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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Elucidating determinants of aerosol composition through particle-type-based receptor modeling" *by* M. L. McGuire et al.

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Anonymous Referee 2

General Comments:

This article describes the application of positive matrix factorization (PMF) to preclustered single particle mass spectral data in order to resolve local and regional sources of particulate matter in Southern Ontario, Canada. Local and regional scale meteorological data and models have been used in combination with the temporality of the

factors obtained and the particle mixing state provided by the mass spectra, to apportion the various single particle types to their respective sources. A nine-factor solution was observed to be the most robust, with most factors assigned to local-to regional or regional scale transport of particulate matter emitted on both sides of the Canada-US border. Dust particles containing nitrate were found to be the most important local source, while significant regional sources include biomass burning associated with forest fires in the Canadian Prairies and anthropogenic carbonaceous emissions from urban areas in Canada and the US. While PMF has been applied to single particle data in some previous studies, this work represents the most methodical and comprehensive approach thus far, and provides a benchmark study that will be useful for others attempting source apportionment using single particle mass spectral data. Choosing the most reasonable number of factors is essential, because, as has been demonstrated here, the iterative addition of factors which appear to artificially split the existing factors can sometimes be justified by examining particle mixing state and the extent of chemical processing during transport. The authors also performed detailed meteorological analysis, which demonstrates the value of using high-resolution trajectory models where available to identify local-to-regional sources of particulate matter.

The authors thank Anonymous Referee 2 for valuable comments and suggestions. All comments and suggestions have been thoroughly considered in order to further improve the manuscript. Responses to your comments are in italics.

Specific comments:

Page 9836, lines 13-15. Considering this statement, were size-resolved variables explored for the different clusters? For example, does splitting the existing clusters into size bins lead to variables with different temporality. This is possibly beyond the scope of this manuscript but may be interesting for bimodal clusters with input from more than one source.

The average mass spectra, size distributions, and temporality of each particle-type

were examined prior to PMF analysis. The size distributions of most particle-types exhibited single modes, some with broad and positively skewed distributions. However several did exhibit clear bi-modal distributions (i.e., C10, C14, C16, C24, C29, C31, C32, and C33). Bi-modal distributions were particularly evident for those from the DUST particle-type family. As bi-linear PMF analysis of particle ensembles does not keep track of which particles (and hence their respective sizes) are apportioned to a given factor, it is not possible to know through PMF how a particle-type size distribution has been split between two factors. However the temporal trend of the fractional contribution of a particle-type to a given factor is available. Comparison of this temporal trend with that of a range of particle sizes for a given particle-type can help to indicate the particle size make up of a given factor.

While performing an analysis on the temporal distributions of the size bins from each particle-type and how they relate to each PMF factor is beyond the scope of this paper, several particle-types, due to their obvious bi-modal distributions, were examined.

In general, separating these distributions based on a clear modal cut point was not useful for the analysis due to low counting statistics for one of the modes (typically the smaller size mode). For instance the most obvious bi-modal distribution was observed for the C29, or the "aged sea-salt" particle type from the DUST family. This clear bi-modal distribution indicated more than one particle history or source origin. Separating it into two distributions based on a 1um cut point, which appeared to delineate the two distributions, yielded two temporal trends: one that was correlated with the Long Range Transport factor (to which 68% of this particle-type was apportioned), and another which was noisy due to low counting statistics (maximum hourly particle count = 3). Given that this particle type only contained 868 particles, with 709 particles greater than the 1um threshold and only 159 below, this result is not unexpected.

To examine bi-modal distributions in more populated particle-types, C10 and C14 from the OC_S_N family were selected for similar analysis, both of which were apportioned in significant fractions to the two Biomass Burning factors, and a smaller fraction of

C10 also apportioned to the Nitrate Dust factor. Both particle-types exhibited slight modes at smaller sizes (0.3μm). However, separating these particle-types into two distributions produced a similar effect, where the counting statistics were not sufficient for the smaller mode to form any meaningful temporal trend for correlation analysis with PMF factors. In contrast, the larger size mode showed good correlation with the two Biomass Burning factors.

