

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 #1

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This paper presents the results from the analysis of size-segregated quartz filter samples collected in Little Rock, AR in the winter and spring of 2013. The filter samples were analyzed for water-soluble organic carbon (WSOC), carbon 13 isotope ratios, and total water-soluble extract. The filter extracts were additionally analyzed by ^1H -NMR (proton-nuclear magnetic resonance) to determine the non-exchangeable protons for five different functional groups. The functional characteristics and sources of WSOC for the various particle sizes were presented and discussed.

Organic aerosols are a hot topic in atmospheric chemistry. Within that WSOC is of even more interest since one of the main sources of WSOC is secondary organic aerosol

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formation, a process which is still not well understood. This paper is trying to better understand the characteristics and sources of WSOC. Many in the atmospheric community would be interested in this paper.

Overall, this is a good paper. My main concern is that the authors make some assumptions about common knowledge, which I think can make it harder for the reader to follow the paper and distract from the great analytical work done by the authors. For example, the section that discusses the various elemental ratios has no references or typical values provided to give the reader context. Only the values determined in this work are presented. Most of these ratios, such as K^+/K and K/Fe , are not routinely used in aerosol work. In the section where some organic compounds are being identified in the ^1H -NMR spectra, the compound trigonelline is identified. However, this compound is not routinely measured, yet there is no discuss about its sources or prevalence in the atmosphere. This is all outlined in more detail below, along with other specific comments that need to be address before this paper can be considered for publication.

Specific Comments: Abstract Page 3630, Line 1 – There should be a hyphen between water and soluble

Page 3630, Line 11 – Suggest adding (^1H -NMR) after resonance since after this the abbreviation is used throughout the abstract

Page 3630, Line 17 – Should methanosulfonate be methanesulfonate?

1.Introduction Page 3631, Line 21 - There should be a hyphen between water and soluble

Page 3631, Line 25 – To be in chronological order the Timonen et al. reference should come first

Page 3632, Line 19 – Should methylsulfonate be methanesulfonate?

Page 3632, Lines 20-21 – I am not sure I understand the part of the sentence from

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polluted sector on. Is it that a factor for the polluted sector and additional contribution from the clean sector were found? This needs to be clarified.

Page 3632, Line 24 – Suggest changing originated to originating

Page 3632, Line 29 – I am not sure I understand what statistical area means in reference to the Little Rock metropolitan area

2.Materials and methods 2.3.Analysis Page 3634, Line 18 – Suggest adding a the before University

Page 3634, Line 19 – The abbreviation for the chemical formula used is not defined

Page 3634, Line 21 – The abbreviation CN is not defined. Also the abbreviations for the chemical formulas used are not defined.

Page 3634, Line 22 – The abbreviation VPDB is not defined

Page 3635, Line 1 – Believe sample and standard should be subscripted

Page 3635, Lines 4-5 – The second thermal optical can be removed

Page 3635, Line 9 – Suggest changing remaining filters were to remaining portion of each filter was. Also, should ultrasound be ultrasonic? Lastly, the abbreviation for the chemical formula used is not defined.

Page 3635, Line 10 – Suggest adding an a before 0.45

Page 3635, Line 11 – Suggest changing transferred in to transferred into

Page 3635, Lines 14-15 - The abbreviations for the chemical formula used are not defined

Page 3635, Line 15 – Suggest changing added in to added into

Page 3635, Line 17 – The abbreviation BBFO is not defined

Page 3635, Line 22 – The abbreviation ACD is not defined

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2.4.Calculations Page 3637, Line 8 – In equation 4 the second α_4 should be α_5

3.Results and discussion Page 3638, Lines 10-11 – OC/EC ratios are site and source specific. Therefore, I am unsure how the authors know that their ratio indicates biomass and coal combustion since I believe they were just sampling regional emissions of both of these.

Page 3638, Lines 11-14 – The ratios of K^+/K , K/Fe , and mineral elements Al, Si, and Ca the authors mention are not ratios routinely examined in aerosol measurements. Since no literature values or references are provided, it is hard to put these into context. How do the authors know their ratios are similar to those previously observed in the region?

