

Interactive comment on “A molecular-level approach for characterizing water-insoluble components of ambient organic aerosol particulates using ultra-high resolution mass spectrometry” by A. S. Willoughby et al.

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Overview: This manuscript describes the molecular composition of ambient organic aerosol from a coastal Virginia site. The water soluble components were extracted in water and acetonitrile. The water-insoluble components were extracted in pyridine. Molecular composition was analyzed by both proton NMR and ESI-FT-ICR-MS. The results indicate water and acetonitrile extract chemically similar organic matter compo-

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nents. However, pyridine extracts a unique fraction of organic matter, containing less polar and more aliphatic components with a large fraction of sulfur containing compounds. The manuscript is well written and easy to follow. The use of pyridine to extract the water-insoluble portion of organic aerosol is a unique contribution to the ESI technique and provides a more complete view of aerosol chemical composition. The complementary use of NMR provides a basis for quantification of organic aerosol components not possible with ESI alone. I support publication in ACP after these comments are considered.

Specific Comments: 1) a. Page 10396 line 12: “. . .comprises up to 90 % of the OM.” Please provide a reference for this statement. Is it because 10 – 70% of the OM is water-soluble as stated in the intro? If so, then 30-90% of the OM should be water-insoluble. b. Page 10415 line 23: Similar comment as above.

We agree that the text is unclear about 90% of OM being water-insoluble. Yes, it is deduced from the idea that if 10-70% of OM is water-soluble, then 30-90% must be insoluble. We will change the text to include the range of 30-90% and provide the references.

2) Page 10405, line 5: Why not show the full spectrum? It would be interesting to see a figure of the full mass spectrum for each solvent type

In the case of our samples, and in the case of many NOM samples, the full spectrum does not provide sufficient useful information to discuss in a manuscript. The important molecular details are buried within each spectrum, and we believe that displaying representative expanded spectra provides a better opportunity to make meaningful comparisons of the different solvents. Thus, in the interest of a succinct manuscript (and lesser publication costs) we chose to omit the full spectra and provide representative expanded spectra. The full mass spectra for each of the solvents will be added to the supporting information for interested readers to view.

3) a. Pages 10405, line 12 – page 10406, line 2: How general is this trend? The

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authors show only information from one nominal mass? What are the results from all the peaks in each solvent? Perhaps a figure such as a Kendrick diagram could show families of major mass defects in each solvent, or a histogram for mass defect for all the peaks in each solvent.

We state (P10405, L7-8) that this peak distribution is representative of odd nominal masses across the spectral range. A histogram (see attached fig. 1) of distribution of the percentage of formulas found within specific mass defect ranges for each of the solvents demonstrates that most of the peaks appear between 0.1-0.2 mass defect. As described in the text, the PSOM clearly shows the highest percentage of peaks in the 0-0.1 mass defect region. This figure will be included in the supplementary information for readers interested in verifying this trend.

A KMD (CH2) plot of every peak assigned a molecular formula proved difficult for a reader to digest and is not included here. A KMD plot using a subset of the data (see attached fig. 2) reveals that many of the peaks at $m/z = 427$ shown in fig. 2 of the manuscript are part of large series (at least 10) unique to the solvent of interest suggesting that the results are representative of the entire sample. Collectively, these series span almost the entire mass range of molecular formulas identified in this study (200-800 m/z). This plot will not be included in the revised text but is included here for the reviewer.

b. page 10405, line 19 –page 10406, line 2: This section ends with the authors informing us that information in the magnitude of peaks is unknown and not to be used. However, page 10405 lines 19 – 29, analyzes the differences in peak intensities. Please reconcile.

Yes, this discrepancy should be clarified. Our intention was not to give the impression that peak magnitudes do not provide useful information, rather that peak magnitude depends on the interrelated issues of compound ionizability, solvent, and sample composition and should be viewed cautiously. For simplicity, we do not explicitly consider

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peak magnitudes in the remaining data presentation. In the revised manuscript, the final sentence of this paragraph will be deleted and replaced with a sentence such as the following “While these differences in peak magnitude can provide useful information, the remainder of the discussion of the data focuses on differences in the presence and absence of peaks in water, pyridine, and acetonitrile extracts to provide a qualitative view of WIOM components detected by ESI-FTICR-MS.”

4) a. Page 10407, line 16 – 18: There needs to be more discussion of the fact that an ionizable functional group is required for detection in ESI. The authors have no knowledge of how much material extracted into pyridine was detected by ESI, meaning that there can be a large fraction of material that is water-insoluble and not detected by ESI-MS. Therefore, it should be stressed throughout the manuscript that it is the water insoluble fraction that can be detected by ESI-MS. b. Page 10407, lines 13-14: again this sentence needs to mention that you are looking at the water-insoluble organic matter that can be detected through ESI-MS.

We agree that the ability to detect only ionizable compounds is an important limitation of the instrument. Reviewer #2 also mentioned that we need to articulate this more clearly. We will revise the text in this section to expand on this limitation and indicate that the compounds we are discussing throughout the manuscript are only those that can be efficiently ionized by ESI.

