

Interactive  
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## ***Interactive comment on “Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data” by I. M. Ulbrich et al.***

**I. M. Ulbrich et al.**

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### **Response to Comments by V. Lanz (Part 2)**

We thank V. Lanz for his additional comments on the manuscript. Our response has been divided into two parts to fit within the allowed page length for Author Comments prescribed by ACPD (15 pgs.). This part includes responses through #10 of V. Lanz's comments. Excerpts from his comments appear below in italics. Our responses follow each excerpt. Changes to the manuscript appear in bold.

A) *Verification of factor interpretations Abstract, p. 6731, lines 4-5: "It is critical to use correlations between factor time series and external measurement time series to support factor interpretations". According to my experience, this correlation might not*

Full Screen / Esc

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Interactive Discussion

Discussion Paper



always be enough to ensure an accurate interpretation of PMF retrieved factors: the correlation between factor scores and the auxilliary data series can be due to several reasons (e.g., as both reflect human activities, meteorology etc.) More options can be considered, such as the comparison measured vs. modelled emission ratios (e.g.,  $POA_{modelled}/NO_{x,meas.}$  vs.  $POA_{meas.}/NO_{x,meas.}$ ), diurnal, weekly or seasonal cycles (boxplots of the scores) etc. as advocated earlier (Lanz et al., 2007, 2008a, 2008b.). This could be mentioned.

[Response]: We did not say, nor did we mean to imply that correlations with time series (TS) are sufficient as the only metric for interpreting factors. Rather, we are aware of several PMF papers (non-AMS) that do not use time series of tracers for validation of the results even when these time series are available. In that context we are strongly suggesting that this is a very important (necessary but not sufficient) test of the results. This conclusion arises especially from the results of the synthetic data cases when too many components are requested in PMF, in which output factors that were non-existent in the input still have mass spectra (MS) that correlate highly with many database mass spectra, and have realistic-looking time series. This specific result is a new piece of information that was not available from previous studies, which is why it is emphasized in the current paper, which focuses in the methodological aspects as much as on the atmospheric results.

We agree with V. Lanz that time series correlation alone does not necessarily give meaning to a factor, as those may indeed also arise from human activity or meteorological reasons, or also PMF splitting behavior. For these reasons, we strongly agree that there are additional necessary tests beyond comparisons of spectra and time series. In fact we already used most of those suggested by V. Lanz in our 2005 paper about factor analysis of this dataset [Zhang et al., ACP, 2005]. As we state on P6748, L15-20 of the current paper, the current results for OOA-I and HOA are very similar to those of Zhang et al. and (L19-20): "All interpretations of the factors made by Zhang et al. (2005a, c) hold for these factors." In fact, most of our 2005 paper presents multiple

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

pieces of evidence to support the interpretation of the HOA and OOA(-I) factors, since this was the first published factor analysis of AMS spectra and we were encountering skepticism about the results. See section 3.1.4., p. 3295 on Zhang et al. (ACP, 2005) for a discussion of the HOA/CO, HOA/EC, HOA/NO<sub>x</sub>, and OOA/SO<sub>4</sub> for this study and comparison with ratios from the literature. Diurnal box plots are presented in Fig. 1 of that paper.

Beyond the tests suggested by V. Lanz, additional tests that we already performed in our 2005 paper include comparison with the results of other apportionment methods such as the EC-tracer method (Fig. 10-12 in Zhang et al. (2005) and associated discussion), comparison of estimated O/C and OM/OC of the factors to those from the literature (Fig. 9), comparison of the estimated size distributions of the factors with each other and with the literature (Fig. 5-8), comparison of the size distribution of the increase in OOA with the condensational sink during a period dominated by photochemical processing (Fig. 15), correlation of the amount of OOA increase with the ozone increase during that period, and comparison of the increase in the total organic spectrum during that period with the average OOA spectrum for the campaign (Fig. 16). We will briefly mention the importance of using these additional tests in the revised manuscript. Because these analyses are not included in the present work, we feel that it would inappropriate to list them in the abstract.

