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Interactive comment on “Molecular characterization of free tropospheric aerosol collected at the Pico Mountain Observatory: a case study with long range transported biomass burning plumes” by K. Dzepina et al.

Anonymous Referee #2

Received and published: 29 October 2014

Anonymous Review: This manuscript describes the characterization of free tropospheric aerosol particles collected at the Pico Mountain Observatory. It describes data obtained using a suite of instruments (OC/EC analyzer, ion chromatograph, aethalometer, particle counter, FLEXPART retroplume analysis, etc.) to identify two samples collected on subsequent days with very different air mass histories and chemical characteristics. One sample was influenced by biomass burning from the northwestern United States, and the other showed a primarily marine influence. These two samples were studied in extensive detail using Fourier transform ion cyclotron resonance mass

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spectrometry (FTICR MS) and compared to each other and data from the literature. The dataset from these unique and difficult to obtain samples represent valuable information that can be a great asset to the community. The manuscript is, for the most part, clearly written, but it is unnecessarily long and at times unfocused - reading more as a cataloguing of FTICR MS data from two samples rather than concentrating on a discussion of the implications of these data on processes in the atmosphere. The manuscript will be suitable for publication in ACP if the following comments are addressed.

Detailed Comments: Title: the title gives the impression that it will study multiple biomass burning plumes, but only one of the samples contains a biomass burning plume. The title should be changed to reflect this. Methods:

1. There is no need to discuss methods for analyses and activities that are not presented in the results. Details about the 18 samples collected but not used (lines 23-24, page 24760), analysis of organic and inorganic (F-, Br-, NO₂-, PO₄³⁻) anions (page 24761), that the field site is difficult to get to (line 20, page 24760), that positive ion mass spectra were analyzed but not discussed, and anything else that isn't germane to the presented results are not needed.
2. Along these same lines, the details for the measurements of ethane and propane, and the SEM analyses (and any other measurements included in the results) should be added to the methods.
3. Page 24762, line 10: What percentage of WSOM do Strata X SPE cartridges isolate? How do Strata X SPE cartridges eluted with acetonitrile compare to other SPE cartridges (e.g., C-18, PPL, etc.) and elution solvents in terms of the characteristics of organic matter that they extract?
4. Equations: There are several problems with the equations in the manuscript. Presumably, these are typographic errors, and the calculations were made correctly. However, the calculations should be checked to ensure this is the case, and the numbers in the manuscript are correct. Additionally, the text needs to be changed to reflect the

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following:

- Equation 1, the Kendrick Mass is calculated using the exact mass of compound C not the observed mass.

- Equation 2, the Kendrick Mass Defect is calculated by subtracting the nominal Kendrick Mass from the Kendrick Mass (not vice versa): $KMD = KM - \text{Nominal Kendrick Mass}$

- Equation 4 is incorrect in the text. The o and s are subtracted in the numerator. It should read:

$$AI = DBEI/CAI = (1 + c - o - s - 0.5 * h)/(c - o - s - n)$$

- Equations 5 and 6 are incorrect. In equation 5, the O and C should be lowercase as designated by the defined elemental composition. In equation 6, the O and H should be replaced with h and c. Further, equations 5-8 can be combined into one equation replacing O/C, H/C, DBE, and OM/OC with X then defining X as O/C, H/C, DBE, or OM/OC in the text following the equation.

5. The AI calculation as used in the manuscript assumes that all oxygen atoms are in the form of carbonyl bonds which is not true for aerosol WSOM where carboxyl and alcohol (as well as nitrate and sulfate) functional groups are abundant. The modified AI described in Koch and Dittmar (2006) assumes that half of the oxygens are in C=O bonds and half are in C-O bonds, a more likely scenario. Regardless of whether the modified AI is used, this assumption about the bonding of oxygen should be stated explicitly.

6. Throughout the manuscript, WSOC should be changed to WSOM to reflect that water soluble organic matter is being characterized rather than water soluble organic carbon which typically refers to a quantity of carbon.

7. Page 24768, lines 2-11: There are a few problems with the rationale in these arguments. The OM/OC ratio of 1.8 takes into account the entire OM. What has been

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analyzed by FTICR MS here is the WSOM that is isolated by the extraction technique. One would expect WSOM to be higher because it inherently excludes low oxygenated hydrocarbon compounds (in addition to the highly oxygenated, low MW compounds cited by the authors). Do Strata X cartridges bias against high O/C compounds? If no, the actual OM/OC ratio in the aerosol OM at this site may be much lower than the value of 1.8 used here.

8. Page 24768, lines 18-23: These correlations are cited in the abstract but are only presented as a supplementary figure. This seems to be a disconnect in its value to the paper. In lines 21-23, the correlations are described as indicating that the measurements follow the same trends which is self-evident. More in depth analysis and interpretation of the implications of these results and their importance in the atmospheric conditions or processes at this site are needed. Otherwise, the correlations should be removed from the manuscript.

9. Section 3.2, first paragraph: this information belongs in the methods section.

10. What is the purpose of the ethane and propane mixing ratios? This needs to be made clear to the reader. The methods need to be added to the methods section as well.

11. Perhaps Figure 4 should be altered to note that contributions that each particle type are attributed to each sample. The numbers are difficult to follow in the text.

