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Comment

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.

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Received and published: 3 June 2014

acp-2014-C447

Response to Anonymous Referee #1

General Comments:

The manuscript by McGuire et al. applied positive matrix factorization to the full mass spectral matrix from a quadrupole AMS dataset collected at an urban industrial site.

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While such an approach was reported previously by Chang et al. (2011) and Sun et al. (2012), this work presented more detailed evaluations and highlighted its advantages by comparing the results from PMF organics only. This approach was more powerful in source apportionment analysis when it's used along with CPF and PSCF. With this, new insights into the sources and processes of submicron aerosols, in particular the amine and OOA factors were gained. New findings also include the estimation of a RIE of 6.0 for amine and the separation of local sulfate from regional sources. The manuscript was well written and presented clearly, and the approach would be beneficial to the AMS community. I recommend publication for ACP.

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.

Specific Comments:

(1) The collection efficiency needs to be further justified although it didn't affect the PMF analysis in this work. Higher mass fraction of ammonium nitrate than 30% doesn't necessarily guarantee a CE closing to 1 based on the composition-dependent CE ($= \max(0.45, 0.0833 + 0.9167 \times \text{ANMF})$, Middlebrook et al., 2012). Why didn't the authors use NR-PM₁ + BC vs. PM_{2.5} (Fig. 2) to justify CE?

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_{2.5} 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. The text of the main manuscript and of the Supplement, as related to new discussion around CE, is presented below.

Added to manuscript (P5088, line 27):

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“The collection efficiency of the AMS is often estimated by comparison of the measured mass with that of a collocated instrument. If collocated external PM_1 mass measurements are unavailable, CE is often assumed by comparison of the combined AMS sub-micron PM mass and BC with an external measure of $PM_{2.5}$. Middlebrook et al., have also shown that a composition dependent CE can be estimated from the bulk aerosol composition (Middlebrook et al., 2012). These two options were investigated to determine whether a CE other than a default of 1 could be applied to the data, and the results of this investigation are presented in the Supplement. Ultimately, this analysis did not yield a reliable estimate of CE; as such no correction was applied to these data, and a default, simple integer collection efficiency of unity was assumed for this campaign. This value has been used in other studies (Lanz et al., 2007; Richard et al., 2011; Chirico et al., 2011), and reflects a lower bound for the non-refractory mass concentration. While an accurate estimate of collection efficiency is required for overall mass determination, it remains an integer value (either constant, or composition dependent) applied to the total mass concentration, and ultimately does not affect the primary study conclusions with respect to identifying and characterizing factors.”

Added to Supplementary Material (new section):

S1 AMS Collection efficiency

“The collection efficiency of the Aerodyne Aerosol Mass Spectrometer (AMS) is often estimated by comparison of the measured mass with that of a collocated instrument. If collocated external PM_1 mass measurements are unavailable, CE is often assumed by comparison of the combined AMS sub-micron PM mass and BC with an external measure of $PM_{2.5}$. Middlebrook et al., have also shown that a composition dependent CE can be estimated from the bulk aerosol composition (Middlebrook et al., 2012). These two options were investigated to determine whether a CE other than a default of 1 could be applied to the data.

For the simplest option, a reliable measure of $PM_{2.5}$ is required. Although CRUISER

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was equipped with a TEOM providing high time resolution $PM_{2.5}$ measurements, the suitability of using these $PM_{2.5}$ measurements for scaling was questioned as the TEOM was operated at $30^{\circ}C$, resulting in the possibility of significant semi-volatile material losses. This was investigated through comparison of daily averaged CRUISER TEOM $PM_{2.5}$ measurements with daily integrated speciation sampler filter measurements from Environment Canada's National Air Pollution Surveillance (NAPS) network; a slope of 0.48 ($r^2 = 0.47$) indicated that the CRUISER TEOM likely under measured by approximately 50% on average during the campaign. A more suitable measure of $PM_{2.5}$ for scaling was sought. A TEOM located in nearby Dearborn, Michigan was the best alternate measurement available. Although this TEOM was located 6.5km to the north-east of the Windsor measurement site, this TEOM was equipped with a filter dynamic measurement system (FDMS), thereby significantly reducing the effect of semi-volatile material losses (Grover et al., 2005).

