

***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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Received and published: 28 February 2021

1. Introduction: Although the proposed method includes a new concept for data analysis, this manuscript should better recognize the contribution of other recent SP-AMS studies that performed fullerene detection near sources and that integrated BC signals in PMF for BC and OA source analysis.

I have added some recent SP-AMS studies from the following references which stated

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the detection of fullerenes near sources and integrated BC signals by applying PMF for OA and BC sources.

Wang, J., Onasch, T.B., Ge, X., Collier, wang S., Zhang, Q., Sun, Y., Yu, H., Chen, M., Prevot, A.S. and Worsnop, D.R., 2016. Observation of fullerene soot in eastern China. *Environmental Science & Technology Letters*, 3(4), pp.121-126.

Carbone, S., Onasch, T., Saarikoski, S., Timonen, H., Saarnio, K., Sueper, D., Rönkkö, T., Pirjola, L., Worsnop, D. and Hillamo, R., 2015. Characterization of trace metals with the SP-AMS: detection and quantification. *Atmospheric Measurement Techniques Discussions*, 8(6).

Liu, D., Joshi, R., Wang, J., Yu, C., Allan, J.D., Coe, H., Flynn, M.J., Xie, C., Lee, J., Squires, F. and Kotthaus, S., 2019. Contrasting physical properties of black carbon in urban Beijing between winter and summer. *Atmospheric Chemistry and Physics*, pp.6749-6769.

Onasch, T.B., Fortner, E.C., Trimborn, A.M., Lambe, A.T., Tiwari, A.J., Marr, L.C., Corbin, J.C., Mensah, A.A., Williams, L.R., Davidovits, P. and Worsnop, D.R., 2015. Investigations of SP-AMS carbon ion distributions as a function of refractory black carbon particle type. *Aerosol Science and Technology*, 49(6), pp.409-422.

2. Instrumentation: HR-SP-AMS has been deployed in many field studies with different configurations and operation modes. I do believe the tungsten vaporizer was removed from the instrument in this work as only BC-containing particles were detected. It would be very beneficial to readers who are not familiar with this instrument if the authors can explicitly describe whether the HR-SP-AMS was operated in the presence or absence of tungsten vaporizer and what can be detected with this specific configuration.

I have added these few lines in introduction chapter. Thank you for pointing this. In this study, the HR-SP-AMS used was not the same as the C-ToF-AMS (Compact Time-of-Flight Aerosol Mass Spectrometer) described in Reyes et al., (2018). The HR-SP-AMS

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was operated under an intracavity, CW laser vaporiser (with the tungsten vaporiser removed), which vaporises the refractory BC (rBC) and its associated non-refractory particulate species along with metal nanoparticles (Onasch et al., 2012; Carbone et al., 2015).

3. Lines 126-127: As there were only limited work to report metal detection in ambient particles using HR-SP-AMS, it is recommended to include a list of metal peaks that have been investigated and/or detected in this work.

Thank for your comment. In line 183, I have mentioned four different metals that have been detected by HR-SP-AMS, please see below: “This high-resolution analysis on SP-AMS data also detected various metal pollutants such as Iron (Fe), Titanium (Ti), Strontium (Sr) and Caesium (Cs)”.

4. Lines 131-134: Please define fullerene peaks. If UMR data is used for large m/z , what is the possible error for determining fullerene signals?

Thank you so much for your suggestion regarding this comment, I have improved it now; This lower frequency delivered data up to $m/z=3200$ rather than 380, with the intention of characterising the fullerene signals described by Onasch et al. (2012) at the expense of overall signal-to-noise. The data presented in this paper are a combination of the standard ‘V’ mode for the lower m/z peaks, processed using the PIKA high resolution analysis tool, and the long pulser period ‘V’ mode for the fullerene peaks, processed using unit mass resolution (UMR) method. The reason for using UMR method instead of HR was that the peaks in this m/z regime were not sufficiently resolved, due to the $m/\Delta m$ limit of the mass spectrometer. Instead, the UMR method can integrate all the available signals and is therefore more robust. However, the ability to resolve multiple peaks per nominal integer m/z provided useful additional data in the low m/z regime. The ‘W’ mode data was deemed not to have a sufficient signal-to-noise ratio to contribute to this work.