With respect to further support for the interpretation of OOA-II, besides the mass spectrum and the comparison of its time series with nitrate and chloride (already included in the manuscript), we will include the diurnal cycle along with those of nitrate and chloride in the revised paper (likely in the supplementary info). Additional discussion of this topic is below in response to further comments. We do not believe that the ratios of OOA-II to nitrate or chloride observed in this study have a fundamental significance, but rather result from the particular source strengths, aging and volatility distributions, temperature, RH, etc. during this study. For this reason we did not report those ratios in this paper. The interested reader can still see the approximate ratios from Fig.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

5 and compare to other studies. For example we observe ratios of OOA-II/NO<sub>3</sub> ~1 while Lanz et al. (2007) observe a ratio ~2.5. We will briefly compare these ratios in the revised paper. (As an aside, non-refractory chloride is not reported on that paper, but it would be of interest to know whether a correlation of OOA-II with NR chloride is observed or not for that dataset). Finally, we also have preliminary results using two different methods that indicate that the size distribution of OOA-II is also consistent with our interpretation, however we decided not to include this information in the submitted paper as it would need much additional space in the paper as well as additional work to finalize it, and it is only of tangential interest to the methodological results of this paper. One of the size-distribution analysis techniques is similar to that used in our Nemitz et al. paper (AS&T, 42:636-657, 2008).

*B) Three-factorial solution of the real Pittsburgh data: OOA-II vs. HOA From an atmospheric science view, I believe an important section of this manuscript is the "3-factorial solution" (best solution as selected by the authors) within chapter 3.1 (Real Pittsburgh data). The interpretation of these 3 three factors (OOA-I, OOA-II, and HOA) is very well-founded and could additionally be supported, e.g. the interpretation of OOA-II and HOA:*

*OOA-II - as reported in this study - is dominated by m/z's (18), 43, 44, and 57 (Fig. 5, panel a). While m/z 43 may represent both oxidized ( $C_2H_3O^+$ ) or hydrocarbon-like ( $C_3H_7^+$ ) aerosol components originating from different sources, mass fragment 57 has been suggested as a marker for primary combustive (diesel) sources ( $C_4H_9^+$ ) in many previous studies. Mass fragment 44 represents mostly non-gaseous  $CO_2^+$ , a signal that is likely due to highly oxidized substances such as di- and polycarboxylic acids. Primary vehicle exhaust can be the principal source of the di-carboxylic acids in urban areas (Yao et al., 2004), potentially causing the enhanced m/z 44 signal here as well.*

[Response]: Yao et al. (2004) state that "the ratio of C3/C4 in atmospheric particles is a useful indicator to differentiate primary (vehicular) sources from secondary sources. [...] Primary vehicle exhaust was the principal source of the dicarboxylic acids in the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive  
Comment

winter at these two urban sites [in Hong Kong...]. In the summer, the average C3/C4 ratio [suggests] a large contribution of secondary sources to particulate dicarboxylic acid formation." Yao et al. (2004) also cite an earlier study and note, "Yao et al. (2002) reported that the C3/C4 mass ratios from a suburban site and two urban sites in Hong Kong were generally larger than unity, suggesting that the primary vehicle emissions were not the major source of dicarboxylic acids in the atmospheric particles at these sites." Since our study took place in late summer / early fall and at a location (like Hong Kong) strongly influenced by regional secondary aerosols, we expect that these small acids will be dominated by secondary sources and not primary ones in our study.

In addition, note that those small acids that are typically measured by GC-MS or IC only account for a small fraction of the OOA mass detected by the AMS: e.g. Takegawa et al. (2007) report that only 14% of the  $m/z$  44 signal is accounted for by several acids and oxoacids for a dataset in Tokyo. This is consistent with the low mass fractions (of total OA or OC) from those acids reported in many studies. Thus we would not expect that the variability or sources of those acids would play a determining role on the AMS signal, which is sensitive to the total OA mass.

