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Atmospheric
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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 1

General Comments:

This paper describes one of the most comprehensive analyses of ATOFMS field campaign data to appear in the literature to date. The single particle mass spectral dataset has first been clustered into 33 particle types which have then been subject to PMF analysis to further group the particles into source related types. While this approach has been reported previously, this is one of only rather few papers to have used the approach. The authors are to be congratulated on their very thorough approach to data analysis and a well thought out interpretation. The use of CPF plots and PSCF analysis has proved useful in assigning sources to the PMF factors.

The authors thank Anonymous Referee 1 for valuable comments and suggestions. All comments and suggestions have been thoroughly considered so as to further improve the manuscript. Responses to your comments are in italics.

Specific comments:

(1) The analysis of the ATOFMS data is purely in terms of particle number counts, yet air quality regulations are in terms of mass. The authors refer to size dependent transmission losses in the ATOFMS and indicated that they looked into the possibility of correcting for these losses. The resulting data did not lead to robust PMF solutions and hence the particle data were left unscaled for PMF analysis. This is a rather surprising finding and some explanation would be helpful. No indication is given of how the correction was applied. Were independent measurements of the particle number size distribution made alongside the ATOFMS?

The sentence from P9841 L26-29 was elaborated upon to provide further detail regarding the scaling method for subsequent PMF analysis, as well as independent particle size distribution measurements made during the BAQS-Met campaign:

“As the ATOFMS is known to experience size-dependent transmission biases (Allen et al., 2000; Wenzel et al., 2003), the possibility of correcting for these biases was investigated for the purpose of performing semi-quantitative particle apportionment using the enhanced scaling method presented by Jeong et al. (2011). This scaling method corrects for the size-resolved transmission bias by scaling up ATOFMS particle number concentrations using independent, collocated APS and FMPS particle number size distributions, both of which were available during this campaign.”

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As the question regarding the lack of robustness from PMF of scaled ATOFMS particle counts was raised by both referees, and is of interest to the ATOFMS community, results and discussion from PMF analysis of the scaled particle-types have been added to the Supplement. A synopsis of this analysis has been added to the manuscript immediately following the above changed passage on P9841. The results and discussion added to the Supplement are presented below, and new plots illustrating these results are included as Figs 2-5 below.

Added to Supplement:

Sect. 3: PMF of scaled particle-types

“An enhanced ATOFMS particle scaling procedure has been developed by Jeong et al., and is presented in a companion manuscript (Jeong et al., 2011). This method was used to scale single particles from this study for the purpose of quantitative PMF analysis of scaled particle number concentrations. The following section briefly describes the scaling procedure.”

“A scaling factor was applied to each particle, which is given by the ratio of the number of particles measured by the APS and FMPS to the ATOFMS:

For D $_a$ > 0.52 μm, $S_{Da,j} = N_{j(APS)}$/ N$_{j(ATOFMS)}$

For D $_a$ < 0.52 μm, $S_{Da,j} = N_{0.1-0.52\mu m(FMPS)}$/ N$_{Da<0.52\mu m(ATOFMS)}$

where N$_{j(APS)}$ and N$_{j(ATOFMS)}$ are the hourly total particle number concentrations as measured by the APS and ATOFMS measurements in the size bin (j) respectively; N$_{0.1-0.52\mu m(FMPS)}$ is the hourly total number concentration of particles in the range from 0.1-0.52μm (aerodynamic diameter) measured by the FMPS. Further details of these calculations can be found in Jeong et al., 2011. Note that calculations in Jeong et al. were performed using volume concentrations for the purposes of later arriving at mass concentration. In this analysis, scaling calculations were made using number concentrations. Calculations using volume concentrations were also explored although

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were found to provide highly similar results to number concentration. The analysis was thus kept in terms of number concentration to enable comparison with unscaled PMF analysis results."

"The particle-type assignments as determined by cluster analysis (section 2.3 of the manuscript) were used for the scaled particle analysis, and thus the only change to the data was the total hourly number counts for each particle-type. Consequently, the particle scaling resulted in modified particle-type time series for PMF analysis. Both the data and error matrices were prepared using the methods presented in section 2.4 of the manuscript. Furthermore, since solutions for C3=0 (as used in the unscaled analysis) would not converge, a C3 of 0.05 was used."

