

## ***Interactive comment on “Enhancing non-refractory aerosol apportionment from an urban industrial site through receptor modelling of complete high time-resolution aerosol mass spectra” by M. L. McGuire et al.***

**M. L. McGuire et al.**

m.mcguire@utoronto.ca

Received and published: 3 June 2014

acp-2014-C579

Response to Anonymous Referee #2

### **General comments:**

The paper titled “Enhancing non-refractory aerosol apportionment from an urban industrial site through receptor modeling of complete high time resolution aerosol mass

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spectra” by McGuire et al. deals with the atmospheric aerosol source apportionment in Windsor (Ontario) making use of positive matrix factorization applied both to the organic and inorganic AMS mass spectra. 6 sources were separated using this approach, including factors related with inorganic components (like sulfate-OA, nitrate-OA and chloride), a HOA related with traffic, a site-specific component with amine peaks and an oxygenated OA fraction. The paper is well written and describes detailed analysis especially concerning the comparison of PMF results obtained with and without the introduction of the inorganic fractions in the source apportionment matrix. This approach is still quite new although it has a lot of potentialities that should be systematically investigated in most of AMS-PMF analysis. Therefore I recommend the publication of McGuire et al. work after replying to some technical comments.

*The authors thank Anonymous Referee #2 for valuable comments and suggestions. All comments and suggestions have been thoroughly considered so as to further improve the manuscript.*

Specific and technical comments:

(1) When referring to the amine containing factor, the work of Hildebrandt et al. (2011) should be cited as well.

*We thank the referee for bringing this work to our attention. The work of Hildebrandt et al. (2011) has been cited in the manuscript when referring to the Amine factor.*

(2) There are many more papers than the one reported by the authors assessing the cooking source identification in urban areas. How were the selected references chosen? The authors should consider quoting also the work of Sun et al. (2011), Mohr et al. (2012), Crippa et al. (2013), etc.

*We thank the referee for identifying this oversight. The list of references has been expanded to include more relevant references, and the works of Sun et al., (2011), Mohr et al. (2012), and Crippa et al., (2013) have been cited in the manuscript when*

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referring to identification of cooking sources.

(3) The discussion about the CE estimation should be extended reporting some graphs and evaluations (possibly in the supplementary material), although the choice of adopting a CE equal to 1 is in this case reasonable.

*We thank the referee for this comment, and have provided some further investigation into collection efficiency estimation. Per the suggestion of the Anonymous Referee #1, the method of AMS sub-micron PM + BC vs. PM<sub>2.5</sub> was investigated. Furthermore, the composition dependent CE method by Middlebrook et al. (2012) was also further explored. The results of this investigation have been presented in a new section in the Supplement (S1 AMS Collection efficiency). The text of the main manuscript and of the Supplement, as related to new discussion around CE, is presented in the response to comment (1) from Referee #1.*

(4) Did the authors apply any downweighting procedure when combining together the inorganic and organic matrix in one PMF experiment? As for m/z 44 a downweighting procedure is required when running PMF because some organic peaks are calculated from m/z 44 (Allan et al., 2003; Ulbrich et al. 2009). The same applies to some SO<sub>4</sub> peaks (e.g. m/z 80-81-98 are calculated from the signal at m/z 48-64). Can the authors clarify their approach on this issue?

*Following the approach of Chang et al., the authors determined that a downweighting procedure for specific peaks was not required for the PMF<sub>FullMS</sub> data matrix, as was required for the PMF<sub>OrgMS</sub> matrix (Chang et al., 2011). Such downweighting procedures would be required if the PMF<sub>FullMS</sub> matrix was constructed through addition of individual species matrices, as each of these matrices would be calculated through application of the fragmentation scheme, resulting in some peaks calculated from other reference peaks. Downweighting of selective organic or inorganic peaks was avoided in the PMF<sub>FullMS</sub> analysis, as the PMF<sub>FullMS</sub> matrix resulted from the subtraction of the "Air" and "Water" components from the original "All" matrix. In other words, the*