5. Lines 137-138. There are a few previous field studies that included BC frag-

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ments for source apportionment/identification analysis of ambient BC and OA but they may not explicitly highlight this application in the manuscript. However, those publications should be cited here. Thanks for your suggestion. This citation is added in the manuscript. Saarikoski, S., Carbone, S., Cubison, M.J., Hillamo, R., Keronen, P., Sioutas, C., Worsnop, D.R. and Jimenez, J.L., 2014. Evaluation of the performance of a particle concentrator for online instrumentation. *Atmospheric Measurement Techniques*, 7(7), pp.2121-2135.

6. (a) Figures: Although Figure 4 is good for visualization, it is recommended to report the Pearson correlation coefficients between different BC measurements here. This comment also applies to other time series comparisons throughout the manuscript.

Thank you so much for this suggestion. I will add following tables in the supplementary information section.

6b. Furthermore, Figures 2-5 can be combined into a single graph with different panels so that the time series of different species can be easily compared. Figures 6 and 7 can be combined as well (i.e., showing HR-MS for lower range m/z in Figure 6).

Thanks for your suggestion, I have combined figures 2, 3, 4 and 5 in one panel.

7. Section 3.5: Re-organization of this section is required. In particular, it is recommended to discuss the PMF factor profile and time series together instead of separating them into two sub-section as both of them provide information for sources of BC and OA. For example, Figure 8 (time series of PMF factors) is required at the beginning of Section 3.5 when describing which OA factors were strongly associated with the bonfire night or other emissions. The mass spectral profile alone did not provide sufficient evidence to support the scientific argument.

Thank you so much for your suggestion. I have reorganised this section now (See revised manuscript).

8. Line 234: The meaning of HULIS here is unclear. Figure 6 only shows "BC and

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HULIS” factor. The terminology throughout the manuscript should be consistent.

In order to provide the clearer meaning of HULIS, I am adding further explanation to this; HULIS is a class of organic molecules that can be formed by photochemical oxidation and oligomerisation of volatile organic compounds in the atmosphere (Aiken et al., 1985; Hoffer et al., 2004) and biomass burning (Lin et al., 2010), with a characteristic peak at m/z 44 (McFiggans et al, 2005). Potential origins of HULIS in the atmosphere are diverse, including (primary) biomass burning (Graber and Rudich, 2006; McFiggans et al, 2005; Mukai and Ambe, 1986; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002), terrestrial (Simoneit, 1980) and marine sources (Cini et al., 1994; Cini et al., 1996; Calace et al., 2001; Cavalli et al., 2004), , and secondary organic aerosol formation (condensation, reaction, oligomerisation, etc.) (Gelencser et al., 2002; Jang et al., 2002; Jang et al., 2003; Tolocka et al., 2004; Hung et al., 2005). Moreover, HULIS as an atmospheric aerosol has already been reported in previous literature (Decesari et al., 2000, 2007). Along with this the work of Havers et al. (1998), wherein the term HULIS was coined. Examining a standard reference air dust as well as airborne particulate matter, Havers et al. (1998) attributed 10% or more of aerosol organic carbon to macromolecular substances HULIS similar to humic and fulvic acids. Aiken, G.R., McKnight, D.M. and Wershaw, R.L. (1985). Humic substances in soil, sediment, and water. Geochemistry, Isolation and Characterization. New York: Wiley

9. Lines 243-245: Both factors 2 and 3 consist of fullerene peaks. Please further elaborate how the fullerenes help to differentiate domestic burning and biomass burning during the bonfire event (e.g., any distinct peaks or mass spectral pattern that can be used?). It seems that the lower m/z fragments are more than sufficient to tell the differences between the two OA factors. What does “hydrocarbon like fullerene” mean?

