Answers to Anonymous referee no. 1

This paper presents a new approach by using fullerenes and metals in PMF analyses of HR-SP-AMS data and shows that BC from more than one biomass burning sources can be separated. The work can be a good contribution to the aerosol chemistry, however, there are quite a number of important issues to be addressed first before considering its possible publication in ACP. Please see below:

(1) This work uses fullerenes and metals to help the BC source apportionment via SPAMS, however, it is surprised that the authors seem to completely overlook a few important papers very closely related with your current analyses. Necessary citations and incorporation of findings from these studies has to be added in your work. And I also suggest the authors to do a more thorough search on the recent SPAMS studies. These papers at least include: Distribution of carbon cluster ions in different BC types (Aerosol Sci Tech 2015;49:409-422); detection, quantification and source apportionment of fullerenes by using SP-AMS (Environ Sci Technol Lett 2016,3,121-126); Characterization of OA via BC fragments and metals detected by SP-AMS (Atmos. Chem. Phys., 20, 5977–5993, 2020); Source identification of BC by using SP-AMS (Atmos Environ 2018,185,147-152); Another study combining SP-AMS and SP2 data to apportion BC into different sources (Atmos Chem Phys 2019,19,6749-6769).

Ans: Thank you so much for your feedback and suggesting me some new research articles to include in my journal. I will consider your suggestion and add these citation work in my manuscript.

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.
Wang, J., Onasch, T.B., Ge, X., Collier, S., Zhang, Q., Sun, Y., Yu, H., Chen, M., Prévôt, 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.

(2) Line 115: What is the role of a catalytic stripper? And why data under this mode is not used then?

Ans: Thanks for asking. The catalytic stripper was used in the setup and has already published in Danton Liu's paper. It was not included for this research work publication. The only reason to quote in my manuscript is, it's been used in another study. I have also tried analysing catalytic stripper data but did not get sensible results. So, I have excluded that data.

(3) Line 120：Why no ionization efficiency was not obtained? Due to what difficulty? If other studies can determine the IE, then why this work cannot? It is not explained clearly to the readers. If the IE or RIE of different species, especially fullerenes, are not determined, this is a fatal issue. This reviewer doubts the credibility of PMF results and subsequent analyses.

Ans: Thank you so much for your comment. At the time, we tried but it did not work properly so we cannot go back and recalibrate. Also, RIE did not affect PMF analysis results and it's not at all fatal issues.

(4) Section 2.2: Some necessary technical details are still missing here: what is the chemical resolution, and how does this allow you to detect the ions with low signals? For example, different metals? What is the time resolution? And what are the detection limits of different species by using SP-AMS? At last, did the SP-AMS here only detect BC-containing particles? Then it is not clearly specified that the SP-AMS is operated

with only laser vaporizer? Or with laser and tungsten vaporizer? Is the thermal vaporizer physically removed? The different modes significantly influenced the aerosol components detected (Check and cite if necessary: Atmos. Meas. Tech. 2014, 7, 4507−4516; Atmos Chem Phys 2019,19,447-458)

Ans: Thank you so much for the feedback. In terms of technical details, High Resolution SPAMS detected the metal signals such as Sr, Fe, Cs and Ti. The time resolution, as I have mentioned in my manuscript was from 29th Oct-11th Nov 2014. Also, I have clearly stated that in this study, the SP-AMS was only operated with the laser vaporiser only in combination with the electron impact source and measures both refractory and nonrefractory components along with metal nanoparticles and it's also cited (Onasch et al., 2012).

(5) Section 2.3: m/z up to 3200 was determined, however, the m/z range of your PMF results is only up to 1000. Can you explain?

Ans: Thank you so much for your comment. The reason for 1000 m/z range of this PMF analysis is that above m/z 1000 the signals were not approachable, and it was only noise so that's why we have ignored them and only added m/z up to 1000 by clearly showing the separate BC sources.

(6) Figure 4. More details are needed. How did you determine BrC for example?

