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Interactive comment on “Changes in organic aerosol composition with aging inferred from aerosol mass spectra” by N. L. Ng et al.

Anonymous Referee #2

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This manuscript attempts to reconcile the “triangle plot” of atmospheric OA composition [Ng et al., 2010] with the Van Krevelen diagram description of OA composition [Heald et al., 2010], and use PMF factors to gain further insight into the aging process. There is certainly a need to harmonize the community’s understanding of OA evolution that is developing from these different studies. However, the work presented in this manuscript is technically flawed and misses the mark in terms of providing further scientific insight into the OA aging process. The results presented in this manuscript are too poorly established to be publishable at this time. Detailed comments follow.

1. The discussion and justification for relating f43 and H:C (the central concept of this paper) is extremely inadequate. Only a small fraction of total H is contained in the m/z 43 peak, and thus the choice of f43 seems arbitrary and counterintuitive (compared to

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say the use of m/z 44 which contains a large fraction of the measured oxygen for the O:C determination).

- a. Page 7097, line 9: can the authors provide a reference for the sentence “The m/z 43 ion is predominantly due to non-acid oxygenates”? This sentence does not seem to be consistent with a lot of the data on the AMS spectral database (<http://cires.colorado.edu/jimenez-group/AMSsd/>): for example, gultaric acid (which has only acid groups) has a fair amount of m/z 43 (almost certainly C₂H₃O⁺). Can the authors demonstrate that indeed f₄₃ correlates with non-acid oxygenates?
2. The fit of f₄₃ to H:C for OOA appears far more uncertain than suggested in the manuscript. First, what justification is there for fitting a polynomial function constrained at H:C=1? What would a linear fit look like? What is the R² of this fit? In Figure 2 there are a great number of points (from lab studies) that lie outside the +/- 10% line leading to potentially substantial errors in H:C. It would be informative to see a scatter plot of H:C obtained from the high res vs. the H:C obtained using this fit. Such a plot could be used to estimate error in estimated H:C and this uncertainty added to Figure 3. The data in Figure 2 are only shown for bulk OOA – would the plot & fit be similar if only SV-OOA or LV-OOA were included?
3. Investigation of the evolution of PMF factors in the Van Krevelen diagram is an over-interpretation of the degree of chemical information contained in these factors.
 - a. PMF factors are a mathematical representation of compositional endpoints. They do not represent a physical continuum. Thus investigating the evolution of OOA alone is misleading and unphysical – HOA and OOA likely co-exist in all field samples and aging of these occur simultaneously.
 - b. While PMF analysis can provide great qualitative insight into OA properties, it cannot be quantitatively compared across different field sites (unlike f₄₄, f₄₃, O:C, H:C, etc). PMF factors do not represent constant mass spectra, but rather vary with PMF fitting across sites. Thus SV-OOA at one site, might in fact be more comparable with LV-OOA

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at another.

c. Furthermore, the fitting of the mass spectra dictates the line in Figure 3. A different SV-OOA (with higher H:C) and different LV-OOA (with lower H:C) could be fit to the same spectra to produce a steeper slope in the Van Krevelen diagram.

4. Flawed comparison with the study of Heald et al. [2010]

a. Page 7100 lines 1-7: Related to point 3a, the discussion here is misrepresentative – you cannot compare the evolution of OOA factors alone (Figure 3 of this manuscript) with the TOTAL OA composition slope of -1 in Heald et al. [2010].

b. The data in both Figures 5 & 6 appear more consistent with a -1 slope than a -0.5 slope. What is the fitted slope for the chamber data alone in Figure 6?

c. Page 7100, lines 15-19: The authors refer to Figure 2 of Heald et al, but completely ignore Figure 3, which shows all (not average) data from several sites. In all of these plots, the slope of -1 is exceedingly clear (though as the paper describes, there's a leveling off at high O:C for the Mexico City data). A line with a slope of -0.5 would fit the data very poorly. These three datasets cannot be ignored in the present paper.

d. Figure 5 (and associated discussion): There are some very worrisome discrepancies between the data shown in Heald et al. [2010] and the data shown in this plot. As discussed above, Figure 3a of Heald et al shows that the Riverside data fall very clearly along a line with slope of -1. Mathematically, the PMF factors should also fall along this line, unless their contribution to total OA is minor. The fact that the Riverside OOA factors shown here do not fall on this line strongly suggests the factors were either obtained incorrectly or have been misinterpreted.

e. Further, the “Mexico City Ground” OOA2 and OOA1 factors in Figure 2 of Heald et al. connect to each other with a line with a slope that appears to be much closer to -1 than -0.5. Yet these data do not appear in Figure 5 of this paper. Why?

5. Figure 1: Does f43 refer to UMR or HR data? Captions throughout are unclear.

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6. Figure 6: The significance of the trace species shown here is unclear. The composition of these species (which make up very little of the total SOA mass) would be swamped by species unaccounted for here (eg. oligomers) in the total OA composition. It therefore seems inappropriate to compare these individual species to AMS data.
7. Figure 6: The numbering of individual compounds is misleading. It suggests some progression from molecule 1 to 9, when clearly no such evolution occurs.
8. Figure 6: what would this figure look like if H:C were determined from the f43 fit of Figure 2?
9. The supplementary materials are short and should have been integrated into the main text.

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