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Atmospheric
Chemistry
and Physics
Discussions

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

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We thank the reviewers for their comments. Responses to specific reviewer comments are given below. Reviewers’ comments are included in italics and author responses are in plain text. Changes to text in manuscript are shown in bold.

Review 1:

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” (f44 vs.

f43, where fX 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. f43 that when combined with a published parameterization for O/C vs. f44 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 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.

R1.1. 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?

Tracer correlations and spectral intercomparisons from multiple campaigns suggest that ambient HOA in urban and rural sites is dominated by POA, while ambient OOA is dominated by SOA (e.g., de Gouw et al., 2005; Zhang et al., 2005; Herndon et al., 2008; Aiken et al., 2009; Ulbrich et al., 2009). Individual precursors do produce SOA with varying characteristics (e.g. Chhabra et al., 2011; Lambe et al., 2011) and alkane SOA does look like SV-OOA with a little more aging (Lambe et al., 2011). Since ambient aerosol is formed from a mix of precursors, we focus on the trends observed in the overall ambient SOA mix in this manuscript. Thus, while the composition observed by de Gouw et al. (2011) is very interesting, it seems to be dominated by lightly aged alkane SOA, which may be of limited relevance for other locations where evaporated crude oil is not the main source of the SOA.

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R1.2. 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 < f43 < 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 < f43 < 0.25, then why force the curve to a value of H/C = 1.0 at f43 = 0? To my eyes, the curve should be much closer to a straight line with values of H/C 1.7 at f43 = 0.25 and H/C 1.3 at f43 = 0. The curves drawn in Figure 3 seem to support this conclusion, since the mean of the transformed data extrapolates to H/C 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 f43 = 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.

This is a question brought up by both reviewers and we agree with the reviewers that the fit details needed to be clarified. The fit was done for both ambient and chamber data. The goal was to find a self-consistent parameterization that fit both types of data. Since ambient aerosols represent an ensemble mix of individual precursors and it is clear from Chaabra et al. (2011) and Lambe et al. (2011) that laboratory SOA data points contain variability that is dependent on the precursor, we focused on finding the parameterization that best represented the ambient data points and still reproduced the overall precursor trends observed in the laboratory data within the stated uncertainties of the parameterization.

The chamber SOA and ambient OOA data points shown in Fig. 2 were weighed equally in the fits. As both reviewers noted, a linear fit does reproduce most of the data to within

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10% (See Fig. R1). However, a comparison of the fit residuals for the ambient and chamber data points showed that the fit to the ambient data points was systematically worse than that of the chamber data points, particularly at the low f43 values (See Fig. R2). Since the ambient data points have some curvature at low f43 values, polynomial fits were also performed. This is also true for the binned data (see Fig. R3 and Fig. R4). The polynomial fit with fixed intercept reproduced most of the data to within 10% (as in the case of the linear fit) and was significantly better at reproducing the ambient data. Thus, we chose the polynomial fit with a fixed intercept of 1 when f43=0.

A value of f43=0 can be obtained from SOA under both low and high levels of oxidation (i.e. low O:C as well as high O:C). A fixed H:C intercept of 1 was chosen based on SOA species likely to yield f43=0 at these two oxidation extremes. m/z 43 has two contributions (C3H7+ from alkane moieties at low levels of oxidation and C2H3O+ from oxidized species at high levels of oxidation).

- At low levels of oxidation, the most likely SOA hydrocarbon skeleton that can yield f43 = 0 is an aromatic skeleton without large alkyl groups. Simple aromatics without large alkyl groups have H:C around 1.

- At high levels of oxidation, m/z 43 and m/z 44 are the most prominent peaks in SOA spectra and the m/z 44 to m/z 43 ratio increases with aging (Ng et al., 2010). The ion m/z 44 is thought mostly due to acids (Duplissy et al., 2011). Hence, highly aged SOA is likely to have f43=0 only if its acid content is high. The species with the highest acid content observed in the aerosol phase is oxalic acid (HOOCCOOH), which has an H:C of 1 (Kroll et al., 2011).

We agree with the reviewers that the methods described above were not explained clearly enough in the current manuscript. The need for the polynomial fit and the intercept of 1 are not immediately obvious in Fig. 2 because the continuous laboratory data are represented in the figure by many more points than the ambient data and the importance of reproducing the ambient data was not stated explicitly. In order to address the reviewers' comments and to clarify the methods used in the parameterization, we have explored a more transparent means of parameterizing the data in the revised version. In this method we appropriately weight the ambient and laboratory data points with respect to each other at the start of the fit. This can be done by binning and averaging the continuous data for each laboratory experiment so that the total number of laboratory data points is similar to the number of ambient data points used.

This is the detailed methodology for the parameterization

1. The data shown are results from multiple chamber experiments (i.e. for each precursor, multiple experiments are performed). For each chamber experiment, the f43 values are binned with a f43 increment of 0.02 and the average values for H:C and f43 are calculated for each bin. The binned averages are then used in the parameterization.

2. As pointed out by Reviewer 2, some of the data are outside the +/-10% uncertainty. Those points are mainly at the beginning of the chamber experiment where there is low signal to noise. In order to minimize the effect of these noise data points on the parameterization, only data from the peak aerosol growth until the end of the experiment are used.

3. The ambient data (solid circles) and binned laboratory data (solid diamonds) are fitted with a polynomial function without constraining the intercept. Note: The linear fit is shown in Fig. R3 just for comparison purposes; only the polynomial fit is used in the revised manuscript.

The results from the polynomial and linear fit of these data (ambient + binned laboratory data) are shown in Fig. R3. The residuals for both ambient and binned laboratory data are calculated and shown in Fig. R4. Again, the polynomial fit does a better job of fitting the ambient data than the linear fit, particularly at low values of f43. It is also clear that while the polynomial fit reproduces the ambient data points better, it also still reproduces the laboratory data points to within the stated 10% uncertainty of this parameterization. Since the number of ambient data points at the low f43 values is similar to the number of binned lab data points, the unconstrained polynomial fit reproduces the ambient dataset well. It is satisfying to note that the intercept of the unconstrained polynomial fit is 1.01, which is not significantly different from the value of 1 to which the original polynomial fits was constrained. Moreover, the new polynomial fit does not differ substantially from the original polynomial fit and does not affect the discussions/conclusions of this work.