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*PMF<sub>FullMS</sub> matrix was not constructed from application of the fragmentation scheme to create "Org", "SO<sub>4</sub><sup>2-</sup>", "NO<sub>3</sub><sup>-</sup>", "Cl", and "NH<sub>4</sub><sup>+</sup>" matrices which could be added together to generate a "Full MS" matrix, but was a result of the subtraction of the "Air" and "Water" components subtracted from the original "All" matrix. As mentioned in the manuscript, the error matrix for the PMF<sub>FullMS</sub> analysis was constructed by summing in quadrature the original "All<sub>err</sub>", "Air<sub>err</sub>", and "Water<sub>err</sub>" matrices. The rationale for this approach has been further clarified in the main manuscript, as detailed below:*

*Added to P5091 of manuscript, line 10: "The data and error matrices for the PMF<sub>FullMS</sub> analysis were prepared following principles outlined by Chang et al. (2011). The data matrix was calculated in nitrate equivalent (NO<sub>3eq</sub>) mass (refer to section 2.3) and calculated by taking the entire raw MS matrix ("All"), and from it, subtracting the mass spectral matrices of species not of interest to the analysis (i.e., air and water), leaving the contributions from fragments associated with NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl-, and organics. Downweighting of selective organic or inorganic peaks as is required when conducting the PMF<sub>OrgMS</sub> analysis was avoided in the PMF<sub>FullMS</sub> analysis as the PMF<sub>FullMS</sub> matrix resulted from the subtraction of the "Air" and "Water" components from the original "All" matrix. In other words, the PMF<sub>FullMS</sub> matrix was not constructed from application of the fragmentation scheme to create "Org", "SO<sub>4</sub><sup>2-</sup>", "NO<sub>3</sub><sup>-</sup>", "Cl", and "NH<sub>4</sub><sup>+</sup>" matrices which could be added together to generate a "Full MS" matrix, but was a result of the subtraction of the "Air" and "Water" components subtracted from the original "All" matrix."*

(5) At page 5093 (line 2), the authors discuss the Q/Q<sub>exp</sub> variation in the f<sub>peak</sub> range -10,+10. Since this metric varies ca 1%, the authors are comparing mathematically equivalent solutions. They should investigate a broader f<sub>peak</sub> range to possibly identify different solutions. Ulbrich et al. (2009) recommend analyzing an f<sub>peak</sub> range corresponding to a Q/Q<sub>exp</sub> variation of at least 10%. This applies to all f<sub>peak</sub> analysis reported in this paper.

*The authors thank the referee for this comment. Although the range of FPeak values*

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used in this study corresponded to a variation in  $Q/Q_{exp}$  of 1%, this range was deemed sufficient for this study. It was reported in Ulbrich et al., (2009) that some researchers recommend exploring a range of FPeaks resulting in a 10% difference from the minimum  $Q/Q_{exp}$  value from the central rotation in order to identify alternate solutions. However, it has also been discussed more recently by Paatero et al. (2013) that using a defined percentage difference in Q values for assessing variations in Q values may not be sufficient, as an appropriate percentage will depend on the individual dataset. For instance, rotational variations and associated Q values will likely differ significantly between AMS-generated datasets (which display a very high degree of internal correlational structure) and integrated filter data (which shows a lower degree of internal correlation). As this is likely to vary based on the dataset, it has been suggested that it may not be helpful to base such assessments on a defined percentage value, and that assessments should be conducted based on empirical evidence (Paatero et al., 2013).

A range of  $Q/Q_{exp}$  of  $\sim 1\%$  was deemed suitable for the analysis performed by Ulbrich et al. (2009), and the same range was found suitable in this study. This range was helpful in assessing possible alternate solutions. The robustness of alternate solutions was assessed based on correlations with reference MS and TS of external tracers (Figures S-1.6 and S-1.7 in ACPD Supplement). Unfortunately, no further a priori information (e.g., zero values in factor time series) was available to constrain and potentially justify an alternate solution. Correlations showed that the greatest changes in correlations occurred in the solutions within FPeak values of  $\pm 4$ . Past these points, correlation coefficients levelled off. As discussed in the manuscript, although there were slight gains in positive FPeak values, these changes were deemed insufficient to choose them over the central rotation.