Page 3638, Lines 14-15 – The authors mention that the high molar ratio of ammonium to sulfate suggests complete neutralization of sulfate and nitrate. The ratio is over 2, which suggests a non-acidic aerosol. But nitrate is not even included in this. Would it be better to determine and discuss the molar ratio of ammonium/(nitrate + sulfate)?

3.1.Size distribution Page 3638, Line 18 - There should be a hyphen between water and soluble

Page 3639, Lines 1, 2, and 7 – The units should be $\mu g C/m^3$

3.2.Functional characterization Page 3641, Line 6 – Suggest adding the word range after 1.8ppm

Page 3641, Line 8 – Suggest changing proton to protons

Page 3641, Line 9 – A period is missing at the end of the sentences

Page 3641, Lines 12-14 – The authors mention that long-chain alkanolic acids, aldehydes, and alkanes were particles with diameters less than 0.96 μm . Is this referring to the samples analyzed by the authors? It is not clear based on the sentence before it and the fact a reference is provided.

Page 3641, Lines 22-23 – Should this line indicate that these species were not ob-

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served in the coarse particles? The plots referred to in Figure 2 are for the larger size particles and the previous sentence is discussing coarse acetate and formate observed in soil dust.

Page 3642, Line 8 - There should be a hyphen between water and soluble

Page 3642, Line 14 – I believe it should be (Fig. 2a-c)

Page 3642, Lines 16-17 – I believe it should be Fig. 4a-b and c-d

Page 3642, Line 26 – There should be a ppm after 3.77 and 3.91

Page 3643, Line 17 – Suggest changing diameter to diameters

Page 3643, Line 23 – I am not sure I understand the phrase not visible of solvent residue. Is it trying to indicate that the H-3 at 4.64 ppm was not visible due to interference from solvent residue?

Page 3643, Line 24 – Suggest changing of ultrafine and fine 1H-NMR to of the ultrafine and fine particle 1H-NMR spectra

Page 3643, Line 28 to Page 3644, Line 3 – I am not sure I am completely following the discussion in these lines. The samples analyzed by the authors were not heavily impacted by biomass burning, it was more background biomass burning that was sampled. So then what does the discussion of H-C-X have to do with the determination of protons from levoglucosan? Is it that the previous assignment was wrong?

Page 3644, Line 15 – The authors mention that trigonelline was identified in the NMR spectra. Could the authors tell us more about this compound? It is not commonly measured in aerosol samples. So a mention of its prevalence in atmospheric samples could give the reader a better context.

3.3.Source reconciliation Page 3645, Line 26 – I believe it should be Table 2 that is referenced

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Page 3646, Line 1 – Suggest adding the word different before OC

Page 3646 Line 23 through Page 3647, Line 12 – I believe this section is referring to Table 3, but at no point in the text is Table referenced

Page 3646, Line 29 – Suggest changing WSOC that can be interpreted by the condensation to WSOC, that can be interpreted as a result of condensation

Page 3647, Line 6 – Suggest changing an MMAD to a MMAD

3.4.WSOC reconstruction Page 3647, Line 23 – The slope mentioned in the text is not the same as indicated in Figure 7a

Page 3647, Line 24 – Suggest changing an CV(RMSE) to a CV(RMSE)

4.Conclusions Page 3648, Line 16 – Suggest changing characteristic of water soluble to characteristics of water-soluble

Page 3648, Line 20 – Suggest changing and water soluble to and the total water-soluble

References Page 3651, Line 1 – I believe this is an extra line and can be removed

-The Decesari et al., 2011, Miyazaki et al., 2009, and Pietrogrande et al., 2013 references are missing from the list.

Tables Table 1 -The units for elemental carbon should be ug C/m3 -I believe the range for temperature and pressure is being shown in parentheses, but it is not indicated in the caption or column heading

Table 2 -In caption, suggest adding the word Mean before Particle -The units for WSOC should be ug C/m3

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