To clarify the details of the parameterization, the following paragraph is added to Section 2 in the revised manuscript:

“The laboratory data are time-dependent data (continuous data over the course of each experiment) and account for more points in Fig. 2 than the ambient data. The variability in the chamber data points reflects precursor-dependent differences in SOA. In order to weight the laboratory data equally with ambient data, for each laboratory experiment the f43 values are binned with a f43 increment of 0.02 and the average values for H:C and f43 are calculated for each bin. The binned averages from each experiment are then used in the parameterization. While both linear fit and polynomial fits reproduce all the data (both laboratory and ambient data) to within 10% uncertainly, the polynomial fit is chosen as it reproduces the ambient data better and captures the curvature of the ambient data at lower f43 values. The polynomial fit has an intercept of 1.01, indicative of the H:C composition of SOA species likely to yield f43 =0 under low and high oxidation conditions. The ion at m/z 43 can arise from either C3H7+ (from alkyl groups) or C2H3O+ (from non-acid oxygenates) fragments. At low levels of oxidation, the most likely SOA hydrocarbon skeleton that can yield f43 = 0 is an aromatic skeleton without large alkyl groups. Simple aromatics without large alkyl groups have H:C around 1. At high levels of oxidation, m/z 43 and m/z 44 are the most prominent peaks in SOA spectra and the m/z 44 to m/z 43 ratio increases with aging (Ng et al., 2010). The ion m/z 44 is thought mostly due to

acids (Duplissy et al., 2011). Hence, highly aged SOA is likely to have f43=0 only if its acid content is high. The species with the highest acid content observed in the aerosol phase is oxalic acid (HOOCCOOH), which has an H:C of 1 (Kroll et al., 2011).”

R1.3. Page 7099: The only comment made in the text about Figure 4 is that oxidation 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.

We thank the reviewer for pointing out this oversight. We have added the following text to the revised manuscript:

“SV-OOA components have higher H/C and lower oxidation states than LV-OOA components for almost all sites, with the separation being clearer for the oxidation state. These results are consistent with the distributions of O/C for the different components (Jimenez et al., 2009). Within each category some variation is observed, reflecting the diversity of sources and degrees of aging observed in different field sites. For datasets for which only total OOA was retrievable, its properties lie in between those of SV-OOA and LV-OOA.”

R1.4. 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 NOx 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.

This is a very good point and we agree with the reviewer. We made the following changes based on the reviewer’s suggestion.

a) In Abstract:

“In this study, we find that the OOA components from all sites occupy an area in the Van Krevelen space, with the evolution of OOA following a shallower slope of ~−0.5, consistent with the additions of both acid and alcohol/**peroxide** functional groups without fragmentation, and/or the addition of acid groups with C-C bond breakage.”

b) In Section 3.1:

“If the functional group addition occurs on a CH2 group without C-C bond breakage, this slope can be caused by e.g., the addition of 3 OH groups and 1 C=O group or the addition of 2 OH groups and 1 COOH group. If formation of peroxide is involved, the slope can arise from the addition of 1 OOH group, 1 OH group, and 1 C=O group, or the addition of 1 OOH group and 1 COOH group. Formation of peroxides would be expected if aging proceeds under low-NOx conditions (e.g., Surratt et al., 2006). Furthermore, hydroperoxides react readily with aldehydes (and with ketones under acidic conditions) to form peroxyhemiacetals (and peroxyacetals) (Johnson et al., 2004, 2005), which could also explain the additional of carbonyl groups.”

Also,

“Therefore, an OOA aging mechanism that is consistent with measurements (laboratory + field data) is that the ensemble average of the transformation involves both the net addition of COOH and OH/**OOH** functional groups.”

c) Conclusions:

“The observed OOA slope of ~-0.5 is consistent with several simple mechanisms such as the net addition of both COOH and OH/**OOH** functional groups without fragmentation (i.e. C-C bond cleavage).

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R1.5. 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?

While providing a conceptual model for the aging process would be very useful, we do not think that we have enough data to disentangle these details based on our results. However, a key advance in this work is that separating the OOA components from HOA and other POA components allows for separating out the effects of physical mixing of SOA and POA from aging of SOA. Moreover, the general trends in OOA aging could provide useful constraints for models that explicitly investigate the relative importance of these processes. We have added the following text to the conclusions of the manuscript to reflect this discussion.

In Conclusions:

"Aerosol aging can proceed through various pathways including condensation/evaporation, oxidation, particle-phase reactions, and mixing of different air masses. While our results remove the contribution from mixing between OOA and primary OA components, they do not allow us to discriminate between the other aging pathways; the general trends in OOA aging obtained in this study could, however, provide useful constraints for models that explicitly investigate the relative importance of these processes together in the overall evolution of SOA."

R1.6. 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.

In the few cases in which we have derived component-resolved size distributions, it does seem like the aged OOA has a larger size distribution than the fresher OOA (e.g., Nemitz et al., 2008). Some community members feel that this is a strong indication of the importance of cloud SOA formation, which would lead to organic material in the "droplet mode." However, we do not think we have enough data to make a general argument on this. More aged aerosols will have been longer in the atmosphere and increases in size can arise from condensation of SOA, coagulation and/or particle-phase SOA chemistry. In addition, other processes such as deposition and condensation of inorganics may also be responsible for the increase in size. This should be a topic of future research with case studies in which the air mass history is well constrained.

Review 2:

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.

We thank the reviewer for the detailed comments which point to aspects of the paper that are unclear and need to be clarified. However, we disagree with the reviewer's suggestion that the work in this paper is technically flawed and that this paper does not offer further scientific insight into the OA aging process. The detailed responses below demonstrate that all technical methods used in this manuscript can be readily justified, and that we can clearly address all the specific criticisms from the reviewer. The new scientific insights into the OA aging process offered in this manuscript are:

1) The parameterization of H:C in terms of f43: This is an important advance as it allows for making direct connection between the “triangle plot” (Ng et al., 2010) and Van Krevelen (Heald et al., 2010) methods of describing the evolution of OA composition with aging. It also allows for direct intercomparisons between the large body of existing and future unit mass resolution ambient AMS and ACSM (Aerosol Chemical Speciation Monitor) (Ng et al., ACP 2010, EST 2011) datasets with high resolution AMS datasets.