To understand the effect of the site difference between the two sites, daily integrated filter measurements were compared. It was found that on a 24hr average basis, the two sites correlated well for the days measured, with an r^2 of 0.96. However, a slope of 1.12 indicated that the Dearborn measurements were $\sim 12\%$ higher than those in Windsor, indicating that there was some difference between the two sites. The Dearborn daily average FDMS TEOM measurements were compared to the integrated filter measurements from the same site, and it was found that again they compared well with an r^2 of 0.89. However, a slope of 1.24 indicated that the FDMS TEOM may have been biased somewhat high. Ultimately, good agreement was found between the daily averaged measurements of the Dearborn FDMS TEOM and the Windsor NAPS speciation sampler (r^2 of 0.92), although the FDMS measurements appeared to be 34% higher (slope = 1.34). This may have been a combination of the FDMS TEOM being biased somewhat high, combined with the actual differences in $PM_{2.5}$ between the sites ($\sim 12\%$). Nonetheless, comparison between the Dearborn FDMS TEOM and the CRUISER TEOM highlighted the unsuitability of the CRUISER TEOM mass measurements for scaling purposes, as very low agreement was found between the two ($r^2 =$

0.16, slope = 1.73), likely due to significant semi-volatile material losses. Comparison between the combined AMS submicron PM and BC masses with the Dearborn FDMS TEOM measurements revealed an estimated CE of 0.45 (Figure 1a). However, only a moderate r^2 of 0.64 was found between them, indicating that there was still significant variation, likely due to composition effects.

The Middlebrook et al. approach was explored to determine if a composition dependent CE could yield better agreement with the FDMS TEOM. Two key inputs are helpful to execute and validate this calculation, namely reliable measurements of sampling line RH, and a representative measurement of external mass from a collocated instrument. Unfortunately, sampling line RH was not measured in this study. Fortunately the Middlebrook algorithm contains a provision for lack of sampling line RH measurements, by assuming a constant RH. Comparison of FDMS TEOM measurements from Dearborn with composition dependent CE corrected submicron AMS measurements with BC was performed, and is shown in Figure 1b. While this test did increase the slope, it was still only 0.85, which could possibly be explained as the difference between the two sites. However, the agreement with the FDMS TEOM did not improve, but rather decreased slightly to r^2 of 0.63. A better agreement between the measurements following application of this composition dependent CE was expected. It is possible that the assumption of a constant sampling line RH was insufficient to determine an effective composition dependent RH in this case: as a nafion dryer was not used, variability in the sampling line RH, particularly with high RH, likely introduced further variation on CE (Middlebrook et al., 2012). As a constant RH was assumed, this additional variability could not be accounted for. Thus, with the CE reported to be dependent on RH particularly at higher RH values, the composition dependent CE did not appear to have improved the results, and as such was thus not applied to the data.

Ultimately, no CE correction was applied to these data, and a default, simple integer collection efficiency of unity was assumed for this campaign. This value has been used in other studies (Lanz et al., 2007; Richard et al., 2011; Chirico et al., 2011), and

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reflects a lower bound for the non-refractory mass concentration. While an accurate estimate of collection efficiency is required for overall mass determination, it remains an integer value (either constant, or composition dependent) applied to the total mass concentration, and ultimately does not affect the primary study conclusions with respect to identifying and characterizing factors.”

(2) The sum of mass fractions for NO_3^- in Figure 7d is not equal to 1.

We thank the referee for identifying this oversight. We notice that indeed the sum of mass fractions for NO_3^- in Figure 7d from the manuscript very slightly exceeds 1 due to rounding errors. This rounding issue has been addressed, and an updated Figure is presented in Figure 2 below.

(3) P 5085, line 20, spell out “O/C”

We thank the referee for noting this discrepancy. The oxygen to carbon (O/C) ratio has been spelled out in this sentence.

