Technical Note: A new approach to discriminate different black carbon sources by utilising Fullerene and metals in Positive Matrix Factorisation analysis of High-Resolution Soot Particle Aerosol Mass Spectrometer data

Zainab Bibi[1]*, Hugh Coe[1], James Brooks[1], Paul I. Williams[1,2], Ernesto Reyes-Villegas[1], Michael Priestley[1, a], Carl Percival[1, b], James D. Allan[1, 2]*

[1]Department of Earth and Environment Science, The University of Manchester, Manchester, M13 9PL, K.
[2]National Centre for Atmospheric Science, The University of Manchester, Manchester, M13 9PL, UK.
[a] now at: Department of Chemistry and Molecular Biology, University of Gothenburg, 40530 Gothenburg, Sweden.
[b] now at: Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

Correspondence to: zainab.bibi@manchester.ac.uk, james.allan@manchester.ac.uk

Abstract. Atmospheric aerosol particles are known to have detrimental effects on human health and climate. Black carbon is an important constituent of atmospheric aerosol particulate matter (PM), emitted from the incomplete combustion process and cause significant effects on air quality and human health. Source apportionment of BC is very important, to identify the fraction of BC that has an anthropogenic origin and to evaluate the influence of different sources. The High-Resolution Soot Particle Aerosol Mass Spectrometer (HR-SP-AMS) instrument uses a laser vaporiser, which allows the real-time detection and characterisation of refractory BC and its internally mixed particles such as metals, coating species and rBC subcomponent in the form of Fullerene. In this case study, the soot data was collected by using HR-SP-AMS during Guy Fawkes Night on 5th November 2014. Positive matrix factorisation (PMF) was applied in order to positively discriminate between different wood-burning sources for the first time, in this case, BC from domestic wood-burning and bonfires, which no existing black carbon source apportionment technique is currently able to do. Along with this, the use of the fullerene signals in differentiating between soot sources and the use of metals as a tracer for fireworks has also been investigated, which has not significantly contributed to the BC concentrations. The addition of fullerene signals and successful PMF application on HR-SP-AMS data apportioned BC into more than two sources. These bonfire sources are hydrocarbon-like Fullerene, biomass burning organic aerosol, HULIS (humic-like substance) and non-bonfire sources such as hydrocarbon-like OA and domestic burning. The result of correlation analysis between HR-SP-AMS data with previously published Aethalometer, MAAP and CIMS data provides an effective way of quickly gaining insights in relations between the variables and also provide a quantitative estimate of the source contributions to the BC budget during this period. This research study is an important demonstration of using HR-SP-AMS for the purpose of BC source apportionment.

1 Introduction

35   Aerosol particles in the atmosphere are known to have very harmful effects on the air quality, human health and climate (Highwood and Kinnersley, 2006). One of the most important components of atmospheric aerosol particles is Black Carbon (BC), i.e. soot, which has extremely detrimental impacts on the human health and air quality (Janssen and Joint, 2012). BC's main emission source is through the incomplete combustion of fossil fuel and biomass, involving transportation, open biomass burning, power generation sources, and residential heating sources (Bond et al., 2011; Cooke et al., 1999; US EPA, 2012). In

40   the atmosphere, BC can be mixed with organic and inorganic aerosol species, either at the point of emission or gas-to-particle conversion processes in the atmosphere.

    As well as harmful impacts on human health, BC can also absorb cancer-inducing pollutants such as volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) due to its carbonaceous nature and large surface area. As a result of its smaller size, can be deposited in weasands and lungs, leading to severe health problems (Cao et al., 2012; Dachs

45   and Eisenreich, 2000). According to hypothesised mechanisms, the ultrafine BC is the cause of abnormal cardiovascular functions and endothelial senescence at the molecular level (Buchner et al, 2013). Along with being harmful on human health, it also affects the visibility, reduces agricultural productivity, harms ecosystems and exacerbates global warming (Grahame and Schlesinger, 2010).

    Most BC sources are of anthropogenic origin, but source apportionment is important to establish which specific sources are

50   responsible. There are multiple measurement techniques available for this purpose but are subject to considerable uncertainties (Martinsson et al, 2014). Different techniques have been used for the source apportionment of BC. One of the most widely used techniques is the multiwavelength Aethalometer, which was first described by Hansen et al, (1984). Later Sandradewi et al (2008) described how Aethalometer can be used to apportion different sources of light-absorbing aerosols such as wood-burning, which in contrast to traffic emissions, absorbs additional light in the UV region, over what would be expected in the

55   near-infrared region. Another source apportionment method is to measure the radiocarbon (14C) content (Hellborg et al., 2003). This method has not been used widely because it requires very specialist equipment (Barescut et al., 2005).

    Positive Matrix Factorisation can in principle, identify multiple categories of soot; however, it needs a large data set and relevant chemical data of several species. Advancements in different measurement techniques has been deployed by the addition of Soot Particle Aerosol Mass Spectrometer (SP-AMS) for the online ambient measurements of refractory black

60   carbon (rBC) (Onasch et al., 2012). In general, the SP-AMS can be operated with the both laser and tungsten vaporiser or with only laser vaporiser.

    The current study aims to develop the source apportionment tool, which will subsequently improve our understanding of sources of atmospheric soot. For this purpose, Bonfire night 2014 in Manchester was taken as a case study because it is known that there were at least three sources of BC (traffic, domestic wood-burning, bonfires and potentially fireworks) and weather

65   conditions that night favoured the high concentrations of primary emissions. This event has been described in previous studies (Liu et al, 2017: Priestley et al, 2018a; Reyes et al, 2018). 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).

70   In terms of air quality, it has been recognised that Bonfire night is one of the most polluted days in the UK. Every year, this event is celebrated on 5th November (or on a weekend day near this date) where open fires are lit and fireworks are set off at individual households, as well as large community events. These bonfire activities have a strong flaming segment which roughly start during the evening and lasts for up to 2 hours. The fires after flaming are not refuelled, therefore leading to an extended phase of smouldering as the fires are left to completely burn and die down (Dyke et al.,1997; Mari et al., 2010;

75   Pongpiachan et al., 2015).

Different research case studies have previously been published about the Bonfire night around the UK. For example, Clark (1997) studied the PM_{10} concentrations emitted during the Bonfire night event in different parts of UK. In Oxford, dioxins measurements in the ambient air were conducted by Dyke et al (1997). Colbeck and Chung (1996) targeted the particle size distribution. The polycyclic aromatic hydrocarbons (PAHs) were measured in Lancaster (Farrar et al., 2004), while in 2018,

80   Reyes et al (2018), studied insights into nitrate chemistry during the bonfire night by applying the chemical ionisation mass spectrometry measurements and aerosol mass spectrometry simultaneously. Observations of the Nitro-compounds including nitrate, amide and isocyanate were studied during the bonfire night in Manchester (Priestley et al., 2018a). In previous studies, specifically during the bonfire event and general aerosol measurements, several different source apportionment techniques have been performed. Aethalometer AE31 model was performed to do the source apportionment analysis and successfully

85   apportion the rBC into BC from wood-burning and BC from the traffic emissions (Reyes et. al., 2018). During the same study, Multilinear Engine-2 and PMF tools were also used over the AMS data through the source apportionment interface (SoFi version 4.8 as presented by (Canonaco et al., 2013) in order to find the organic aerosol sources according to proposed strategies by Reyes et al., (2016) and recommendations made by Crippa et al. (2014). Liu et al., (2019) also studied the BC sources from wood-burning and diesel traffic emissions using an SP2 to examine the BC particles' mixing state and optical properties.

90   In order to test the ability of HR-SP-AMS to apportion rBC (with multiple BC types) the data was collected during bonfire night from 29th Oct-11th Nov 2014 at the University of Manchester. As a result of strong meteorological conditions, very high and mixed concentrations of pollutants were observed. Traditionally the PMF tool is applied to conventional AMS data (as with Reyes et al., 2018) but the objective of this study is to demonstrate a new way to source apportion black carbon based on highly time resolved mass spectrometric composition data of the population of particles that contain black carbon and uses

95   information on the composition of black carbon and information on internally mixed Fullerene and condensed material. Fullerene are a class of exclusively high molecular weight carbon clusters (C60 and C70 etc.) having a unique hollow cage-like structure. which were discovered by Kroto et al., (1985) for the first time. They were identified as ionised particles in low-pressure fuel rich flat premixed acetylene and benzene–oxygen flames by molecular-beam sampling combined with mass

spectrometer analysis (Gerhardt, Loffler and Homann, 1988). These have been reported previously in HR-SP-AMS data but whether they are formed in the flame or during the vaporisation process is not clear (Fortner et al., 2012).

2 Methodology

2.1 Sampling site overview

Measurements were conducted at the South Campus University of Manchester (53.467°N, 2.232°W) before, during and after the bonfire night event on 5th November as described in the previous publications (Liu et al., 2017; Reyes et al., 2018). The sampling station is surrounded by the nine public parks. Different instruments were set up for the online measurement of ambient aerosols and gases. A Compact Time-of-Flight Aerosol Mass Spectrometer (cTOF-AMS) was used to measure all PM_1 components as described by Reyes et al., 2018. A Time-of-Flight Chemical Ionisation Mass Spectrometer (ToF-CIMS) was used to measure the gas phase concentrations of aerosols (Priestley et al., 2018b). BC source apportionment was performed by using Aethalometer AE31 which measured the absorption of light at seven different wavelengths (Reyes et al., 2018) while a MAAP was used to measure the concentrations of BC emitted during the bonfire event and inform the corrections needed to process the AE31 data (Collaud Cohen et al, 2010).