In a study of primary particles from vehicle emissions and other sources (including meat cooking and paper and plastic burning) sampled by HR-ToF-AMS, Mohr et al. (ES&T submitted 2008) note, "All of these sources have low total  $m/z$  44 and this signal is not dominated by the  $\text{CO}_2^+$  ion." When measured in the AMS, ambient OOA mass spectra have typically  $\sim$ 10-15%  $\text{CO}_2^+$ , whereas primary emissions from several diesel and gasoline vehicles is  $\sim$ 0.3%  $\text{CO}_2^+$  (Mohr et al., 2008). Thus even if such acids are present in vehicle POA, they are typically trace species and not major components of the mass. Similarly carbonyls in PM emissions from motor vehicles have been quantified at about  $2 \text{ mg km}^{-1}$  (Jakober et al., 2006) while OM emissions are of the order of  $400 \text{ mg km}^{-1}$  (Kirchstetter et al., 1999). This confirms that while some oxygenated species are present in vehicle PM, their fraction and associated oxygen content are far smaller than for SOA/OOA. We conclude that the presence of  $m/z$  44 in the OOA-II

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

spectrum strongly supports secondary, rather than primary, OA.

A different way to look at the same evidence is using the oxygen-to-carbon atomic ratios (O/C) recently determined from high-resolution AMS data. We have measured O/C  $\sim$  0.03-0.04 from directly sampled vehicle emissions (Mohr et al., 2008) and determined O/C  $\sim$  0.06-0.10 for urban HOA (Aiken et al., ES&T 2008). Both of these values are much lower than the values 0.5-1 for ambient OOA (Aiken et al., 2008), again indicating that vehicle emissions are not a significant direct source of ambient OOA. The higher values for urban HOA compared to directly sampled vehicle emissions may be due to the inclusion of e.g. meat cooking OA together with vehicle POA in the urban HOA determined by PMF, or to e.g. some oxidation of the vehicle POA via atmospheric aging.

*At first glance, the time series of OOA-II further seems to be somewhat correlated with the TS of HOA (given the more or less simultaneous peaks for HOA and OOA-II, e.g. on 9/11, 9/13, 9/14, 9/19 etc.). From Fig. 5, Panel b) I would expect that OOA-II is also correlated to NO<sub>x</sub> and CO.*

[Response]: While OOA-II is indeed somewhat correlated with CO and NO<sub>x</sub>, the shape of the OOA-II events is best matched by the semivolatile inorganic species. The TS of HOA and OOA-II with the primary and inorganic traces are available at <http://tinyurl.com/5oy8nh> (pgs. 2-3). The correlation between OOA-II and the primary tracers is likely explained by meteorological conditions: periods with low dispersion, low boundary layer, and lower temperatures both trap the primary emissions of POA, CO, EC, and NO<sub>x</sub>, and cause the partitioning to the gas-phase of the products of the photochemistry from the previous day, such as HNO<sub>3</sub> and fresh SOA. Examination of scatter plots between nitrate and OOA-II show two distinct branches with different slopes, indicating that this relationship may be influenced by different emission ratios or processes during these two events.

*On the other hand, m/z 57 might also represent C<sub>3</sub>H<sub>5</sub>O<sup>+</sup> and the correlation of HOA*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



and OOA-II may perfectly reflect the rapid partitioning of semivolatile OVOCs (down-mixed during the early morning hours?) into the freshly emitted HOA particles. No doubt, the results reported here will stimulate further discussions about the chemistry and temporal behaviour of differently aged SOA.

[Response]: Total  $m/z$  57 does indeed have contributions from both a hydrocarbon-like fragment ( $C_4H_9^+$ ) and an oxygenated fragment ( $C_3H_5O^+$ ), as first shown explicitly by DeCarlo et al. (2006) for Riverside, California using the high-resolution AMS. In this study with unit mass resolution data, 68% of  $m/z$  57 is represented by HOA and 18% by OOA-II. The signal at  $m/z$  57 is dominated by  $C_4H_9^+$  for motor vehicles, and this ion also represents a high fraction for several other POA sources, while for chamber SOA this signal is dominated by  $C_3H_5O^+$  (Mohr et al., 2008). Thus it is very likely that the HOA signal at  $m/z$  57 for HOA is dominated by  $C_4H_9^+$ , while the (smaller) contribution of OOA-II to total  $m/z$  57 is dominated by  $C_3H_5O^+$ .