This range was also helpful for assessing the relative degree of rotational ambiguity amongst factors. It was determined that the Chloride factor showed the greatest amount of uncertainty, with up to 20% fractional species variation, as shown in Figure S-1.5 from ACPD Supplement. While the other factors showed greater stability than the

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Chloride factor, rotations nonetheless caused up to 10% fractional species variation. Thus, although the range of rotations appeared to produce somewhat mathematically equivalent solutions, there was sufficient variation in this range, as was found in Ulbrich et al. (2009), for this range to be useful for the purposes of this study.

The utility of this FPeak range in helping to justify the central rotation as most suitable, and also to help identify the relative degree of rotational ambiguity amongst factors, has been added to the Supplement and is as follows:

Added to Supplement, Section S2  $PMF_{FullMS}$  solution justification:

Paragraph 3: "Despite the wide range of tested FPeak values, the range of variation in  $Q_{robust}/Q_{exp}$  was reasonably low (0.793-0.805, or  $Q/Q_{exp} \sim 1\%$ ). This range was similar to that explored in Ulbrich et al. (2009), and was deemed suitable for the purposes of this analysis, as it caused sufficient perturbation to help justify the central rotation as the most suitable, and also determine the relative degree of rotational ambiguity amongst factors."

Paragraph 4: "Overall, the greatest variation was found within solutions of FPeak of  $\pm 4$ . Although a very minor improvement in correlation was noted for the FPeak of +2 value, this was not deemed sufficient to justify use of this value."

Paragraph 5: "Similar to the variation in mass spectra, the greatest variation in correlations between time series was found between Fpeaks of  $\pm 4$ . As no significant justification could be found for the selection of an alternate solution other than the base run, the central FPeak rotation (FPeak = 0) was chosen."

Added to Supplement, Section S3  $PMF_{OrgMS}$  solution justification

Paragraph 2: "Furthermore, despite the wide range of tested FPeaks, the range of variation in  $Q_{robust}/Q_{exp}$  is reasonably low (0.776-0.780). However, as with the  $PMF_{FullMS}$  analysis, this variation was deemed sufficient for the purposes of this analysis for determining the relative degree of rotational ambiguity amongst factors. The variation in

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the fraction of  $m/z$  44 to the factor mass spectrum (F44) was also examined (Table S-3.1). Variation was low for both the HOA and Amine factors, where values were low. For the OOA factor, it varied more significantly from the central rotation value of 0.15, ranging from 0.12 to 0.16. These values still fell within the range of values reported for OOA factors from around the world ( $\sim 0.10$ - $0.20$ ) (Ng et al., 2011). Furthermore, factor profile correlations across FPeaks with the reference HOA and OOA mass spectra showed negligible variation in correlation coefficients across rotations, indicating the central rotation was appropriate. Correlations between external time series and factor time series across FPeaks showed slightly more variation, but any improvement in correlation was still insufficient to justify choosing another solution over of the central rotation (Figure S-3.3 from ACPD Supplement). Variations in factor profiles and mass spectra were greatest for the solutions immediately adjacent to the central rotation (FPeak  $\pm 2$ ), indicating this FPeak range was sufficient for this analysis.”

(6) Page 5112: the authors should report the R2 instead of R (although correlations coefficients are not very high). Can the authors additionally report the correlation of HOA with toluene?

*Correlations with auxiliary data have been reported as  $r^2$  values instead of  $r$  values in the manuscript. The correlation of the HOA factor with toluene has been reported in the manuscript ( $r^2 = 0.32$ ).*

(7) Table 2: F44 represents the fraction of  $mz44$  to total org or the fraction of  $mz44$  in a MS (see page 5015). Why is the ratio  $f44$  to org reported in Table 2?