2.2 Instrument Overview:

In this case study, the High-Resolution Soot Particle Aerosol Mass Spectrometer (HR-SP-AMS) was used, which is a combination of Single Particle Soot Photometer (SP2) and High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). Based on the design used in SP2, the SPAMS is equipped with an intracavity laser vaporiser Nd: YAG (1064 nm), that heats up and vaporise both core and coating particles, which was collected before, during and after the Bonfire night event in UK, concurrent with the previous measurements. In order to vaporise the refractory particles types that are not detected by the standard AMS, the new vaporiser is designed, to detect the vaporised species through electron ionisation for the generation of chemical ion, thus keeping the vaporisation and ionisation steps separate. The intracavity laser vaporiser allows AMS to characterising the refractory chemical components of ambient aerosol species (organics and inorganics), particularly, including light absorbing refractory Black Carbon (rBC) particles (Onasch et al., 2012; 2015). A catalytic stripper was also attached to the aerosol sampling lines, which switched between catalytic stripper and direct measurements after every 30 minutes (Liu et al., 2017). In our case, the results have been analysed by using the direct measurements only. During the experiment, a measurement of the ionisation efficiency was not obtained owing to technical difficulties associated with generating a suitable test aerosol, however, this only affects absolution quantification and not the ability of the instrument to apportion fractions of the signal, which is the subject of investigation here. Therefore, this dataset should still serve as a technical proof-of-concept for factorisation. The HR-SP-AMS data were analysed using the data analysis toolkit TOF-AMS HR Analysis 1.20O (DeCarlo et al., 2006). The high-resolution feature of toolkit allow the direct separation of most ions from the organic and inorganic

species at the same nominal mass by charge ratio, the separation of BC family from its coating species, the direct identification of organosulfur and organic nitrogen content and also the quantification of many different types of their organic fragments (isotopes) such as CxHy, CxHyOz, CxHyOzNp (Aiken et al., 2007). This high-resolution analysis on SP-AMS data also detected various metal pollutants such as Iron (Fe), Titanium (Ti), Strontium (Sr) and Caesium (Cs).

The instrument alternated between three mass spectrometer configurations: The standard 'V' mode, high-resolution 'W' mode (DeCarlo et al., 2006) and an alternative 'V' mode whereby the orthogonal extractor was pulsed every 95 instead of 34 μs. 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.

2.3 Positive Matrix Factorisation

Positive Matrix Factorization (PMF) is an advanced factor-analysis technique developed by Paatero and Tapper (1994). In the previous researches, PMF has been used extensively to apportion organics with the standard AMS data but not so often to apportion BC from SP-AMS data (Crippa et al., 2012; Saarikoski et al, 2014). In this research study Positive Matrix Factorization (PMF) was applied on HR-SP-AMS data to apportion BC in to more than two sources. PMF assumes that a matrix of data can be explained by a linear combination of "factors" with characteristic profiles and varying temporal contributions (Paatero and Tapper, 1994; Ulbrich et al., 2009). The analysis was conducted using the PMF Evaluation Tool (Ulbrich et al., 2009; Zhang et al., 2011).

Because of the lower signals and the combination of different data retrieval method used for the fullerene signals (UMR rather than HR), greater emphasis had to be placed on these signals. Because UMR was used, we were unable to apply the detailed error model of Corbin et al. (2015), so we took an empirical approach. This was done by applying an additional 'model error' to the error matrix, i.e. an error term proportional to the signal intensity instead of its square root, as per the standard AMS error model (Ulbrich et al., 2009; Comero et al, 2009). The model error value was increased from 0 to 0.10 to reflect that the data and uncertainties have a lognormal distribution and to upweight the fullerene signals (Corbin et al., 2015). (see supplement). As well as placing greater emphasis on the smaller fullerene signals, the application of this model error also increased the number of "weak" variables, defined as having SNR below 2 (Paatero and Hopke, 2003; Ulbrich et al., 2009), which were down weighted by a factor of two. No variables were "bad" in the sense of having SNR < 0.2 (Paatero and Hopke, 2003). Additional details and residual plots are available in the supplementary material.

3 Results

3.1 Weather measurements and overview of highly polluted time-period:

The weather data is as presented by Reyes et al, (2018), and results showed quiet stagnant conditions with the low temperature of 4°C, high relative humidity of 85% alongside the wind speed of 1.5 m s^{-1} and varying wind directions. This type of weather condition facilitates the increasing amount of pollution in the atmosphere. During the periodic stagnation weather phenomenon, the very high concentrations of BC was also observed with the signal of 3400 s^{-1} during the bonfire event at 10:20 pm as compared to (100 s^{-1} – 500 s^{-1} before Bonfire and 250 s^{-1} - 300 s^{-1} after bonfire night) fig 1. The time-period of the bonfire night when the pollutants were very high is called as high pollutant concentration time-period.

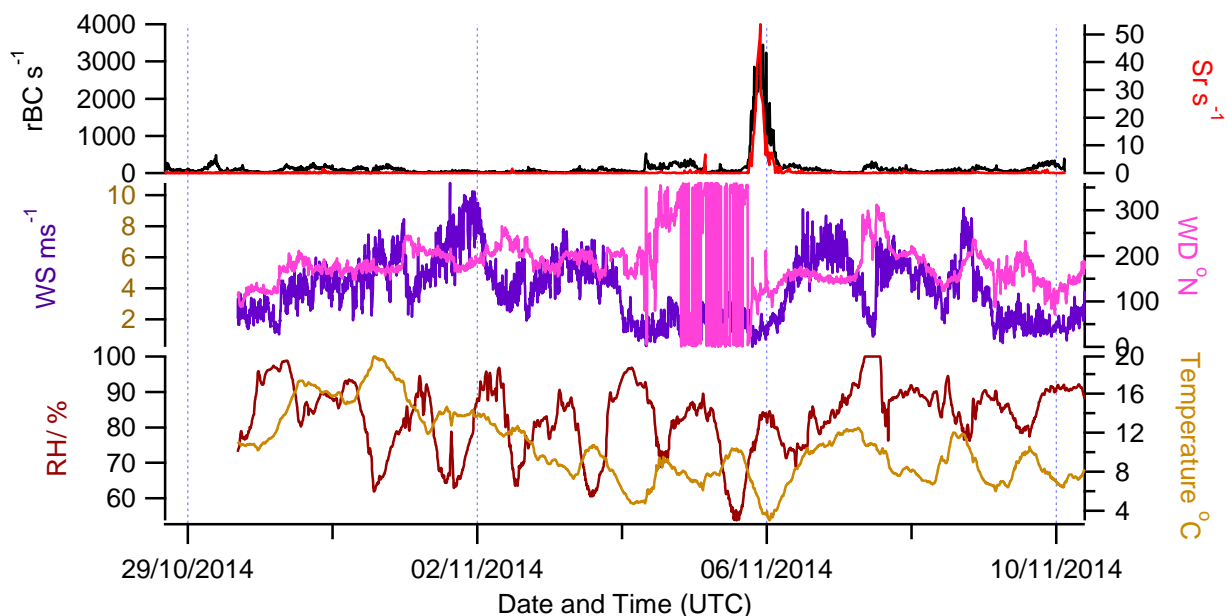



Figure 1: Meteorological measurements Relative humidity (RH), Temperature, Wind direction (WD) and Wind speed (WS) along with the time series of BC and Strontium (Sr), a firework tracer emitted during the bonfire night.

3.2 Time Series of different variables concentrations observed during the BF event:

3.2.1 Firework burning tracer:

To attempt to identify a unique tracer for fireworks, the HR-SP-AMS data was analysed for metals. Reyes et al., (2018) concluded that fireworks were not a major factor in the overall mass concentrations but could not directly support this assertion with the data available. However, HR-SP-AMS can potentially offer insight through its ability to detect metals. Fireworks release several pollutants such as manganese, cadmium, strontium, aluminium, and other suspended particles, carbon

180 monoxide, carbon dioxide and sulphur dioxide etc. (Lemieux et al., 2004; Shi et al., 2011). These metal compounds are in the form of metal salts such as potassium chlorates, perchlorates, strontium nitrates, potassium nitrates, barium nitrates, sodium oxalate, manganese, sulphur, iron, aluminium etc. These metals are mainly used to give different bright colours; for example, Sr can be used for giving red colour to the fireworks (Mclain, 1980). During the analysis, different metal peaks, such as Iron (Fe), Strontium (Sr), Caesium (Cs) and Titanium (Ti), that could be associated with the fireworks were detected (fig 2a). The

185 Sr was most unambiguously associated with the fireworks due to the fact that there is no other signal present in the atmosphere outside of Bonfire night. Other metals may have other sources, such as mineral or brake dust in the case of iron, may be receiving signal interference from other mass spectral peaks. The highest peak of Sr concentrations i.e. 53.6 s^{-1} was detected as compared to the concentrations of Sr, before and after Bonfire event (1.6 s^{-1} and 0.9 s^{-1}).

3.2.2 HR Time series of BC and its coating species

190 Figure 2b shows that the signals associated with refractory BC (rBC) and its coating species (Org, SO_4, NO_3, Chl and NH_4) were particularly very high during the bonfire night. The HR-time-series of the whole sampling time-period shows that the majority of non-refractory PM_{BC} signal was mainly organic matter, having very high concentrations, followed by Chl, SO_4, NH_4 and NO_3. It has been worth mentioning that the signals of these aerosols were very high during the bonfire night as compared to before and after time period except the NO_3 signal which was 0.8 s^{-1} before bonfire event on 30th October at 8:30

195 am and 1.8 s^{-1} after bonfire night on 7th November at 4:15 pm. The high Chl peak was strongly related with the open fire burning that happened on the Bonfire night. Wood-burning is an important source of chloride in the atmosphere (Lobert et al, 1999). Fireworks can also be a likely source of Chl, because chlorates and perchlorates can provide oxygen for the combustion of fireworks. Also, the high peak of nitrate can be linked with the combustion sources such as wood-burning and biomass burning emissions (Reyes et al. 2018). The concentrations of organic aerosol started increasing at 8:30 pm to 9:00 pm (highest),

200 while concentrations of rBC were increasing after 1:50 hour later.

3.2.3 Correlation analysis of rBC with other pollutants

The HR-SP-AMS data was compared against those of other instruments such as AE31, CIMS, MAAP and AMS presented in the previous studies (Reyes et al, 2018; Priestley et al., 2018a) and a statistically significant correlation (see table S2, S3, S4 in supplementary information) was found between the black carbon measured by three different instruments, i.e. rBC from

205 HR-SP-AMS, eBC from MAAP and eBC and BrC from AE31. The BC measured by AE31 and MAAP was named as eBC (equivalent BC) according to (Petzold et al., 2013) recommendations. Reyes et al., 2018 measured eBCwb and eBCtr at 470 nm and 950 nm with the mass absorption cross-section (MAC) of 31.1 m^2 g^{-1} and 15.4 m^2 g^{-1} while eBC from MAAP was measured at 630 nm with MAC of 6.67 m^2 g^{-1}. A very high concentration of rBC and eBC was measured from all instruments that could detect these. The peak of Brown Carbon (BrC) measured by AE31was also very high during the event night and

210 indicates a wood-burning source (details found at Reyes et al., 2018).

