

Interactive comment on “Functional characterization of the water-soluble organic carbon of size fractionated aerosol in the Southern Mississippi Valley” by M.-C. G. Chalbot et al.

Anonymous Referee #2

Received and published: 24 April 2014

Summary:

Size-segregated aerosols were collected using a high-volume impactor sampler in Little Rock, Arkansas. Samples were collected over a short period in the winter/spring of 2013. A thorough analysis of these samples was performed, including bulk WSOC, ¹³C isotopes, and proton-NMR spectra. Supporting data was used from the IMPROVE network that included meteorological parameters, OC/EC concentrations, and common inorganic ion concentrations. Analysis showed a clear chemical segregation between coarse and fine-mode particles, with a mixture of biomass burning and anthropogenic carbon dominant in the fine mode and potentially biological aerosols (pollen) in the

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coarse mode. While this conclusion is certainly not novel or unexpected, the analysis of HNMR spectra by attributing specific compounds to strong resonant peaks for each size fraction is valuable to the community. Particularly, sugars from biogenic aerosol are tentatively assigned ‘fingerprints’ to the often-cited Decesari [2007] source apportionment plot (Figure 6). Carbon isotope analysis is also a nice contribution to the literature. These aspects warrant publishing in ACP with minor revisions for clarification and emphasis.

Major Comments:

1.) 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 were 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- μ m diameter particles, is it possible for particles of this size to penetrate the inlet and be sampled quantitatively?

2.) 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?

3.) 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.

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Minor comments:

Page – Line

3634 – 22 define VPDB

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?

3636 – 11 What is a Lundgren diagram?

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?

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

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

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

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

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

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!

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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?

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

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

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.

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.

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?

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