2) The integrated use of PMF components from worldwide studies to allow for an average description of trends in ambient SOA composition with aging. The ambient SOA composition trends are followed in a manner that is analogous to and can be compared with chamber SOA experiments. Key aspects of this analysis include

- the use of factor analysis to separate out trends in distinct components (SV-OOA, LV-OOA, and HOA for example) that contribute to total OA. By separating OOA components from HOA components (surrogates for primary OA) we remove the effect of physical mixing of secondary and primary OA in the observed trends. This provides us with a unique opportunity to examine ambient SOA chemical trends on their own which differs from and complements the work of Heald et al. (2010), which examined Van Krevelen trends for total OA.

- the integration of OOA measurements from multiple sites to build an overall picture of the continuum of ambient SOA chemical evolution that is not subject to site-specific meteorology, source, or mixing effects.

- the determination that the continuum of ambient OOA composition follows a Van Krevelen slope of ~-0.5 as O:C increases. This slope is shallower than the slope of -1 expected for mechanisms that involve addition of carboxylic acids alone without C-C bond breaking. These changes in SOA composition are consistent with net additions of both acid and alcohol/peroxide functional groups without fragmentation, and/or the addition of acid groups with C-C bond breakage.

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R2.1. 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 say the use of m/z 44 which contains a large fraction of the measured oxygen for the O:C determination).

The fact that a small fraction of the total H is contained in the m/z 43 ion is not an obstacle for using it as a tracer for H:C, if we can show that H:C is indeed correlated with f43. For example, f60 levels of the order of 1% are used as a tracer for biomass burning organic aerosol (BBOA) (e.g. Cubison et al., 2011, and others), even though they represent a very small fraction of the actual BBOA. Similarly with the use of other tracers by many other researchers, e.g., cholesterol or hopanes or methyltetrols, which are often used as molecular markers of different types of OA and typically account for a few percent or less of the mass of those OA types.

The manuscript is modified to reflect this discussion as follows:

In Section 2,

"Measured O:C is well parameterized in terms of the ion at m/z 44, which accounts for much of the measured oxygen in OOA. For the H:C parameterization, we explored the use of m/z 43, which is the next most intense ion in OOA component spectra. While the ion at m/z 43 does not necessarily contain a large fraction of measured total hydrogen in OOA, it does correlate well with H:C as shown in Fig 2. In this case, m/z 43 functions as a tracer for H:C analogous to the use of f60 (fraction of m/z 60 to the total signal in the mass spectrum) as a tracer for biomass burning organic aerosols (BBOA) (e.g., Cubison et al., 2011), even if this ion usually represents a small fraction of the actual BBOA."

R2.2. 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*

The reviewer might have made a mistake when examining the glutaric acid mass spectrum. That mass spectrum is shown in Fig. R5. It does NOT contain a fair amount of m/z 43, on the contrary, f43 only accounts for 2% of the total signal.

It has been shown that f44 increases with the mass fraction of COOH (Duplissy et al., 2011). When examining the values of f43 of the standards listed in the database, it is found that f43 relatively low (<0.04) regardless of the mass fraction of COOH, suggesting that f43 (mostly C2H3O+) arises from non-acid oxygenates.

R2.3. 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?

Please see a detailed response to this topic on R1.2 above.

R2.4. 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. R2.4.a. PMF factors are a mathematical representation of compositional endpoints.

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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.

The separation of HOA and OOA using PMF of AMS spectra is, in fact, one of the main achievements of this technique, and the reason why the scientific community has embraced it enthusiastically, leading to ~100 publications using it and its results in the last 6 years. Although the separation is never perfect, it is more than sufficient to allow studying the aging of OOA separately from the contribution from HOA. In fact, this topic has been discussed in many recent studies (e.g., Jimenez et al., Science, 2009; Ng et al., 2010). When taking the OOA components from all sites together, the different f44 and O:C values observed for all the OOA components reflect the fact that there is indeed a continuum of OOA properties in ambient aerosols, and this continuum at each individual site can often be apportioned into SV-OOA and LV-OOA components according to the details of the aerosols observed at that particular site (e.g. Lanz et al., 2007; Ulbrich et al., 2009; Ng et al., 2010).

Chamber studies, in particular, can separate the OOA aging since typically there is no HOA present. The consistency between the aging observed in ambient and chamber studies is further evidence that PMF is working well in terms of extracting OOA from the mixed ambient aerosol. OOA has been shown to be a good surrogate for SOA (see e.g. Jimenez et al., 2009 and references therein) and many of the chamber experiment are designed to study the formation and evolution of SOA.

The manuscript has been modified and additional text has been added to more explicitly state the usefulness of examining the OOA component evolution separately as follows:

a) In the Abstract:

“Heald et al. (2010) examined the evolution of total OA in the Van Krevelen diagram. In this work total OA is deconvolved into components that correspond to

primary (HOA and others) and secondary (OOA) organic aerosol, which allows for the examination of the chemical composition trends of the OOA components alone in the Van Krevelen diagram. Deconvolution of total OA composition allows for removing physical mixing effects with primary OA components from OOA trends and provides a unique means of following ambient secondary OA composition that is analogous to and can be compared with trends observed in chamber studies of SOA formation.”

b) In the Conclusions:

“This work also provides ambient composition information that is analogous to and can be compared with trends observed in chamber secondary OA experiments and detailed molecular-level studies.”

R2.4.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 at another.