Reyes et al., (2018) used AMS to estimate the concentrations of Particulate Organic Oxides of Nitrogen (PONs), i.e. 2.8 μgm^{-3} 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. The study also identified two PON factors into primary PON and secondary PON by applying ME-2 source apportionment on organic aerosol concentrations from different sources after modification of fragmentation table. Figure 2d shows the time-series of rBC, Primary Particulate organic oxide of nitrogen (pPON) and Secondary Particulate organic oxide of nitrogen (sPON). The result in fig 2d showed that the concentration of up to 2.8 μgm^{-3} for PON was detected which was over the detection range as reported by Bruns et al. (2010). Moreover, BC was also detected with very high signals of 3400 s^{-1}. The reason behind this high correlation is that, rBC is a primary pollutant, so it is well correlated with the primary PON as both are directly emitted from the bonfire event. While the correlation of rBC with the sPON is not very good, i.e. $r^2 = 0.35$, because the secondary pollutants appeared later.

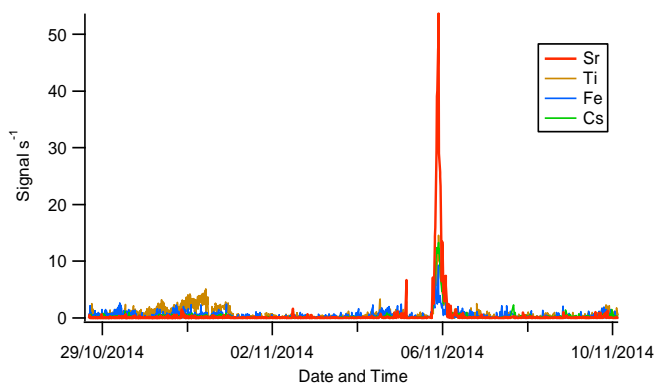
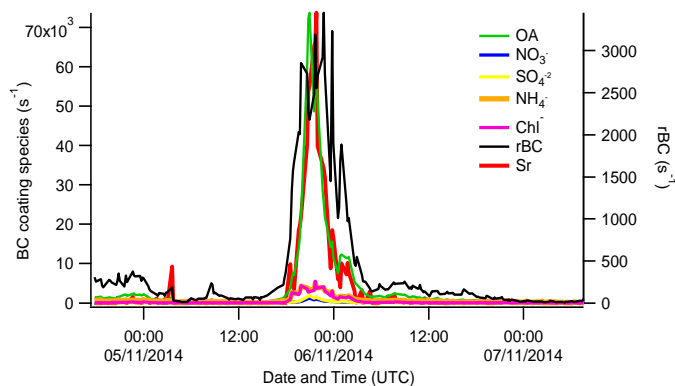
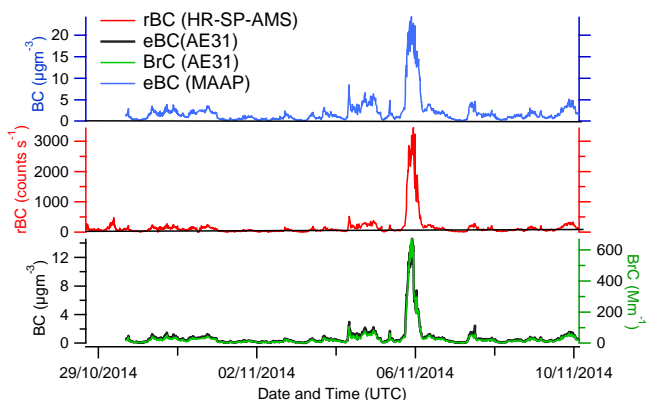
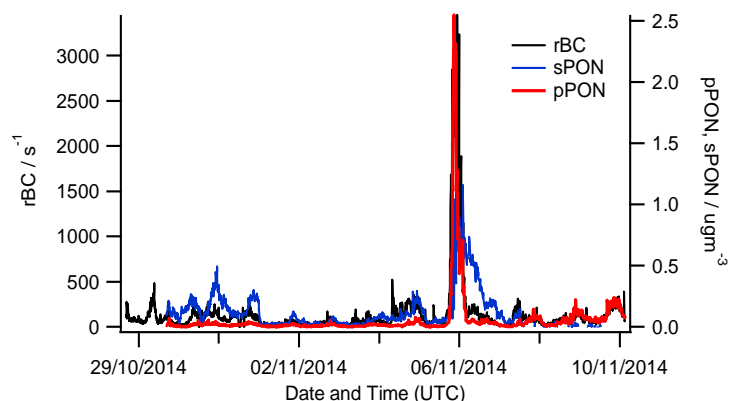



Figure 2. Timeseries of different variables observed during bonfire event. 2a. Time series of various metal pollutant concentrations, 2b. Time series of High Resolution rBC concentrations and its coating species (Organics and Inorganics), 2c. Time series of Black Carbon measured by different instruments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

3.3 BC Source apportionment analysis

3.3.1 PMF factorisation result

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,

225 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.

Later, PMF was performed with the inclusion of Fullerene data and for the selction of optimum number of factors, a

230 stepwise approach was used, beginning with a 2-factor model and successively adding factors up to a maximum of six. In our case, five-factors gave the best solution based on the criteria of Q/Q_{exp} near 1, the squares of scaled residuals' total sum and all the matrix points fitted within their expected error (Paatero et al., 2002). The rotational ambiguity of the five-factors solution was explored by varying the f-peak between -2.0 and +2.0 with fpeak interval of 0.2. Along with that the changes in the fractional contribution of the PMF factors was very small for all the factors, indicating that changing f-peak value over a

235 range of 2 and -2, (away from 0) did not affect the overall results of PMF analysis. The solution for fpeak=0 was used for all subsequent work, as also recommended by Paatero et al. (2002).

The results in Fig 3 shows the results obtained after adding the fullerene signals. 5 factors were resolved, that are plotted separately as Bonfire night factors and non-bonfire night factors. Factor 1 (BC and HULIS), Factor 5 (HOA-like Fullerene) and factor 2 (Biomass Burning OA) are the bonfire night factors having very high peaks detected only during the bonfire night

240 while factor 4 (Hydrocarbon-Like OA) and factor 3 (domestic wood-burning), are the two non-bonfire night factors, which are behaving completely independently, as their peaks have been observed before, during and after the bonfire night. While there is still activity in HOA associated with the night, this is much reduced compared to the PMF without Fullerene included, giving confidence that this resolved the traffic source more successfully. The domestic burning source can be related to activities such as household wood combustion.

245 In order to test whether any of the factors could be associated with fireworks, PMF analysis was also performed to force the inclusion of Sr in the factorisation. For this purpose, the Sr concentrations were upweighted by multiplying the total

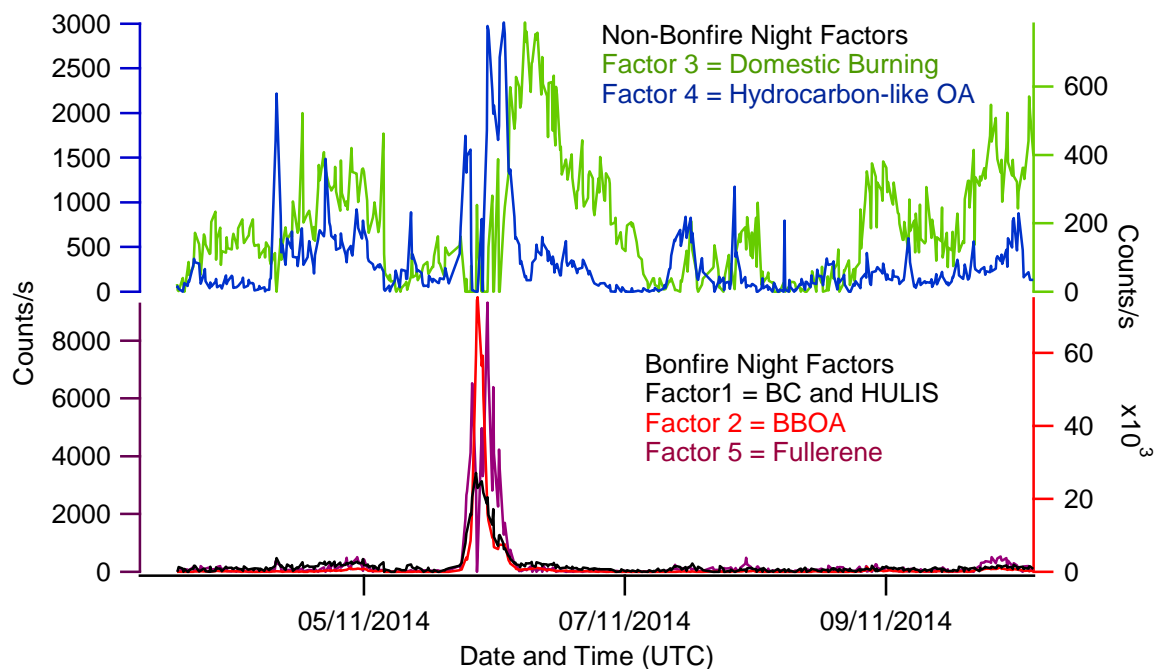
concentrations of Sr (but not the associated error) by 10, 100 and 1000, but despite this, a factor containing Sr was not found. This implies that none of the HR-SP-AMS factors could be associated with fireworks.

 Figure 3: The time series of (a) non-Bonfire night factors and (b) bonfire night factors obtained by PMF analysis of the HR-SP-AMS data.

Fig 4 shows the profile concentrations and mass spectra of five different factors. Three of them (BC and HULIS, biomass burning OA and Fullerene) are directly linked with the bonfire night while HULIS and other two (domestic burning and traffic emissions) are referred to as non-bonfire night sources. 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.

265   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. Factor 4 resembled Hydrocarbon like organic

270 aerosols (HOA) and is related to the traffic emissions (fossil fuel combustion), presenting the high signals at m/z 55 and m/z 57 typically aliphatic hydrocarbons (Canagaratna et al., 2004). Diesel exhaust is typically dominated by re-condensed engine lubricating oil and consists mainly of n-alkanes, branched alkanes, cycloalkanes, and aromatics (Canagaratna et al., 2004; Chirico et al., 2010), leading to high signal at the ion series $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$. In particular, m/z 57 is a major mass fragment and often used as a tracer for HOA (Zhang et al., 2005).