We also note that, as discussed in the paper, the retrieval of smaller components necessarily has higher uncertainty, since e.g. they can "absorb" e.g. variations in the spectra of other components, etc. Since there is some overlap in the time series of HOA and OOA-II, it is possible that the  $m/z$  57 signal in the OOA-II in this dataset is a "bleed" of the HOA spectrum which has high  $m/z$  57. In the Lanz et al. (2007) paper, the spectrum of OOA-II has very little  $m/z$  44 (<0.5%), which would be very unusual for a real SOA spectrum (Aiken et al., 2008), and is likely due to similar imperfections of PMF solutions in which the solutions solve the mathematical model but may not represent distinct particle sources directly, instead approximating groups of particles (e.g., representing similar combustion particles or endpoints of continuous photochemical aging processes; see point C below).

*It might be fruitful in this context to calculate the diurnal boxplots (as absolute and relative contributions) of the three factors' scores (OOA-I, OOA-II, and HOA) and show or describe them. This could also give an additional answer to the gasoline vs. diesel particle question (two birds with one stone). Factor interpretations could be corroborated*

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

by diurnal boxplots: e.g., for the Zurich data the traffic factor (extracted from organic aerosol as well as from gas-phase data) showed a different weekend vs. weekday pattern with respect to its daily cycle (Lanz et al., 2007 and 2008b).

As stated in our response to point (A), the HOA and OOA-I factors are very similar to those described by Zhang et al. (2005a) and all interpretations of the those factors found in Zhang et al. (2005c) are still valid, including the diurnal cycles shown in figure 1 in that paper. As discussed above, diurnal plots for the 3-factor solution will be added to the supplemental information of the revised manuscript.

This short study has only 10 weekdays and 5 weekend days, and the differences in their diurnal cycles are hampered by limited statistics and a few large events in some of the components. Thus a weekday/weekend analysis for this dataset is not representative enough to warrant its inclusion in the paper.

*C) Split vs. coerced sources/spectra* One drawback of using the chi square-metric underlying PMF2 is that it places no restriction on the complexity of the model, making it potentially prone to overfitting. The authors input 2 and 3 profiles, respectively, in order to generate synthetic data. Within the applied PMF model, they increased the number of assumed source profiles to higher values,  $p > 2$  and  $p > 3$ , respectively, and describe what happens. Then, the authors rightly found that the split factors may correlate well with real profiles.

On the other hand, it can be expected that in reality the situation is vice versa (and even more frequent): Much more sources (with distinct spectral fingerprints) actually have an influence on the OA at the receptor-site than can be/are specified within receptor models; widely different organics from various source types with varying profiles are present in ambient air (wood burning and biomass combustion particles generated at different conditions, diesel and gasoline exhaust, primary aged particles, secondary and differently aged particles etc.). E.g. for wood/biomass burning, Schneider et al. (2006) reported widely different AMS spectral signatures. Passant (2002) has collected

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



*the profiles of more than hundred volatile hydrocarbon sources . . . - there is no doubt: this certainly yields composite source profiles and various artefacts in bilinear receptor-model outputs due to coercing real sources (with distinct spectra).*

[Response]: We agree that there are more sources of OA than appear to be separable with factor analysis of unit-mass resolution Q-AMS data. One of our goals was to explore the limits of what is separable with the PMF technique. In a way what is being discussed here is the definition of a "component" extracted by PMF. Ideally each source in ambient air would result in a PMF component. However it is clear that PMF analysis of Q-AMS data does not resolve every source. Instead, sources with similar spectra and time series are grouped together into single components. In our Zhang et al. (ES&T 2005) paper we already concluded (p. 4950): "In other words, we believe that underneath the apparent simplicity of each of the two components there likely lies considerable complexity, e.g., compounds that have similar temporal variations or similar mass spectra are likely grouped together. Aerosols having significantly different sources/precursors, e.g., biogenic vs. anthropogenic SOA, or traffic vs power plant emission POA, may not be discriminated by the technique presented here." Thus in our discussions the assumption that similar sources such as diesel and gasoline exhaust are grouped together into one component is implicit. (See a longer discussion on this topic in the response to the Short Comment from B. Resson earlier in this public discussion.) Then the variations in the spectra that we are referring to can arise from e.g. different proportions of diesel and gasoline exhaust PM at different points during the study, in addition to changes in the MS of diesel exhaust with time. In this manuscript we are in fact referring to both possibilities. We will try to further clarify this point in the revised manuscript.