The fact that the PMF components do vary between sites, depending on the sources and degree of aging of the OA at that site, has been recognized for several years, and in fact papers by the current authors have described this phenomenology in detail. See for example Fig. 1 in Jimenez et al. (2009) that shows the distribution of O:C of the different OOAs, or Figs. 1 2 in Ng et al. (EST, 2011) which illustrate the variation of the OOA spectra across sites, or Fig. 4 in the current paper (ACPD version). Since the naming of the OOA components (SV-OOA and LV-OOA) is not absolute, there would inevitably be some overlap between the components from different sites. It is true that doing a single comparison of e.g. the LV-OOA at one site with the SV-OOA at a different site could be confusing. In this manuscript we do not seek to explain the trends in SV-

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OOA to LV-OOA for individual sites or between two sites. Instead, we combine all the OOA components together, treat each as a snapshot of evolution along the OOA continuum and explain the overall trends observed in this continuum. The overall trend observed in the ambient is similar to that observed in chamber studies, and begs for an explanation.

We have added the following text to the introduction of this manuscript to clarify and explicitly state the points summarized above:

"Total OA composition is driven by several effects, including physical mixing effects, condensation/evaporation effects, and photochemical transformation. In this manuscript we deconvolve total OA into distinct primary (HOA and others) and secondary (total OOA, LV-OOA, SV-OOA) components and explicitly examine ambient OOA composition trends alone in a manner that is analogous to and can be compared with chamber secondary OA experiments. By deconvolving total OA into different components, we remove physical mixing effects between secondary and primary aerosol which allows for examination of the evolution of OOA components alone. Unit mass resolution ambient OOA components from Ng et al. (2010) are then transformed to the Van Krevelen space using a new parameterization of H:C in terms of f43 that is derived from and is valid for laboratory SOA and ambient OOA components. The OOA composition at any given site is highly dependent on the meteorology, photochemical aging, and different precursor sources affecting that site. Each component provides a "snapshot" of the OOA as it is formed and aged in the atmosphere, but together the components from multiple worldwide sites define a continuum of OOA properties (Ng et al., 2010; Morgan et al., 2010). We use this integrated analysis of OOA components to examine the trends in Van Krevelen space and the implied changes in chemical composition of ambient OOA."

R2.4.c. Furthermore, the fitting of the mass spectra dictates the line in Figure 3. A

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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.

For each ambient dataset the actual PMF fits are performed on the entire mass spectral matrix (0-300 amu) as a function of time (i.e. not prescribing or forcing the H:C or O:C values in any way). So, species with different mass spectra and temporal trends can be separated in PMF even if they have similar H:C and O:C values. Thus, the Van Krevelen diagram cannot be used to assess the "best" PMF solutions as the reviewer seems to be suggesting.

The PMF solutions shown in Fig. 3 were evaluated according to the very detailed procedures laid out in Ulbrich et al. (2009). PMF provides both SV-OOA and LV-OOA mass spectra and corresponding SV-OOA and LV-OOA time trends. A key diagnostic that was used to identify the "best" PMF solution is the interpretability of the component time trends when compared with tracer time trends (Ulbrich et al., 2009). The PMF solutions that were chosen for all the datasets shown in Fig. 3 were obtained after exploring a range of possible solutions. For each dataset, the chosen solution was obtained by examining correlations between tracer and PMF component time series and the correlations between component spectra and the mass spectral database of known aerosol mass spectra. We generally avoided the use of the FPEAK parameter and thus the "rotational freedom" of the solutions is not systematically forced in any particular way. Thus, we think that the components obtained from these analyses are the "best" and most interpretable PMF solutions that could have been chosen.

R2.5. Flawed comparison with the study of Heald et al. [2010] R2.5.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].

It is clearly acceptable to discuss the comparison with previously published results.

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This is in fact needed for scientific progress. We agree with the reviewer that it needs to be clearly specified that the Heald et al. (2010) paper focused on the evolution of total OA, while our paper focuses on the evolution of OOA alone. We have added new text to address this point, as summarized in responses to comments R2.4a and R2.4b above. However, this point was already discussed in the original ACPD manuscript. The specific text is quoted below:

[Original ACPD Abstract] Heald et al. (2010) suggested that the bulk composition of OA line up in the Van Krevelen diagram with a slope -1; such slope can potentially arise from the physical mixing of HOA and OOA, and/or from chemical aging of these components. In this study, we find that the OOA components from all sites occupy an area in the Van Krevelen space, with the evolution of OOA following a shallower slope of -0.5, consistent with the additions of both acid and alcohol functional groups without fragmentation, and/or the addition of acid groups with C-C bond breakage.

[Original ACPD main text] As most data in Heald et al. (2010) represent the average OA composition at each site, the observed slope of -1 in their study can arise from a combination of physical mixing of HOA and OOA components, and/or chemical evolution of these components. The HOA, SV-OOA, and LV-OOA components from Riverside are highlighted in Fig. 5. It is clear that once the total OA is deconvolved into these components, the evolution of SV-OOA to LV-OOA follows a shallower slope.

To clarify this point further, we have made some additional changes to the manuscript as follows:

In the Abstract:

"Heald et al. (2010) examined the evolution of total OA in the Van Krevelen diagram In this work total OA is deconvolved into components that correspond to primary (HOA and others) and secondary (OOA) organic aerosol, which allows for the examination of the chemical composition trends of the OOA components alone in the Van Krevelen diagram."

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In Section 3.1: The original paragraph comparing the Heald et al. (2010) results with the results from this manuscript is replaced with the following text:

“Heald et al. (2010) examined the evolution of total OA by using the average OA composition at each site and observed a slope of ~-1. Total OA evolution is affected by several factors including physical mixing effects and processes such as oxidation, volatilization and condensation. In this work, by deconvolving the total OA into different components, we are able to separate out the effect of HOA and OOA mixing and focus only on the aging of OOA components alone. On average, the transition from less oxidized to more oxidized OOA follows a slope that is shallower than -1 (~-0.5). In Heald et al. (2010), it is noted that the slope of the Mexico City aircraft data levels off at higher oxidation. The leveling off of the total OA slope at higher O:C, when the OOA fraction of OA is highest, is consistent with the overall trend observed for OOA components alone in this study.”

R2.5.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?

The following text has been added to the manuscript.

In Section 3.2:

“The slope for the chamber a-pinene photooxidation data alone is -0.64. It is noted that results from laboratory studies of other precursors also have slopes shallower than the slope of -1 expected for acid group addition alone (Chhabra et al., 2011; Lambe et al., 2011).”