275   Factor 3 presented a relatively mixed factor source having the high loading of signals at m/z 43, m/z 55, m/z 57 and m/z 60. Therefore, this factor was mainly related to the domestic wood-burning sources because of its high peaks observed before and after the event night. Factor 2 was specifically loaded at m/z 60 and m/z 73 (levoglucosan), indicating the typical source profile of by wood-burning organic aerosols (Alfarra et al, 2007). In previous AMS studies, cooking could be one of the important sources of $PM_{2.5}$ (Sun et al., 2013), but in this study cooking was not identified by PMF because it is not co-emitted with rBC

280 and so is not vaporised by the HR-SP-AMS. The factor 1 having signals at m/z 36 related to BC (the main bonfire emission source) and m/z 44 is highly related to HULIS, showing its contributions from bonfire night as well as secondary sources. The reason for representing HULIS at m/z 44 was its high concentration observed during the event night only (fig 3).

285

290

295

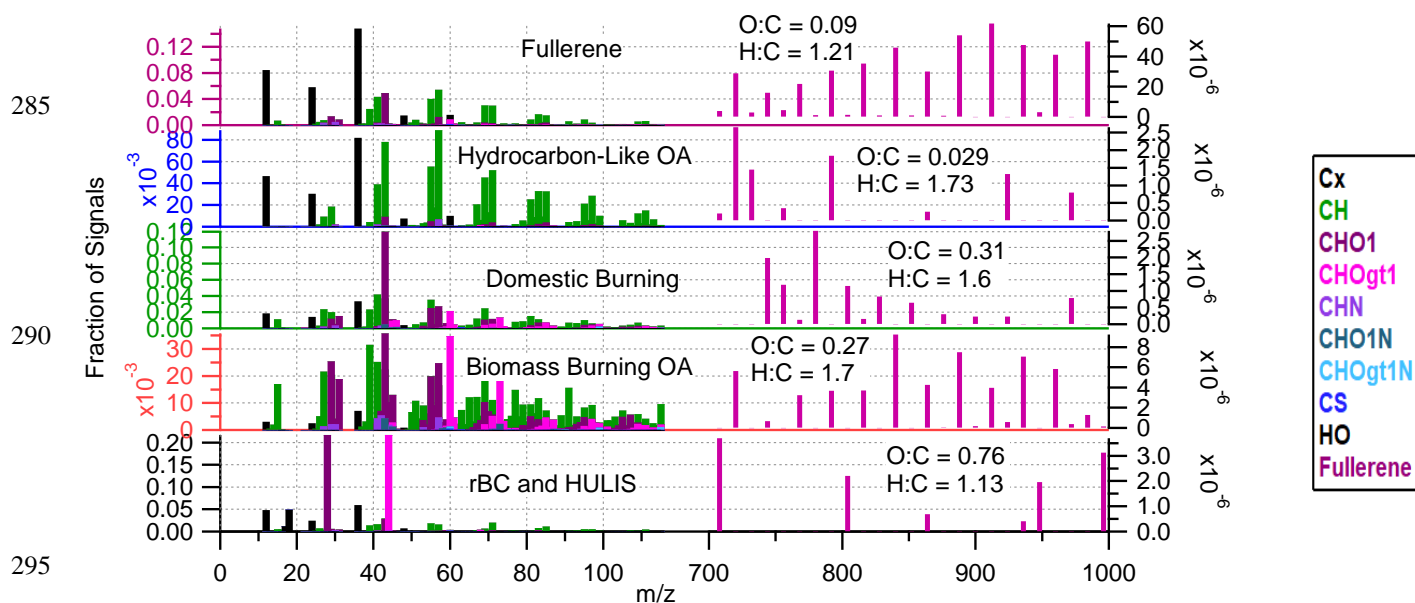



Figure 4: PMF five factors source profile (factor 1 = BC and HULIS, factor 2 = BBOA, factor 3 = Domestic burning OA, factor 4 = Hydrocarbon-Like OA, factor 5 = Fullerene). Note the difference in scales of the fullerene signals (right hand axes).

4 Discussion

4.1 Correlation between different pollutants

Correlation analysis gives an effective way of quickly gaining an idea of how variables are related with one another. The data analysis software 'openair' was used to generate the hierarchical cluster analysis chart (Carslaw and Ropkins, 2012) using the 'corplot' function on the bonfire night data only. Hierarchical cluster analysis (HCA) provides an effective way of understanding of the order how different variables appear due to their similarity in one another. A dendrogram was plotted to provide additional information to help visualising how groups of variables are related to one another. The explanation of all these time series names and how do they measured is given in table 1.

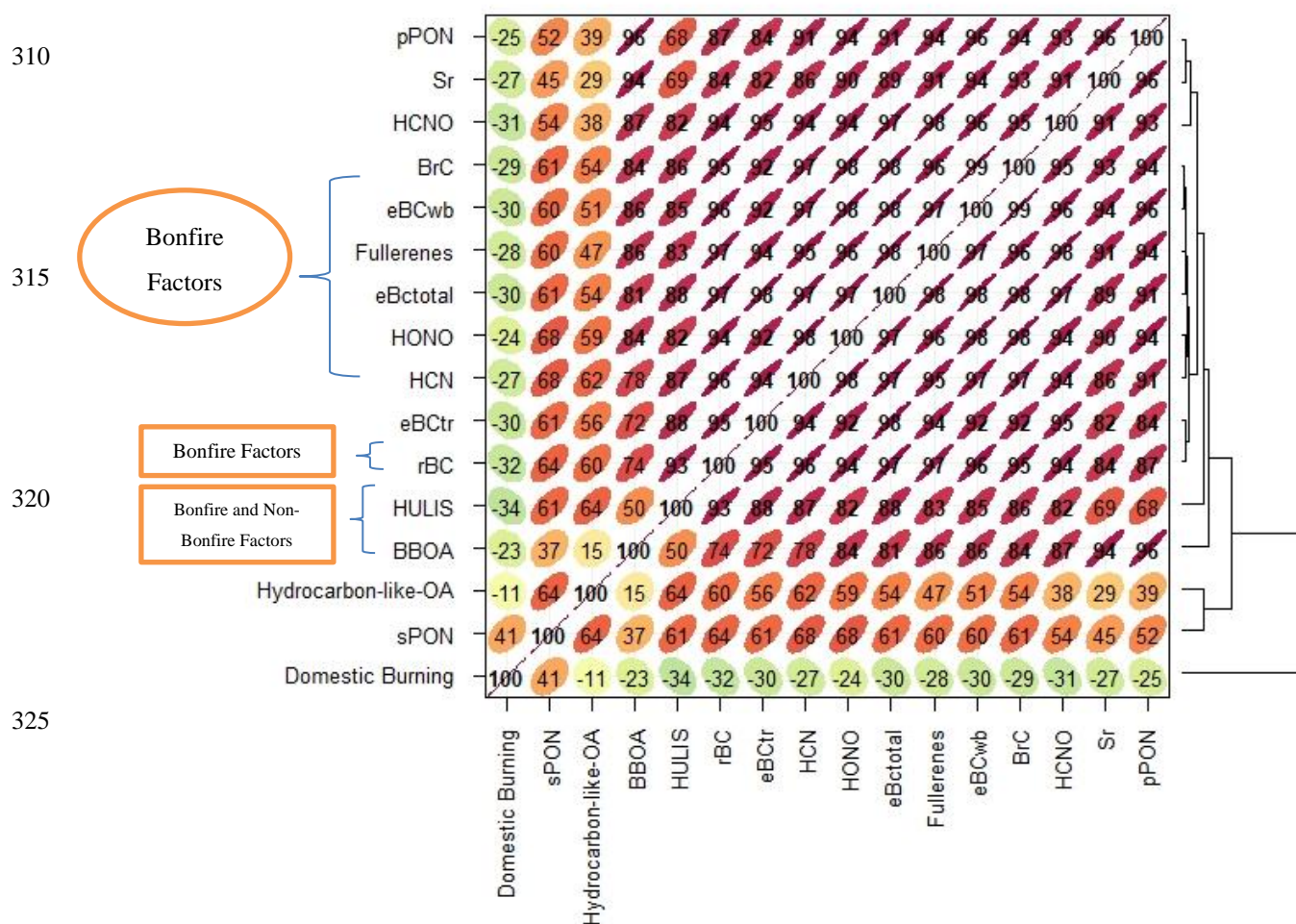



Figure 5: The similarity between different pollutant time series through hierarchical cluster analysis (HCA)

In fig 5, a significant correlation was observed between Fullerene, eBC_{total}, HONO, HCN, rBC. The reason is that all of these are primary pollutants and directly released from the bonfire emissions. HCN and HONO are nitrogen containing gases that were released during the bonfire night from the wood fires (Le Breton et al., 2013; Wang et al., 2016). eBC_{tr} (Black Carbon emission from traffic) has also shown a strong correlation with the rBC because it is also contributed to by primary pollutants and is also influenced by the bonfires. HULIS and BBOA have a very close relationship, which indicates that both are bonfire factors, but on the other hand HULIS also has some relationship with the secondary sources as discussed previously. Hydrocarbon-like OA and sPON have a close similarity because just like sPON, the peak of Hydrocarbon-like OA has been observed before and after the event night. Sr and pPON and HCNO show some similarity, but as discussed previously, 'Sr' is behaving as a separate factor when subject to PMF analysis. Upon closer inspection, it can be seen that while having a high degree of correlation, the peak of Sr occurs at a slightly different time. A correlation was seen between BrC and $eBC_{wb,}$ (Black carbon emissions from wood-burning) which is expected, as BrC is normally associated with wood-burning. And the last factor i.e. domestic burning is behaving as a separate factor and showing no or very less correlation with any sources.

Based on HCA plot, a time series graph was also plotted to investigate the timings of all pollutants having strong relationship among one another (fig 7). The second group which showed the strong correlation was HCNO and factor 5 (hydrocarbon-like Fullerene) with the r^2 value of 0.96. Isocyanic acid (HNCO) is another highly toxic, long-lived gas (lifetime of days to decades; (Borduas et al., 2016) emitted from biomass burning (BB) with similar anthropogenic and biogenic sources as HCN. Alternative urban sources of HNCO are attributed to primary activity such as automotive emission (Jathar et al., 2017), residential heating (BB) (Woodward-Massey et al., 2014), and industrial processes (Sarkar et al., 2016), although is clearly related to the bonfire event here. A reason for the close but not perfect relationship between the groups could be due to their same emission sources but at different stages of the burn during the bonfire night, or possibly different bonfires in the region whose plumes arrived at the site at different times.

