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Atmospheric
Chemistry
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Discussions

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 2: General comments: Wozniak et al. describe the application of ultrahigh resolution mass spectrometry to water soluble aerosol organic matter collected from New York and Virginia. I am concerned that the conclusions drawn here are based on

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the data from only two samples and that there are too few discussions of the limitations of this small data set. Nonetheless, these preliminary results point to some interesting features of WSOC and should serve as a good foundation for more detailed study. The manuscript is generally well-written but the authors should be careful with some of their statements to adhere to precise language and correct usage (described below). The authors should revise the manuscript according to the specific comments but I see no reason why the work should not be published.

Authors Response: This referee shared some of the same concerns as referee #1 regarding the sample size and limitations of the dataset – we thank them for their comments and suggestions. These same issues were addressed above in our response to Referee 1’s general comments, which we hope Referee 2 finds satisfactory.

Specific comments: 1. Abstract (and many other places that follow): The authors appear to equate “peaks”; from the mass spectrum with “compounds”. It is hard to tell if the authors mean that one peak corresponds to one compound or whether they recognize that one peak corresponds (possibly) to a group of compounds. The authors should be very clear in their presentation to indicate that multiple compounds can co-occur at the same peak in the FT-ICR mass spectrum. Although an elemental formula can often be identified due to the ultrahigh resolution of the FT-MS, this elemental formula has many possible structural isomers which cannot be resolved by this technique. In general, the authors should draw a distinction between “peaks”, “elemental formulas” and “compounds” so that the limitations of the analysis are clear.

Authors Response: The referee’s point is a good one. In our analyses, we assign a molecular formula to nearly every peak in the mass spectrum. This formula does not, however, correspond to a structure. There are any number of structures that could be assigned to any given formula, and it is likely that each molecular formula represents a number of structural isomers. In the revised manuscript, we have added a sentence in the introduction that acknowledges that peaks can only be assigned molecular formulas that may represent any of several structural isomers (see section 1, page 5 of revised manuscript). Additionally, we have taken care to edit the entire manuscript to remove the impression that “peaks” are equivalent to “compounds”.

2. Page 6545, line 7: Acidifying the sample to a final pH of 2 can cause esterification and/or hydrolysis of macromolecular material, particularly in the presence of methanol (see McIntyre & McRae, 2005). Can the authors provide an estimate of possible methylation with this protocol?

Authors Response: The referee is correct. McIntyre and McRae (2005) show that ethanol, propanol, and methanol all can induce self-esterification in humic and fulvic acids (i.e., methylation of a carboxylic acid to give an ester). They found that the presence of more acidic functionalities leads to more esterificiation. This phenomenon is more pronounced in positive ion mode than in negative ion mode, and our samples were run in negative ion mode. Additionally, our samples were run within a couple hours of the C18 extractions (and addition of methanol). The results from McIntyre and McRae (2005) indicate that less than 1% of carboxyl groups in Suwannee River fulvic acid reacted within the first 2 hours. Because our samples are WSOC and not fulvic acid, it is expected that this value would be even lower for our samples. Thus, we feel confident that the use of methanol to elute our samples caused little to no bias in our results. In the revised manuscript, we have added a short discussion of this issue (section 2.3, end of first paragraph of the revised manuscript)

3. Page 6545, line 17: Use of ammonium hydroxide is commonplace with negative ion mode ESI MS. However, it can add N to DOM components. The authors should recognize this possible problem with their data and address it in the manuscript.

Authors Response: NH4OH was added, in very small quantities (<0.1% total volume), immediately prior to analysis only to bring the pH up to about 8 to increase the ioniza-

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tion efficiencies. As a result, we feel confident that the incorporation of N to the WSOC was not significant. In the revised manuscript, the small volume added is noted (refer to section 3, first paragraph of the revised manuscript).

4. Page 6546, section 3.1: The authors do not appear to state their assumption that m/z value equates to molecular weight in their analysis. This is only valid if they are certain that z=1 in their spectra. The authors should provide evidence that their spectra represent singly-charged components.

