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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 #3

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This paper presents ultrahigh-resolution MS analysis of aerosol WSOC from a free tropospheric site at the Pico Mountain Observatory. Measurements of aerosol OC, EC, and inorganics are used together with FLEXPOART analysis of air mass histories to classify the overall chemical composition and air mass history of the aerosol sampled at the site. Two events are identified as case studies of biomass influenced and marine influenced airmasses. This data offers a useful opportunity to explore the effect of airmass aging and airmass sources on WSOC composition. The manuscript is well written in sections, but could be tightened to make it clearer and some of the reasoning

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seems to be erroneous and needs to be rechecked. So, I recommend publication only after the following comments are addressed.

Main Comments 1) The argument that the authors present in the abstract (line 19-24) that low O/C ratios in aged aerosol is consistent with evaporation and increased fragmentation does not make sense to me. My understanding is that increased fragmentation results in more oxidized organic aerosol and higher O/C values (see for example, Kroll et al.Nature Chemistry, 3: 133-139). Also, previous work has shown that oxidation is generally accompanied by decrease in volatility of aerosol components. So, I don't understand how evaporation is increasing with aging. The argument about fragmentation is repeated throughout the manuscript and based on the Kroll et al. paper and related papers, I think it is incorrect and should be rethought.

2) I have several questions regarding how the mass spectra of 9/24 and 9/25 are compared: Aging The authors use FLEXPART to expect that there is more aging in the 9/25 airmasses (15 days) than the 9/24 airmasses (>12 days). What is the evidence for this from the mass spectra? It is not clear exactly what criteria in the spectra are being used to indicate aging (what are O/C, H/C, DBE, and Carbon number supposed to do in the aging picture that the authors are trying to present?)

Unique Ions In Figure 10, it looks like the differences between the spectra are due to unique ions on 9/24 ions which have higher O/C values and higher carbon numbers than the unique ions on 9/25. I am not clear on how these differences are reflective of aging. The authors also state but don't provide much information on why the mass >400 amu, that are uniquely intense in the Pico Mtn spectra are really reflective of aging. In fact, if these are unique for this site, it would be interesting to have more description about the likely compositions of these >400 amu ions.

Common Ions In Figure 10 a and b it looks as though there is a difference in the distributions and relative intensities of the common ions <m/z 350 and those >m/z 350. Does this difference mean anything with respect to the airmass histories? This should

be discussed.

3) This work presents O/C and H/C as well as carbon number ranges observed in WSOC from 2 different airmasses. It would be very helpful if these values were put in context of other previous measurements from different airmasses. While the authors mention some comparisons in the text in sections 3.3.2 to 3.3.4, it is hard to quickly get an overview of how the observations at this aged site differ from the other measurements at other sites. For example, what is the difference between this aged site and less aged sites measured in previous campaigns? I recommend the authors present these values as well as values from previous sites (including a brief description of the site type (rural, remote, urban, fress biomass etc..)) in a table so that it will be easier to compare. Since the authors mention DBE and OM/OC, these would be useful to add to this table as well.

4) The DBE values are mentioned, but what is the connection between DBE and oxidation. In the situations where DBEs increase and H/C values go down, couldn't this be reflective of either increased aromaticity OR increased addition of oxygen? Is there a correlation between O/C and and DBEs for this data? The authors mention aromaticity index, but don't really use it or report values throughout most of the manuscript text. The authors mention that DBE increases with aging. Is aging known to add C-C double bonds? If so, authors should reference and should clarify how/why DBEs increase with aging.

5) The WSOC shown in this manuscript generally have high carbon numbers. Most biogenic VOCs have carbon numbers on the low end of the carbon numbers of WSOC species reported in this paper. They point out that the WSOC ions at m/z >400 amu here are unique and likely reflect aging processes during long-range transport. When the authors mention aging, it is not clear whether the authors are suggesting that the large carbon numbers observed here a result of heterogeneous oligomer forming reactions from small carbon number precursors OR do they reflect SOA formation from large carbon number precursors? How different in age are the airmasses observed

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here compared to those observed in other studies? Can the authors provide some information on how much of the large carbon number distribution is affected by clusters form during electrospray rather than oligomers?

6) Words with two ffs next to each other print the two ffs with different font. Equations 5-8 printed out with the letter P randomly placed within each equation.

Other comments

Title: The manuscript actually compares two different airmasses and doesn't focus only on the biomass burning plume so perhaps title should be changed to reflect this.

Section 3.2. It would be easier if the knowledge about the distinct sources (biomass burning influenced and marine influenced) was presented right away after the definition of the time periods. Then the rest of the observations in this section can be used to support why the airmasses are identified as they are.

Section 3.2.1. I see that the absolute concentrations of the VOCs could reflect relative pollution of the two different airmasses, but isn't clear what new information is offered by the ethane/propane ratios.

Page 24778, line 14-28. If there is ion signal everywhere, how do the authors know that the ions being presented are actually from biomass burning products and not isobars? Is there some pattern or diagnostic from this or previous studies that the authors are using to confirm the identity of these ions?

Section 3.3.3. How do the authors know whether the N containing species are nitrates or amines? Do the CHNO ion formulas allow for unique identification of one vs. the other?

Page 24780, Line 27-28. How does unsaturation reflect long range transport related aging? Is the increase in observed unsaturation due to increase in hetoratoms or due to increase in C=C double bonds? What do the authors use to distinguish between these two options?

page 24781, Line 7. In Figure S9, please state the difference between N1 and N2 in the figure legend.

Figure 5b and Figure 7c. What are the strong ions that dominate the signal between 200-300 amu?. These ions are not strong in Figure 5a. Do the authors have any insight into what these ions are ? It would be good to at least mention their formulas.

Figure 6e. Line iii shows decreasing O:C and decreasing H:C and is attributed to functionalization (alkylation) or fragmentation (line 23, page 24775). I don't understand how this can be. fragmentation would increase O/C and decrease H:C. I would also think that alkylation would increase H:C and decrease O:C...

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 24753, 2014.