"In general, all solutions ranging from 1 to 12 factors were not robust, and were thus undesirable. A 9 factor solution was chosen for comparison purposes with the unscaled analysis, and the factor profiles and time series are shown in Figures S11 and S12 respectively. The following paragraphs elaborate on how the solutions were judged in terms of robustness."

"Fig. S13 shows the effect of increasing the number of factors on the scaled PMF solution. For the 9 factor solution, it can be seen that the data are reconstructed with an R^2 *of 0.92, which was less than that found in the unscaled analysis (*R^2*=0.96). The* Q/Q_{exp} *value for this solution was 5.63, which was greater than that of the unscaled analysis. Given that the errors were approximately only 10% less on average than those supplied for the unscaled analysis, and the* Q/Q_{exp} *value for 9 factors was so much larger, it could be seen that the errors generated for the scaled analysis were inadequate for modelling these scaled particle-type time series."*

"The particle-type profiles (Fig. S11) and time series (Fig. S12) for the 9 factor solution from PMF analysis of the scaled data were compared to those from the unscaled data. Many of the particle-types could not be modeled adequately by PMF and consequently were not useful for factor identification. In fact, the OC family of particle types

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was hardly represented by the 9 factor solution, as evidenced by the lack of reproduced particle counts at the beginning of the campaign. It was also difficult to interpret particle-type profiles as they tended to be more broadly distributed across particle-type families within the factors than in the unscaled PMF analysis. No new logical conclusions regarding factor composition were ascertained from this analysis."

"As with the unscaled PMF analysis, the 9 factor solution was subjected to 100 bootstrap runs and was initiated from 100 different seed values. Bootstrapping showed that the solution did not appear reproducible, as none of the runs could be "remapped" onto the base case. Using 100 different random seed values to initiate PMF analysis also showed undesirable results: none of the solutions produced identical Q/Q_{exp} *values (min = 5.51, max = 5.99, median = 5.74) suggesting that each solution was different. The variability in these results indicated that the 9 factor solution was unstable. To verify the instability in PMF solutions in these data and errors, 10 random starts or seeds were used from 1 to 12 factors. In each case, the* Q/Q_{exp} *values differed significantly, in a similar manner to the 9 factor solution."*

"As stated in the manuscript, this undesirable result was attributable to the large scaling factors required to scale up particles from the smallest size bin ($D_a < 0.52 \mu m$*), which experienced the greatest transmission losses. Effectively, scaling caused the times series of each particle type to be dominated by the portion of that particle type within the smallest size bin. Given the lower efficiency of the ATOFMS for these small particles, these time series were often the noisiest. Comparing Figs. S2 and S10 it can be seen that particles with (*$D_a < 0.52 \mu m$*) were scaled up by about 2 orders of magnitude more than larger particles. Thus, PMF analysis was essentially performed on scaled particle-type time series that were dominated by the convolution between a very large scaling factor and a noisy time trend from the smallest hit particles. Further, the temporality of these smaller particles is inevitably dictated by a different set of atmospheric determinants than those impacting the set of particles measured directly by ATOFMS, rendering comparison between these scaled and unscaled solutions unsound. One*

approach to partially control for this effect would be to remove the contribution of the small particles from the dataset, although there still remains several orders of magnitude in difference between number concentrations measured by APS for the most and least populous size bins. A more rigorous approach would be to separate each particle-type into several size bins for PMF analysis, in order to separate out the variability of smaller particles subjected to large scaling factors from larger particle with lower scaling factors. This approach was considered for this dataset although low hourly counting statistics precluded size segregation of each particle type. Such an approach would be worth exploring using data with higher overall particle counts. In summary, the unscaled PMF solution presented in the manuscript emphasizes the characteristics of particles in the size ranges efficiently detected by the ATOFMS, rather than those of ($D_a < 0.52\mu m$) *which were measured with lower efficiency."*

(2) Related to the above point, the methods section indicates that PM2.5 mass concentrations were made using a TSI DustTrak instrument but these data are not presented. It would give added perspective to the paper to add a time series of PM mass to Figure 2.

We have added the $PM_{2.5}$ *time series to Figure 2 from the manuscript. The updated Figure is shown below in Fig. 6.*

(3) A intriguing facet of Figure 2 is that there is a period almost in the centre of the time series where there are no significant counts of any particle type (on 29-30/06/2007). Was significant mass measured during that period? The ATOFMS is known to be far more sensitive to some particle types than others. Was this a period where mass was contributed by particles undetected by the ATOFMS?