We have also addressed both of these points in the synthetic data cases. In the 3-factor synthetic cases (Sect. 3.2.2, pg. 6760, Fig. 13), factors which are actually part of the input, but that have a small fraction of the mass (generally < 5%) get "lost" and their MS or TS are not properly retrieved. This is one case of what V. Lanz describes

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



as "coercing" distinct sources into a single factor. The second point was addressed by the set of 2-factor synthetic cases constructed with a range of correlation between the factors in which we observe that highly correlated factors are retrieved less accurately (especially at non-zero FPEAK values) than factors with less correlation. The overall message is that true factors must both have distinct enough spectra and time series *\*and\** sufficient mass fraction to be successfully retrieved.

Note that, as pointed out in the Discussion of the paper by referee P. Paatero, it is not just the correlation of the factors but also the number and relative location of near-zero values in the factors that affect their retrieveability. We have decided to remove these cases from the final paper and perhaps explore them in a separate paper at a later date; however, the qualitative conclusions we made about the difficulty of separating factors with similar time series or profiles still hold. This finding is consistent with results from others, e.g., Brinkman et al.(2006) state, "When contributions from a pair of sources, such as diesel and gasoline exhaust, were highly correlated in the synthetic datasets, a single factor corresponding to both sources was usually found."

Biomass burning OA (BBOA) is a very important global source of OA, and during some periods it can affect air quality in Pittsburgh, either due to wildfire emissions (Bein et al., 2008, due to large wildfires in Quebec) or to domestic wood burning. However domestic wood burning was estimated to be negligible during the period of our study due to good weather conditions (e.g. the temperature at midnight was never below 15°C during our study, see Supp Info. of Zhang et al., JGR 2005). Consistent with this, Robinson et al. (2006) report: "At the upper limit, biomass smoke is estimated to contribute on average [...] 2% of the ambient OC in the spring and summer. [...] The levels of biomass smoke in Pittsburgh are much lower than in some other areas of the United States, indicating significant regional variability in the importance of biomass combustion as a source of fine particulate matter." Note that a source which contributes only ~2% of the mass is not separable with PMF according to the conclusions in our paper.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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Interactive  
Comment

To address the specific point of BBOA during this study, a plot of the ratio of a common BBOA tracer,  $m/z$  60, to total OA is available at <http://tinyurl.com/5oy8nh> (pg. 4) and will be added to the Supplementary Information of the ACP version. The typical level for  $m/z$  60 / Total OA (abbreviated as "60/Org") for periods without biomass burning influence (or for fresh and aged chamber SOA) is around 0.25–0.3% (DeCarlo et al., 2007; Docherty et al., 2008; Shilling et al., 2008; and also for the SOA spectra in the AMS database). The 60/Org of 20 primary BBOA spectra from laboratory BB (5 from Schneider et al., (2006) and 15 from our FLAME-1 Experiment (unpublished)) is an average of  $2.2\% \pm 1.1\%$ , with a range of 0.5% to 4.4%. Note that all of these spectra were obtained by burning the biomass in open air under conditions that resemble wildfires. Spectra from individual woodstoves may show broader variability, but they also encompass a narrow range of combustion conditions which are very unlikely to be representative of a wildfire. Wildfires or the burning of wood across many homes in an urban area encompass a wider range of conditions which are very likely to result in some enhancement of  $m/z$  60. The average 60/Org in this study is 0.26%, which is similar to values for other studies in the absence of biomass burning. 60/Org is 0.20% for OOA-II, 0.29% for OOA-I, and 0.15% for HOA. This indicates that none of these components is likely to be of primary BB origin, including OOA-II. Aged BB could lose the 60/Org signature after significant photochemical aging (Grieshop et al., 2008), so from that point of view perhaps OOA-I could be of BB origin. However, BB is mostly organic and has low  $(SO_2 + SO_4)/Org$  emissions, and aged BB observed at various locations (e.g. in our recent ARCTAS campaign in the NASA DC-8) has a much lower  $SO_4/Org$  ratio than the 2/1 ratio observed here for the aged regional aerosol and typically still has somewhat enhanced 60/Org. Given the high correlation of  $SO_4$  and OOA-I, it appears very unlikely that the OOA-I arises from BB. Together, these pieces of evidence indicate that BBOA, if present, is very small in this dataset. Any small impacts by BBOA events in this dataset are thus likely below the 5% cutoff in mass, and are likely not separable for this study.