Authors Response: The referee is correct. Our peaks are all singly charged. We know this because of the observation of its 13C isotope at 1.003 higher than the 12C peak. If the peak were doubly charged, the isotope peak would be detected at 0.5 m/z units higher. We have revised the manuscript to state our assumption that m/z value equates to molecular weight (see section 3.1, page 9 of revised manuscript).

5. Page 6546, section 3.1.1: The authors should state the origin of their elemental formula constraints (minimal / maximal elemental ratios). No reference is given for these values.

Authors Response: This comment is similar to comment #4 from referee #1. Please note our response to this above.

6. Page 6546, line 22: I think DBE should always be greater than ($>$) 0.

Authors Response: The referee is correct that DBE should always be greater than or equal to 0. Our Matlab pre-processing file eliminates molecular formulas that have DBE $<$ 0. Formulas that pass the other elemental formula constraints and have DBE ≥ 0 are retained. As a result, the manuscript is consistent with the referee’s comment, and no change was made to the manuscript.

7. Page 6548, line 18: This is the most obvious place of confusion between “peaks” and “compounds”. In this line, the authors appear to equate the two terms and this is not valid.

Authors Response: Corrections have been made to the revised manuscript to address this problem. Please also refer to our response to Referee 2, comment 1 above.

8. Page 6552, first paragraph: The authors should provide the details of the radiocarbon analysis in the methods section since the reference provided here for this analysis is a meeting abstract. Was the radiocarbon analysis performed on the Virginia sample as well? If so, why is that value not presented? Was radiocarbon analysis performed on the C18 extract that was analyzed by FT-MS? If not, the authors should provide a rationale for assuming that the fossil signature of the bulk material was also present in the C18 extract. If radiocarbon analysis was performed on the C18 extract, how does it differ from the bulk sample?

Authors Response: The radiocarbon analyses presented here were performed on samples collected from the New York site during the same week as the NY sample that was analyzed for ESI FT-ICR MS. We do not have radiocarbon data for the Virginia sample or for a sample for a comparable date. While the radiocarbon analyses cited were not performed on samples covering the exact sampling days as the WSOC sample analyzed by ESI FT-ICR MS, two of the three samples analyzed for radiocarbon content were collected during portions of this sampling period, and the third was collected just two days later so there is reason to believe that the Δ14C signatures of these samples are similar (other work conducted by our group confirms that this is the case). The WSOC samples analyzed for radiocarbon signatures were not C18-extracted to remove salts so these samples represent the total WSOC while the sample analyzed by ESI FT-ICR MS was C18-extracted and likely represents about half of the WSOC (Louchouarn et al., 2000; Kim et al., 2003a). Nonetheless, it is reasonable to assume that the C18-extracted sample contains considerable fossil-derived WSOC. Thus, we feel inclusion of the radiocarbon data enhances our discussion of BC and fossil OC contribution to aerosol WSOC and have chosen to retain it in the revised manuscript. We have provided the radiocarbon data mainly for perspective on the WSOC findings here and on possible fossil contributions to the WSOC.

Radiocarbon methodology and sample collection details have been added (see section 2.1, page 6; section 2.2, page 7 of the revised manuscript). Additionally, we have added language in the Results and Discussion acknowledging the different sampling dates and sample treatments for the radiocarbon and ESI FT-ICR MS samples (section 4.4, page 14-15 of revised manuscript).

9. Page 6553, line 8: ESI MS does not always faithfully represent the natural abundance of its constituents within the neutral sample. Thus, the term “dominant” should be used here with care since you cannot be certain that the compounds in high abundance in the FT spectra were numerically dominant in the neutral sample. This caveat should be explained and presented in more detail to avoid confusion with more quantitative analyses.

Authors Response: We agree with this, and the term “dominant” has been replaced with the term “common” in the revised manuscript.

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

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