These results suggest that while larger size modes were likely attributed to the factors to which these particle-types were apportioned to the greatest extent, the lack of counting statistics for the smaller mode precludes the association of smaller particles with any PMF factors or source types.

While this analysis did not produce meaningful results for these data, it is possible that performing it on a larger dataset, may aid in identifying the size make up of PMF factors without resorting to incorporating size-resolved information into the PMF analysis to form a tri-linear PMF analysis.

Page 9841, line 13. The authors mention that reducing particle cluster numbers after running ART-2a through manual recombination resulted in unsatisfactory PMF solutions. Does this suggest that this subjective approach, commonly used for ATOFMS studies, should be reconsidered, or even avoided? Typically higher vigilance factors are used, resulting in higher cluster numbers and thus encouraging manual recombination. A few lines on this would be of interest to other ATOFMS users.

The referee brings up an important point, and we wish to further emphasise why we did not choose to manually recombine particle-types for this type of analysis.

Manual recombination of particle-types following cluster analysis is a common practice which serves the purpose of reducing the number of particle-types to a more manageable number for interpretation. In our opinion, manual recombination is an approximation that can be helpful for general ATOFMS data interpretation, although authors should be clear in stating their recombination process, as the process can impact the

types of conclusions which can be drawn from recombined particle-types.

The typical methodology behind manual recombination involves recombining particle-types based on high similarity between particle-type mass spectra, with some consideration of the time-series, and size distribution data. The underlying assumption behind this recombination process is that particle-types can be manually apportioned to a common source origin and/or chemical processing history based on these similarities. If only mass spectra are considered in the comparison, this may result in the convolution of chemically similar particle-types from different sources into one particle-type, and possibly misinterpretation of particle-type history. This may limit the conclusions to be drawn on the source origins of the particle-type. If all three pieces of information are considered, the possibility of correct manual attribution is increased. However, the inherent assumption is that a given particle type only comes from a single source or process and thus that no apportionment is needed. Our manuscript has demonstrated that this is not the case. Further, errors in recombination can still arise even if all three pieces of information have been considered in this subjective process: it is not always the case that all three particle-type features will be identical, yet recombination is often still performed if for instance two of the three features are deemed similar enough.

Manual recombination for the purposes of PMF analysis was avoided for two reasons. Firstly, if particle-types are recombined using all three particle-type features, manual recombination, to a certain extent, defeats the purpose of PMF. Secondly, it is hypothesized that PMF is sensitive to small errors in the recombination process from subjective comparisons between particle-types. Essentially, recombining time series of particle-types can impact the co-linearity in the PMF matrix. It follows that inaccurately recombining particle-types will directly affect the extent to which useful factors can be extracted using PMF. Hence, errors in the subjective manual recombination process may cause undue errors in the PMF analysis.

To make this distinction in the manuscript, the following sentence has been added for clarity:

P9841, L13 "While manually recombining the particle-types based on their spectral, temporal, and particle size similarities is a common method for reducing their number, for this study this technique was avoided as it yielded PMF solutions without global minima. This is probably caused by the sensitivity of PMF towards small errors in the recombination process from subjective comparisons between particle-types: recombining the time-series of particle-types inherently changes the co-linearity between particle-types in the PMF matrix. It follows that inaccurately recombining particle-types directly affects the extent to which useful factors can be extracted using PMF. Hence, errors in the subjective manual recombination process, which cannot be easily accounted for in the PMF error model, likely result in undue errors in the PMF analysis."

Page 9841, line 26. This section needs to be expanded, or moved to the supporting information and covered in more detail. Size-dependent transmission efficiency problems associated with the aerodynamic lens are typically "scaled up" using concurrent scanning mobility particle sizer or aerodynamic particle sizer measurements, and this was described in detail in the companion paper cited in the manuscript (Jeong et al., 2011a). It is surprising that the scaled particle counts do not lead to equally robust PMF solutions, considering that the raw ATOFMS size distributions are skewed due to the transmission efficiency curve associated with the lens. What about volume estimates or mass estimates, what are the PMF solutions like? The unsatisfactory PMF solutions should be included in the supporting information, along with the authors' opinion on why the scaled datasets do not work as well, or at least give the same results. This will definitely be of interest to the ATOFMS community. The scaled size distributions could also be used in Figure S2 and in the particle size mode descriptions in section 3.3.