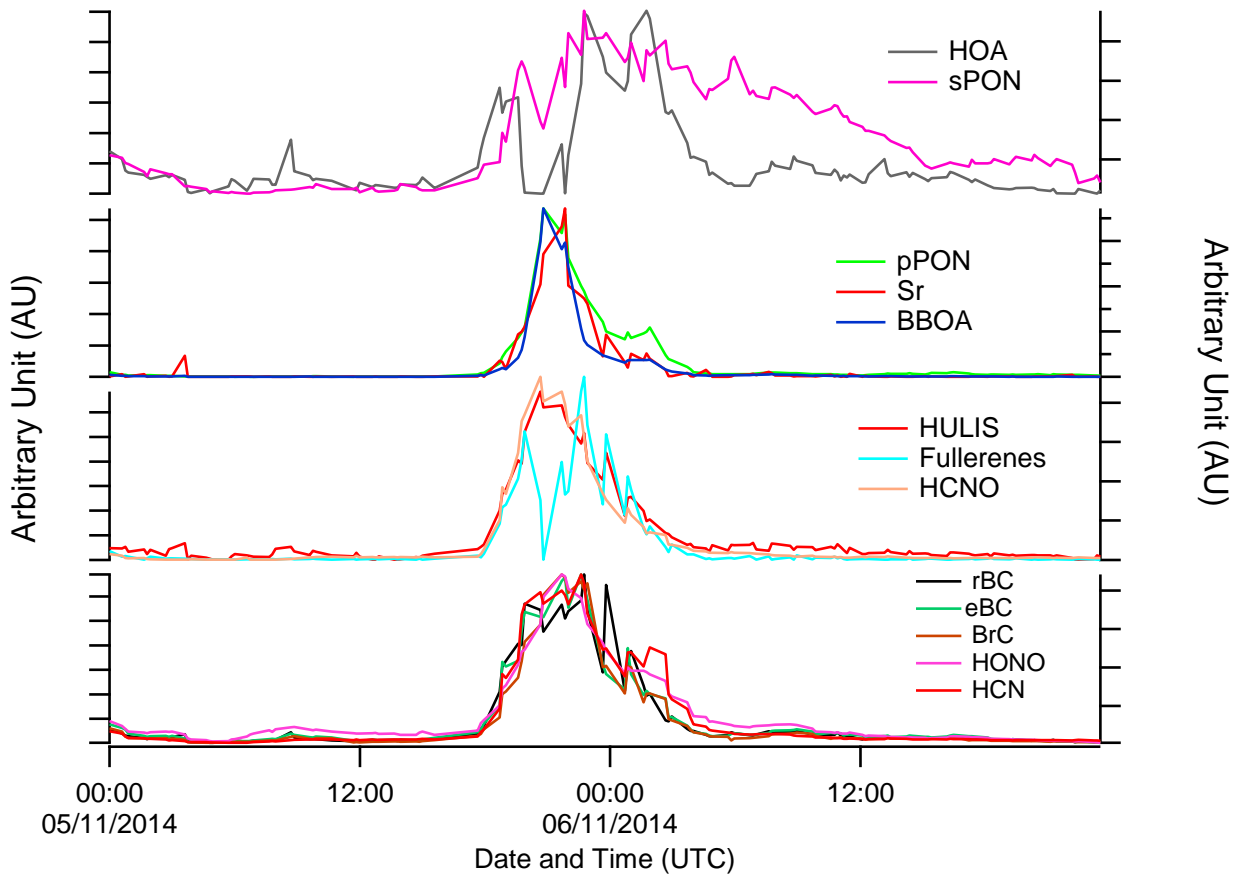



Figure 6: Time series of the pollutants, grouped according to the Hierarchical Cluster Analysis in figure 9.

355

360

365

Table 1: Explanation of the time series used in figure 5 and 6.

FamilyCx (rBC[1])	Refractory Black Carbon	Measured from HR-SP-AMS
eBC)[2]	Black Carbon	Measured from MAAP
BrC [2]	Brown Carbon	Measured from Aethalometer AE31
BC$_{total}$	Total BC from AE31 (eBC$_{tr}$+eBC$_{wb}$)	
eBC$_{tr}$	Black Carbon (traffic emissions)	Measured from Aethalometer AE31
eBC$_{wb}$	Black Carbon (Wood-Burning)	Measured from Aethalometer AE31
HONO[3]	Nitrous Acid	Measured from ToF-CIMS
HCN[3]	Hydrogen Cyanide	Measured from ToF-CIMS
HCNO[3]	Isocyanic Acid	Measured from ToF-CIMS
Fullerene[1]	Fullerene	Measured from HR-SP-AMS from HR-SP-AMS
BC and HULIS[1]	HULIS	Measured from HR-SP-AMS from HR-SP-AMS
pPON[2]	Primary Particulate Organic Nitrate	Measured by Aerosol Mass Spectrometer (AMS) by using 46:30 ratio (Reyes et al, 2018)
sPON[2]	Secondary Particulate Organic Nitrate	Measured by Aerosol Mass Spectrometer (AMS) by using 46:30 ratio.
HOA[1]	Hydrocarbon-like Organic Aerosol	Factor derived by PMF analysis from HR-SP-AMS
BBOA[1]	Biomass Burning Organic Aerosol	Factor derived by PMF analysis from HR-SP-AMS
Sr[1]	Strontium Metal	Measured from HR-SP-AMS
Domestic Burning[1]	Domestic burning	Factor derived by PMF analysis from HR-SP-AMS

[1]rBC, Sr, Fullerene, Hydrocarbon-like OA, Domestic burning, BBOA, BC and HULIS (Current Case study) derived by PMF from HR-SP-AMS

[2]pPON, sPON, eBC and BrC, (AE31), eBC (MAAP) (Reyes et al, 2018)

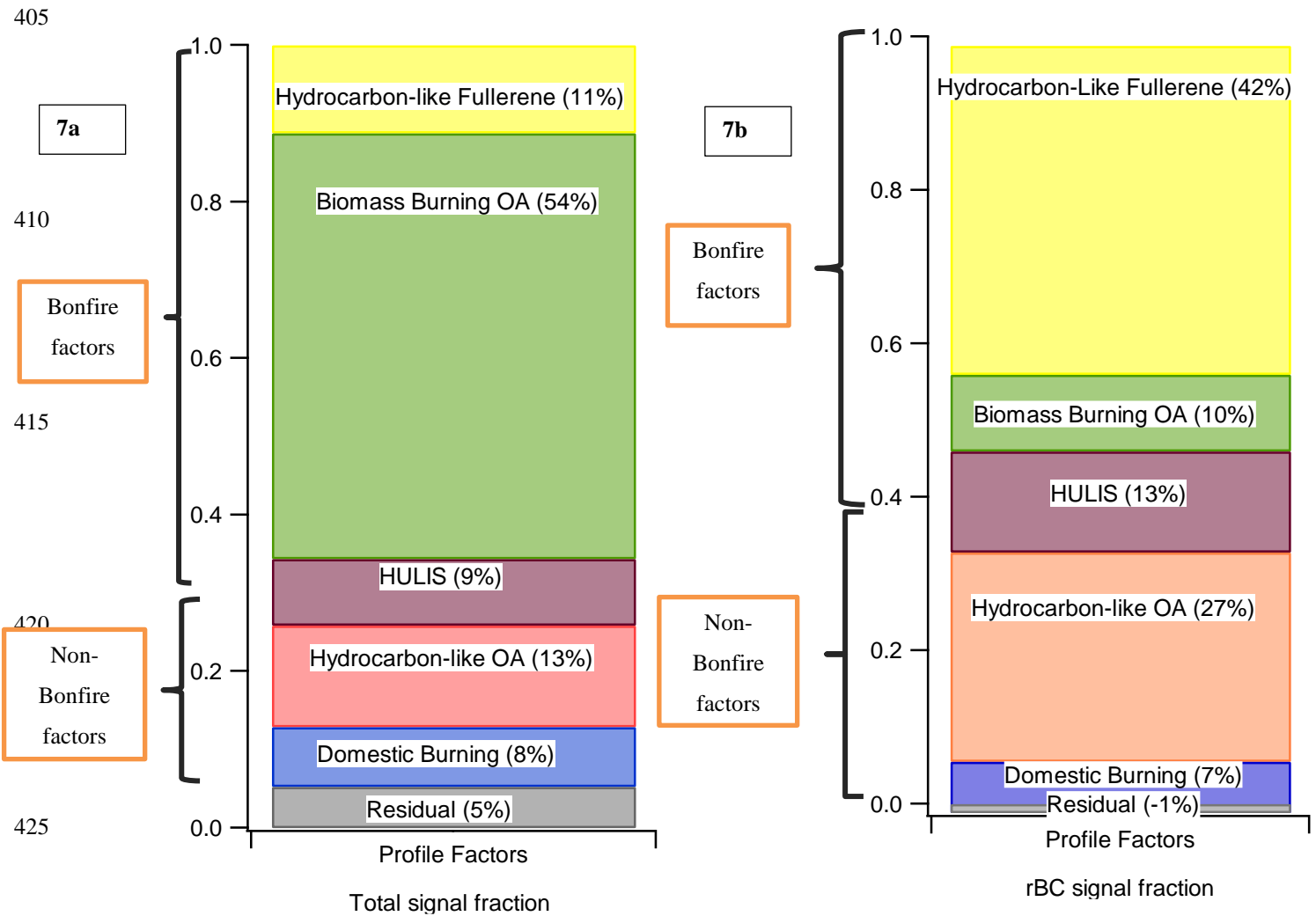
[3]HCN, HCNO, HONO (Priestley et al, 2018a)

Another close correlation was factor 1 (HULIS) with an r^2 of 0.82 with Fullerene. The reason for this high correlation is because of the very high concentration released during the bonfire event. In terms of sPON and factor 4 (traffic emissions), both are showing moderate correlation i.e. r^2= 0.64. The r^2 in this case is much lower than the other grouping because traffic emissions are the primary source, not a secondary source, so their relationship is likely coincidental, maybe modulated by the

boundary layer. The last group of pollutants having close correlation included pPON, Sr and factor 2 (biomass burning OA). In a previous research study (Reyes el al., 2018), ME-2 analysis indicated the presence of two different types of PON, in which particularly pPON are primarily emitted along with BBOA concentrations. According to Zhang et al., (2016), PON are related
375 mainly to the primary sources of combustion.