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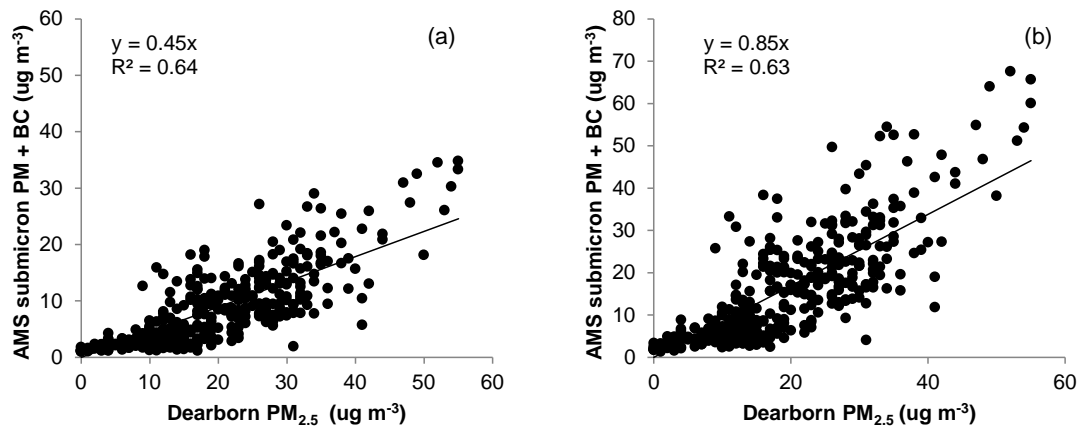


Fig. 1. Figure S-1.1 added to Supplement.

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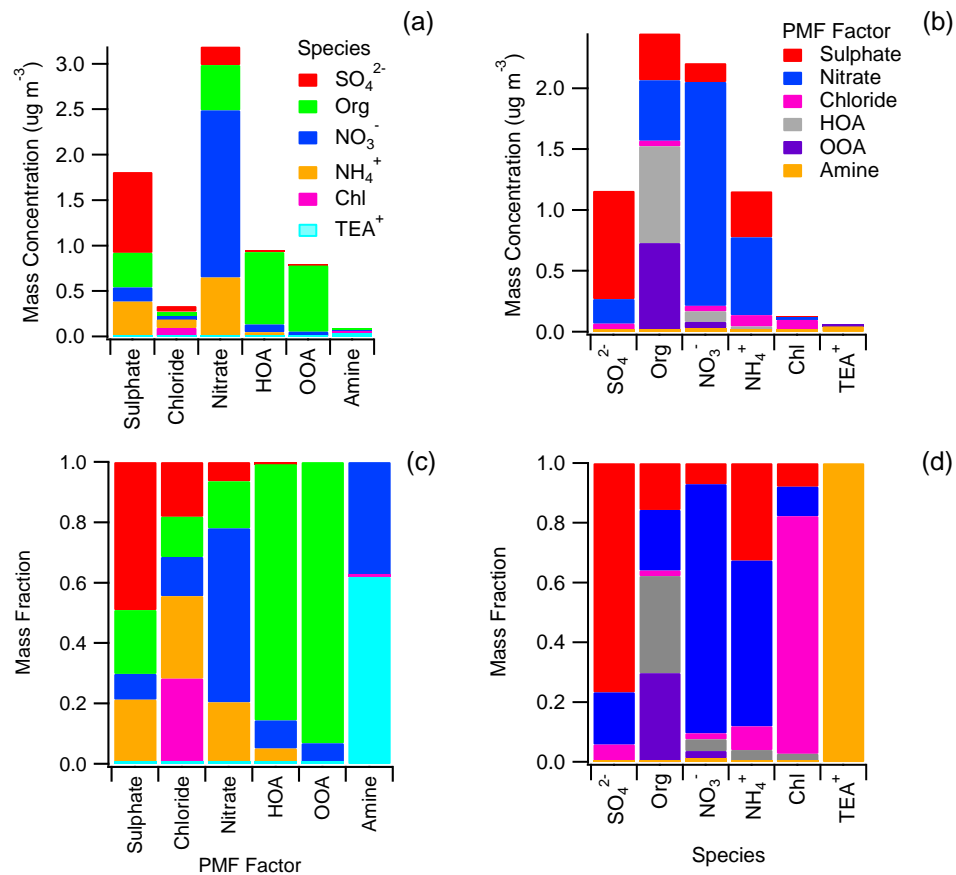


Fig. 2. Updated Figure 7.