

Interactive comment on “Technical Note: A new approach to discriminate different black carbon sources by utilising fullerenes and metals in Positive Matrix Factorisation analysis of High-Resolution Soot Particle Aerosol Mass Spectrometer data” by Zainab Bibi et al.

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SUBJECT: Percentage uncertainty terms (peak width and fitting errors) results in a similar conclusion as PMF model error

TEXT:

Dear authors,

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It is very interesting to see these fullerene and metal ions included in SP-AMS-PMF. I would like to make two comments.

The first comment is trivial. Figure 4 uses a confusing mixture of terminology and units. Absorption measurements are reported as both BC [$\mu\text{g m}^{-3}$] and BrC [/Mm]. I would suggest following the recommendations of Petzold et al. 2013 and renaming BC as eBC, for both AE31 and MAAP, and specifying in the figure legend the measurement wavelength and assumed MAC. Also, the reason that the two eBC instruments are plotted on separate axes could be noted in the legend.

The second comment is to recommend an improvement to the authors' SP-AMS error model based on Corbin et al. 2015a ("C2015") instead of using PMF's "model error" to address SNR issues. I am sure that the authors will already understand my suggestion from this brief statement. However, I would like to take the opportunity of writing this Interactive Comment to summarize C2015's message in simple practical terms:

Currently, the large dynamic range of signals in this data set led the authors to use a PMF "model error" of 0.05 or 0.10. This is illustrated by the signal to noise ratios (SNRs) in Figures S3b, S4b, S5b, which showed extremely high values for some ions. Specifically, the SNR for ions such as C3H8O was about 1000, whereas the SNR for fullerene ions was about 10 (too small to read from Figure S3b). This is a perfect example of the problems described in C2015, and arises when only Poisson counting errors are taken into account. In real-world instruments, Poisson-only error models will almost always overestimate the SNR of large signals, and this problem can be overcome with the inclusion of a percentage error term (Rocke and Lorenzato, 1995). The effect of this percentage error term is easy to understand if the SNR is converted to a percentage. SNRs of 1000 and 10 become percentages of 0.1% and 10%, respectively. Normally, repeated measurements vary by much more than 0.1%, which implies that the SNR of 1000 is an overestimate.

The PMF "model error" of 0.05 or 0.10 acts like a percentage error term (of 5% or

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10% respectively). However, it has no physical basis, beyond implying that the bilinear PMF model does not represent the data accurately. In contrast, including the missing proportional error terms in the SP-AMS uncertainty model would result in nearly the same numerical outcome, but without implying a problem in the actual factorization stage or requiring a subjective decision on how much error to include. Thus, including of peak width and peak fitting errors in AMS-PMF reduces uncertainty in the final result.

Although C2015 discussed a complex Monte Carlo approach to peak-fitting errors, two of the conclusions of that work could be applied here very easily. One is that isolated peaks (no overlap) will always have a couple of percentage uncertainty due to random noise in the m/z calibration (Figure 8 in C2015 implies about 2% or 3%). The other has nothing to do with peak fitting, and only regards peak integration. During peak integration (Eq. 4 in C2015), the peak width w is predicted from an empirical fit to the data (often a linear fit, see Section 2.2 in C2015 and the SI of Corbin et al. 2015b). This prediction of w has an associated proportional uncertainty σ_w/w . In the C2015 data set σ_w/w was 2.5%. This 2.5% may be treated as independent of the earlier 2% or 3% uncertainty in the height of isolated peaks, so the two can be summed in quadrature. So, the total percentage uncertainty (Eq. 6 in C2015) for isolated peaks can be about 5%. This 5% is conceptually equivalent to 0.05 model error. This 5% is likely may be an underestimate for the present study, where the authors have investigated peaks at very high m/z that were not addressed in C2015. (The authors might add a comment on the calibration of these peaks.)

There is only a minor technical difference between model error and total percentage uncertainty: the PMF Evaluation Tool [PET] does the sum linearly instead of quadratically.

In summary: one can expect a few percent of isolated-peak uncertainty in all cases (due to variability in m/z calibration) and another few percent of peak-integration uncertainty (σ_w/w). The latter can be estimated from the peak-width calibration stage in PIKA (by repeating the peak width fit manually, as detailed in Corbin et al. 2015b). This

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provides a simple and objective justification for using model error in PMF.

Again, although I have taken the opportunity to write this out in full, I am sure that the authors understand these details, and that they only add weight to the results of Bibi et al. 2020.

Best regards,

Joel

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