R2.5.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

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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.

Figure 3a in Heald et al. (2011) shows the total Riverside SOAR data. The PMF factors from the Riverside SOAR data are included in our manuscript since we are interested in looking at trends in OOA composition and not trends in total OA composition. As noted in our ACPD manuscript, once the total OA at Riverside are deconvolved into different factors, it is clear that the evolution of the OOA components at Riverside lies along a shallower slope of ~-0.5.

Figure 3b in Heald et al. (2011) are the AMAZE data. The PMF factors from AMAZE are not included in our manuscript as they have not been published yet. In the AMAZE campaign, the air mass is a mix of both in-basin SOA production and out-of-Basin sources. As the out-of-Basin sources are significant for as much as 30% of the entire measurement period (Chen et al., 2009), we cannot use ALL the data from the campaign to describe the evolution of SOA alone.

Figure 3c in Heald et al. (2011) shows the Mexico City data (flight data). While Heald et al. (2011) proposed a slope of -1 for the evolution of total OA, the authors themselves also noted that there is a leveling off in the slope at higher O:C. In our work, by deconvolving the total OA into different components allows us to separate the physical mixing of HOA and OOA and focus only on the evolution of the OOA components. The leveling off of the total OA slope at higher O:C, when the OOA fraction of OA is highest, is consistent with the overall trend observed for OOA components alone. The text has been modified to include this discussion (See the modifications to Section 3.2 under R.2.5.a).

R2.5.d. Figure 5 (and associated discussion): There are some very worrisome dis-

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crepancies 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.

We disagree with the reviewer on this point. Figure R7 shows the Riverside total OA data from Fig. 3a of Heald et al. (2010) along with the PMF factors. It is clear that every black point in the total OA continuous data can, in fact, be represented by a linear combination of the PMF factors, as projected into this space. Thus, one cannot automatically conclude that the factors were obtained incorrectly based on the Van Krevelen Space. Moreover, PMF analyses were performed on the entire mass spectral matrix (0-300 amu) as a function of time (i.e. not based on the H:C or O:C values). The correlated variations in individual ion fragments that justify the need for more PMF factors are not necessarily obvious in the Van Krevelen Space.

The reviewer's statement that *"…..the factors were either obtained incorrectly or have been misinterpreted"* is incorrect. The Riverside PMF components have been described and justified in previous publications. Each of the PMF factors has its own unique mass spectra and time series and the factors were judged as meaningful based on the correlations with external tracers (Docherty et al., 2008; Huffman et al., 2009; Jimenez et al.., 2009). For the Riverside field campaign, PMF was performed on both the regular AMS data (Docherty et al., 2008) (as in the case of all other campaigns shown in this manuscript) as well as on thermal denuder AMS data (Huffman et al., 2009).

The Huffman et al. (2009) manuscript intercompared the two types of PMF and states the following:

"In addition to providing volatility profiles of all PMF-identified components, including the thermally denuded data enhances the contrast between time series of the different components and thus may facilitate their separation. However, including these data may also introduce additional variation in the MS which could distort the PMF fit. The results of PMF analysis from each campaign, both including and omitting the thermally denuded data points, are very consistent. As a result, it appears that any degradation of the PMF solution due to additional variation in the MS after TD-processing is more than compensated by the enhanced contrast between the different components. Thus we conclude that the PMF analysis of the TD-AMS data is successful at recovering the same components that are important under ambient-only conditions. In fact we will show that including the TD data enhances the application of PMF with respect to ambient only data and thus we recommend that future PMF analyses also use TD-AMS data whenever possible."

As shown in Fig. R6 (reprinted from Jimenez et al., 2009), the component mass spectra of these components are distinct from each other. The SV-OOA component that is shown in Jimenez et al. (2009) and in this manuscript is the weighted sum of two of the semi-volatile OOA components (OOA-2 and OOA-3) extracted by Huffman et al. (2009) in TD-AMS PMF. The HOA, SV-OOA, and LV-OOA components in Riverside also have tracer correlations (Docherty et al., 2008; Ng et al., 2010) that are consistent with what has been observed in many other field measurements.

R2.5.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?

The Mexico City ground data presented in Heald et al., (2011) are based on the analysis of 5-days of ground site data (performed early on in the HR-ToF-AMS data analysis software development, when analyzing additional days was very onerous). Two OOA components (SV-OOA and LV-OOA) were obtained from that dataset (Aiken et al., EST, 2008). The Mexico City ground data presented in this work are the ground data from the entire campaign (~3 weeks) and only one OOA component was obtained (see a discussion of this point in Aiken et al., ACP, 2009). We chose to use the results from the entire campaign, as we thought that it would be more representative of the air masses sampled during the entire campaign than the 5-day data. We have, however, included the 5-day data in the revised manuscript as suggested by the reviewer. The OOA slope from the 5-day data is indeed closer to -1 than to -0.5. However, as mentioned earlier, the SV-OOA to LV-OOA slope at each individual site can be affected by several factors including meteorology, mixing and transport, and photochemical transformation. Since our goal is to obtain a description of the overall trend in composition of OOA across multiple sites, we do not think that we should over-interpret this individual slope. Thus, this revision simply adds two more data points to our work and does not change the discussions and/or conclusions of our work.

R2.6. Figure 1: Does f43 refer to UMR or HR data? Captions throughout are unclear.

To clarify this point, the following sentence is added to the figure caption:

“It is noted that f43 refers to ratio of total m/z 43 ($C_3H_7^+$ and $C_2H_3O^+$) to total signal in the component spectrum for the components. The only exception to this are the squalane data. The squalane data points were obtained by heterogeneous oxidation and thus f43 contains contribution from both unreacted squalane as well as oxidized squalane products. In order to follow the production of the oxidized materials, we only show the ratio of $C_2H_3O^+$ to total signal (i.e., $fC_2H_3O^+$) for squalane data to examine its oxidation trends.”

R2.7. 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

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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.