12. Throughout section 3.3: I caution the authors in being clear how they are comparing the results from this study to those from other studies. In addition to differences in WSOM source and processing, WSOM mass spectra can differ depending on the methodologies used in each study (e.g., the extraction conditions (choice of SPE cartridge, eluting solvent, etc.), the tuning parameters of each individual FTICR MS instrument). The best comparisons (especially of abundances, mass ranges, etc.) are made for samples that have been processed and analyzed in the same way over similar time periods.

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13. Throughout section 3.3: The presentation (Figures 6-10) and description of the FTICR MS results is extensive and repetitive and would benefit from a more targeted approach that effectively describes the important, unique features in these samples that can be linked to important potential effects in the atmosphere/environment. Many details included in the presentation have been established in several other FTICR MS studies – such as the high isobaric complexity in samples, that homologous series can be observed in DBE and KMD plots (e.g., page 24775, line 10; page 24776, lines 7-9 – are there specific importances to these series?), and that lines of apparent saturation/unsaturation, oxidation/reduction, and alkylation can be observed in van Krevelen diagrams. Additionally, descriptions of Kendrick plots as, for example, “narrow and uniform” (e.g., page 24774, line 28) are vague and do not have particular value unless they are linked to specific molecular components which one cannot tell from the Kendrick plots themselves. Backing up the vague terminology with more quantitative measures describing the distributions and what they mean molecularly will improve the manuscript. Otherwise, they are simply describing differences in a graph shape.

14. Throughout section 3.3: DBE values are frequently cited as evidence for the unsaturation of samples, and they are evidence for the total number of double bonds. However, because WSOM compounds vary in size within a sample and between studies, DBE is limited in terms of how much structural information it can give. A better idea of WSOM structural components can be gained using the DBE/C ratio (Hockaday et al., 2006), the aromaticity index, or the aromaticity equivalence (Yassine et al. 2014).

15. Page 24774, line 22: Why is it “not likely that nitrooxy organosulfates will be observed after long-range transport?” Do you have a rationale and citation for this?

16. Page 24775, lines 1-4: Why is a “similar distribution in the Kendrick plot” evidence for very aged and processed aerosol WSOM? Further, fulvic and humic acids, which are by definition insoluble in water, have been found in previous studies to be poor analogues for aerosol WSOM and so-called HULIS (Duarte et al., 2007). Unfortunately, the term HULIS persists in the literature, but its similarity to SRFA and other fulvics and

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humics should not.

17. Can the authors provide citations and/or mechanisms for how “fragmentation” can result in higher degrees of unsaturation in the WSOM composition?

18. Page 24783, lines 16-24; Page 24785, lines 5-8; Page 24787, lines 7-9: organosulfates are not specific to marine environments and have been identified in terrestrial environments and from other sources. Furthermore, fatty acids are a major biological component in all manner of life and are not specific to marine environments. This line of reasoning must be further supported, edited to add qualifying statements, or eliminated.

19. Section 3.3.5 is largely redundant with the rest of section 3.3. That said, it contains much of the important comparison of the two samples.

20. The literature is full of marine aerosol or rainwater WSOM studies that have examined the molecular composition. These studies can be compared to the present study to confirm marine sources to the 9/25 sample or to delineate differences between the Pico samples (collected in the middle of the ocean) and these other marine aerosols. See, for example, Altieri et al., 2012; Cavalli et al., 2004; Decesari et al., 2011; Ovadnevaite et al., 2014; Russell et al., 2010; Wozniak et al., 2014

Minor Comments (given the length of the manuscript, many of these are suggestions for shortening it):

Page 24757, lines 10-11: The sentence “Determination of the OA molecular composition is a challenging task.” is redundant with line 1 in this paragraph.

Page 24757, the paragraph beginning on line 17 can be condensed considerably to omit details about FTICR MS that have been covered in a great many previous publications.

Page 24758-9, the final two paragraphs of the introduction should include some further justification of why the measurements are being made. Simply understanding long

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range transport is not an end in itself. The atmospheric community wants to understand long range aerosol transport (and the resulting WSOM chemical characteristics) for their effects in the atmosphere and environment. This needs to be made clear. Further, many of the details on the PMO can be more appropriately moved to the methods section as a site description.

Page 24763, line 23-24: The sentence beginning “the aim of data processing...” is not necessary.

Page 24765 (and in the results): Why are two methods of formula assignments presented and compared? I believe that they were ultimately used in tandem (which seems appropriate). The authors should just state that both methods are used to assign formulas. Any comparison can be moved to the supplementary information.

Page 24765, line 10: The assignment thresholds are presented as percentages. To what are these thresholds being compared? The highest peak in the spectrum? This should be clarified.

References: Altieri et al., 2012; Atmos. Chem. Phys., 12, 3557-3571.

Cavalli et al., 2004; J. Geophys. Res., 109, D24215, doi:10.1029/2004JD005137

Duarte et al., 2007; Atmos. Environ., 41, 8100-8113.

Decesari et al., 2011; J. Geophys. Res., 116, D22210, doi:10.1029/2011JD016204

Hockaday et al., 2006; Org. Geochem., 37, 501-510.

Ovadnevaite et al., 2014; JGR Atmospheres, 10.1002/2013JD021330

Russell et al., 2010; PNAS, 107, 6652-6657.

Wozniak et al., 2014; Atmos. Chem. Phys. 14, 8419-8434.

Yassine et al., 2014; Rapid Commun. Mass Spec. 28, 1-10.

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