*This was added to the original manuscript to help distinguish that the F44 reported here is the fraction of  $m/z$  44 with respect to the organic fraction of a given factor, instead of with respect to the total combined organic and inorganic signal within the factor. The metric name has been changed in the table to F44 from F44/Org, and the table caption has been updated to clarify that, in keeping with other studies, the F44 reported here refers to the fraction of  $m/z$  44 with respect to a factor's organic signal*

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*only. This distinction was already reflected in the manuscript text.*

(8) It would be interesting to summarize with two pie charts/bar graphs the average source contribution to total OA (just taking into account the organic fraction from the coupled PMF) and to PM1 (from the coupled organic-inorganic apportionment). In this way it is easier to compare the PMF results obtained for this site with other literature works. These graphs represent complementary information to Table 2 and Fig.7. The authors should always report and discuss both the OA composition and the source contribution to PM1. A comparison of these results to analogous studies in the area in terms of organic fractions is needed (e.g. is HOA contributing to xxx% to total OA similarly to literature studies?).

*The authors thank the referee for these helpful suggestions. Two pie charts were created, and appended to Figure 12, to highlight the average factor composition of organics in both the PMF of the full mass spectrum and of the organics only (see Figure 1 below for updated Figure 12 from manuscript).*

*Factor organic composition relative to analogous studies (i.e., PMF of the full mass spectrum), in this case mainly that of Sun et al., (2012) is reported for the Sulphate-OA, Nitrate-OA, HOA, and OOA factors. Interestingly, the organic content between most of these factors is highly similar. The following text has been added to the following sections to expand on this point:*

*Added to P5015 of manuscript, line 1: “The organic fraction of the Sulphate-OA factor was extracted for comparison with the organic fraction of other factors, as well as published organic factor MS (Figure 6). Uncertainty in the organic fraction was assessed through rotational analysis, and was found to be low suggesting that these organics were reasonably rotationally fixed. The organic composition amongst factors extracted using the PMF<sub>FULLMS</sub> analysis was assessed against that from other studies. Only one of the past three similar studies, that of Sun et al., (2012), was sufficiently similar for comparison; Chang et al., involved Arctic aerosol, and the analysis by Crippa et al.,*

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only involved the organics and  $\text{SO}_4^{2-}$ . The Sulphate-OA factor contained 21% organics by mass, accounting for 16% of the total measured organics; interestingly this value was the same as that produced in the analysis by Sun et al., (2012). Although both of these studies were conducted in highly urban environments, such an agreement is interesting, considering that different organic factors were found.”

Added to P5106, line 19: “Deconvolution of the Nitrate-OA factor into its component species (Table 2) shows that it was mostly composed of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (78% by mass). However, other species such as organics and  $\text{SO}_4^{2-}$  also comprise a significant mass fraction (16% and 6% respectively). As with the Sulphate-OA factor, the Nitrate-OA factor demonstrated identical organic composition to the  $\text{NO}_3$ -OA factor found in the study by Sun et al., (2012). That both of these largely inorganic factors were highly similar to another study conducted in New York City is a possible indication of consistent internal and/or external mixing between these combined inorganic and organic species in these types of inorganic factors.”

Added to P5112, line 16: “With an organic composition of 85%, it was not as similar to the HOA factor found in Sun et al. (97%), as was for other factors.”

Added to P5113, line 21: “In terms of organic composition, this factor’s organic composition (93%) was most comparable to the LV-OOA factor from Sun et al., (2012), which comprised 94% organics.”

Comparisons of the factor HOA vs. OOA contributions are also provided in the text as follows:

Added to P5115, line 23: “Overall, the organic fraction was mainly split into the HOA and OOA factors, whereby these factors each contributed 53 and 47% relatively to the total OA as assessed by the  $\text{PMF}_{\text{OrgMS}}$  analysis. This nearly 50:50 division between these two organic components was somewhat different than that found in other two component studies in urban areas, with HOA making a greater contribution (Zhang et al., 2007). Such a difference could possibly be attributed to the significant industrial

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activity and traffic contributions from the international border crossing.”

(9) The authors discuss in the SI the impossibility to identify a BBOA factor. Do they expect this source to contribute to this site during wintertime? From the 5 factor solution of  $\text{PMF}_{\text{Org}}$ , the authors claim that the factor Other OA1 cannot be considered as a BBOA source because of the correlation of its time series with the one of Other OA2 factor (although the correlation is not very high as it appears from Fig. S-2.4). The authors should investigate the diurnal pattern of all sources in order to justify the interpretation of all the sources. If the authors expect a BBOA contribution, they could easily verify it looking at the diurnal pattern of this source.

