Review on:

Schum et al.: "Molecular and physical characteristics of aerosol at a remote marine free troposphere site: Implications for atmospheric aging"

The authors describe the analysis of three selected filter samples that were collected within a more comprehensive sampling campaign (a total of 127 filters) at the Pico Mountain Observatory (PMO) on Pico Island / Azores. The samples were chosen because of the high organic carbon (OC) concentration. While major small ions and OC of the three filter samples were measured as well, the focus of the manuscript certainly lies on the analysis using direct infusion electrospray ionization ultra-high resolution mass spectrometry in the negative ion mode (($-$)ESI/UHRMS). Differences in the mass spectra are discussed with regard to a back-trajectory analysis. The authors observe signals in one sample (out of three) that exhibits higher O/C ratios compared to the other two samples that likely have undergone a longer atmospheric transport time (and thus aging). The authors argue that the two samples with the lower O/C ratio were transported in the free troposphere (FT) to PMO, and thus the particle phase state during transport was likely solid. They conclude that "biomass burning emissions", which are directly injected by pyro-convection into the FT, "are longer-lived than emissions in the boundary layer".

General comments:

Overall, the manuscript presents results from an atmospheric measurement station that is certainly very well suited for studying aerosol transformation processes during long-range transport. Furthermore, the authors demonstrate the need for ultra-high resolution mass spectrometry techniques when it comes to ambient measurements of particulate matter. However, I have major concerns regarding a weak reasoning that is used as a basis for their conclusions and implications for atmospheric aging (see my point (1) below). Also, the authors remain too speculative in many cases, or even state arguments that are not supported by their figures (see (2)). Furthermore, I have serious technical concerns that might have an effect on the outcome of the ESI/UHRMS analysis (see (3)).

My major remarks concerning the above mentioned points:

(1) The authors argue that particle phase state is affected by the conditions during atmospheric transport. Their observation of a low O/C in the biomass burning samples (PMO-1 and PMO-3) is reasoned by the phase state of the particles during transport. Although, the authors mention that the PMO-2 sample is originating from another source (from the Eastern United States – dominated by a mix of biogenic and anthropogenic emissions), they argue that the high O/C ratio of this sample is caused by the semi-solid phase state, which allows faster aging during atmospheric transport to PMO. Assuming that the back-trajectory analysis is getting the sources right, the authors don't present a convincing argument why we can use the two different sources (biomass burning organic aerosol (BBOA) vs. anthropogenic/biogenic secondary aerosol (A/BSOA)) as an **identical reference point for the onset of atmospheric aging**!
In the literature it is now well recognized that these two kinds of organic aerosol (BBOA vs SOA from anthropogenic and biogenic VOCs) are already very different on the molecular level at the time when emitted by their sources or formed in the atmosphere: While BBOA is largely composed of lignin- and cellulose-derived

condensed aromatic / polyphenolic structures with low O/C ratios (Lin et al., 2016), numerous studies have shown that the auto-oxidation of (mostly biogenic) VOCs results in highly oxygenated molecules within seconds after the initial attack by an oxidant (Crounse et al., 2013; Ehn et al., 2012; Jokinen et al., 2014). Although it is not yet fully understood what happens to these compounds once they condense, the auto-oxidation mechanism still can explain high aerosol O/C from atmospheric oxidation of VOCs.

My impression is that the authors do not adequately consider or discuss different reasons for their observations and overemphasize the possible link between atmospheric transport and aging efficiency at different altitudes.

To be clear, I am not saying that aerosol phase state does not change aerosol transformation rates, but to extract this effect from ambient observations, one likely needs to consider a larger set of samples (which the authors apparently have).

(2) The authors argue that the aerosol that was captured on the PMO-2 sample travelled at altitudes below 2 km over Eastern U.S. and stayed below 2 km altitude until it reached PMO 2-4 days later (p. 7, l. 251-253). From Figure 1 (e), I cannot see that. For the upwind days 0-5, the mean height of the plume is consistently higher than 2 km. As stated on p.2, l. 65-67, the marine boundary layer (MBL) around PMO ranges between 500 m and 2 km, and thus below the mean height of the plume. However, the authors argue that **PMO-2 air masses travelled within the MBL layer** to PMO, explaining high relative humidity and a semi-solid phase state during transport. Another argument against the transport within the MBL is given by the authors, mentioning that PMO-2 does not reveal any chemical signature from the MBL (p. 6, l. 232-233). Furthermore, the mean height in PMO-3 appears even lower than PMO-2 for the last five days.

(3) The discussed filters were selected because of their high mass loadings of organic carbon (>1 mg OC / quarter filter). After loading the water-soluble (WS) OC extract onto solid phase extraction (SPE) material for purification, the SPE was then eluted by 2 mL of MeCN/H_2O and the extract was used for direct infusion. If we assume that half of the OC is WSOC and assume 100% SPE collection efficiency (neglecting losing the small, polar organic compounds), the concentration of the solution for direct injection ESI would be ~0.25 mg/mL. To me, this appears as a huge concentration in which ion source cluster formation (e.g. x-mers of analytes, clusters with solvents or solvent additives, impurities), can become a serious issue. I understand that SPE was done in order to reduce cluster formation with inorganic ions and that a separation technique was apparently not available. However, the authors could have done straight-forward tests to check the extent of cluster formation in these samples by: (1) sample dilution and checks for non-linear reduction of cluster-signal candidates and (2) MS/MS isolation and recording the fragmentation energy of cluster signal candidates.