Both factors 2 and 3 have fullerene peaks but if we see their y-axis the concentration of fullerene is very low and mainly dominated by other sources, while factor 1 is heavily populated by fullerene peaks, so that’s why I have only considered factor 1 as fullerene (Onasch et al., 2015). Although it is not clear why fullerene signals are sometimes ob-

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served, it does seem to differentiate between biomass burning during the bonfire event and biomass burning from domestic burning. In fig 4, Factor 5 was heavily weighted by hydrocarbon like Fullerene having a peak at m/z 720 (C60+), implying polycyclic aromatic hydrocarbons can transform into soot containing Fullerene during combustion (Wang et al., 2015, Wang et al., 2016; Reilly et al., 2000). This was typically not associated from the traffic source (diesel), so depended on the different type of combustion. References: Reilly, P. T. A.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M. Fullerene Evolution in Flame-Generated Soot. *J. Am. Chem. Soc.* 2000, 122 (47), 11596–11601. Wang, J., Onasch, T.B., Ge, X., Collier, S., Zhang, Q., Sun, Y., Yu, H., Chen, M., Preißner, A.S. and Worsnop, D.R., 2016. Observation of fullerene soot in eastern China. *Environmental Science & Technology Letters*, 3(4), pp.121-126.

10. Lines 287-288: Three bonfire night factors were identified. Were they all from bonfire emissions? If so, it implies that there were different types of bonfire emissions that can provide sufficient temporal variabilities for PMF factor separation. I am wondering if the same number of PMF factors can be obtained if fullerene signals is excluded. More discussion is required to demonstrate the importance of including fullerene signals in PMF analysis.

All of the three factors are bonfire emissions factors (please see the time series spike originated during the bonfire emissions time period).

Factorisation without Fullerenes: Thank you so much for pointing out this comment. I have added the factorisation without fullerene graphs in the supplementary section and their explanation in the result section. Please see below the factorisation results. Firstly, the factorisation was performed without the inclusion of fullerene signals in the data matrix, in order to explore the factorisation without fullerene data. And the results showed five factors solution (fig S1a and S1b) which are BC and HULIS, SV-OOA, BBOA, Hydrocarbon-like OA and domestic burning. In that case, only two unambiguously bonfire night sources of BC were identified, with a degree of 'mixing' between the bonfire night factor and traffic noted in the HOA factor. Also, the SV-OOA and domestic

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burning factors also exhibit mixing in their timeseries as well. As such, the factorisation without fullerene signals was judged to be poor.

11. HULIS factor: The manuscript mention a couple of times that a factor having strong m/z 44 signals can represent HULIS in ambient particles, but I cannot fully follow the flow of argument. My interpretation is that the mass spectral features of the HULIS factor is similar to that of more-oxidized oxygenated OA (MO-OOA) factor identified in most other field studies. I am wondering whether other co-located measurements in this work can provide evidence that the HULIS factor has some specific chemical features that cannot be described as MO-OOA. I understand this can be just a terminology issue. More elaboration is required here.

The first factor is BC and HULIS. Firstly, by observing the time series of this factor, the reader will clearly notice that the highest concentration is during the bonfire emissions. If I interpret m/z 44 as MO-OOA then time series results also show some spikes before and after the bonfire event. Secondly, HULIS is a class of organic molecules that can be formed by photochemical oxidation and oligomerisation of volatile organic compounds in the atmosphere (Aiken et al., 1985; Hoffer et al., 2004) and biomass burning (Lin et al., 2010), with a characteristic peak at m/z 44 (McFiggans et al, 2005). Potential origins of HULIS in the atmosphere are diverse, including (primary) biomass burning (Graber and Rudich, 2006; McFiggans et al, 2005; Mukai and Ambe, 1986; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002), terrestrial (Simoneit, 1980) and marine sources (Cini et al., 1994; Cini et al., 1996; Calace et al., 2001; Cavalli et al., 2004), , and secondary organic aerosol formation (condensation, reaction, oligomerisation, etc.) (Gelencser et al., 2002; Jang et al., 2002; Jang et al., 2003; Tolocka et al., 2004; Hung et al., 2005). Moreover, HULIS as an atmospheric aerosol has already been reported in previous literature (Decesari et al., 2000, 2007). Along with this the work of Havers et al. (1998), wherein the term HULIS was coined. Examining a standard reference air dust as well as airborne particulate matter, Havers et al. (1998) attributed 10% or more of aerosol organic carbon to macromolecular

substances HULIS similar to humic and fulvic acids.

