

Response to Reviewer

Specifications on the sampling strategy are not well described. Please describe more thoroughly the sampling protocol. How many samples were collected during the campaign? What duration where the filters sampled? Are any other sampling biases known, for example weekday/weekend, day/night, during precipitation? How was the flow rate controlled, as any fluctuations could cause sizing uncertainty? What kind of inlet was employed, and what is the size-dependent transmission efficiency of the system? Size distributions indicate that you are sampling up to 30-um diameter particles, is it possible for particles of this size to penetrate the inlet and be sampled quantitatively?

Response: We added the following statements. “We assumed an upper limit of 30 μm for the larger particles, in agreement with the specification for the effective cut-point to standard high volume samplers and to facilitate comparison with previous studies (Kavouras and Stephanou, 2002).” and “Seven-day urban size fractionated aerosol samples were collected every second week with a high-volume sampler in Little Rock, Arkansas in winter and early spring of 2013 (February-March). The sampling duration was selected to reduce the effect of sampling biases (i.e. weekday/weekend or day/night) and obtain sufficient quantities for NMR analysis in each particle size range.”

For Figures 1, 2, 4, 6, 7, do the points represent averages? How many samples are incorporated into these points? It is difficult to assess whether the trends that are described are representative without this information, and including some measure of variability. For the size distributions, I suggest adding error bars to represent this variability. For figures 5-7, do the error bars represent standard deviations?

Response: Figure 2 shows a representative set of NMR spectra. Figure 3 4 is also the reference NMR spectra. There are error bars in figures 5,6 and 7. Error bars cannot be added in Figure 1, but information about the variability are given in Table 1 where mean and standard errors are reported..

Section 3.2 provides a wealth of detail regarding the NMR speciation of samples. Is it possible to tabulate these results to qualitatively allow the reader to see the molecules/species that are predominantly found in each size region? Basically, this would involve summarizing Figures 2-4 into a qualitative summary of the trends that are discussed throughout the section.

Response: This information is already provided in Figure 2

3634 – 22 define VPDB

Response: It is defined

2635 – 11 What is the manufacturer/model for the balance? What is the precision of the gravimetric measurement? Were the measurements done in a temperature/RH controlled environment?

Response: The following statement is added: “A microbalance (Mettler-Toledo, Model: AB265-S) with precision of 10 μg was used in a temperature-controlled environment”

3636 – 11 What is a Lundgren diagram?

Response: A reference is added

3636 – 18 Please comment on the appropriateness of MMAD calculations for a system with only 5 size stages. You might want to consider using the bin midpoint when describing size distributions. For example, is a MMAD of 1.1-um compared to 1.3-um statistically meaningful?

Response: Indeed, we considered the range of particle sizes for each stage in the discussion of the results by only describing large changes in the MMAD that cross into different stages.

3639 – 16+17 ‘two’ is written out, while ‘1 to 2’ is numerical. Please be consistent through the text.

Response: It is corrected

3639 – 16 The statement “H/C values higher than. . . an aromatic signature” probably needs a citation.

Response: A reference is added.

3642 – 23 The use of ‘tentative’ is strange. Is there doubt that the assigned peaks are not correct?

Response: The word “tentative is eliminated.

3646 – 22 It might be beneficial to the reader to add a box to Figure 6 to highlight the samples that are predominantly biological.

Response: An oval shape showing the size fractions, in which a strong signature of biological (pollen) origin was quantified, is added.

3647 – 15 The reference to Eq.5, should this be Eq.4?

Response: It is corrected.

3649 – 8 So, is the separation of urban and biological particles possible if no size information was available? For examples, if someone was using bulk filters (with no size cuts), would NMR be able to provide the relative distribution of carbon mass between biological and urban sources? If so, this should be highlighted!

Response: Qualitatively, the presence of sugars indicated the presence of biological aerosol. On the other hand, quantitatively, the values of the $H-C-O/\Sigma(H-C-)$ and $H-C-C=O/\Sigma(H-C-)$ ratios would be influenced mostly by the fraction with the highest concentrations, which in our case was the fine and ultrafine particles. Conclusively, the existing framework as it is described by Decesari determines the most predominant source of organic aerosol.

Table 1 What is the meaning of a molar ammonium/sulfate ratio greater than 2. Is there significant excess ammonium and what is it associated with?

Response: Values of the molar ammonium/sulfate ratio greater than 2 indicate that the amount of ammonium is sufficient to neutralize SO_4^{2-} and a fraction of NO_3^- (depending on NO_3^- levels), as we described in the manuscript (end of last paragraph in Section 3).

Figure 1 Can you comment on the minimum observed in H/C at approximately 2-um?

Response: Addressed in previous comment requiring a reference for the low H/C molar ratio.

Figure 1 I would suggest using an x-axis range of 0.1-30 μm . Plotting to 0.01 seems unreasonable.

Response: It is fixed.

Figure 2 Can you comment on the peak at 2.25 ppm? This seems to dominate the spectra in the middle size ranges but I don't believe it is discussed in the text.

Response: At this point, we cannot attribute the peak at 2.25 ppm to a specific chemical compound. The abundance of the peak decreases as particle size increases.

Figure 4 What causes the broadening of the NMR peaks when compared to the reference spectra? This is especially evident for the glucose cluster at 3.4ppm.

Response: Figure 4e and f shows the segments of the reference spectra for the four compounds. There are reference spectra of individual compounds that are merged rather than the NMR spectra of a solution composed of the four compounds. The broadening of the baseline in atmospheric samples may be associated with the presence of organic compounds with low concentration. We revised the statement as follows to clarify this point: "The spectra are characterized by a combination of sharp resonances of the most abundant organic species and convoluted resonances of many organic compounds present at low concentrations." and "Fig. 4e and f show the combination of individual NMR reference spectra for glucose (HMDB00122), sucrose (HMDB00258), fructose (HMDB00660) and levoglucosan (HMDB00640) retrieved from the Human Metabolome Database (HMDB) NMR databases (Whishart et al., 2009)."

Figure 7 How many points are incorporated in the 0-200 nmol/m³ range for panel a? If you fit with only these points, do you get a similar linear fit (slope), i.e., are the two points at high WSOC dominating the good fit and determined slope?

Response: By excluding the two highest points (that represent particles with diameter less than 0.96 μm), the slope changed by 6% and the CV(RSME) increased to 1% which is still excellent.