Particle mass was measured during the period mentioned by the reviewer, and is now presented in the revised Figure 2. However, as stated on P9838 L175-19, no ATOFMS data was analyzed by PMF for the period of 28-30 June 2007: "The ATOFMS was operated from 19 June - 11 July 2007, and measured particles in the approximate range *of 0.1 to 3μm using the AFL100 aerodynamic focusing lens, except for a brief period from 28-30 June 2007 when the ultrafine lens (AFL030) was used. Only ATOFMS measurements made with the AFL100 were used for this publication." To clarify this point we have highlighted the period of "no data" in all figures including ATOFMS time series with this time period to indicate when no data from the AFL100 was available for PMF analysis.*

(4) There has been rather little attempt to compare the individual particle types with those reported in earlier work with the ATOFMS by other groups. Prather's group has published a large number of particle signatures including some from source studies. It would be useful for the reader to know how closely the particle types identified in this work map onto those in earlier published studies and particularly those which were source related. For example, did any of the EC, OC or organic particle types compare closely with those determined by Prather's group in engine exhaust?

The particle types were not described in detail within the manuscript as this only described the outcome from an intermediate step of the dual data analysis procedure. The particle types were presented in the Supplement. Comparisons to published source spectra have been made more explicit in the Supplement where required, and the manuscript where applicable, for source-related particle types. The changes are documented below.

Changes to the Supplement:

Section 2.1 – EC_OC Particle-Type Family – P3, L20 "Such aged EC particle types, containing significant oxidized organic and sulphate content, have been reported in numerous ambient ATOFMS field campaigns (Dall'Osto and Harrison, 2006; Moffet et al., 2008; Healy et al., 2010). They have been typically reported as aged primary EC emissions."

Section 2.2 – EC Particle-Type Family – P3, L26 "In general, this particle-type resembled particles generated from source diesel emissions studies (Spencer et al., 2006;

Toner et al., 2006) due to its small diameter and EC ion fragments. While such a small diameter EC particle type typically suggests fossil fuel combustion emissions, it was unusual that a strong peak at m/z 23 [Na^+] was present without other ions typical of diesel emission (e.g., Ca^+ and $PO_3{}^-$) (Spencer et al., 2006; Toner et al., 2006), This specific particle-type has only been observed in two other ambient studies (Dall'Osto and Harrison, 2006; Moffet et al., 2008), whereby in both it could not be conclusively identified. Regardless, the aforementioned characteristics of this particle-type strongly suggest it is associated with diesel fuel combustion emissions."

Section 2.3 – OC_S_N Particle-Type Family – P 4, L30 "Based on these characteristic ions, all particle-types from this family (with the exception of C5) resembled particles reported from biomass burning source characterization studies (Silva et al., 1999; Healy et al., 2010)."

Section 2.4 – OC Particle-Type Family – P5, L23 "Thus these particle-types could not be attributed to a specific source class."

Section 2.6 – FIREWORKS Particle-Type Family – P7, L1 "Alkali and alkaline earth metals such as Na, Mg, Ca and Ba have been associated with the combustion of fireworks (Vecchi et al., 2008; Joly et al., 2010). Due to the presence of these metallic species, the most populous particle-type from this family, C12, was nearly identical to ambient pyrotechnic particles measured by ATOFMS in Riverside, California (Liu et al., 1997)."

Section 2.7 – DUST Particle-Type Family – P7, L13 "These particle types were characterized by very high peaks associated with several dust related species, such as m/z +23 [Na^+], 27 [Al^+], +40 [Ca^+] and +56/57 [$CaO/CaOH^+$], and were very similar to aluminium and calcium rich dust particles measured in several other ATOFMS field studies (Guazotti et al., 2001; Dall'Osto et al., 2004; Dall'Osto et al., 2006, Sullivan et al., 2007)."

Changes to the Manuscript:

P 9853, L2 "Moreover, the dominant particle-type C12 (FIREWORKS), contained all the aforementioned ions, as well as minor contributions from ions more characteristic of fireworks emissions (e.g., m/zs +63/65 [Cu^+], +88 [Sr^+], +138 [Ba^+], and +154 [BaO^+]); this particle-type was highly similar to particles measured in a fireworks plume in Riverside, California (Liu et al., 1997)."