Ans: The Aethalometer AE31 was used to determine BrC and it has already published in Reyes et al., 2018.
(7) Figure 5. How to determine PON etc? A citation of previous work is not enough.

Ans: Particulate organic oxides of nitrogen (PONs) were estimated using the m/z 46 : 30 ratios from aerosol mass spectrometer (AMS) measurements, according to previously published methods (published in Reyes et al., 2018).

(8) Figure 6. You have a high-resolution SP-AMS, why not use different colors to differentiate different ion categories? (Figure 7 is redundant). This helps justification of your PMF results and better for readers to judge and understand your results. Also, the justification of your PMF results is not clear. I am not sure for example, why factor 5 is fullerenes, and why factor 1 is BC and HULIS, and so on？ The O/C and H/C are too high, and they seem to be wrong. This has to be addressed well, otherwise, analyses based on the PMF are not trustworthy.

Thank you so much for the suggestion. Sure, I will use different colours to differentiate the ion categories. I have added some more details to explain why factor 1 is BC and HULIS and others as well.
Yes, you are right, I have mistakenly added the wrong values of O:C but H:C values are correct. Thank you so much for pointing this, I have now added the correct values.

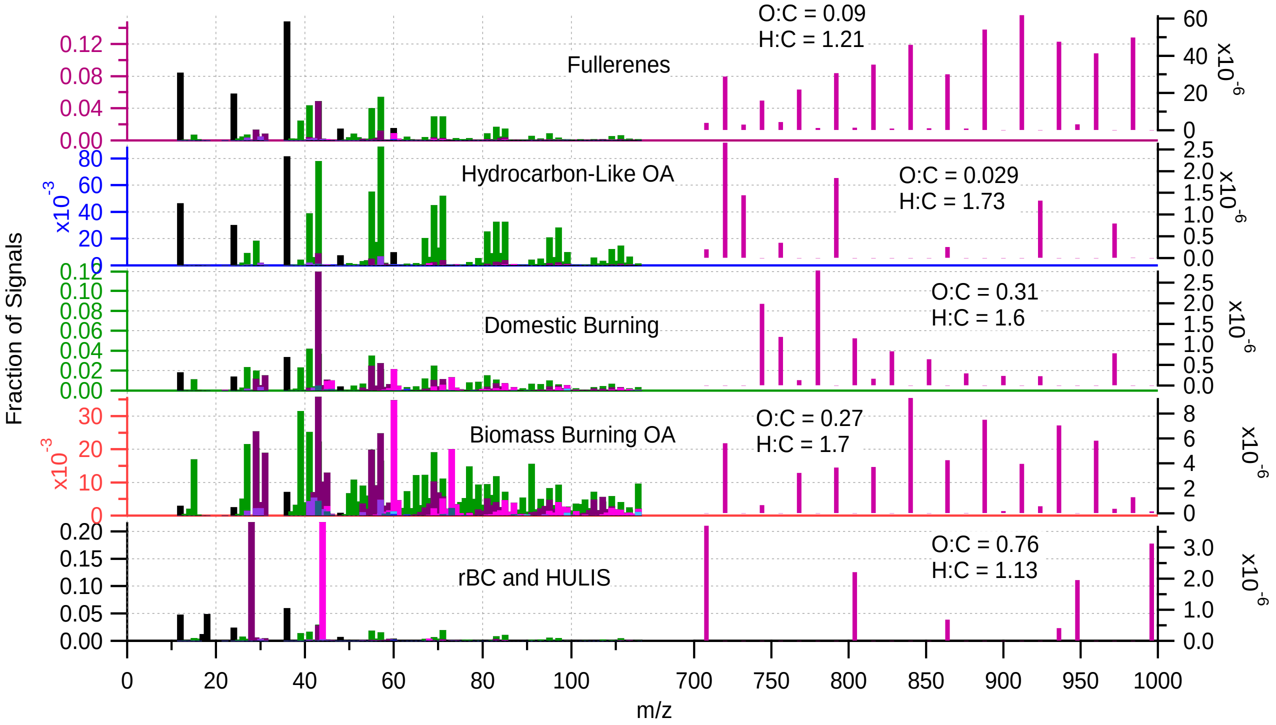


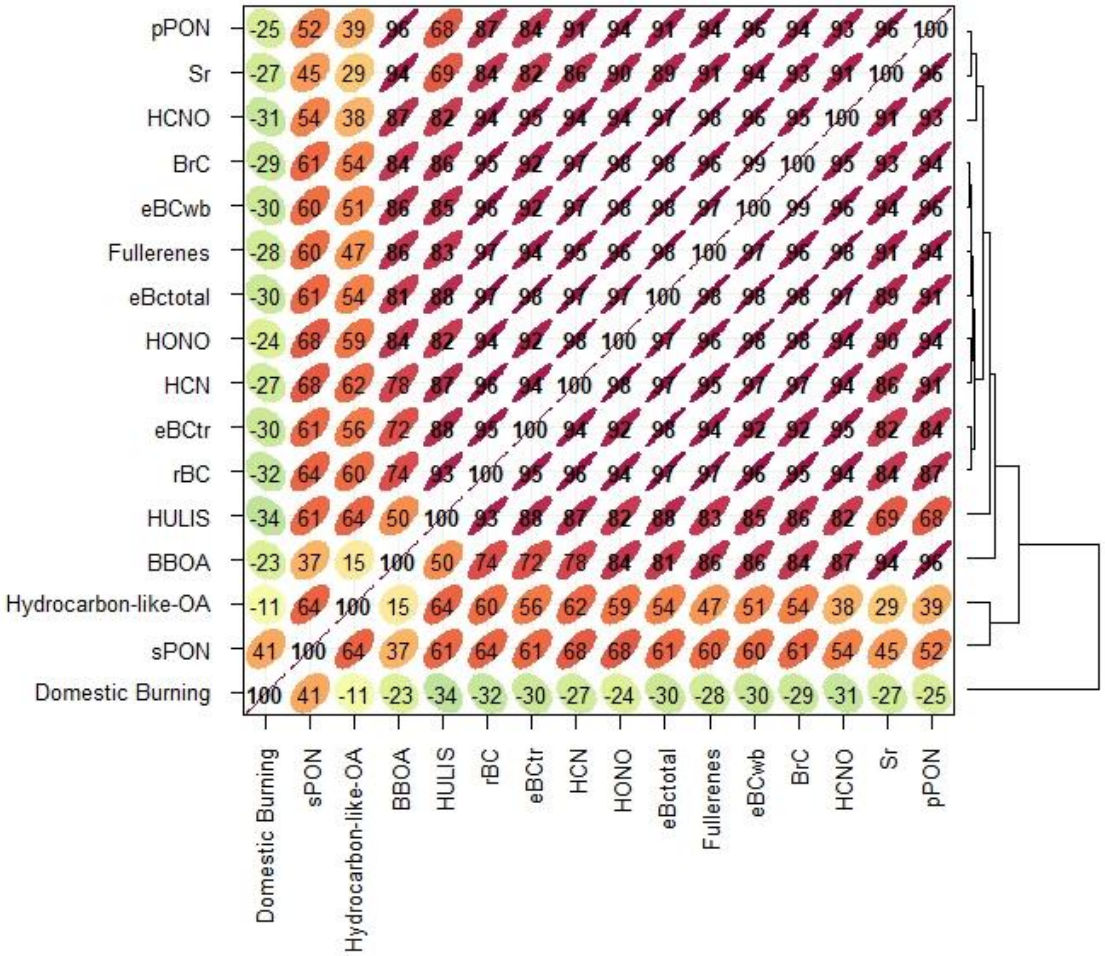
Figure 4: PMF five factors source profile (factor 1 = BC and HULIS, factor 2 = BBOA, factor 3 = Domestic burning OA, factor 4 = Hydrocarbon-Like OA, factor 5 = Fullerene). Note the difference in scales of the fullerene signals (right hand axes).