We thank the referee for this comment, and have provided additional diurnal plots to further examine the possibility of a biomass burning factor in the  $\text{PMF}$  analysis of the organic mass spectrum. The Supplementary Material has been updated with this further analysis, and the updated sections are provided below.

Added to Supplement, section S3  $\text{PMF}_{\text{OrgMS}}$  analysis solution justification:

Paragraphs 6-7: “The time series of the factors from the three to six factor solutions (Figures 2 to 5 below) were further examined through analysis of diurnal trends. Diurnal trends of the OOA and Other OA factors were examined most closely to determine if there was additional definitive information regarding their nature. In the four factor solution (Figure 3), the OOA factors’ diurnality decreased, with the addition of the Other OA1 factor, which showed a more pronounced diurnal trend with daytime lows. This effect was also observed in the five and six factor solutions (Figures 4 and 5), where the Other OA1 and 2 factors both showed similar diurnality. This diurnal pattern was consistent with the semi-volatile nature that was suspected of the organics from the three factor solution OOA factor. It should be noted that these nighttime patterns were not necessarily consistent with nighttime residential wood burning, where mainly higher evening contributions would be expected. Thus, although these diurnal trends provided some further information to characterize OOA and Other OA factors in higher order

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solutions, they did not provide a definitive determination of a characteristic source or process.

*Correlations with external tracers provided further information of the effect of increasing the number of factors on the whole solution (Table S-3.4). The addition of more OA factors in the four and five factor solutions leads to higher correlations between the Other OA 1 and 2 factors in the 4 and 5 factor solutions respectively, with black carbon, NO, CO, and PNC. However, at the same time, the correlation between HOA and these key combustion species also decreases, indicating that the HOA factor is being split to some degree as well. The impact on the HOA factor, along with the difficulty in justifying the MS of the additional OA factors in the higher order solutions led to the three factor solution being chosen.*

*Although a biomass burning factor would be a logical observation during this wintertime campaign, it was not necessarily expected at this site. First, a literature review of past studies (mostly of integrated filter measurements) in the Windsor/Detroit area, showed that biomass burning has only been identified in three out of eight known past studies (Brown et al., 2006; Peré-Trepat et al., 2007; Gildemeister et al., 2007; Hammond et al., 2008; Wade et al., 2008; Morishita et al., 2011; Slowik et al., 2011; Pancras et al., 2013). Second, measurements were taken at a highly urban, industrial site; it is possible that industrial and traffic sources overwhelmed contributions from biomass burning, making it difficult to resolve them by PMF. Furthermore, it is possible that residential biomass burning is mainly occurring in residential areas at a distance from this highly urban site; this would allow for the oxidation and breakdown of biomass burning associated organic compounds during transit, also reducing the ability to resolve such contributions. Thus, although there appeared to be some evidence for biomass burning contributions, alternate solutions could not be accepted, as the evidence for a biomass burning factor was deemed too weak, and higher order solutions resulted in possible factor splitting and a decreased overall solution quality.”*

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 5081, 2014.

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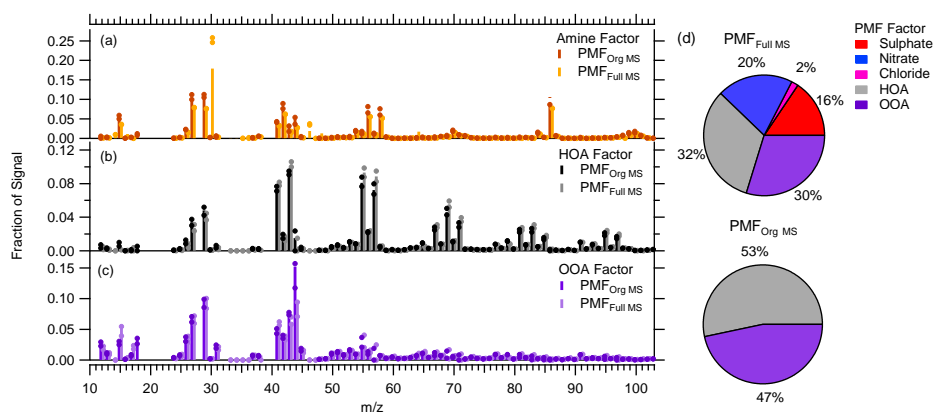


Fig. 1. Updated Figure 12 from manuscript.