The firework tracer Sr has shown some correlation with pPON and BBOA, but their peaks occurred at slightly different times. So, in spite, of the high correlation, this implies that they're not identical. It could be that if the firework display occurred at the beginning of the bonfire event their emissions maybe coincident with the pyrolysis emissions on bonfire begin to be lit, as distinct from the smouldering emissions later (Haslett et al., 2017), however, without specific knowledge of the timings of the
380 events that contribute to these emissions, it is difficult to conclude this. Coupled with the fact that Sr could not be incorporated with any of the factors in this study, this would be consistent with the notion that fireworks are not the soot sources reported here or in Reyes et al. (2018).

4.2 Relative contributions of the different factors to the HR-SP-AMS signal and the BC budget:

This data can be used to estimate the relative contributions of the different sources to the overall signal and the black carbon
385 assuming that the divergence of the aerosol in the beam is the same for all particle types and hence the efficiency is same for all particle types. Fig 8(a) illustrates the total signal fraction of BC accounted by each BC sources released during the Bonfire event. The total mass fraction was obtained directly by the PMF analysis. The five factors have been divided into two different categories i.e. Bonfire factors and non-Bonfire factors. The Bonfire factors are HOA-like-Fullerene and BBOA, while HOA and domestic burning are the non-bonfire sources and HULIS having contributions from both. The biggest contribution from
390 the event was BBOA, contributing 54% out of total signal fraction followed by traffic emissions (13%), HOA-like-Fullerene (11%), HULIS (9%) and domestic burning (8%). Fig 8(b) shows the mass fraction of only black carbon from each PMF factor profile. The BC only mass fraction was calculated by multiplying the total signal fraction with the fraction of rBC in each factor and then renormalise to 1. According to analysis, HOA-like-Fullerene contributed the highest fraction i.e. 42% followed by the non-bonfire factor HOA (traffic emissions) with 27% contribution. The HULIS and BBOA have 13% and 10%
395 contribution respectively while domestic burning has the least part with 7% only. Therefore, it has been clearly found that the two major sources of BC are HOA-like-Fullerene and traffic emissions. While in fig 9 shows the quantitative data of BC signals in µg m^{-3} after scaling them to the AE31 eBC$_{950}$ data. This time series was generated by following the same procedure for BC signal fraction out of total signal fraction and normalising to the total BC signal. According to the time series, BC from Fullerene and BBOA showed the highest signals during the bonfire night-time period followed by HULIS, domestic burning
400 and traffic emissions.

7(a) shows the relative contributions of total mass fraction to HR-SP-AMS signal and Fig 7(b) shows rBC mass fraction accounted for by each PMF factors.

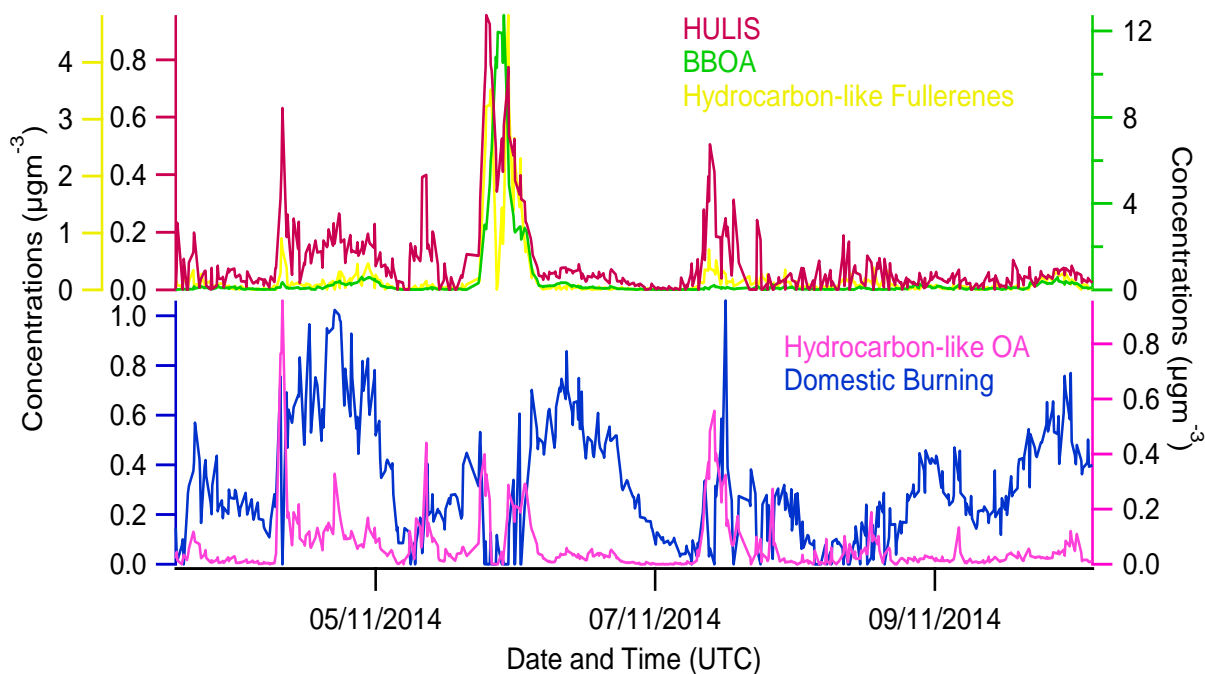



Figure 8: The contributions of BC signals in µg/m³ after normalising it to the concentrations of eBC₉₅₀ from aethalometer (AE31) (Reyes et al, 2018).

5 Conclusion

This study has shown that for the first time, the inclusion of fullerene data in PMF applied to HR-SP-AMS data can be used to apportion soot into five sources during an even superimposing emissions from a bonfire event on urban pollution. The five soot sources can be divided into bonfire night factors (HOA-like Fullerene, HULIS, BBOA) and non-bonfire night factors (i.e. domestic wood-burning, hydrocarbon-like organic aerosol and some HULIS). Metals were also observed at the time of fireworks display such as Fe, Ti and Cs and Sr. But Sr was most unambiguously associated with the fireworks, due to the fact, that there is no other source of Sr signal present outside of Bonfire night. metal was taken as a tracer for the fireworks. The addition of fullerene signals and increasing the model error value from 0 to 0.10 reduces the uncertainty/error in the PMF factor solution and provides the best factorisation results. The fullerene data was successfully incorporated into rBC signals and linked with the bonfire emissions directly while Sr metal signals did not incorporate into rBC or any other factors, implying it was not contributing as a source. Also, the inclusion of Fullerene signals also helped to differentiate between different factors. The results correlate well with the other BC and soot proxies provided by other instruments presented in previous papers and can be used to estimate the relative contributions of the different sources to total BC. This technique will be useful in the future studies to better differentiate between the different soot sources in complex polluted environments.

6 References

450 Aiken, G.R., McKnight, D.M. and Wershaw, R.L: Humic substances in soil, sediment, and water. Geochemistry, Isolation and Characterisation. New York: Wiley. 1985

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental Analysis of Organic Species with Electron Ionization High-Resolution Mass Spectrometry. Anal. Chem., 79, 8350– 8358. 2007.

Alfarra, M. R., Prevot, A. S. H., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V. A., Schreiber, D., Mohr, M., and
455 Baltensperger, U.: Identification of the mass spectral signature of organic aerosols from wood burning emissions, Environ. Sci. Technol., 41, 5770-5777, 10.1021/Es062289b, 2007.

Barescut, J.C., Gariel, J.C., Péres, J.M., Olivier, A., Tenailleau, L., Baron, Y., Maro, D. and Fontugne, M.: Measurement of the carbon 14 activity at natural level in air samples. Radioprotection, 40(S1), S791-S796, 2005.

Bond, T. C., C. Zarzycki, M. G. Flanner, and Koch, D. M.: Quantifying immediate radiative forcing by black carbon and
460 organicmatter with the Specific Forcing Pulse,Atmos. Chem. Phys.,11(4),1505–1525, doi:10.5194/acp-11-1505-201, 2011.

Borduas, N., Place, B., Wentworth, G. R., Abbatt, J. P. D., & Murphy, J. G.: Solubility and reactivity of HNCO in water: Insights into HNCO's fate in the atmosphere. Atmospheric Chemistry and Physics, 16(2), 703–714. https://doi.org/10.5194/acp-16-703-2016, 2016.

Buchner N, Ale-Agha N, Jakob S, Sydlik U, Kunze K, and Unfried K, et al.: Unhealthy diet and ultrafine carbon black particles
465 induce senescence and disease associated phenotypic changes. Exp Gerontol, 48(1), 8–16, 2013.

Bruns, E. A., Perraud, V., Zelenyuk, A., Ezell, M. J., Johnson, S. N., Yu, Y., Imre, D., Finlayson-Pitts, B. J., and Alexander, M. L.: Comparison of ftir and particle mass spectrometry for the measurement of particulate organic nitrates, Environ. Sci. Technol., 44, 1056–1061, https://doi.org/10.1021/es9029864, 2010.

Calace, N., Petronio, B. M., Cini, R., Stortini, A. M., Pampaloni, B., and Udisti, R.: Humic marine matter and insoluble
470 materials in Antarctic snow, Int. J. Environ. Anal. Chem., 79, 331–348, 2001.

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., and Worsnop, D. R.: Chase studies of particulate emissions from in-use new york city vehicles, Aerosol Sci. Tech., 38, 555–573, https://doi.org/10.1080/02786820490465504, 2004.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: SoFi, an IGOR-based interface for the efficient
475 use of the generalised multilinear engine (ME- 2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6, 3649–3661, https://doi.org/10.5194/amt-6-3649-2013, 2013.

Cao, J., Xu, H., Xu, Q., Chen, B. and Kan, H.: Fine particulate matter constituents and cardiopulmonary mortality in a heavily polluted Chinese city Environ. Health Perspect., 120 (3), 373-378, 2012.

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

Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J. P., and Dell'Acqua, A.: Advances in characterisation of size-resolved organic matter in marine aerosol over the North Atlantic, J. Geophys. Res.-Atmos., 109, D24215, doi:10.1029/2004JD005137, 2004.

485   Chirico, R., DeCarlo, P. F., Heringa, M. F., Tritscher, T., Richter, R., Prevot, A. S. H., Dommen, J., Weingartner, E., Wehrle, G., Gysel, M., Laborde, M., and Baltensperger, U.: Impact of Aftertreatment Devices on Primary Emissions and Secondary Organic Aerosol Formation Potential from in-use Diesel Vehicles: Results from Smog Chamber Experiments. Atmos. Chem. Phys., 10:11545–11563, 2010.