The lack of a robust solution for PMF analysis of the scaled ATOFMS particle counts (scaled as detailed by Jeong et al., 2011), is a point that was also raised by Referee 1, and was discussed in the response to that Referee. Thus Referee 2 is kindly asked to review the response to Referee 1. Results and discussion from PMF analysis of the scaled particle-types has been added to the Supplement, and a synopsis of these

results has been added to the manuscript to P9841. Figs. 2-5 shown in the response to Referee 1 illustrate the findings from this analysis.

PMF analysis of volume estimates were also explored in the study. However, following scaling, volume estimates were subject to the dominance of scaling factors from the smallest particles as described in the response to Referee 1. As obtaining mass estimates involved applying a constant density factor (as described in Jeong et al., 2011), this conclusion also applied for the mass estimates.

The scaled size distribution of all particles measured during the campaign has been added as Figure S10, and is shown in Fig. 5, in the response to Referee 1. The unscaled size mode ranges for each particle-type family were added to sect. 3.1 of the manuscript.

Page 9864, lines 16-30. Alongside the recommendations provided in this section, it would be interesting to gauge the authors' opinions on the inclusion of other online measurements (e.g., EC, OC, PM mass, NOx etc.) in the PMF analysis and how this might affect the results.

Other online measurements, such as EC, OC, PM mass, and trace gases in the PMF analysis were included in two of the three receptor modeling studies of ATOFMS particle-types from the literature (Eatough, et al., 2008; Healy et al., 2010). In these studies, fractions of each of the species from the additional online measurement methods were apportioned to PMF factors.

While this approach has yielded interpretable solutions in previous work, the addition of these variables in a PMF data matrix may not always lead to an improved interpretation of ATOFMS particle-type factors. The reason for this is attributed to the bias and sensitivity implicit in each analytical measurement method. Often, the temporality between online measurements such as the ones mentioned above does not necessarily correlate well with that of ATOFMS particle-type temporal trends. The result of which is the lack of cross-apportionment between different types of data to the same factor, and

the creation of new factors composed mostly of the additional online measurements. This effect can be exacerbated if the contribution of one type of data to the data matrix greatly outweighs another.

The aforementioned effect was explored by Slowik et al. (2010) in a study that sought to combine non-refractory aerosol mass spectral measurements from two separate mass spectrometric instruments: an Aerodyne c-ToF-AMS and VOC measurements from a PTR-MS. Given that the m/zs useful from the AMS greatly outnumbered those from the PTR-MS (270 vs. 10 respectively), correction in the PMF calculation was required to accommodate this unequal weighting . If such a precaution was not taken, the temporality from the AMS data dominated both the calculation of the PMF solution, as well as the interpretation of the modeled result. To ensure balanced weighting of the two datasets within the PMF analysis, the errors for the PTR-MS were diminished by dividing the PTR-MS specific uncertainties by this factor. This resulted in a more equal contribution of residuals from both types of data to the Q value.

Inclusion of additional variables to the ATOFMS data matrix was considered for this analysis, and this type of weighting was considered to account for the imbalance in the datasets. However, in order to ensure good cross-apportionment of the external online measurements and ATOFMS particle types, a good degree of correlation is required between them. Since most of the correlation coefficients (85%) between the external online measurements and ATOFMS particle-type time series did not exceed a moderate level (Pearson r = 0.4), their inclusion in the PMF analysis would result in the creation of new factors. Without moderate cross-apportionment to other factors, their inclusion could not be justified. As such, post-PMF correlation analysis was deemed to be the best method for including other online variables in the analysis.

