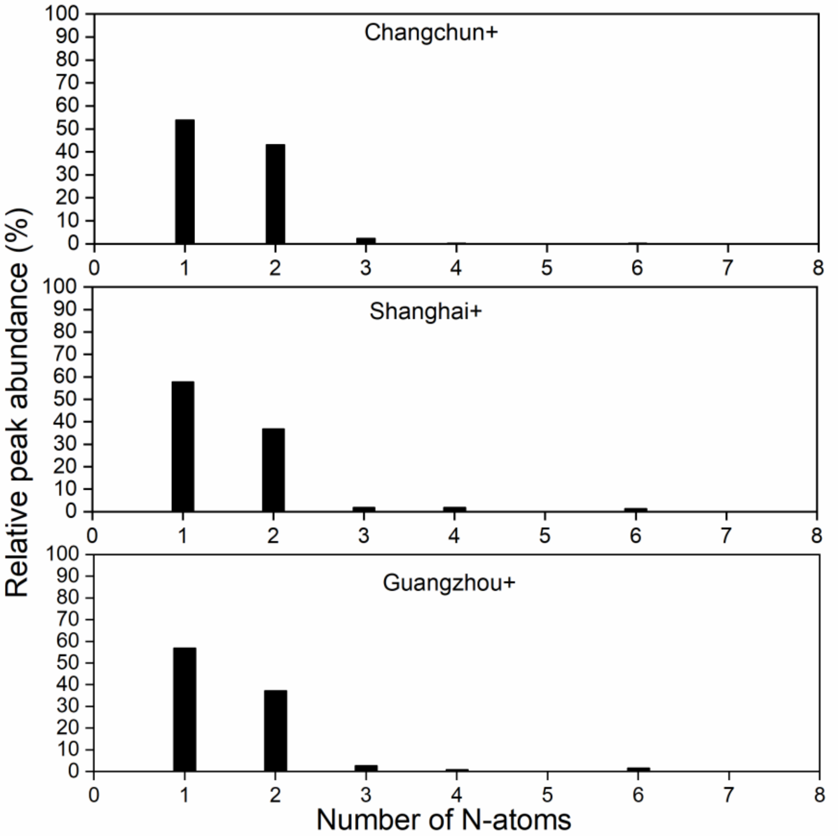

Figure S5. Classification of CHON+ compounds into different subgroups according to nitrogen atoms number in their formulas. The y-axis indicates the relative contribution of each subgroup to the sum of peak abundance of all CHON+ compounds.

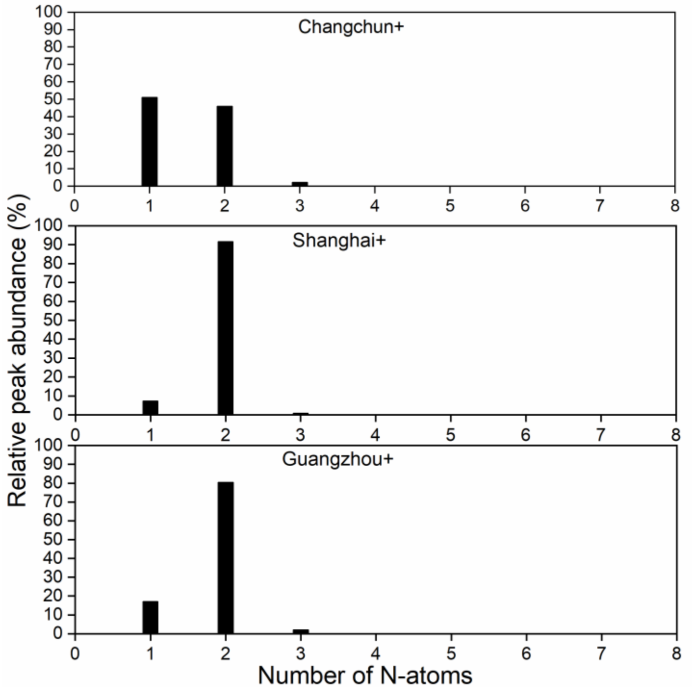

Figure S9. Classification of CHN+ compounds into different subgroups according to nitrogen atoms number in their formulas. The y-axis indicates the relative contribution of each subgroup to the sum of peak abundance of all CHN+ compounds.

7. Throughout the text, differences are stated to be significant but no significance tests are performed. I would recommend re-phrasing to avoid implying a level of analysis that was not carried out.

Response: The word ‘significant’ is now carefully used and the sentences related to ‘significant difference’ is now rephrased throughout the manuscript.