We disagree with the reviewer on this point. It has been shown in Chhabra et al. (2011) that many SOA systems show good agreement between AMS elemental composition measurements and elemental composition of identified species, when a majority of the SOA mass has been speciated. For a-pinene ozonolysis, >90% of SOA mass has been identified by GC-MS technique (Yu et al., 1999). As shown in Chhabra et al., (2011), the species identified by Yu et al. (1999) show close agreement to AMS data. Many of the same products identified in a-pinene ozonolysis have also been identified in a-pinene photooxidation and there is also close agreement between AMS elemental composition and that of identified products in the photooxidation system. Therefore we believe that the use of these tracer species is significant and useful in the context of our paper.

R2.8. Figure 6: The numbering of individual compounds is misleading. It suggests some progression from molecule 1 to 9, when clearly no such evolution occurs.

To clarify this point, the figure caption has been modified to read:

"The numbers correspond to individual molecular products in a-pinene SOA, with their structures being shown on the right. **It is noted that the increasing number correlates with higher O:C and higher generation of oxidation, but it does not represent literally the order in a reaction chain.**"

R2.9. Figure 6: what would this figure look like if H:C were determined from the f43 fit of Figure 2?

The original ACPD Figure 2 indicates that the flow tube H:C values are approximately 10% lower than predicted by the parameterization while the chamber data is approx-

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imately 5% lower than predicted by the parameterization. Thus, estimating H:C from the f43 fit would have the effect of flattening the overall a-pinene slope slightly. These small changes will not affect the main point which is that a-pinene SOA evolves along a slope that is shallower than the -1 slope expected for addition of carboxylic acid groups alone without C-C bond breaking.

R2.10. The supplementary materials are short and should have been integrated into the main text.

We have moved Fig. S1 to the main text as suggested. We keep Fig. S2 as supplementary material. While Fig. S2 adds information to the current work, parameterization of primary components is out of the scope of this work and we do not want to distract the readers with a figure that is similar to Fig. 2 of the main manuscript.

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

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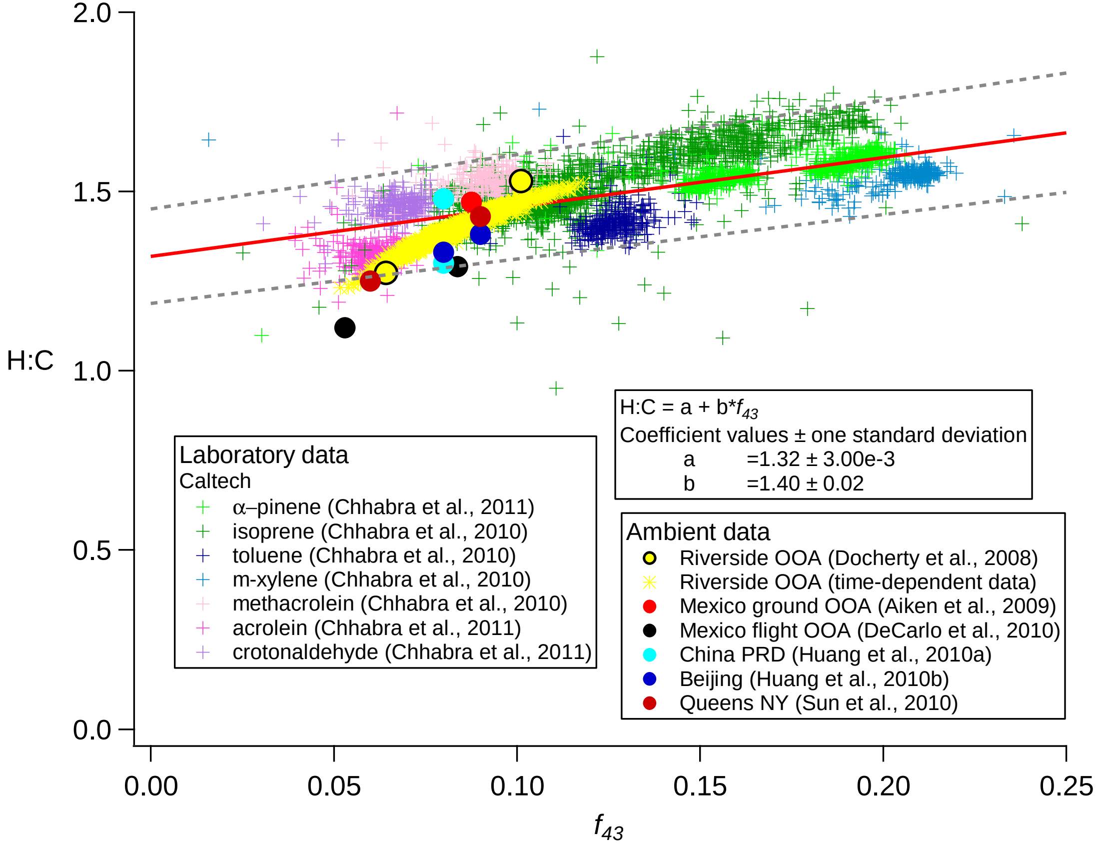

Figure R1. A linear parameterization of H:C in terms of f_{43}. The dotted gray lines are ±10% from the fitted line.

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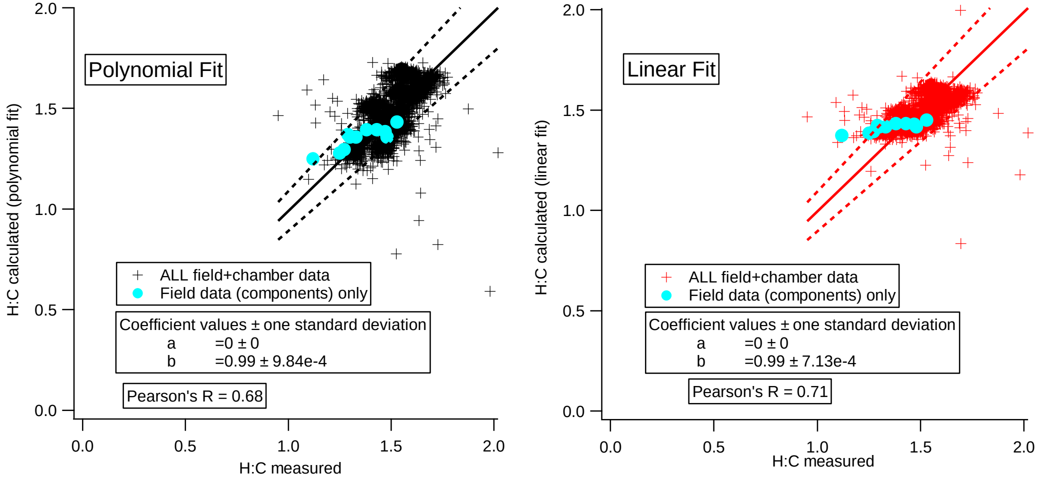

Figure R2. Scatter plots of calculated (polynomial fits and linear fits) vs. measured H:C. The field data are highlighted in light blue. It is clear that the polynomial fit is better at representing the field data.