*Further, it is possible that, e.g., at p=3 factors the profile of an additional 4th (real)*



source is (mathematically) approximated by linear combinations of the first three factors extracted by PMF (not to be confused with the "mixing artefact").

Future studies may detail this latter situation. In the current abstract, discussion and conclusion part, this situation could possibly be mentioned as well.

[Response]: We agree. This point is addressed by our response to the beginning of part C above.

#### D) Unusual vs. outlying spectra

*It is possible that a very small fraction of samples in the real Pittsburgh dataset represents pure/absent sources (or distinct spectra) (geometrically spoken — see papers by R.C. Henry — these samples would represent the vertices/edge-points of a solution simplex spanned by the source vectors). These samples in question would then represent unusual but crucial data points (in order to recover real source profiles) and should, therefore, rather be up-weighted than down-weighted. By using the robust mode in PMF2, this source information may be lost (depending on the data structure) ... possibly causing the loss of retrievable/interpretable source profiles and/or influencing their shape. Did the authors consider this possibility? In other words: are there any differences in the results of the robust and non-robust mode pointing to this possibility?*

[Response]: We already stated on pg. 6747, lines 11-12: "We explored the [...] use of the robust mode in PMF (in which outliers in the iterative fit ( $|e_{ij}/\sigma_{ij}| > 4$ ) are not allowed to pull the fit with weight  $> 4$ ). Differences in the factor MS and TS were minor in all cases." Comparison of the 2- to 4-factor solutions of the real Pittsburgh dataset modeled in the robust and non-robust modes are available at <http://tinyurl.com/5csnnj>, posted in response to the comments from Anon. Ref. 1 (pgs. 2-4). Because the factors obtained in the robust and non-robust modes are virtually identical, we do not suspect that use of the robust mode has compromised the analysis.

We explored the possibility of a few unusual distinct spectra during our work for the

Full Screen / Esc

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Interactive Discussion

Discussion Paper



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Interactive  
Comment

2005 papers, in particular using cluster analysis (Murphy et al., 2003), which is a sensitive technique to detect very different spectra. In fact the custom principal component analysis software that we used for our early work had a cluster analysis algorithm which the user could apply to identify such cases. For this dataset, there was only one brief and intense plume of reduced aerosol that lasted ~60 min. on one night. The spectrum of this source was similar but not identical to HOA, and its inclusion in the factor analysis led to some distortion of the HOA retrieval. This is presented in Zhang et al. (ES&T, 2005), on p. 4940 and in Fig. S1 in the supplementary information of that paper. Since this was a unique short-lived source, and we are attempting to retrieve the main contributors to OA mass over the 2-week period with PMF, we also excluded that period from PMF analysis here. We will mention the usefulness of cluster analysis as a preprocessing tool for PMF in the revised manuscript.