P9855, L16 "Biomass burning emissions were proposed as the source class given that all the corresponding particle-types closely resembled particles generated from source characterization studies (Silva, et al., 1999; Healy et al., 2010), and satisfied three defining criteria: large [K^+] peaks, large organic carbon signals in the positive ion mass spectrum, and clear contributions from organic acid fragments, such as formate, m/z -45 [$CHO_2{}^-$], and acetate, -59 [$C_2H_3O_2{}^-$]."

P9861, L26 "Interestingly, particle-type C11 (EC), which mostly resembled particles from source diesel fuel emission studies (Spencer et al., 2006), was mostly apportioned to this factor."

(5) The behaviour seen for nitrate is very interesting but should be compared with that reported by Dall'Osto et al. (Dall'Osto M, Harrison RM, Coe H, Williams PI and Allan JD, 2009, Real time chemical characterization of local and regional nitrate aerosols, Atmos. Chem. Phys., 9, 3709-3720). It would be useful to compare the particle mass spectra but also the behaviour of nitrate as Dall'Osto and co-workers also reported long-ranged transported and local nitrate particles and a diurnal pattern of nitrate association and release from particles.

We thank the referee for highlighting this similarity, and have considered it for comparison with this study.

An interesting resemblance is noted between the nitrate associations observed in this study, and those observed during the REPARTEE-I study (Dall'Osto, et al., 2009). In both studies, diurnal associations of nitrate with particles of local and regional origins were observed. First, the nitrate partitioning behaviour observed between the EC OC

Day and Night factors in this study is analogous to the behaviour observed between the Long Range Transport (LRT) nitrate and nitrate LRT core particle-types from the REPARTEE-I study. Second, the association of nitrate with locally derived particles is similar to a degree in this study in the Nitrate Background factor and in the Local Nitrate particle-type from the REPARTEE-I study.

Thus the following sentences have been added to the manuscript to elaborate on this comparison:

P9860, L22: "This effect of nitrate partitioning to pre-existing particles has been previously reported by Dall'Osto et al. from the REPARTEE-I field campaign in London (2009). In the aforementioned study, two particle-types showed anti-correlated temporal trends, similar to the EC OC factors reported here: a Long Range Transport (LRT) Nitrate particle-type peaked at night, while a LRT Nitrate core particle-type peaked during the day. During the REPARTEE-I study, the two particle-types were distinguished by nitrate uptake at night, and volatilization during the day, the same effect which led to the two EC OC (Day and Night) factors in this study. In both studies, these particle-types were transported to the site from either local-to-regional or regional sources during PM episodes, were mainly carbonaceous in nature, and displayed similar geometric mean sizes (approximately 0.60μm)."

P9862, L5: "Nighttime partitioning of nitrate in locally derived particles has been previously reported during the REPARTEE-I campaign in London (Dall'Osto, et al., 2009). In the aforementioned study, a Local Nitrate particle-type was observed, which contained significant K and EC, and was designated as locally produced due its small modal diameter (0.30μm). This Local Nitrate particle-type displays some similarities to those from the Nitrate Background factor, mainly in the nitrate uptake to pre-existing locally emitted particles. However, some differences are observed. In this study, particles from the dominant particle-type C11, may not have been strictly locally emitted as the largest source of diesel emissions is located on the local-to-regional scale in Windsor. Furthermore, the methodology presented in this study highlighted the strong external *mixing in this factor, suggesting that nitrate uptake was non-discriminatory, partitioning to pre-existing background particles from a range of particle-types from different source-classes, both carbonaceous and non-carbonaceous."*

(6) On page 9855, line 20, the particle of m/z -59 [C2H2OO-] is described as formate. There is clearly an error here particularly as the suggested elemental composition does not give this mass number.

We thank the referee for noting this error. This sentence has been changed to: "Biomass burning emissions were proposed as the source class given that all the corresponding particle-types closely resembled particles generated from source characterization studies (Silva, et al., 1999; Healy et al., 2010), and satisfied three defining criteria: large [K$^+$*] peaks, large organic carbon signals in the positive ion mass spectrum, and clear contributions from organic acid fragments, such as formate, m/z -45 [CHO*$_2^-$*], and acetate, -59 [C*$_2$*H*$_3$*O*$_2^-$*]."*

(7) Particle type C29 has a composition suggestive of aged sea salt. Is this likely at a location so far inland?