Cini, R., Innocenti, N. D., Loglio, G., Oppo, C., Orlandi, G., Stortini, A. M., Tesei, U., and Udisti, R.: Air-sea exchange: Sea
490   salt and organic micro components in Antarctic snow, Int. J. Environ. Anal. Chem., 63, 15–27, 1996.

Cini, R., Innocenti, N. D., Loglio, G., Stortini, A. M., and Tesei, U.: Spectrofluorometric Evidence of The Transport Of Marine Organic-Matter In Antarctic Snow Via Air-Sea Interaction, Int. J. Environ. Anal. Chem., 55, 285–295, 1994.

Cooke, W. F., C. Liousse, H. Cachier, and Feichter, J.: Construction of a 1º X 1º fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, J. Geophys.Res.,104(D18), 22137–22162, 1999.

495   Carslaw, D.C. and Ropkins, K.: Openair—an R package for air quality data analysis. Environmental Modelling & Software, 27, 52-61, 2012.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., De- Carlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C.,
500   Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14, 6159– 6176, https://doi.org/10.5194/acp-14-6159-2014, 2014.

Clark, H.: New directions. Light blue touch paper and retire, Atmos. Environ., 31, 2893–2894, https://doi.org/10.1016/s1352-
505   2310(97)88278-7, 1997.

Colbeck, I. and Chung, M.-C.: Ambient aerosol concentrations at a site in se england during bonfire night 1995, J. Aerosol Sci., 27, Supplement 1, S449–S450, https://doi.org/10.1016/0021- 8502(96)00297-2, 1996.

Collaud Coen, M., Weingartner, E., Apituley, A., Ceburnis, D., Fierz-Schmidhauser, R., Flentje, H., Henzing, J. S., Jennings, S. G., Moerman, M., Petzold, A., Schmid, O., and Baltensperger, U.: Minimising light absorption measurement artifacts of the
510   Aethalometer: evaluation of five correction algorithms, Atmos. Meas. Tech., 3, 457-474, 10.5194/amt-3-457-2010, 2010.

Comero, S., Capitani, L. and Gawlik, B.M.: Positive Matrix Factorisation (PMF)–An introduction to the chemometric evaluation of environmental monitoring data using PMF. Office for Official Publications of the European Communities, Luxembourg, 59, 2009.

Corbin, J. C, Othman, A., D. Haskins, J., D. Allan, J., Sierau, B., R. Worsnop, D., Lohmann, U. and A. Mensah, A.: Peak
515 fitting and integration uncertainties for the Aerodyne Aerosol Mass Spectrometer, Atmos. Meas. Tech. Discuss., 8(4), 3471–
3523, doi:10.5194/amtd-8-3471-2015, 2015. "C2015"

Dachs, J. and Eisenreich, S.J.: Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic
hydrocarbons Environ. Sci. Technol., 34, 3690-3697, 2000.

DeCarlo, P F, Kimmel, J R, Trimborn, A, Northway, M J, Jayne, J T, Aiken, A C, Gonin, M, Fuhrer, K, Horvath, T, Docherty,
520 K S, Worsnop, D R, & Jimenez, J L.: Fielddeployable, high-resolution, time-of-flight aerosol mass spectrometer. Analytical
chemistry, 78, 8281–8289. 2006.

Decesari, S., Facchini, M. C., and Fuzzi, S.: Characterisation of water-soluble organic compounds in atmospheric aerosols: a
new approach, J. Geophys. Res., 105, 1481–1489, 2000.

Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E., and Facchini, M. C.: Source attribution of
525 watersoluble organic aerosol by nuclear magnetic resonance spectroscopy, Environ. Sci. Technol., 41, 2479–2484, 2007.

Dyke, P., Coleman, P. & James, R.: Dioxins in ambient air, bonfire night 1994.Chemosphere, 34 (5–7), 1191–1201. 1997.

Farrar, N. J., Smith, K. E. C., Lee, R. G. M., Thomas, G. O., Sweetman, A. J., and Jones, K. C.: Atmospheric emissions of
polybrominated diphenyl ethers and other persistent organic pollutants during a major anthropogenic combustion event,
Environ. Sci. Technol., 38, 1681–1685, https://doi.org/10.1021/es035127d, 2004.

530 FORTNER, E. C., BROOKS, W. A., ONASCH, T. B., CANAGARATNA, M. R., MASSOLI, P., JAYNE, J. T., FRANKLIN,
J. P., KNIGHTON, W. B., WORMHOUDT, J., WORSNOP, D. R., KOLB, C. E. & HERNDON, S. C. Particulate Emissions
Measured During the TCEQ Comprehensive Flare Emission Study. Industrial & Engineering Chemistry Research, 51, 12586-
12592, 2012.

Gerhardt, P., Loffler, S. and K. H. Homann, "The formation of polyhedral carbon ions in fuel-rich acetylene and benzene
535 flames," in: 22nd Symp. (Int.) on Combustion, Combustion Inst., Pittsburgh, 395–401, 1988.

Gelencser, A., Hoffer, A., Krivacsy, Z., Kiss, G., Molnar, A., and Meszaros, E.: On the possible origin of humic matter in fine
continental aerosol, J. Geophys. Res.-Atmos., 107, D12 4137, doi:10.1029/2001JD001299, 2002.

Graber, E. R., and Rudich, Y.: Atmospheric HULIS: How Humic-Like are They? A Comprehensive and Critical Review.
Atmos. Chem. Phys., 6:729–753, 2006.

540 Grahame TJ, and Schlesinger RB.: Cardiovascular health and particulate vehicular emissions: a critical evaluation of the
evidence. Air Quality, Atmosphere and Health, 1:3–27, 2010.

Graham, B., Mayol-Bracero, O. L., Guyon, P., Roberts, G. C., Decesari, S., Facchini, M. C., Artaxo, P., Maenhaut, W., Koll,
P. and Andreae, M. O.: Water-soluble organic compounds in biomass burning aerosols over Amazonia - 1. Characterisation
by NMR and GC-MS, J. Geophys. Res.-Atmos., 107, D20 8047, doi:10.1029/2001JD000336, 2002.

545 Hansen, A. D. A., Rosen, H. and Novakov, T.: The Aethalometer – An instrument for the real-time measurement of optical
absorption by aerosol particles. The Science of the Total Environment. 36, 191-196, 1984.

HASLETT, S. L., THOMAS, J. C., MORGAN, W. T., HADDEN, R., LIU, D., ALLAN, J. D., WILLIAMS, P. I., SEKOU, K., LIOUSSE, C. & COE, H.: Highly-controlled, reproducible measurements of aerosol emissions from African biomass combustion. Atmos. Chem. Phys. Discuss., 1-33, 2017.

550 Hellborg, R., Faarinen, M., Kiisk, M., Magnusson, C. E., Persson, P., Skog, G., and Stenström, K.: Accelerator mass spectronomy-an overview. Vacuum. 70, 365-372, 2003.

Hoffer, A., G. Kiss, M. Blazso, and Gelencser, A.: Chemical characterisation of humic-like substances (HULIS) formed from a lignin-type precursor in model cloud water, Geophys. Res. Lett., 31, 2004.

Highwood, EJ and Kinnersley, R.P., When smoke gets in our eyes: The multiple impacts of atmospheric black carbon on 555 climate, air quality and health. Environment international, 32(4), pp.560-566, 2006.

Hung, H. M., Katrib, Y., and Martin, S. T.: Products and mechanisms of the reaction of oleic acid with ozone and nitrate radical, J. Phys. Chem. A, 109, 4517–4530, 2005.

Havers, N., Burba, P., Lambert, J., and Klockow, D.: Spectroscopic characterisation of humic-like substances in airborne particulate matter, J. Atmos. Chem., 29, 45–54, 1998.

560 Jang, M. S., Carroll, B., Chandramouli, B., and Kamens, R. M.: Particle growth by acid-catalysed heterogeneous reactions of organic carbonyls on preexisting aerosols, Environ. Sci. Technol., 37, 3828–3837, 2003.

Jang, M. S., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalysed particle-phase reactions, Science, 298, 814–817, 2002.

Janssen, N.A. and Joint, WHO: *Health effects of black carbon* (pp. 1-86). Copenhagen: WHO Regional Office for Europe, 565 2012.

Jathar, S. H., Heppding, C., Link, M. F., Farmer, D. K., Akherati, A., Kleeman, M. J., et al.: Investigating diesel engines as an atmospheric source of isocyanic acid in urban areas. Atmospheric Chemistry and Physics, 17(14), 8959–8970. https://doi.org/10.5194/acp-17- 8959-2017, 2017.

Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E.: C60: Buckminsterfullerene. Nature, 318 (6042), 570 162−163. 1985

Le Breton, M., Bacak, A., Muller, J. B. A., O'Shea, S. J., Xiao, P., Ashfold, M. N. R., Cooke, M. C., Batt, R., Shallcross, D. E., Oram, D. E., Forster, G., Bauguitte, S. J.-B., Palmer, P. I., Parrington, M., Lewis, A. C., Lee, J. D., and Percival, C. J.: Airborne hydrogen cyanide measurements using a chemical ionisation mass spectrometer for the plume identification of biomass burning forest fires, Atmos. Chem. Phys., 13, 9217–9232, https://doi.org/10.5194/acp-13-9217-2013, 2013.

575 Lemieux, P.M., Lutes, C.C., & Santoianni, D.A.: Emissions of organic air toxics from open burning: a comprehensive review. Prog. Energy Combust. Sci. 30 (1), 1–32, 2004.

Lin, P., Huang, X.-F., He, L.-Y., and Yu, J.-Z.: Abundance and size distribution of HULIS in ambient aerosols at a rural site in South China, J. Aerosol Sci., 41, 74–87, 2010.

Liu, D., Whitehead, J., Alfarra, M. R., Reyes-Villegas, E., Spracklen, D. V., Reddington, C. L., Kong, S., Williams, P. I., Ting, Y.-C., Haslett, S., Taylor, J. W., Flynn, M. J., Morgan, W. T., McFiggans, G., Coe, H., and Allan, J. D.: Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, Nat. Geosci., 10, 184–188, https://doi.org/10.1038/ngeo2901, 2017.

