Response to Reviewer #1

Abstract Page 3630, Line 1 – There should be a hyphen between water and soluble
Response: It is corrected

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

Page 3630, Line 17 – Should methanosulfonate be methanesulfonate?
Response: It is corrected

Page 3631, Line 21 - There should be a hyphen between water and soluble
Response: It is corrected

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

Page 3632, Line 19 – Should methylsulfonate be methanesulfonate?
Response: It is corrected

Page 3632, Lines 20-21 – I am not sure I understand the part of the sentence from 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.
Response: We revised the statement as follows: "methanesulfonate (MSA), amines, clean marine samples, polluted air mass and clean air masses."

Page 3632, Line 24 – Suggest changing originated to originating
Response: It is corrected

Page 3632, Line 29 – I am not sure I understand what statistical area means in reference to the Little Rock metropolitan area
Response: The term statistical refers to the definition of metropolitan area by the US Census that has been adapted by the US EPA. Because the term is only used in the US, we eliminate it.

Page 3634, Line 18 – Suggest adding a the before University
Response: It is corrected

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

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

Page 3634, Line 22 – The abbreviation VPDB is not defined
Response: It is corrected

Page 3635, Line 1 – Believe sample and standard should be subscripted
Response: It is corrected

Page 3635, Lines 4-5 – The second thermal optical can be removed
Response: It is corrected

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.
Response: It is corrected

Page 3635, Line 10 – Suggest adding an a before 0.45
Response: It is corrected

Page 3635, Line 11 – Suggest changing transferred in to transferred into
Response: It is corrected

Page 3635, Lines 14-15 - The abbreviations for the chemical formula used are not defined
Response: It is corrected

Page 3635, Line 15 – Suggest changing added in to added into
Response: It is corrected

Page 3635, Line 17 – The abbreviation BBFO is not defined
Response: It is corrected

Page 3635, Line 22 – The abbreviation ACD is not defined
Response: It is corrected

Page 3637, Line 8 – In equation 4 the second alpha4 should be alpha5
Response: It is corrected

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.
Response: The conclusions relies on the analysis of ten years of PM2.5 chemical speciation data from the same site and the source apportionment using positive matrix factorization. This analysis has been published last year at Atmospheric Chemistry and Physics and it is cited in the manuscript (Chalbot et al.,2013a). To clarify this point, we revised the statement as follows: "The OC/EC ratio (4.58 ± 1.06) was comparable to those observed in the same region for the 2000-2010 period (Chalbot et al., 2013a) that identified biomass burning and traffic as the most important sources of carbonaceous aerosol in the region."

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?
Response: In the revised manuscript, we provide additional information on soluble potassium being a tracer of biomass burning and the range of the K/Fe values. New references are also cited.

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)?

Response: This is true. We eliminated the discussion about nitrate.

Page 3638, Line 18 - There should be a hyphen between water and soluble
Response: It is corrected

Page 3639, Lines 1, 2, and 7 – The units should be ug C/m3
Response: It is corrected

Page 3641, Line 6 – Suggest adding the word range after 1.8ppm
Response: It is corrected

Page 3641, Line 8 – Suggest changing proton to protons
Response: It is corrected

Page 3641, Line 9 – A period is missing at the end of the sentences
Response: It is corrected

Page 3641, Lines 12-14 – The authors mention that long-chain alkanoic acids, aldehydes, and alkanes were particles with diameters less than 0.96 um. 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.
Response: It refers to previous studies. We revised the statement as follows: "It was previously observed that long chain (C_6-C_{30}) *n*-alkanoic acids, *n*-aldehydes and *n*-alkanes accumulated in particles with d_p < 0.96 μm (Kavouras and Stephanou, 2002)."

Page 3641, Lines 22-23 – Should this line indicate that these species were not observed 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.
Response: We revised the text as follows: "These species were observed in the coarse fraction (Fig. 2e-f) but not in fine and ultrafine particles (Figs. 2a-c)."

Page 3642, Line 8 - There should be a hyphen between water and soluble
Response: It is corrected

Page 3642, Line 14 – I believe it should be (Fig. 2a-c)
Response: It is corrected

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

Page 3642, Line 26 – There should be a ppm after 3.77 and 3.91
Response: It is corrected

Page 3643, Line 17 – Suggest changing diameter to diameters
Response: It is corrected

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
Response: It is corrected

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?
Response: The discussion for H-C-X is not associated with the detection of levoglucosan. We separated the test in two paragraphs.

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.
Response: We added additional discussion on the presence of trigonelline on the leaves of oak trees, the prevailing type of trees in the monitoring areas and its detection in pollen particles at the study area. New references are cited.

Page 3645, Line 26 – I believe it should be Table 2 that is referenced
Response: It is corrected

Page 3646, Line 1 – Suggest adding the word different before OC
Response: It is corrected

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
Response: It is cited

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
Response: It is corrected

Page 3647, Line 6 – Suggest changing an MMAD to a MMAD
Response: It is corrected

Page 3647, Line 23 – The slope mentioned in the text is not the same as indicated in Figure 7a
Response: It is corrected

Page 3647, Line 24 – Suggest changing an CV(RMSE) to a CV(RMSE)
Response: It is corrected

Page 3648, Line 16 – Suggest changing characteristic of water soluble to characteristics of water-soluble
Response: It is corrected

Page 3648, Line 20 – Suggest changing and water soluble to and the total watersoluble
Response: It is corrected

Page 3651, Line 1 – I believe this is an extra line and can be removed
Response: It is corrected

The Decesari et al., 2011, Miyazaki et al., 2009, and Pietrogrande et al., 2013 references are missing from the list.
Response: They are included in the revised manuscript.

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
Response: It is corrected and the caption is modified to accurately describe the values for meteorological and air pollution parameters.

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

Response to Reviewer #2

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. Figur3 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/Σ(H-C-) and H-C-C=O/Σ(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 SO42- and a fraction of NO3- (depending on NO3- 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 um. 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.