*Specific comments (continued, comp. 'Comments (Part I)')*

4) p. 6731, lines 25-27: *at this instance, it could be instructive to mention that  $^{14}\text{C}$  analyses and receptor modelling of organic AMS spectral data were combined (Lanz et al., 2008a)*

[Response]: This part of our introduction is describing non-AMS source apportionment techniques. The Szidat et al. paper cited in those lines used  $^{14}\text{C}$  for source apportionment. The Lanz et al. (2008a) paper used two  $^{14}\text{C}$  samples as another tracer to verify and help interpret the factor analysis results of AMS data and to estimate the fossil carbon contribution to OOA, but this reference does not seem appropriate at this point in the paper.

5) p. 6731, line 27: *the time-resolution of radiocarbon ( $^{14}\text{C}$ ) analysis is in the range of several hours rather than several days.*

[Response]: The  $^{14}\text{C}$  analysis used in Lanz et al. (2008a) consisted of two samples with 17- and 40-hour sample times. We will change "3-5 days" to "**many hours to several days**".

Full Screen / Esc

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Interactive Discussion

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[sic] 7) p. 6733, lines 25-29: It would be more accurate to state: "Lanz et al. (2008) applied a hybrid receptor model [...] specified by the Multilinear Engine".

[Response]: We will change the two words as suggested.

8) p. 6734, line 1, OOA-nomenclature: the ratio of  $m/z$  44-to- $m/z$  43 in OOA found in winter (Lanz et al., 2008a) was 2:1, which is in between OOA-I ( $m/z$  44:  $m/z$  43  $\sim$  3:1) and OOA-II ( $m/z$  44:  $m/z$  43  $\sim$  0:1) found in Zurich summer (Lanz et al., 2007). Therefore, we labelled it OOA rather than OOA-I.

[Response]: Since the spectra of OOA-I and OOA-II have only been reported in 4 published works (Lanz et al. 2007, Cottrell et al., 2008, Nemitz et al. 2008, and this work), no rigorous way to define OOA-I and OOA-II exists at this point. Our interpretation of the MS presented in Lanz et al. (2008a) is that it is much closer to OOA-I's that have been reported for which  $m/z$  44  $>>$   $m/z$  43, as opposed to OOA-II's for which  $m/z$  44 is comparable or smaller than  $m/z$  43. However, for consistency with Lanz et al. (2008a), and since only one OOA was identified in that study, we will change "OOA-I" to "OOA" in this sentence.

9) p. 6734, line 2: "more advanced". I did not fully comprehend what is "more advanced" than what? With respect to what criterion?

[Response]: The output of Bayesian source-apportionment methods is a probability distribution for each element of the source profiles and source time series, instead of single scalars. Thus the output contains the information necessary for a statistical evaluation of the uncertainty of the output, which is difficult in PMF. Bayesian models can also incorporate prior information in a natural and probabilistically rigorous way, by specification of the "prior distribution" for each variable. Bayesian methods are expensive computationally, and the more complex output requires greater review by the researcher. Their application to source apportionment problems is still in its early stages. More information about Bayesian methods for source apportionment can be found in e.g. Lingwall et al. (2008). We will add a brief description along these lines to

Full Screen / Esc

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Interactive Discussion

Discussion Paper



the revised paper.

10) p. 6735, line 14: what is meant by "internal correlation" here? The correlation of two species within the PMF data matrix? This would also be the case for certain chromatographic data (along with the high precision etc.).

[Response]: We note that the AMS produces signal intensities vs.  $m/z$ , and it does not report "species." The phrase "internal correlation" refers to the inherent correlation between some  $m/z$ 's in AMS data created by patterns of fragmentation of molecules in the vaporization and ionization processes in the AMS. For example, hydrocarbons always produce fragments in a "picket fence" pattern (McLafferty and Turecek, 1993). The whole collection of characteristic fragments molecules is always produced, with intensities that depend on the specific species; one would not expect to measure just  $m/z$  41, 43 and not 55 or 57 or 69 for a particle-phase hydrocarbon. The correlation is internal because these ions arise from the fragmentation of the same molecules. This is different from data from other techniques, in which different species (e.g. benzene and toluene) may be correlated in time, but do not have to be detected simultaneously because of the mechanics of the detection process. We will clarify this phrase in the revised manuscript.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 6729, 2008.

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8, S6433–S6447, 2008

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