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Atmospheric Chemistry and Physics 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.

Anonymous Referee #2

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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 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 The authors should revise the manuscript according to the specific comments but I see no reason why the work should not be published.

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. 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? 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. 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. 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. 6. page 6546, line 22: I think DBE should always be greater than ($>$) 0. 7. page 6548, line 18: This is the most obvious place of confusion between “peaks” and “compounds”. In this

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line, the authors appear to equate the two terms and this is not valid. 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? 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.

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Interactive Comment