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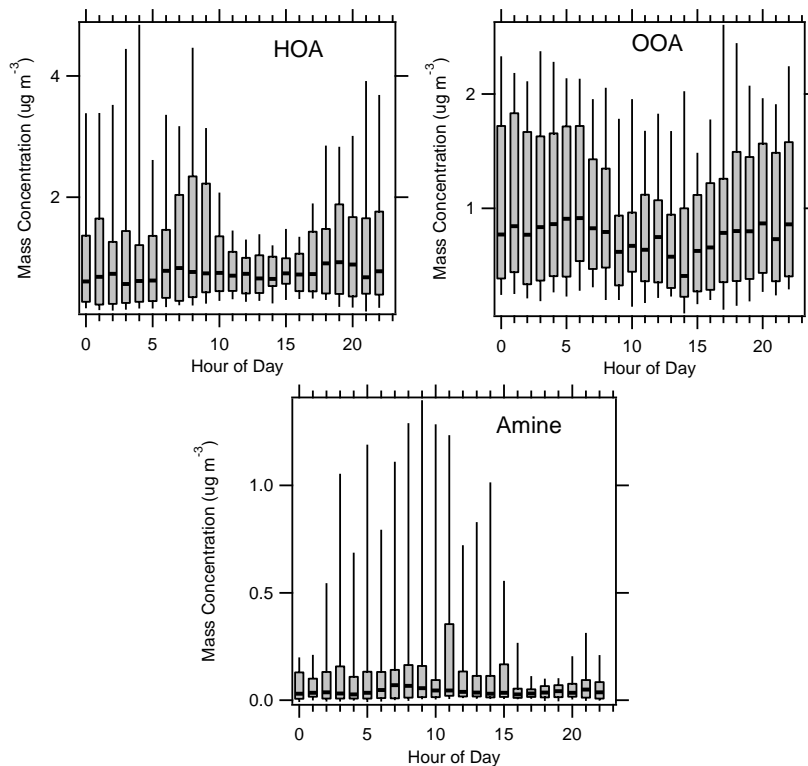
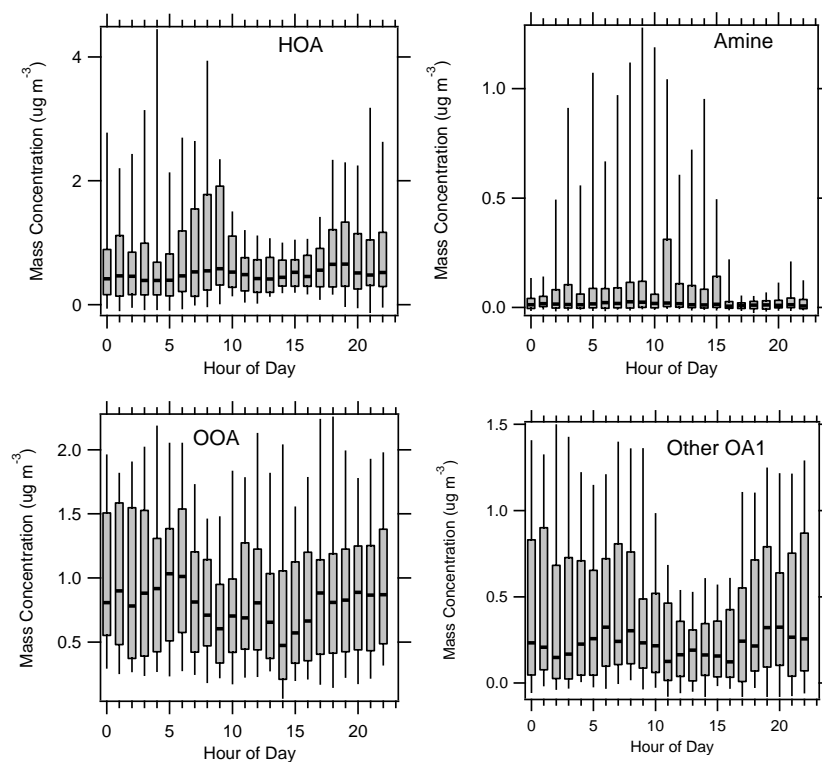


