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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 #1

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General Comments

This paper explores changes that occur in organic aerosol composition with aging using a large AMS data set on elemental composition (H/C and O/C ratios) and key mass spectral marker peaks (m/z 43 and m/z 44) obtained from field and laboratory studies. The goal is to link the information encompassed in so-called “triangle plots” (f_{44} vs. f_{43} , where f_X refers to the fraction of total ion signal in m/z X) and Van Krevelen plots (H/C vs. O/C) for use in understanding aerosol aging. This is done by developing a parameterization for H/C vs. f_{43} that when combined with a published parameterization for O/C vs. f_{44} allows triangle plots to be transformed into Van Krevelen plots. The results of this analysis are discussed and interpreted in terms of possible changes in the functional group composition of the aerosol during aging. The explanations of

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the trends seem reasonable and should provide some useful constraints on possible atmospheric sources and mechanisms of SOA formation and aging. The manuscript is concise and well written and contains needed references and figures. I think it should be published in ACP after the following comments have been addressed.

Specific Comments

1. Page 7097: In the discussion about OOA and HOA, OOA is equated with SOA and HOA is equated with POA. Results from the recent Science paper by de Gouw et al. (2011), however, indicate that alkane-derived SOA can look like HOA. How might this impact these results?

2. Page 7098: It seems to me that the use of $H/C = 1.0$ for potential aromatic SOA precursors as a constraint in the parameterization is completely arbitrary. Why not use 1.6 for terpenes or 2.0 for alkanes? This choice appears to have a large effect on the resulting curve, which to my eyes does not fit the data as well as it could. If one weights each data point equally (which may or may not be appropriate, but the authors do not explain how they did it), then in the region between $0.05 < f_{43} < 0.12$ there are almost no points below the fitted curve, but a large number above it. If one is only interested in fitting the region $0.05 < f_{43} < 0.25$, then why force the curve to a value of $H/C = 1.0$ at $f_{43} = 0$? To my eyes, the curve should be much closer to a straight line with values of $H/C \sim 1.7$ at $f_{43} = 0.25$ and $H/C \sim 1.3$ at $f_{43} = 0$. The curves drawn in Figure 3 seem to support this conclusion, since the mean of the transformed data extrapolates to $H/C \sim 1.5$ at $O/C = 0$. This suggests to me that the data are telling you that the y-intercept of $H/C = 1.0$ in Figure 2 is much too low. It seems that the y-intercepts of Figures 2 and 3 should be similar, since one would expect $O/C = 0$ when $f_{43} = 0$. This seems like a serious issue that the authors need to address, since I would expect that the results and conclusions are sensitive to the parameterization, and others in the community are likely to use this parameterization.

3. Page 7099: The only comment made in the text about Figure 4 is that oxidation

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state is a useful metric for describing the chemistry of SOA. I suggest supporting this statement by elaborating on what new and useful information is obtained from Figure 4.

4. Page 7101: Why is no mention made of the possible addition of OOH groups? These provide twice the oxygen of an OH group, and if aging occurs in low NO_x regions then one would expect the formation of hydroperoxides more than alcohols. Furthermore, since hydroperoxides react readily with aldehydes (and ketones when acid is present) to form peroxyhemiacetals (and peroxyacetals), this might also help to explain the addition of carbonyl groups.

5. I suggest that the authors provide a description of their conceptual model for the aging process. Is aerosol composition changing with age because (1) new products are condensing, (2) the particles are undergoing heterogeneous oxidation, (3) compounds are being lost from the particles, and (4) aqueous and organic condensed phase chemistry is occurring? Do the results suggest anything about which of these processes might be important?

6. Are aged particles generally larger than young ones? It seems that if this is the case then it may indicate that aging occurs predominantly by condensation or condensed phase chemistry.

Technical Corrections

I did not find any technical errors.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7095, 2011.

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