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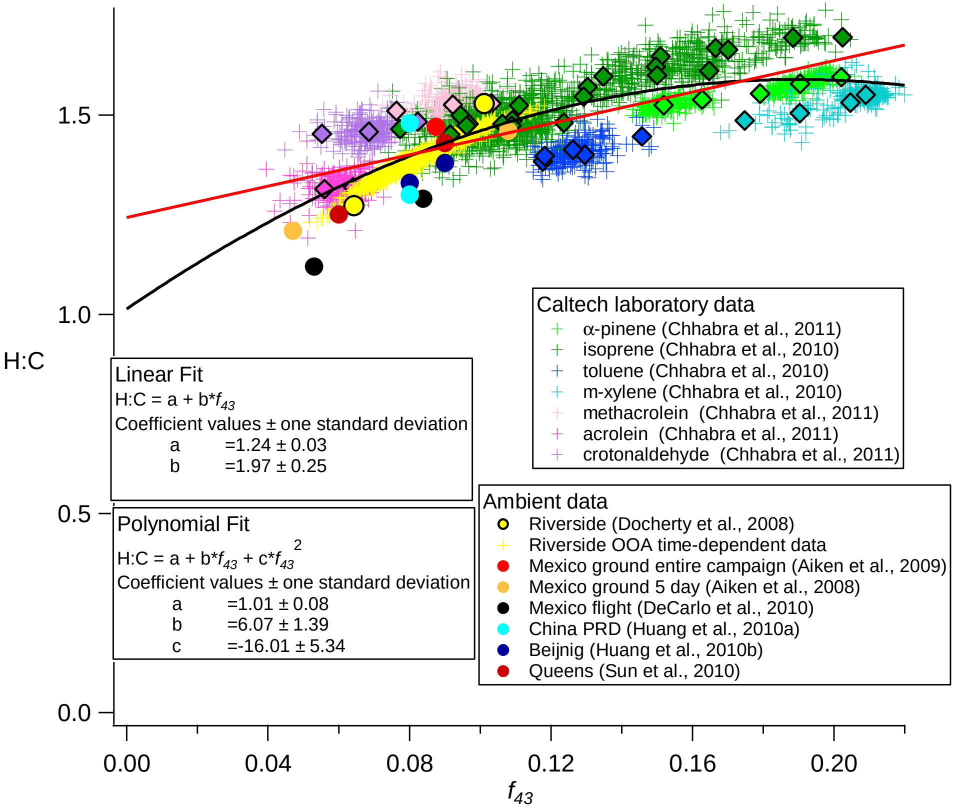

Figure R3. Revised parameterization using both ambient data (solid circles) and binned laboratory data (solid diamonds). The time dependent laboratory data points are shown for reference only and are not used in the parameterization. Both linear and polynomial fits are shown for comparison here. In the revised manuscript, only the polynomial fit is used.

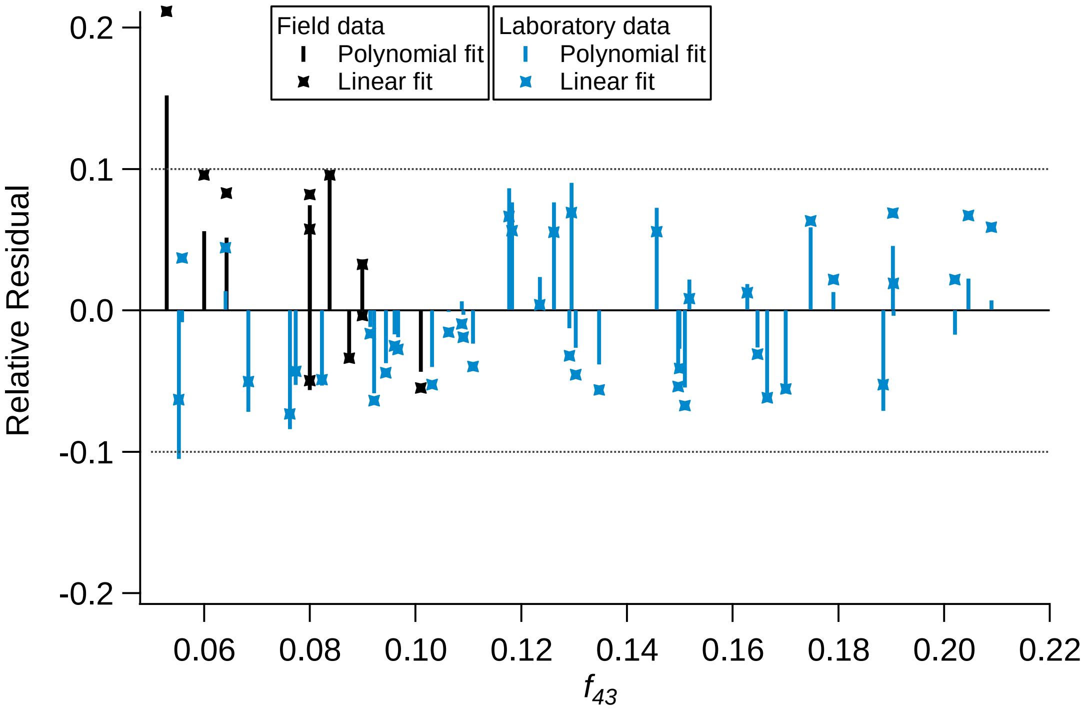

Figure R4. Relative residuals (calculated by (fit-measured)/measured) for both field data and binned laboratory data from polynomial/linear fits. Note that the polynomial fit (black data) represents the field data better, especially at low f_{43} values.

