

***Interactive comment on “Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry” by A. S. Wozniak et al.***

**A. S. Wozniak et al.**

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The authors would like to thank the referees for their helpful and insightful reviews and comments and their suggestions provided, which have resulted in significant improvements in the revised manuscript.

Referee 1 Overall Comment This paper is generally well written, with appropriate citations, figures, and tables. The abstract also is adequate. My major concerns (detailed subsequently) are that the paper is probably better suited for a journal focused on

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analytical chemistry and that the limited conclusions are based on mostly qualitative analysis of one sample in each of the two locations.

General Comment I am very concerned about the use of one sample from each location to garner any conclusions at all about the utility of this technique and its output. In my opinion, the authors should focus this paper more on technique development (specifically on extraction efficiencies and an increased number of calibration samples). That would make it more suitable for publication in an analytical chemistry journal. Sample analysis from the ambient atmosphere could then be addressed more quantitatively in a future manuscript. With unknown extraction efficiencies and such, it is not clear how much this manuscript as it now stands really tells us about the nature of WSOC in ambient particulate organic matter.

Authors Response: This manuscript provides detailed molecular characterization of two aerosol WSOC samples that provide information that have specific implications for aerosol WSOC and general implications for aerosol research. The two samples analyzed here, though collected at two different sites and times, show highly similar patterns in the types of elemental formulas that are present in the aerosol water-soluble organic carbon (WSOC) component (please refer to Figures 1, 2, and 3). The similarity of these samples actually makes them replicates of a sort, and suggests that the WSOC component of aerosols may have a similar, general origin. While we agree with the referee that more replicates would be desirable, the small number (2) does not in our opinion negate the value of this study, which sought to show both proof-of-concept and provide initial results on the detailed chemical nature of aerosol WSOC. In addition, the data from these two samples and the implications of the findings and interpretations, while qualitative in nature, help to identify a valuable and fruitful avenue for future research (e.g., in identifying BC, SOA compounds, characterizing ambient aerosols under varying environmental conditions, etc.) for better understanding the origins and composition of aerosol OC and WSOC. We also note that more detailed publications of the temporal and spatial variability in WSOC characteristics by our group are an-

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anticipated as part of a much larger spatial and temporal study; however, for purposes of the initial proof-of-concept and demonstration of the application of ESI FT-ICR MS to aerosol and aerosol WSOC studies, we chose to limit the number of samples analyzed to these samples from two different sites (and which we further note yielded thousands of data points from the ESI FT-ICR MS work alone).

As stated in the manuscript, ESI FT-ICR MS is a qualitative analysis, and quantitative information on the mass spectra is simply not possible to obtain at this time. While quantitative information on the absolute abundances of individual compounds would be ideal, the type of ultrahigh-resolution information obtained by ESI FT-ICR MS simply can not be obtained by an alternative quantitative method. However, this type of ultrahigh precision characterization information will presumably serve to inform both more targeted and more quantitative studies and analyses for future work.

Since the initial submission of this manuscript, WSOC extraction using the same method has been repeated on material remaining from the aerosol samples, and these data are reported in the revised manuscript along with OC and BC data for the aerosol samples (see section 4.1, page 10, and new Table 1 of revised manuscript). As stated in the initial and revised manuscripts (see section 2.3, page 7-8 of revised manuscript), based on previous studies of dissolved organic matter extractions, we estimate the recovery of WSOC to be between 42 and 60% of the carbon after C18-extraction and re-elution (Louchouart et al., 2000; Kim et al., 2003a).

Finally, on the basis of 1) its relevant subject matter and 2) the papers that are routinely published by Atmospheric Chemistry and Physics, this manuscript appears to fall within the aims and scope of the journal as stated on the Atmospheric Chemistry and Physics website (<http://www.atmospheric-chemistry-and-physics.net/>). As a result, we feel that this manuscript is actually ideally suited for ACP. In addition, the manuscript provides important initial findings on the development of a potentially powerful new analytical technique (ESI FT-ICR MS) for characterizing the organic composition of aerosol water soluble organic carbon (WSOC)), and for the possible primary and secondary sources

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of the soluble, and more mobile, aerosol organic phase. ESI FT-ICR MS provides ultrahigh precision molecular information that will presumably be of significant benefit to the atmospheric organic geochemical community.

Specific Comments: 1. Page 6541, do aerosols not also affect the radiative balance of the Earth by absorbing outgoing planetary longwave radiation?

Authors Response: We thank the referee for this comment, which is correct. There is indeed an aerosol-outgoing longwave radiation climate effect. The manuscript now adds language acknowledging this effect (section 1, p. 2 of revised manuscript).

2. Page 6543, have any comparisons been done comparing the BC measured using this technique and other techniques (such as an aethalometer or measuring EC using a thermal-optical technique)? That would certainly lend credence to their characterization of some of the WSOC as being BC. It would also allow for a comparison of total BC to that which is water soluble (as is done with WSOC vs. OC).