We agree with the referee that such a particle type assignment is unexpected given the inland location. However, in other ATOFMS particle-type studies from Toronto, Ontario, Canada (located 500km to the northeast, and equally as inland as Harrow), we have identified sea salt particles originating from Hudson Bay. Chemically processed salt particles, suspected to be of marine origin, have also been observed in Stockton, New York in a filter-based receptor modeling study (Sunder Raman and Hopke, 2007). Therefore, a sentence has been added to sect. 2.7 in the Supplement describing this particle type:

P7, L26: "While it is unexpected to observe marine aerosol as far inland as Harrow, Ontario, chemically processed salt particles suspected to be of marine origin have been reported in nearby inland areas such as Toronto, Ontario and Stockton, New York (Rehbein et al., 2010; Sunder Raman and Hopke, 2007)."

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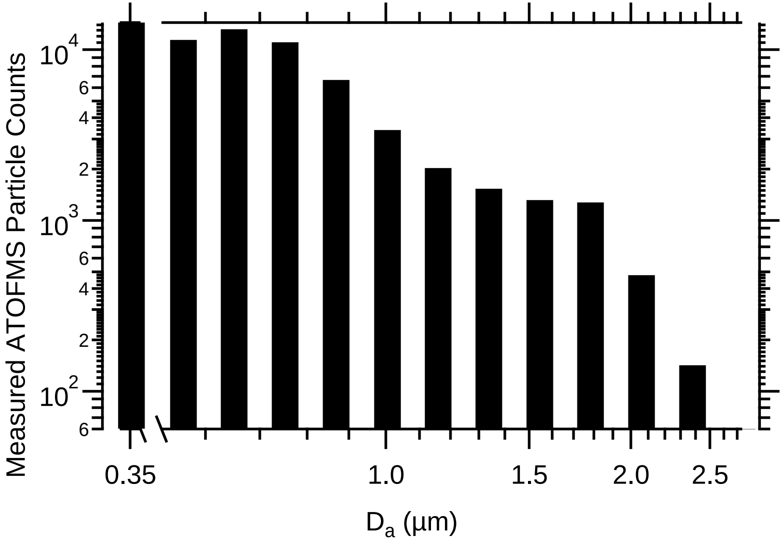

Fig. 1. Figure S2 changed in the Supplement for comparison with size bins from the scaled data presented in Figure S12. Size distribution of particles desorbed and ionized by ATOFMS during BAQS-Met.

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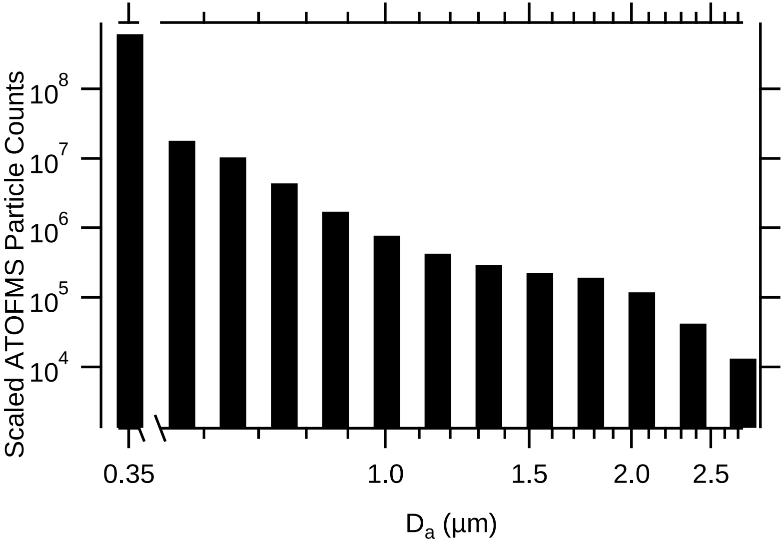

Fig. 2. Figure S10 added to the Supplement. Size distribution of particles desorbed and ionized by ATOFMS and then scaled according to the method of Jeong et al. (2011) during the BAQS-Met campaign.