(9) How about the diurnal patterns of your factors?

Ans: The data for this study is only for few days, and it is already obvious from the time series that the signals were very high during the bonfire night specifically, when the fire log burning, and fireworks started. And there is no point of doing diurnal plots because it is obvious that it will be dominated by bonfire night.

(10) Figure 9 is not clear, please replace with a high resolution one

Ans: Thank you so much for pointing this out. I have replaced this figure in the manuscript (Please see below).



	Domestic Burning	sPON	Hydrocarbon-like-OA	BBOA	HULIS	rBC	eBCtr	HCN	HONO	eBctotal	Fullerenes	eBCwb	BrC	HCNO	Sr	pPON
pPON	-25	52	39	96	68	87	84	91	94	91	94	96	94	93	96	100
Sr	-27	45	29	94	69	84	82	86	90	89	91	94	93	91	100	96
HCNO	-31	54	38	87	82	94	95	94	94	97	98	96	95	100	91	93
BrC	-29	61	54	84	86	95	92	97	98	98	96	99	100	95	93	94
eBCwb	-30	60	51	86	85	96	92	97	98	98	97	100	99	96	94	96
Fullerenes	-28	60	47	86	83	97	94	95	96	98	100	97	96	98	91	94
eBctotal	-30	61	54	81	88	97	98	97	97	100	98	98	98	97	89	91
HONO	-24	68	59	84	82	94	92	98	100	97	96	98	98	94	90	94
HCN	-27	68	62	78	87	96	94	100	98	97	95	97	97	94	86	91
eBCtr	-30	61	56	72	88	95	100	94	92	98	94	92	92	95	82	84
rBC	-32	64	60	74	93	100	95	96	94	97	97	96	95	94	84	87
HULIS	-34	61	64	50	100	93	88	87	82	88	83	85	86	82	69	68
BBOA	-23	37	15	100	50	74	72	78	84	81	86	86	84	87	94	96
Hydrocarbon-like-OA	-11	64	100	15	64	60	56	62	59	54	47	51	54	38	29	39
sPON	41	100	64	37	61	64	61	68	68	61	60	60	61	54	45	52
Domestic Burning	100	41	-11	-23	-34	-32	-30	-27	-24	-30	-28	-30	-29	-31	-27	-25

Figure 5: The similarity between different pollutant time series through hierarchical cluster analysis (HCA)

Answers to comments to anonymous referee 2

Major comments:

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 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., Prévôt, 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., Mensah01, 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 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/Δm limit of the mass spectrometer. Instead, the UMR method can integrates 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 fragments 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.

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_(ugm^{-3})	0.95
HROrg	Org_(ugm^{-3})	0.92
HRNH$_4$	NH$_4$_(ugm^{-3})	0.92
HRNO$_3$	NO$_3$_(ugm^{-3})	0.86
HRSO$_4$	SO$_4$_(ugm^{-3})	0.91
HRChl	Chl_(ugm^{-3})	0.99

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.

