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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular and physical characteristics of aerosol at a remote marine free troposphere site: Implications for atmospheric aging" *by* Simeon K. Schum et al.

Anonymous Referee #2

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Schum et al. present a unique dataset collected on Pico Mountain Oberservatory to study the physiochemical properties of aerosol in the remote marine free troposphere. They analyzed three aerosol samples that had elevated organic carbon concentration, and attributed the differences in their molecular and physical characteristics to emission sources as well as their transport pathways. They observed a lower O/C ratio in two samples that they believed were likely from biomass burning plumes that were transported mostly in the free troposphere, and the aerosols were in a solid state that resisted oxidation. Before this work is published in ACP, the authors need to provide careful clarification and further discussion of several important aspects in this manuscript. Please find the comments below.

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Discussion paper

Major comments

1. The O/C values for PMO-1 and PMO-3 are surprisingly low for particles that had been transported for 7-10 days. In Section 2.3, the authors pointed out that “losses of highly water soluble, low molecular weight organic compounds are expected”. Highly water soluble compounds are presumably quite polar and thus should have higher O/C. Authors need to address how the SPE artifacts affect the overall sample O/C. The same issue applies to the artifacts of water extraction that the water-soluble compounds in the samples were preferably collected for the subsequent analysis. Please provide a discussion of possible bias, what is roughly the fraction that had been extracted versus not-extracted, and how it might affect the results of the analysis.

2. The authors use the method developed by DeRieux et al. to estimate particle phase state and heavily rely on the result to explain their findings. However, the authors use this method without further comment and discussion, especially regarding its uncertainty. Solid, semisolid and liquid state are qualitative descriptions which do not provide much insight into diffusion time-scale of water or organic molecules into/out of particles. Diffusion is a key process that determines the evolution of particle composition, and the connection of phase state and diffusivity involves multiple-step estimations with large uncertainties, as shown in a couple of studies [1][2]. Is it possible that the uncertainty of the method is large enough that it changes the major conclusions of this paper? The authors need to provide a much more comprehensive discussion of these issues.

Minor comments

1. In line 20, “This suggests that biomass burning emissions injected into the free troposphere are longer-lived than emissions in the boundary layer." The term "longer-lived" is vaguely used here, as well as in a couple places in the main text. Do the authors mean the particles from biomass burning have lower oxidation state, or the authors are referring to the chemical life time of the compounds from biomass burning that were transported in the free troposphere?

2. In Section 3.1, chloride is presented in Table 1 but not discussed in the main text. Some studies show that biomass burning can produce chlorine-containing particles [3][4].

3. In Figure 1 (c), the air mass spent a couple of days over Europe, and based on (f), the height of the air mass was quite low during those days. Could there be any influence from emissions from Europe on the sample?

4. In Section 3.2, regarding the CO source apportionment in Figure S1, what is the uncertainty associated with the CO modeling?

5. In Section 3.3, line 285-287, 78% of the formulas in PMO-2 are found to be common with sample from the boundary layer aerosol, and PMO-3 has similarity of 76%. Are 78% and 76% significantly different? This piece of information might not be a strong evidence to support the conclusion that PMO-2 was largely influenced by North America outflow transported within the boundary layer while PMO-3 was not.

6. In Figure 2, an obvious difference of the three spectra is the much higher fraction of high molecular weight materials in PMO-2. Little is discussed about the sources of the high molecular weight compounds in the text. Are they from oligomerization? In contrast, Lee et al. [5] observed abundant high molecular weight compounds from biomass burning in Canada using an aerosol mass spectrometer.

7. In section 3.5, line 387, "Volatility can also play a role in the phase state". This expression is vague. Do the authors mean phase state depends on volatility? Or they both relate to structures of molecules in particles? Please make clarification.

8. In section 3.5, line 392, "This highlights the correlation between O/C and volatility, where volatility is expected to decrease as O/C increases." What about fragmentation?

9. Lastly, how generalizable are these findings in the paper in terms of predicting the oxidation state of aerosols having different transport pathways?

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