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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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Anonymous Referee #2 Received and published: 25 May 2014

Overview: The manuscript presented by Willoughby et al. titled “A molecular-level approach for characterizing water-insoluble components of ambient organic aerosol particulates using ultra-high resolution mass spectrometry” describes the elemental formula compositions of three extractions of OA using water, acetonitrile and pyridine. The extractions were done in parallel and not in tandem, thus overlap of compounds

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that are soluble in multiple solvents or water is expected. The acetonitrile extracts were not obviously different than the water extracts and H-NMR quantitative data was not feasible, thus the manuscript describes most thoroughly the negative ion ESI-FT-ICR MS compositions of the water and pyridine extractions. They propose that the water-insoluble OM may contain most of the fossil material and possibly up to 90% of the OM, thus it's important to study. This statement is a bit of a stretch, since atmospheric oxidation will likely alter the fossil material rendering it more water-soluble with time. The cited studies used in this claim are also somewhat limited, thus this statement is too strong given the lack of concrete knowledge. Another key point of this paper is the presentation of a NMR method for quantification of the OM from different solvent extracts. The results indicate up to ~60% of the OM from these studies was water-soluble and pyridine soluble. It's not clear which samples had which values or what is the associated error on the measurement. As stated in the manuscript the focus is on determination of the water-insoluble OM, but the extracts were apparently only analyzed using negative ion electrospray after NH₄OH and MeOH dilutions. Thus it is probable that a large fraction of the water-insoluble compounds did not ionize. This limitation is not obvious to non-experts. Overall, assuming these limitations are more clearly articulated, this manuscript presents substantially interesting results for the audience of Atmospheric Chemistry and Physics and should be published. A few additional comments are provided below for additional consideration.

Reviewer #1 made a similar comment that the discussion of the instrumental limitations should be more explicitly discussed. We agree that these limitations are important and we will thoroughly review the manuscript to be sure these limitations are more adequately conveyed.

P10416, L2-4: The sentence about PSOM is misleading. It is the solvent that extracts the CHOS compounds with greater efficiency. Why is this? Is it related to the fact that pyridine is an organic base and assumed organosulfates are an acid? Perhaps this point can be made clearly in the manuscript. The more efficient extraction of the

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assumed organosulfates is counterintuitive since as you indicate may be important for hygroscopicity and CCN.

Reviewer #1 also commented on our assertion that pyridine preferentially extracts sulfur containing compounds and suggested that pyridine could be selective for aliphatic compounds, and those aliphatic compounds may be prone to reactions with co-generated sulfur species. We believe that pyridine's affinity for aliphatic compounds as well as acid/base chemistry may be allowing for a greater detection of CHOS compounds in the PSOM. We will revise the text to acknowledge both possibilities.

TSP samples were collected here. Is it possible the larger PM is more biologically influenced?

It is possible that we are collecting more biologically influenced particles, but confirmation of this would require additional measurements (e.g., microscopic or biomarker analyses) and is outside of the scope of this manuscript. We collected at times where pollen counts were low, so we do not expect that there was an overwhelming amount of plant-derived biological matter in the samples.

The PPL extraction method was recently reported in Wozniak et al., ACPD 2014. In that paper, they reported the use of strong acids for a pH adjustment of the water used to rinse and extract the cartridges. Was the pH adjustment used here? In that paper, they also stated that the addition of NH₄OH to the extracts lead to problems with the ESI. Thus, they reported results without pH adjustment. Please comment on the method differences.

Both papers use the PPL extraction methods described in Dittmar et al., 2008. We do acidify the samples to a pH of 2 before PPL extraction as stated in Wozniak et al., ACPD 2014 and in Dittmar et al., 2008. The pH adjustment is required to optimize OM retention by PPL. It is common practice in our laboratory to optimize instrumental response for each sample set and that includes testing a representative sample with and without the addition of NH₄OH. In some cases, adding NH₄OH will enhance

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the ionization of peaks attributed to inorganic salts that suppress the ionization of organic matter peaks in ESI. Wozniak et al., ACPD 2014, which notably analyzed aerosol WSOM collected over the marine environment and is expected to have a different composition than the samples analyzed here, compared spectra obtained with NH₄OH and without and found that omitting NH₄OH gave better quality spectra, so they analyzed all samples without the pH adjustment. During optimization of the samples presented here we found that the addition of NH₄OH gave better quality spectra as evidenced by increased spectral signal for organic matter peaks.