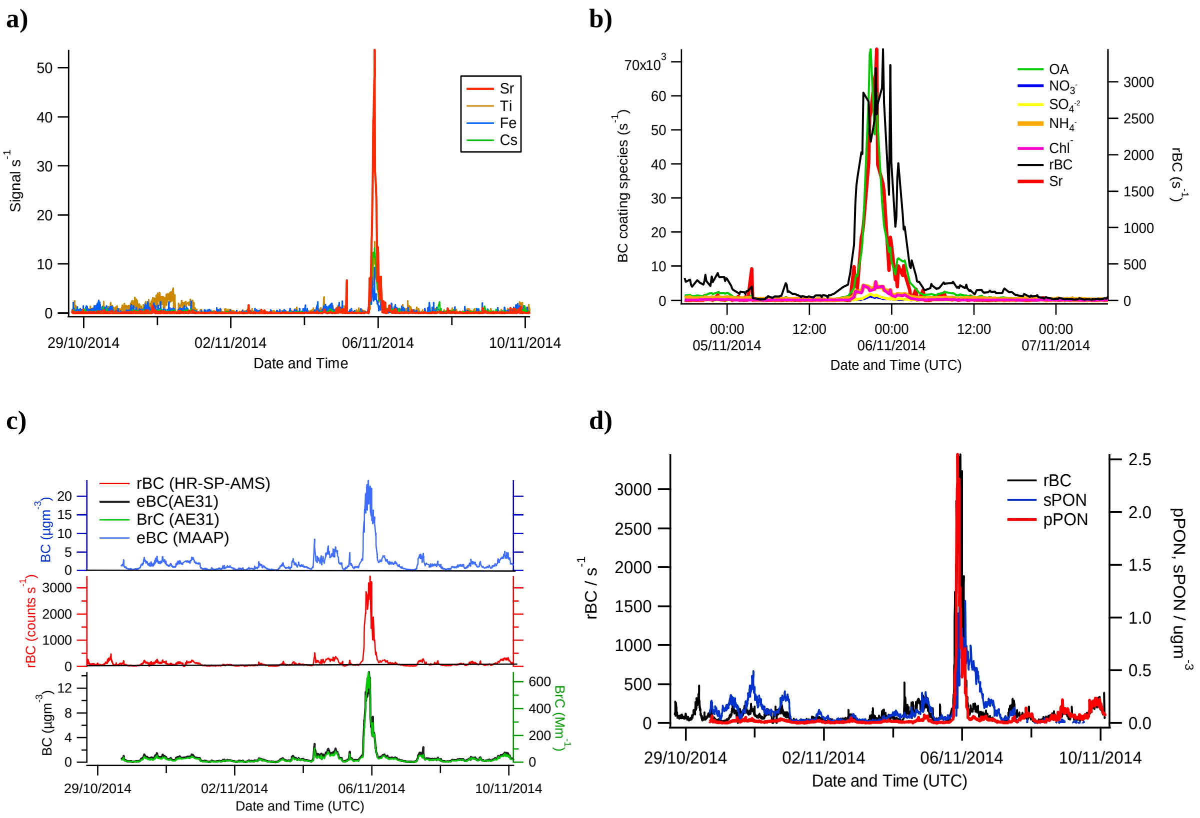


Figure 2. Timeseries of different variables observed during bonfire event. 2a. Time series of various metal pollutant concentrations, 2b. Time series of High Resolution rBC concentrations and its coating species (Organics and Inorganics), 2c. Time series of Black Carbon measured by different instruments 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.

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 provid3e 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 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 observed, 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 (C_{60}^{+}), 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., Prévôt, 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 burning factors also exhibit mixing in their timeseries as well. As such, the factorisation without fullerene signals was judged to be poor.

PMF Factorisation factors solution without inclusion of Fullerenes signals:

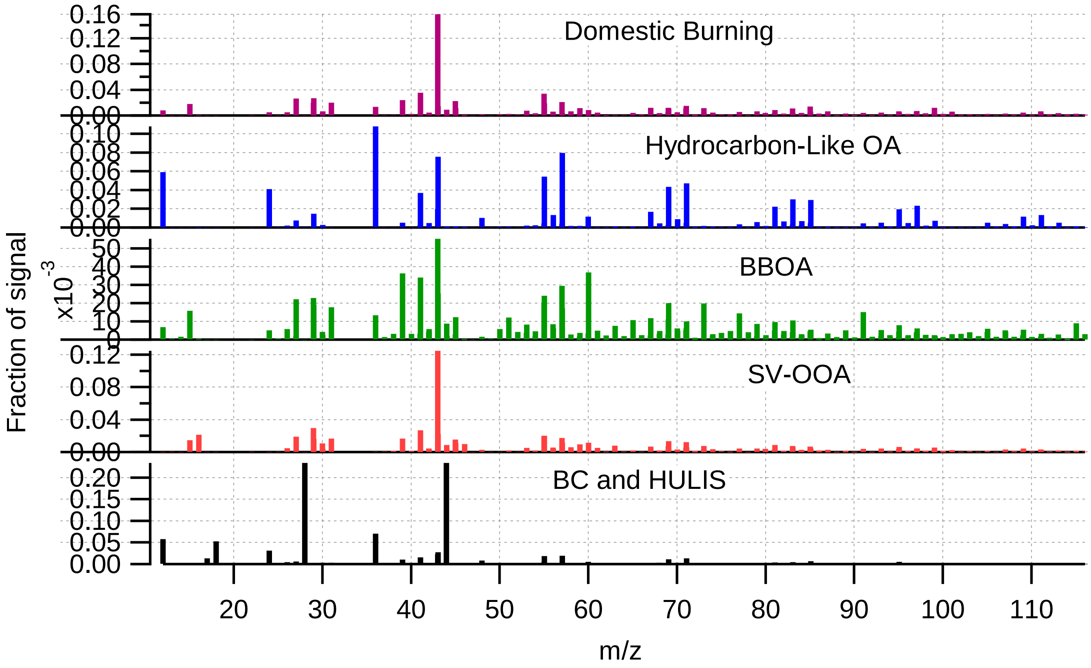


Figure S1a Mass Spectra of five factor solution (without inclusion of fullerene signals).

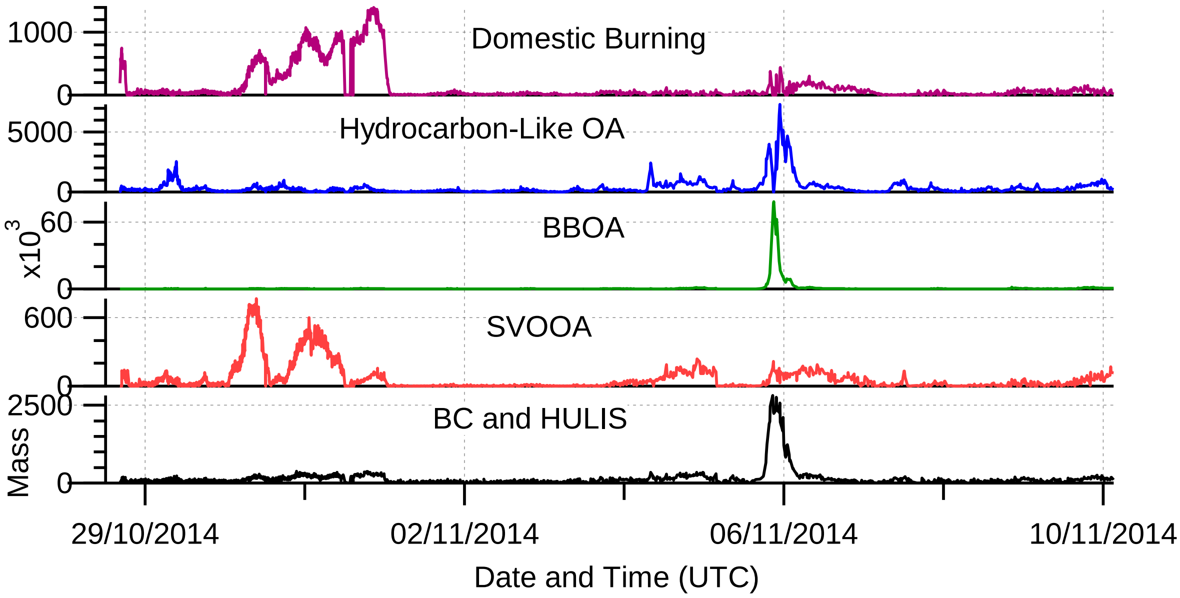


Figure S1b time series of five factors (without the inclusion of fullerene data).

11. HULS 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.