Fig. 2. Figure S-3.8 added to the Supplement. Diurnal trends for the PMF<sub>Org MS</sub> three factor solution.

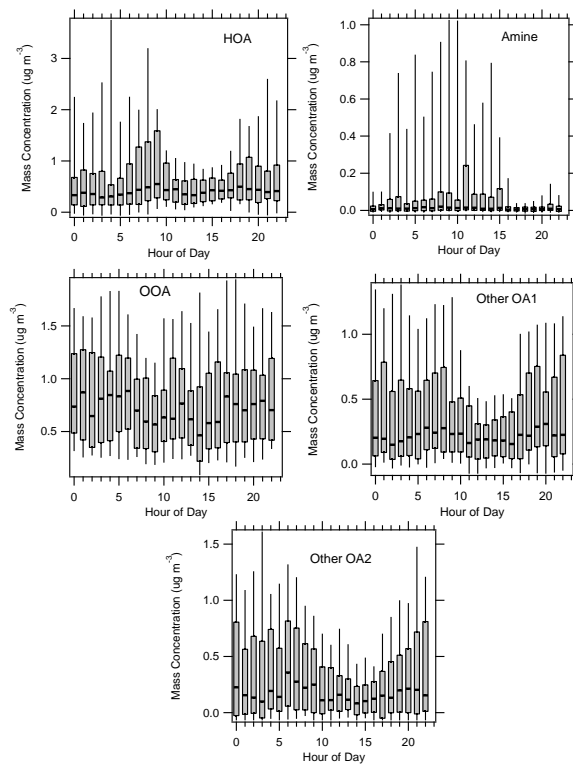
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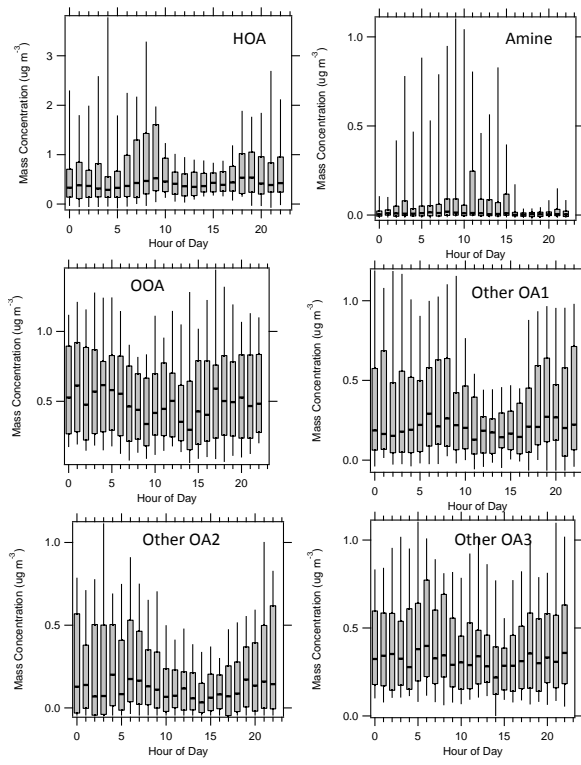
**Fig. 3.** Figure S-3.9 added to the Supplement. Diurnal trends for the PMFOrG MS four factor solution.

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**Fig. 4.** Figure S-3.10 added to the Supplement. Diurnal trends for the PMFOrG MS five factor solution.

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**Fig. 5.** Figure S-3.11 added to the Supplement. Diurnal trends for the PMFOrG MS six factor solution.