5) Page 10409, lines 11-13, also Page 10413 lines 8- 11, also Page 10416 lines 2-3: I do not think that the authors can prove that pyridine is preferably extracting sulfur containing compounds. It could also mean that the more aliphatic molecules, i.e. extracted in pyridine, are more prone to contain sulfur. This could be due to co-generation of SO₂ and carbonaceous aerosols (soot), or burning of sulfur containing diesel.

The reviewer makes a good point that the selectivity may not be for the sulfur, rather the aliphatic material that may be prone to reactions with sulfur. We will revise the text to acknowledge this possibility.

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6) page 10409 line 25 –page 1410 line 7-9: a. There could be a large quantity of aromatic compounds that are not detected by ESI-MS that would still be defined as water-insoluble. Similar to comment 4, the authors should draw attention to the measurement of insoluble OM that is detectable by ESI-MS. b. The authors do not have NMR data for the aromatic region extracted in pyridine to back up the statement that "...WIOM may not absorb light as efficiently as WSOM."

We agree with the reviewer in that we can only speculate about the presence of aromatic compounds in the sample. The revised text described in our response to comment #4, we will note that an unknown quantity of low O/C aromatic compounds are among those that would go undetected by this technique. We will add a qualifying statement such as "Unless the WIOM contains a significant portion of non-ionizable (by ESI) aromatic compounds, the WIOM analyzed in this study may not absorb light as efficiently as the WSOM. We speculate that the aromatic character in these samples is low due to a lack of a strong combustion source. Unfortunately we cannot verify true aromatic content using these methods due to the signal from pyridine in the aromatic region of the ¹H NMR spectrum."

Technical Comments: Page 10394, Line 3: Change "...human emissions, and the effect..." to "human emissions. The effect"

The suggested change has been made.

Page 10394, Line 6: Delete comma after and

The correction has been made.

Page 10395, line 10: Abbreviation "OM" has not been defined.

The reviewer is correct, and it has now been appropriately defined in this location.

Page 10398, Line 16-17: Change "...(ThermoFinnigan), where quantification..." to "...(ThermoFinnigan). Quantification..."

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The suggested change has been made.

Page 10399, Line 21-23: This sentence is very colloquial. Please explain why acetonitrile interfered. Something along the lines of, "Acetonitrile interferes greatly with our measurement strategy because... Due to... it was not possible to determine the extraction efficiency."

The problems with using acetonitrile as a solvent for ¹H NMR are explained in the results section (P 10403, L 6-13). We agree that this explanation should be presented here in the methods and have revised the sentence to include this explanation and use more formal language. The revised sentence will read: "Acetonitrile interferes with our ¹H NMR quantification strategy due to a strong signal from acetonitrile hydrogen (occurring at ~2 ppm) that overlaps with the signal from organic matter (occurring between 0.1-4.4 ppm). This overlapping signal impedes our ability to determine the amount of proton signal derived from the sample and precludes a reliable calculation of extraction efficiency."

Page 10403, line 25-26: Please provide a reference for shifting peaks due to solvent interactions.

We have added the following reference: Sanders, J. K. and Hunter, B. K.: Modern NMR spectroscopy: a guide for chemists, Oxford University Press Inc., New York, NY, 1993.

Page 10404, line 2-3: It is not clear what the following refers to, "... (a ratio of 4 for both WSOM and PSOM)."

We agree that this can be clarified. We will change the text to read "... (a CH₂/CH₃ ratio of 4 for both WSOM and PSOM)."

Page 10404, line 5-7: What electron withdrawing functional groups would you be talking about that are likely in OM?

Many functional groups commonly found in OM would contain protons that appear in this region including alcohols, ethers, esters, carboxylic acids, aldehydes, ketones,

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amines, and amides. We will add text that gives examples of these functional groups.

Page 10406, line 24-28: Please provide references for both statements.

We have added the citation Koch and Dittmar (2006) for the statement regarding the aromaticity index values. We have added the citation Andrae and Gelencsér (2006) for the statement about the role of aromatic compounds in light-absorption.

Page 10408, line 11: Change "...sampling site, and they show..." to "...sampling site. They show..."

The suggested change has been made.

Page 10409, lines 5-8: How can they be outside the window of ESI-FTICR-MS if they are detected in the PSOM formulas?

We agree that the wording is unclear. We will remove the statement "...outside the analytical window of ESI-FTICR-MS..." for clarity. We will change the wording to read "...indicating that they are truly water-insoluble compounds or do not ionize well in water due to being suppressed by other WSOM components with higher ionization efficiencies."

Page 10409 lines 16 -14: What about compounds that are found in both PSOM and ASOM, any comments on the chemical composition of WIOM found in both organic solvents?