Although, I understand that MS/MS cannot be done on all ion signals, there are some "suspicious" signals standing out in Figure 2 (the signals > 0.3 rel. abundance) that should have been checked using MS/MS when doing direct injection.

Ion source cluster formation would introduce a bias on the calculated glass transition temperature (T_g) by artificially increasing the average number of carbon per molecule. Furthermore, the overall T_g is already biased toward higher values since small molecules are very likely lost during the SPE procedure (l. 158-159). The manuscript misses in its current form a critical evaluation of these points and its implications on aerosol phase state and aging.

Finally, it would have been interesting to measure also in the positive ESI mode, in which one can observe levoglucosan or nitrogen-heterocycles that are expected in biomass burning aerosol samples.

Moreover, it is not clear how the blank signal of the DI/ESI-UHRMS was determined. I would expect a measurement of a blank filter that undergoes the whole procedure incl. transport from the field site, sample preparation procedure in laboratory (sonication, filtration, SPE, etc). Only a good blank measurement allows determining the significance level at which individual signals are present in the samples and identifying those signals that emerge from sample preparation. Here, it is especially important since the paper discusses the number of identified compounds between the different samples. If a compound was identified as "not present" in one sample, does that mean after blank subtraction? It is not described what were procedures involving a blank filter, nor are mentioned the criteria and the thresholds for this kind of filtering!

Overall, I cannot recommend the article to be published in ACP, since the conclusions reached remain far too speculative and are not convincingly supported by the presented data. I miss a more critical discussion and evaluation of other potentially important processes (both atmospheric and instrumental) throughout the manuscript. The description of the mass spectrometry analysis is not sufficiently complete and leaves the reader with open questions (e.g. What was the workflow of the data analysis? What did they use as blank samples?). Last but not least, the presentation and language is in many cases not precise.

Specific comments

p.3, l. 106-109: Please provide a reference stating that long-range transported aerosol is generally acidic in nature. Furthermore, negative ESI is not only sensitive to organic acids, but also to important biomass burning markers (e.g. nitro-phenols (Iinuma et al., 2010)). Have you seen nitro-phenols or similar biomass burning tracers in the biomass burning samples?

p. 5, l. 169: The two references describe different criteria for the molecular formula assignments:
    Dzepina et al.: max. 100 C, 400 H, 100 O, 3 N, and 1 S.
    Mazzoleni et al.: max. 70 C, 140 H, 25 O, 3 N, and 1 S.
The elemental windows for nitrogen and sulfur seem very strict. The used limits exclude for example the identification of nitrogen-heterocycles with four nitrogen (e.g Kampf et al., 2012). Given the clear isotopic signature of sulfur, why was not more sulfur allowed? Were the isotopic patterns used to confirm the molecular formulas in case multiple elemental compositions appeared within the instrumental accuracy limits?

p. 5, l. 172: According to Putman et al., allowing nitrogen for compounds larger than 500 amu results in multiple results within 1 ppm. Does that mean that the number of elements allowed was chosen such strict that only one molecular formula per signal was obtained?

p. 6, l. 205-222: As mentioned by the editor, this paragraph is not well structured and needs rewriting.

p. 8, l. 308: Is the high O/C of the CHNO species potentially driven by organic nitrates?

p. 8, l. 310-311: Does the common number of identified molecules in a certain group (here CHNO) really tell us something about the similarity of samples? This is mentioned several times in the manuscript, and I don't understand why intensity of compounds is not given more weight in the discussions.
Why not visualizing the similarity of two different samples by simple scatter plots of the intensity of all ions of sample A vs intensity of all ions of sample B. This would also allow determining the Pearson correlation coefficient.

p. 8, l. 319: also here: Is the high O/C of the CHOS species potentially driven by organic sulfates? What would be the O/C after accounting for organic sulfates? Is it then still different from the CHO value?

p. 9, l. 334 ff.: The oxygen that originates from organic nitrates and sulfates artificially increases the oxidation state of carbon.

p. 10, l. 394: Was the glass transition temperature determined only for single molecules and not for the intensity weighted population of all ion signals? Obviously the atmospheric particles are mixtures and therefore only the glass transition temperature derived from the whole spectrum is meaningful. Accounting for the fact that small organics are lost during the SPE (which would reduce T_g of the mixture), what would be the effect on T_g of the mixture if one assumes that 10, 20 or 50% of total OC consist of small organics?

Figure 3: The three dots with H/C<0.6 are cyan in PMO-1, which should mean unique in PMO-1. Why are these three signals in PMO-2 and PMO-3 then grey (common signals)?

Technical corrections

Figure 1: The Figure quality is not appropriate.

Figure 2: X-axis ticks are missing for (a),(b),(d) and (e). It seems as the highest peaks in (b) and (c) are cut at the top, or are they all the same height?

Figure 4: X-axis ticks are missing for (a), (b), (d) and (e).

Figure 4: The y-label is <u>number</u> of formulas. The caption is not clear on that. What is the "normalized abundance"? On what is it normalized?

Figure 6: X-axis ticks are missing for PMO-1.

Literature

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extremely oxidized pinene reaction products in chamber and ambient air, Atmos. Chem. Phys., 12, 5113–5127, doi:10.5194/acp-12-5113-2012, 2012.

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