The reported method reproducibility is stated to be good with 67% of the assigned formulas in common between duplicate analyses. This seems very low to me. Higher reproducibility may be found with higher S/N thresholds. Thus, why do you consider 67% to be good or adequate?

The method reproducibility was stated to be greater than 67% in agreement with a study by Sleighter et al. (Analytical Chemistry 2012). That study evaluated the reproducibility of peaks detected by (-)ESI-FTICR-MS in 10 representative natural organic matter types and recommended that a minimum value of 67% be used to establish samples as reproducible at a S/N of 3. The corresponding reproducibilities are higher at higher S/N thresholds, but increasing the S/N threshold omit significant numbers of organic matter peaks thereby needlessly reducing the amount of molecular information that is obtained. The peak reproducibilities calculated for these samples were 84%, 71%, and 69% for WSOM, PSOM, and ASOM, respectively.

P10404: A higher relative abundance of unsaturated carbon was observed in the NMR of the water-soluble OM and this is expected to contribute to higher light absorption. Given the FT-ICR MS data, what is the more likely form of the carbon unsaturation?

Signals in that region of the NMR can be attributed to hydrogen that are attached to carbon adjacent to a C=C or in alpha or beta position to a C=O, and it is difficult to distinguish between the two. Certainly, much of the signal in this NMR region corre-

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sponds to hydrogen attached to carbon adjacent to C=C bonds (olefinic compounds). The FTICR-MS data show the majority of olefinic formulas to correspond to CHO and CHON formulas. Signal in this ^1H NMR region could also include ketones and carboxylic acids which are known to be constituents of aerosol OM. LeClair et al. (2012) showed that olefinic compounds frequently show a neutral loss of a CO₂ group, indicating carboxyl groups, and we can speculate that much of the unsaturation is due to carboxylic groups on compounds with and without nitrogen containing functionalities. Unfortunately, we cannot be more specific without doing further studies.

P10405: How were the more H deficient molecular formulas eliminated? The observation of more S-containing compounds is counterintuitive given the SP2 bonding of the pyridine.

H-deficient formulas were not specifically eliminated from consideration of formula assignment. As stated in the manuscript, peaks at low mass defects, as a general rule, typically correspond to formula assignments that are H-deficient or O-rich. In this instance, using the measured mass and the formula assignment rules described in the methods, the molecular formulas corresponded to CHOS formulas. No reasonable H-deficient formulas corresponded to the measured mass.

P10406: Molecular characteristics (of the OM extracted by) each solvent. Please clarify. The labels for the subset of PSOM and ASOM corresponding to uniquely extracted compounds are confusing. Perhaps you can write PSOM-WI or WI-PSOM instead of PSOM-WIOM. Or alternatively, one could write PSOM-WSOM indicating the PSOM minus the WSOM.

We understand that abbreviating it as PSOM-WIOM could be interpreted as PSOM minus WIOM rather than the PSOM that is water-insoluble. We thank the reviewer for the suggestion and will change the abbreviation to be more intuitive. The PSOM-WIOM and ASOM-WIOM, meant to represent the water insoluble OM unique to pyridine and acetonitrile extracts will now be referred to as WIOM_{pyr} and WIOM_{Macn}, respectively.

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What are the molecular weight range differences between the extraction compositions?

The molecular weight ranges are 200-800 m/z to in each of the extracts, which is largely defined by the instrumental parameters and is stated on page 10402 line 10. Peaks are sparsely found above 800 m/z in the case of this sample set, so those peaks are not considered for formula assignments. The average m/z for all assigned formulas is very similar and is between 425 and 450 m/z in each solvent extract.

A well-known limitation of the solid phase extraction methods is the loss of highly water soluble compounds that are rinsed away with the salts. Thus, it would be interesting if the PSOM or ASOM molecular weight ranges were lower. Unless, the FT-ICR mass spectrometer does not trap the low MW ions well. In either case, these limitations should be stated.

There are no major differences between the observed masses. The instrument does not adequately resolve peaks below ~200 m/z, so we do not consider them for formula assignments. As stated in the previous comment, the average m/z for all of the solvents is between 425 and 450 m/z. We also looked at the total formula distribution over the mass range (see attached fig. 1), and there is no apparent dominance at lower masses by either of the solvents. I believe that the reviewer makes a good point, and it is possible and likely that lower molecular weight species are extracted by the organic solvents because of the lack of SPE. However, our FTICR does not detect those species effectively, so we were not able to assess that. We will add text that states the molecular weight limitations of the instrument, and that the SPE could be removing those species.