Authors Response: Because ESI FT-ICR MS is not a quantitative technique, no direct comparisons can be made between this technique and any other technique. However, we now have BC data for the total aerosol samples that have been added to the revised manuscript. BC of the total aerosol component in both samples was measured using a chemo-thermal oxidation method (CTO-375; Gustafsson et al., 1997). BC was present in both samples at low levels ( $\%BC = 100 \cdot BC/OC = 2\%$  for the VA sample, 5% for the NY sample). The CTO-375 method measures only highly condensed BC and in a recent interlaboratory BC methods comparison of several reference materials consistently showed lower levels of BC compared to chemical and thermal-optical methods (Hammes et al., 2007). Thus, these BC estimates are likely conservative estimates of the total aerosol BC content in these samples. Masiello (2004) speculated that in contrast to the CTO-375 method, ultra-high resolution mass spectrometry is able to detect the full range of BC materials. The small number and peak magnitudes of identified BC elemental formulas indicates that only a small portion of the total aerosol BC is

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water-soluble.

These new results are now reported along with OC and WSOC data and OC, WSOC, and BC methodology (see section 2.2, page 6 for methodology; section 4.1, page 10 and section 4.5, page 14 for discussion, and new Table 1 of revised manuscript).

3. Page 6545, are there any effects of the acidification and subsequent neutralization of the sample as described in the experimental/analytical section?

Authors Response: This comment is similar to specific comments #2 and 3 from referee #2 below. Please refer to our response to these comments below.

4. Page 6546, what are the bases for the O/C, H/C, etc. ratios used for elimination of calculated molecular formulae?

Authors Response: The rules used for eliminating calculated molecular formulae are based on similar rules reported in Koch et al., 2005 and Kujawinski and Behn, 2006. The molecular formula calculator outputs molecular formulae that match the observed m/z data without regard for whether the molecular formulae are chemically or geochemically logical. These conservative rules are designed to eliminate molecular formulae unlikely to be observed in nature.

The manuscript now cites the work of Koch et al., 2005 and Kujawinski and Behn 2006 as the basis for these rules (see section 3.1, page 9 of revised manuscript).

5. Page 6547, by ignoring the m/z less than 223, are the authors asserting that compounds at these m/z are not present? Or just that they are unable to see them due to extraction efficiencies? This m/z cut-off, for example, would eliminate pinic acid as a WSOC constituent. This harkens back to my general point about the need for more quantitation to support the conclusions.

Authors Response: In fact, we did not wish to assert that compounds at m/z less than 223 were not present in our WSOC samples. These compounds are simply not detected by ESI FT-ICR MS. There are two reasons for this. The main reason is due to

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the ICR cell. Low  $m/z$  peaks have very high frequencies, so it is difficult to increase these ions to sufficient amplitude so that they induce a high enough current onto the detector plates to get a signal. The second reason is the quadrupole, where ions of a specified  $m/z$  range are allowed to pass through before being accumulated in the hexapole before being transferred to the ICR cell. Our samples were analyzed in broad-band mode, meaning we used a very wide  $m/z$  range (100–2000). Ions below 223 are discriminated against due to the low mass end of the quadrupole efficiency. As a result, we use this  $m/z = 223$  as the starting point for our spectra. This  $m/z$  cut-off is likely to eliminate many WSOC compounds; however, as stated above, these analyses are not intended to be quantitative. While these analyses may miss these low molecular weight compounds, they provide invaluable, ultrahigh resolution, qualitative information on the higher molecular weight portion of aerosol WSOC, a previously overlooked portion of aerosol WSOC. Another technique, such as LC-MS, could be used in conjunction with ESI FT-ICR MS to detect these low MW compounds, albeit not at the same ultra-high resolution, but these analyses are not within the scope of this manuscript.

We have added a sentence to the manuscript explaining why compounds at  $m/z$  less than 223 are not present in our samples (see section 3.1, page 10 of revised manuscript).

6. Page 6550, in the Van Krevelen plots there is certainly a good deal of overlap between the characteristic aerosol types (the ovals in Figure 3). Given that, how much does this analysis really tell us about the WSOC that made it through the extraction procedure?

Authors Response: Significant information and insight can actually be gleaned from the van Krevelen diagrams and their analysis. van Krevelen plots are an extremely useful method of visualizing thousands of data points in order to learn more about the entire sample without having to examine each individual molecular formula. In this instance, the van Krevelen plots are very instructive in terms of characterizing high molecular weight aerosol WSOC. First, the van Krevelen plots tell us that the

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molecular formulas of compounds present in aerosol WSOC are quite heterogeneous and do not fit easily into any traditional geochemical classes of compounds. Second, these plots indicate that sulfur containing compounds appear to have higher H/C and O/C ratios than nitrogen containing and C-H-O compounds that make it through the extraction procedure. Third, they provide evidence that these sulfur containing compounds may be organosulfate compounds suggested in previous studies (Romero and Oehme, 2005; Gilardoni et al., 2007) providing a line of evidence that organosulfate compounds (as opposed to condensed sulfurous hydrocarbons for example) may be common components of aerosol WSOC. Fourth, the plots indicate that tannin- and cellulose-like compounds from terrestrial plant biomass are not identified in these samples, and condensed hydrocarbons are only minor components of aerosol WSOC in these samples. Finally, they further tell us that proteins are not major components in our samples. Thus, while there is overlap in the characteristic aerosol types (this is not unexpected), the van Krevelen diagrams are extremely useful in characterizing the elemental distributions of molecular formulas in our samples.

7. Page 6552, the radiocarbon analysis seems out of place. Either expand it (techniques, analysis, implications) or get rid of it.

Authors Response: This comment is similar to comment #8 from referee #2 below. Please refer to our response to that comment below.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6539, 2008.

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