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.: Contrasting physical properties of black carbon in urban Beijing between winter and summer. Atmospheric Chemistry and Physics, pp.6749-6769, 2019.

Lobert, J.M., Keene, W.C., Logan, J.A. and Yevich, R.: Global chlorine emissions from biomass burning: Reactive chlorine emissions inventory. Journal of Geophysical Research: Atmospheres, 104 (D7), 8373-8389, 1999.

Mari, M. et al.: Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data. Science of the Total Environment, 408(11), 2387–2393, 2010.

Martinsson, J.: Using the Aethalometer for Source Apportionment of Carbonaceous Aerosols. Lund University, Division of Nuclear Physics, 2014.

Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning aerosols over Amazonia – 2. Apportionment of the chemical composition and importance of the polyacidic fraction, J. Geo phys. Res.-Atmos., 107, D20 8091, doi:10.1029/2001JD000522, 2002.

McFiggans, G., Alfarra, M. K., Allan, J., Bower, K., Coe, H., Cubison, M., Topping, D., Williams, P., Decesari, S., Facchini, C., and Fuzzi, S.: Simplification of the representation of the organic component of atmospheric particulates, Faraday Discuss., 130, 341-362, 10.1039/b419435g, 2005.

Mclain, J.: Pyrotechnics: From the viewpoint of solid-state chemistry (Book). Philadelphia, Pa., Franklin Institute Press, 1980.252, 1980.

Mukai, H., and Ambe, Y.: Characterisation of a Humic Acid-Like Brown Substance in Airborne Particulate Matter and Tentative Identification of its Origin. Atmos. Environ., 20:813–819, 1986.

Onasch, T.B., Trimborn, A., Fortner, E.C., Jayne, J.T., Kok, G.L., Williams, L.R., Davidovits, P. and Worsnop, DR: Soot particle aerosol mass spectrometer: development, validation, and initial application. Aerosol Science and Technology, 46(7), 804-817. 2012.

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, DR: 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. 2015

Paatero, P., and Tapper, U.: Positive matrix factorisation: A non-negative factor model with optimal utilisation of error estimates of data values, Environmetrics, 5, 111-126. 1994.

Paatero, P., Hopke, P. K., Song, X. H., and Ramadan, Z.: Understanding and Controlling Rotations in Factor Analytic Models, Chemom. Intell. Lab. Syst., 60, 253–264, 2002.

Paatero P. and Hopke P.K.: Discarding or down-weighting high-noise variables in factor analytic models. Analytica Chimica Acta, 490, 277–289, 2003.

615 Petzold, A., Ogren, J. A., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A. and Zhang, X.-Y.: Recommendations for the interpretation of "black carbon" measurements, Atmos. Chem. Phys., 13(16), 8365–8379, doi:10.5194/acp-13-8365-2013, 2013.

Pongpiachan, S. et al.: Assessing risks to adults and preschool children posed by PM2.5- bound polycyclic aromatic hydrocarbons (pahs) during a biomass burning episode in Northern Thailand. Science of the Total Environment, 508, 435–
620 444, 2015.

Priestley, M., Le Breton, M., Bannan, T. J., Leather, K. E., Bacak, A., Allan, J. D., Brazier, T., Reyes-Villegas, E., Shallcross, B. M. A., Khan, M. A., De Vocht, F., Shallcross, B. M., Brazier, T., Khan, M. A., Allan, J., Shallcross, D. E., Coe, H., and Percival, C. J.: Manchester, UK bonfire night 2014: Air quality and emission ratios during an anthropogenic biomass burning event using a time of flight chemical ionisation mass spectrometer, in preparation, 2018a.

625 Priestley, M., Breton, M.L., Bannan, T.J., Leather, K.E., Bacak. A., Reyes-Villegas. E., Vocht, F.D., Shallcross, B.M.A., Brazier, T., Khan, M.A., Allan, J., Shallcross, D.E., Coe, H., & Percival, C.J.: Observations of isocyanate, amide, nitrate and nitro compounds from an anthropogenic biomass burning event using a ToF-CIMS, Journal of Geophysical Research Atmospheres, 2018b.

Reilly, P. T. A.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M.: Fullerene Evolution in Flame-Generated Soot. J. Am. Chem.
630 Soc., 122 (47), 11596−11601. 2000.

Reyes-Villegas, E., Green, D. C., Priestman, M., Canonaco, F., Coe, H., Prévôt, A. S. H., and Allan, J. D.: Organic aerosol source apportionment in London 2013 with ME-2: exploring the solution space with annual and seasonal analysis, Atmos. Chem. Phys., 16, 15545–15559, https://doi.org/10.5194/acp-16-15545- 2016, 2016.

Reyes-Villegas, E., Priestley, M., Ting, Y.-C., Haslett, S., Bannan, T., Le Breton, M., Williams, P. I., Bacak, A., Flynn, M. J.,
635 Coe, H., Percival, C., and Allan, J. D.: Simultaneous aerosol mass spectrometry and chemical ionisation mass spectrometry measurements during a biomass burning event in the UK: insights into nitrate chemistry, Atmos. Chem. Phys., 18, 4093-4111, 2018.

Saarikoski, S., Carbone, S., Cubison, M.J., Hillamo, R., Keronen, P., Sioutas, C., Worsnop, DR and Jimenez, J.L.: Evaluation of the performance of a particle concentrator for online instrumentation. Atmospheric Measurement Techniques, 7(7), pp.2121-
640 2135. 2014

Sandradewi, J., Prévôt, A.S., Szidat, S., Perron, N., Alfarra, M.R., Lanz, V.A., Weingartner, E. and Baltensperger, U.R.S.: Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter. Environmental science & technology, 42(9), 3316-3323, 2008.

Sarkar, C., Sinha, V., Kumar, V., Rupakheti, M., Panday, A., Mahata, K. S., et al.: Overview of VOC emissions and chemistry
645 from PTR-TOF-MS measurements during the SusKat-ABC campaign: High acetaldehyde, isoprene and isocyanic acid in
wintertime air of the Kathmandu Valley. Atmospheric Chemistry and Physics, 16(6), 3979–4003. https://doi.org/10.5194/acp-
16- 3979-2016, 2016.

Shi, Y.L., Zhang, N., Gao, J.M., Li, X., & Cai, Y.Q.: Effect of fireworks display on perchlorate in air aerosols during the
Spring Festival. Atmos. Environ. 45 (6), 1323–1327, 2011.

650 Simoneit, B. R. T.: Eolian particulates from oceanic and rural areas – their lipids fulvic and humic acids and residual carbon,
in: Advances in Organic Geochemistry, edited by Douglas, A. G. and Maxwell, J. R., Pergamon Press, Oxford, 343–352, 1980.

Sun, Y.L., Wang, Z.F., Fu, P.Q., Yang, T., Jiang, Q., Dong, H.B., Li, J. and Jia, J.J.: Aerosol composition, sources and
processes during wintertime in Beijing, China. Atmospheric Chemistry and Physics, 13(9), pp.4577-4592, 2013.

Tolocka, M. P., Jang, M., Ginter, J. M., Cox, F. J., Kamens, R. M., and Johnston, M. V.: Formation of oligomers in secondary
655 organic aerosol, Environ. Sci. Technol., 38, 1428–1434, 2004.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from
Positive Matrix Factorization of aerosol mass spectrometric data, Atmospheric Chemistry and Physics, 9, 2891–2918, doi:
www.atmos-chem-phys.net/9/2891/2009/, 2009.

US Environmental Protection Agency.: Report to Congress on Black Carbon March 2012 Department of the Interior,
660 Environment, and Related Agencies Appropriations Act, 2010, 2012.

Wang, L. W., Wen, L., Xu, C. H., Chen, J. M., Wang, X. F., Yang, L. X., Wang, W. X., Yang, X., Sui, X., Yao, L., and Zhang,
Q. Z.: Hono and its potential source particulate nitrite at an urban site in north china during the cold season, Sci. Total Environ.,
538, 93–101, https://doi.org/10.1016/j.scitotenv.2015.08.032, 2015.

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

Woodward-Massey, R., Taha, Y. M., Moussa, S. G., & Osthoff, H. D.: Comparison of negative-ion proton-transfer with iodide
ion chemical ionisation mass spectrometry for quantification of isocyanic acid in ambient air. Atmospheric Environment, 98,
693–703.   Retrieved   from   http://www.sciencedirect.com/science/article/pii/S1352231014007079,
https://doi.org/10.1016/j.atmosenv.2014.09.014, 2014.

670 Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M. C., Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A., Meszaros, E.,
Hansson, H. C., Rosman, K., and Zebuhr, Y.: Inorganic, organic and macromolecular components of fine aerosol in different
areas of Europe in relation to their water solubility, Atmos. Environ., 33, 2733– 2743, 1999.

Zhang, X. L., Y. H. Lin, J. D. Surratt, P. Zotter, A. S. H. Prevot, & R. J. Weber.: Light absorbing soluble organic aerosol in
Los Angeles and Atlanta: A contrast in secondary organic aerosol, Geophys. Res. Lett., 38, doi:10.1029/2011GL049385, 2011.

Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., and Jimenez, J. L.: Deconvolution and Quantification of Hydrocarbon-Like and Oxygenated Organic Aerosols Based on Aerosol Mass Spectrometry. Environ. Sci. Technol., 39:4938–4952, 2005.

Zhang, J. K., Cheng, M. T., Ji, D. S., Liu, Z. R., Hu, B., Sun, Y., and Wang, Y. S.: Characterisation of submicron particles during biomass burning and coal combustion periods in Beijing, China, Sci. Total Environ., 562, 812–821, https://doi.org/10.1016/j.scitotenv.2016.04.015, 2016.

7 Authors Contribution

Zainab Bibi performed the data analysis and wrote the paper. James D. Allan and Paul I. Williams designed the experiment and operated the SP-AMS. Ernesto Reyes Villegas, Michael Priestley and Carl Percival provided measurements and data from other instruments. Zainab Bibi was supervised by James D. Allan and Hugh Coe, with Ernesto Reyes Villegas and James Brooks assisting with PMF analysis.

8 Data Availability

Data is archived at the University of Manchester and available on request'. It will be posted publicly before submission of the final manuscript.

9 Acknowledgement

This work was supported by NERC grant COM-PART (NE/K014838/1) for data collection. Zainab Bibi's PhD was funded by a Dean's Award Scholarship from the University of Manchester Faculty of Science and Engineering.

Figure 9: The logo of Copernicus Publications.