

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 #2

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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 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 composi-

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tions 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.

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

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

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

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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.

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?

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?

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.

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.

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

LeClair et al., 2012 provides an MS/MS evaluation of several CHOS, CHNO and

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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.

P10414: The discussion of aliphatic compounds in WSOM would be improved with comparison to other studies beyond Wozniak et al.

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

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

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