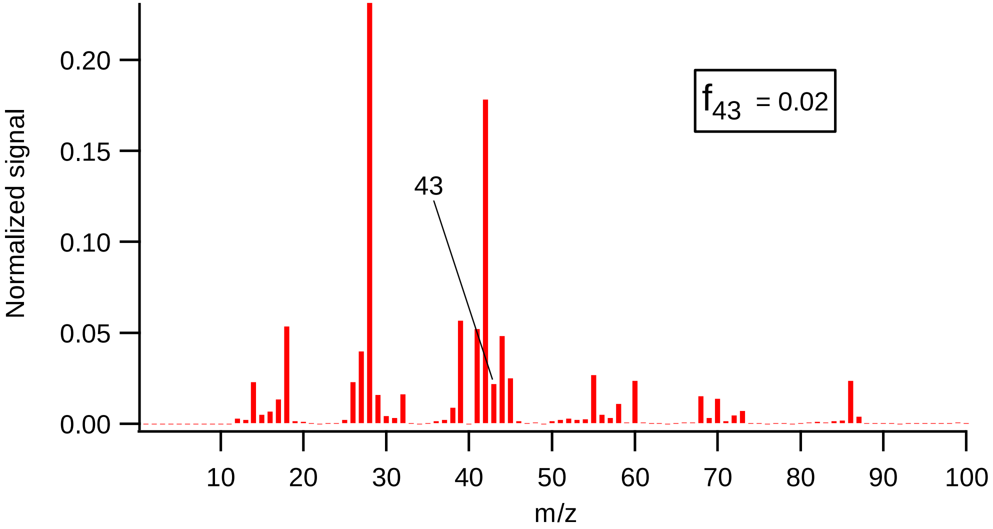

Figure R5. Normalized glutaric acid mass spectrum.

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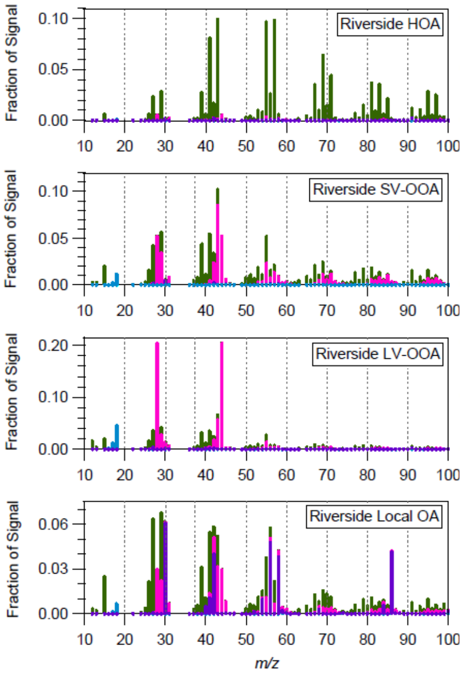

Figure R6: This is Figure S1 in Jimenez et al., (2009), showing the distinctive mass spectral features of the PMF factors.

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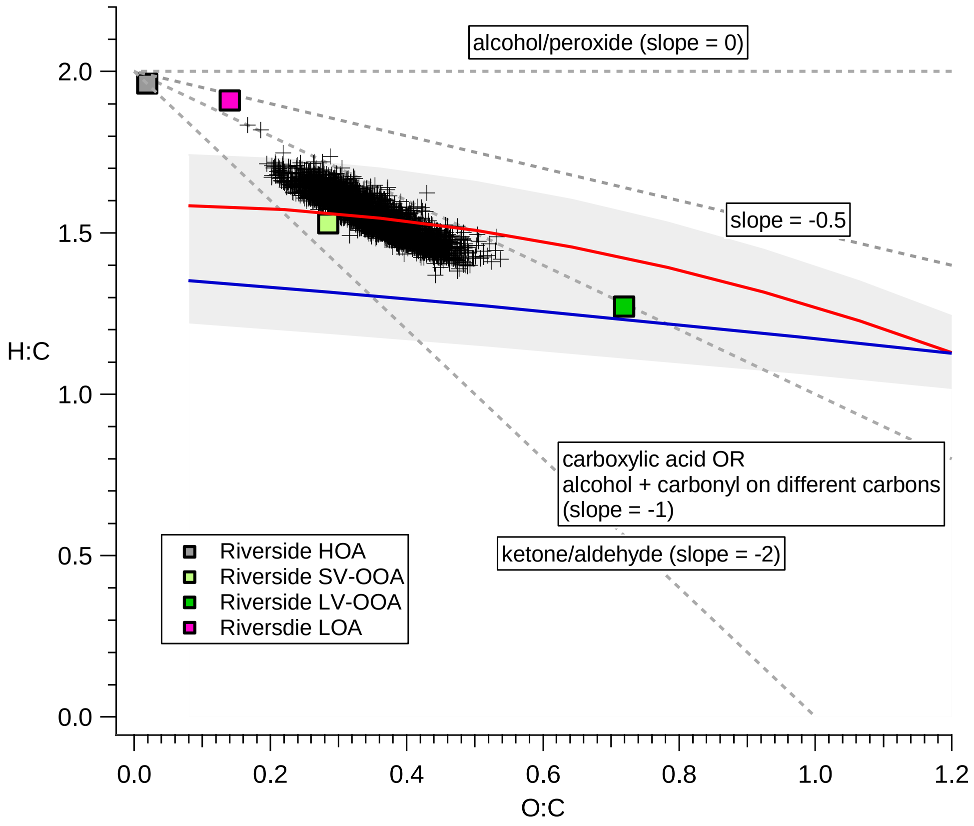

Figure R7. Representation in the Van Krevelen diagram of all data points from Riverside (as in Heald et al., 2010) and factors obtained from PMF analysis.