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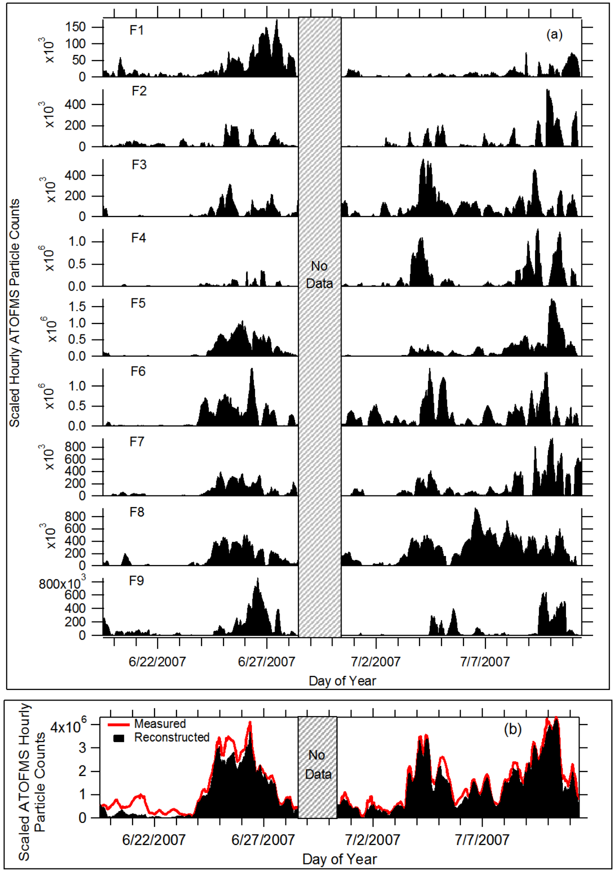

Fig. 3. Figure S11 added to the Supplement. Time series of the nine factor solution for the scaled particle-types (a) and PMF reconstructed scaled hourly ATOFMS particle counts (b).

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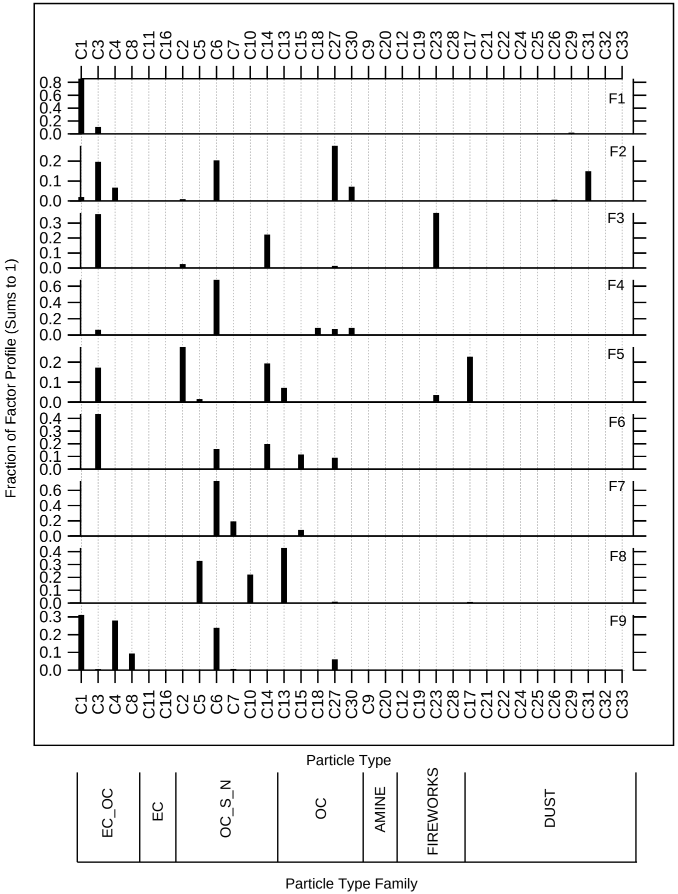

Fig. 4. Figure S12 added to the Supplement. Factor particle-type profiles of the nine factor solution for the scaled particle-types.