This comparison, while interesting, is of minor importance relative to the focus of the manuscript, identifying OM formulas that are uniquely WIOM. For simplicity, we focused the data discussion on the differences between the water and solvent and not the similarities/differences between the two solvents. 400 formulas were identified as common between ASOM and PSOM. The formula distribution is similar to that of PSOM-WIOM with more than 90% of the formulas being aliphatic or olefinic and CHOS formulas showing the highest contributions followed by CHO formulas and lesser contributions from the N and P-containing formulas. We will add a few sentences about this compar-

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ison in the revised manuscript.

Page 10409 line 20 -22: Similar atomic distribution to what?

The atomic distribution of the ASOM-WIOM formulas is similar to that of the WSOM formulas. We will clarify this in the revised text.

Page 10410 line 24: Has the abbreviation NOM been used or defined before? If not please define.

The abbreviation had not been defined. It was the only use of the abbreviation, so we will change it to read natural OM.

Page 10410 line 28-19: As mentioned in the preceding paragraphs, the authors suggest a lack of aromatic compounds. I am confused with the mention of aromatic rings.

We agree with the reviewer in that the mention of aromatic rings here is confusing. Many other FTICR-MS studies have described this region of the van Krevelen diagram as the region where lignin compounds would plot. However, as we state, we don't expect there to be a significant amount of lignin in the sample. Other studies have classified this region as SOA compounds, lignin-like, or CRAM (carboxylic rich alicyclic molecules). We believe that CRAM may be a more representative classification of this OM, and will change the text to reflect this. Describing it as CRAM will not conflict with the lack of aromatic material in the samples, and is consistent with the fact that many of these compounds are classified as olefins. This region may contain SOA compounds, but these will be present throughout the van Krevelen diagram, and we do not have direct evidence for them being secondary in nature.

Page 10411 line 6-9: Can NMR data help with determining N-H bonds versus C-H bonds near an NO₃ functional group?

C-H protons adjacent to a nitrate functional group and C-H protons adjacent to amine groups are expected to give signals with significantly different chemical shifts (at least 1 ppm), and should be easily distinguishable from one another. Unfortunately, C-H bonds

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near a nitrate group are expected to have a signal very close to that of the water signal (~ 4.8 ppm) and the signal for C-H bonds near an NO₃ group are likely suppressed with the water-suppression pulse program used in this study.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 10393, 2014.

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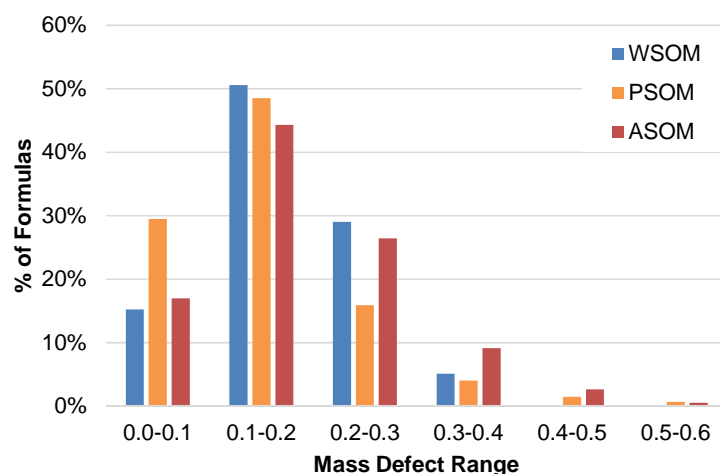


Fig. 1. The distribution of the percentage of formulas found within specific mass defect ranges for each of the solvents

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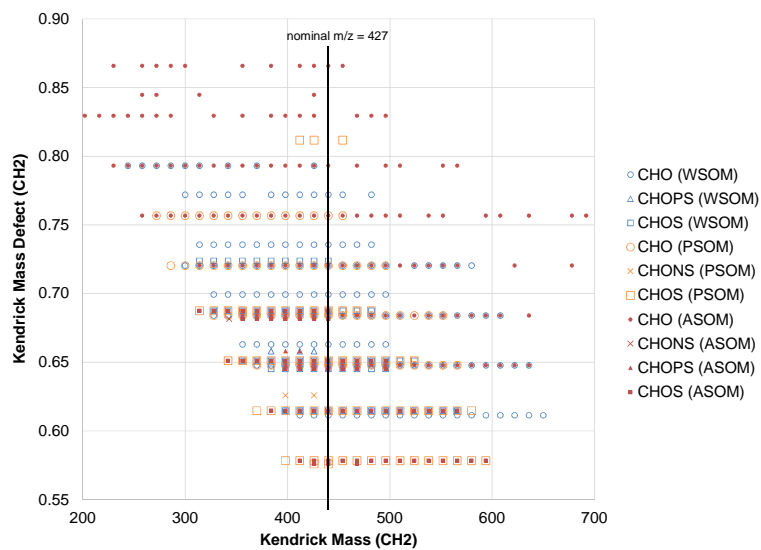


Fig. 2. A Kendrick mass defect (CH2) plot for the formulas identified for peaks shown in Fig. 2 of the manuscript

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