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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

Received and published: 19 May 2014

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 components. 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

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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.

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

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

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

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matter that can be detected through ESI-MS.

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.

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."

Technical Comments:

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

Page 10394, Line 6: Delete comma after and

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

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

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."

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

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Page 10404, line 2-3: It is not clear what the following refers to, "...(a 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?

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

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

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

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?

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

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

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.

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

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