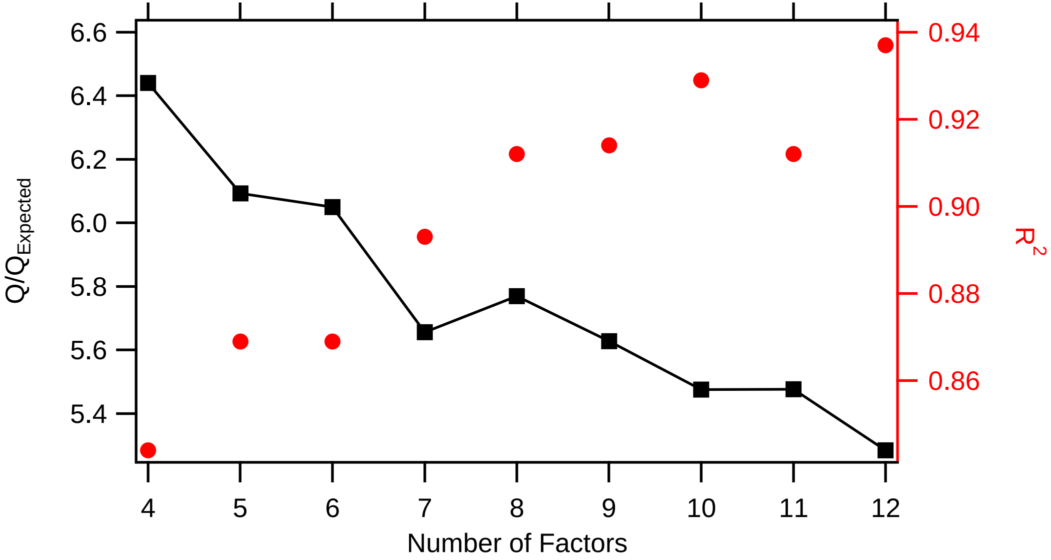

Fig. 5. Figure S13 added to the Supplement. The impact of increasing the number of factors on the scaled PMF solution in terms of R2 and normalized Q value.

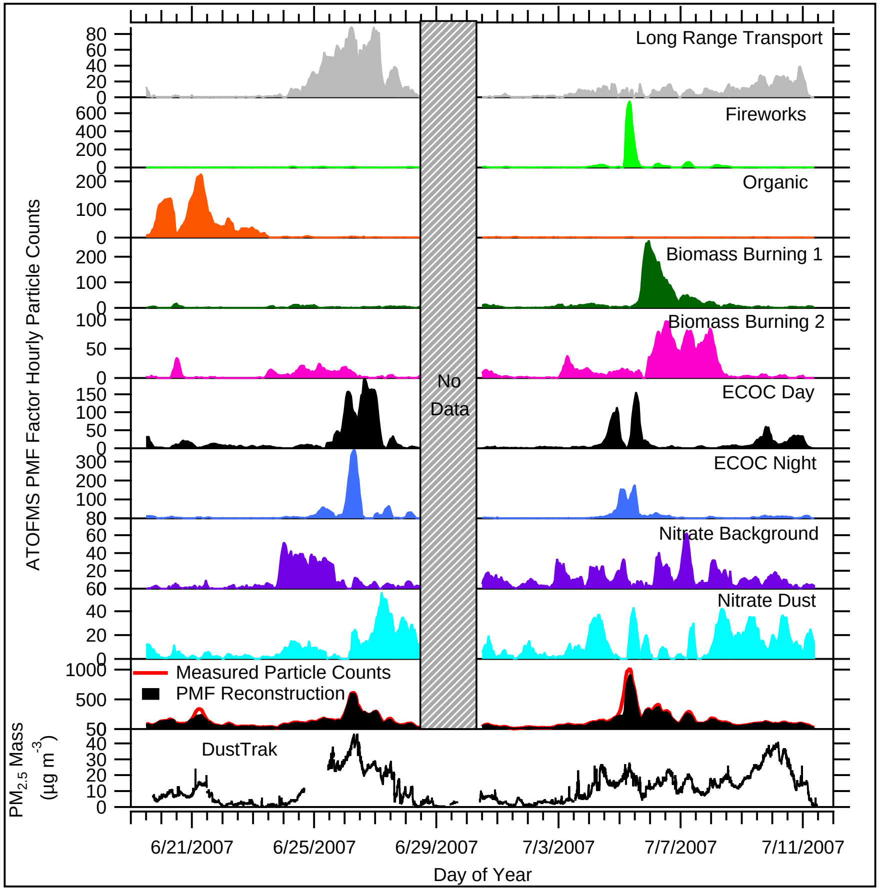

Fig. 6. Updated Figure 2 from the manuscript.