Minor comments: 1. Line 280. I think m/z 73 instead of m/z 71 for typical biomass burning factors. 2. Line 337: Please define BCtr. 3. Line 345: Please define BCwb. Thank you so much for pointing out these minor mistakes. m/z 73 instead of m/z 71 is corrected eBCwb is the equivalent Black carbon emitted from wood-burning sources. eBCtr is the equivalent Black Carbon emitting from traffic emissions.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2020-890/acp-2020-890-AC2-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-890>, 2020.

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Table S1: Pearson correlation coefficients between different BC measurements such as BC (HR-SP-AMS) with BC and BrC (AE31) and BC (MAAP)

BC (HR-SP-AMS)	
	Pearson Coefficient
BC (AE31)	0.98
BrC (AE31)	0.96
BC (MAAP)	0.95

Table S2: Correlation between BC (HR-SP-AMS) and CIMS measurements

HR-SP-AMS	CIMS DATA		
	HCN	HCNO	HONO
	Pearson Coefficient	Pearson Coefficient	Pearson Coefficient
rBC (HR-SP-AMS)	0.88	0.77	0.89

Table S3: Correlation between HR-Aerosols species Vs Aerosol and Gases (AMS)

HR Aerosol Species	Aerosol and Gases	Pearson Coefficient
rBC	BC ₂ ($\mu\text{g m}^{-3}$)	0.95
HROrg	Org ₂ ($\mu\text{g m}^{-3}$)	0.92
HRNH ₄	NH ₄ ₂ ($\mu\text{g m}^{-3}$)	0.92
HRNO ₃	NO ₃ ₂ ($\mu\text{g m}^{-3}$)	0.86
HRSO ₄	SO ₄ ₂ ($\mu\text{g m}^{-3}$)	0.91
HRChl	Chl ₂ ($\mu\text{g m}^{-3}$)	0.99

Fig. 1. Table 1 shows the Pearson correlation coefficients between different BC measurements

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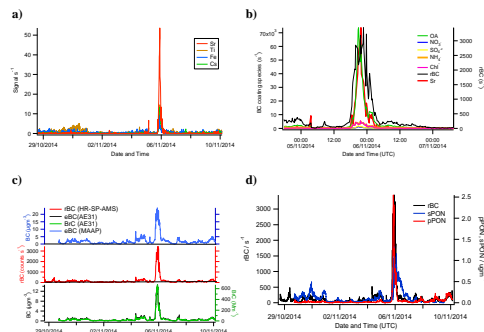


Figure 2. Timeseries of different variables observed during bonfire event. 2a. Time series of various metal pollutant concentrations, 2b. Time series of High Resolution rBC concentrations and its coating species (Organics and Inorganics), 2c. Time series of Black Carbon measured by different instruments i.e. HR SP-AMS (rBC), AE31 (eBC and BrC) and MAAP (eBC), 2d. Time series of rBC, primary (pPON) and secondary (sPON) organic nitrate.

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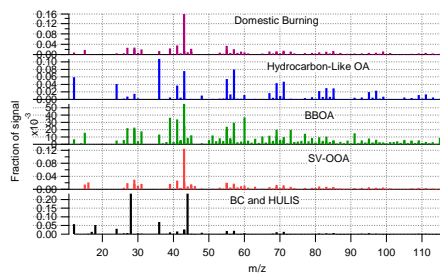


Fig. 3. Mass Spectra of five factor solution (without inclusion of fullerene signals).

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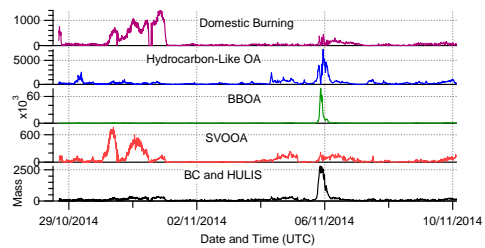


Fig. 4. Time series of five factors (without the inclusion of fullerene data).

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