LeClair et al., 2012 provides an MS/MS evaluation of several CHOS, CHNO and CHNOS compounds. They did not find the associated nitrate and sulfate losses for all of the compounds thus they suggest the terms organosulfates and organonitrates are not wholly accurate.

We recognize that not all compounds containing N and/or S will be organonitrates or

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organosulfates, and state that more reduced forms of the atoms could be present. We use the O/N and O/S ratios to determine whether it is even possible for the compound to contain a nitrooxy or sulfate group, and state that it is a possible structural feature. The implication is that it is a possible structure and that there are other possible structures, but the reviewer's comment suggests clarification is warranted. The LeClair study referenced by the reviewer did indeed find that 15% of S containing formulas and 58% of N, S containing formulas did not show neutral losses consistent with sulfate functional groups. Similarly, 37% of CHON formulas did not show HNO₃ losses consistent with organonitrates. This does support the idea that many CHOS, CHON, and CHONS formulas do not represent organosulfates, nitrooxyorganosulfates, and organonitrates. It should be noted, however, that the above percentages do suggest that very large percentages of these formulas do represent organosulfates, nitrooxy-organosulfates, and organonitrates. Taking this comment into account, the text will be revised to more clearly acknowledge that while not all of these compounds are actually organosulfates (etc.) but that their formulas are consistent with an abundance of these compounds. The LeClair reference will be cited in the text both as evidence for the probable abundance of these compounds and as evidence that the N and S formulas likely take additional forms as well.

P10414: The discussion of aliphatic compounds in WSOM would be improved with comparison to other studies beyond Wozniak et al. Look at LeClair – they define aliphatic/olefinic/aromatic the same way.

This comment is general in nature and therefore somewhat difficult to address. The discussion on page 10414 concentrates on the WIOM having higher contributions from aliphatic compounds than WSOM and references the Wozniak radiocarbon paper as evidence for aliphatic compounds being largely insoluble. The LeClair paper examined filtered fogwater OM (equivalent to WSOM) components and doesn't provide a direct comparison. Nonetheless, we will review this section and the LeClair paper (among others) and edit it as necessary adding references.

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Please enlarge Figure 2 in the ACP version of the manuscript.

We will enlarge the figure size in the publication.

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

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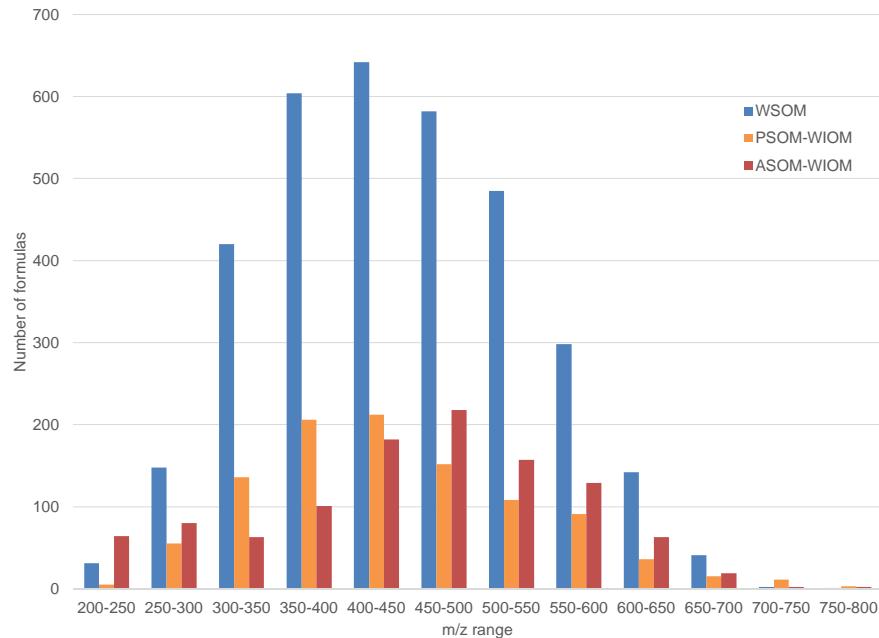
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Fig. 1. A histogram of the number of formulas present across the entire mass range, split into 50 mass unit segments. The average mass for each solvent is found between 425–450 m/z .

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