The following sentences have been added to the manuscript:

P9843, L18: "Inclusion of other online measurements (e.g., $PM_{2.5}$ mass, EC/OC, trace gases) has been a useful method in previous PMF of ATOFMS studies towards im-

proving source characterisation (Eatough et al., 2008; Healy et al., 2010). Given the potential benefits of including other online measurements, this practice was considered for this analysis. However, in order to ensure good cross-apportionment of the external online measurements and ATOFMS particle types, a good degree of correlation is required between them. Since most of the correlation coefficients (85%) between the external online measurements and ATOFMS particle-type time series did not exceed a moderate level (Pearson r = 0.4), their inclusion in the PMF analysis would result in the creation of new factors. Without moderate cross-apportionment to other factors, their inclusion could not be justified. As such, post-PMF correlation analysis was deemed to be the best method for including other online variables in the analysis."

Minor comments:

Page 9834, line 16. Remove apostrophe

We believe the referee was referring to P9833 (CTM's). This has been changed to CTMs.

Page 9837, lines 21-24. Please rephrase. The ATOFMS does measure refractory aerosol components.

The sentence has been changed to: "An Aerodyne Time-of-Flight Aerosol Mass Spectrometer (c-ToF-AMS) (Aerodyne, Billerica, MA, USA) was used to characterize the non-refractory aerosol fraction, and a TSI 3800-100 Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) (TSI, Inc., Shoreview, MN, USA) was used to characterize both the non-refractory and refractory aerosol fractions."

Page 9848. The use of both R and R2 values is confusing. It may be best to use one or the other for continuity.

We acknowledge the referee's concerns regarding the use of two different coefficients for statistical analysis. After considering the recommendation, we wish to keep the coefficients as presented in the discussion manuscript to distinguish between the types

of comparisons being made, as well as the conclusions which were drawn.

The correlation coefficient (Pearson's r) was chosen to represent the degree to which the two time series from similar factors in adjacent PMF solutions were correlated with one another in time. By contrast, the coefficient of determination (R^2) or linear regression coefficient was chosen for comparison between the measured and modeled particle counts to determine the amount of variance in the measured data that could be explained by the sum of the modeled factors. We have changed the text in sect. 3.3 to better distinguish between the two statistical coefficients.

P9847, L14: "In this analysis, the Pearson product-moment correlation coefficient (r) was calculated between the time series of highly comparable factors in adjacent PMF solutions (Table 3). An effect was observed if the r value decreased with the factor addition; a moderate effect was determined if 0.90 < r < 0.95, and a significant effect if r < 0.90. Hence two different coefficients were used: the coefficient of determination (R^2) to ascertain the variance in the measured particle counts that was explained by PMF modelled particle counts, and Pearson's r to compare the degree of similarity between time-series of like factors from adjacent PMF solutions."

Page 9849, line 3. Remove apostrophe

This has been changed.

Page 9853, line 4. Replace "m/z's" with "m/z".

This has been changed.

Page 9854, line 4. Replace "m/z's" with "m/z".

This has been changed.

Page 9857, lines 14-16. Rephrase this sentence, possibly "air masses which passed over the Canadian Prairies 48 h previously".

This has been changed per the recommendation.

Page 9860, lines 19-21. Rephrase this sentence

This has been changed to: "On the whole, the ECOC Night particle-types contained significant amounts of nitrate and ammonium, in contrast to the relatively low amounts of these species in the dominant particle-types of the daytime factor."

Page 9860, line 27. Would "uptake" be better than "deposition"?

This has been changed per the recommendation.

Page 9877, Figure 3. The C1 contribution to the Long Range Transport is difficult to see here, perhaps shift the x-axis. The third factor is named "Primary Organic" here while it is simply "Organic" elsewhere.

Figure 3 has been modified per the recommendation, and Primary Organic has been changed to Organic.

Page 9882, Figure 8. "Primary Organic" is used again here. The authors should stick to one label.

This has been changed.

Supporting Information, page 3, line 2. Rephrase possibly "as their chemical composition and temporality were definitive". *This has been changed per the recommendation.*

Supporting Information, page 3, line 11. Remove apostrophe

This has been changed.

Supporting Information, page 3, line 18. Rephrase possibly "precluded their assignment as fresh or unprocessed particles".

This has been changed per the recommendation.

Supporting Information, page 4, line 31. Superscript +

This has been changed.

Supporting Information, page 5, line 25. Remove apostrophe

This has been changed.

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