

SP-AMS PMF with fullerenes

James Allan

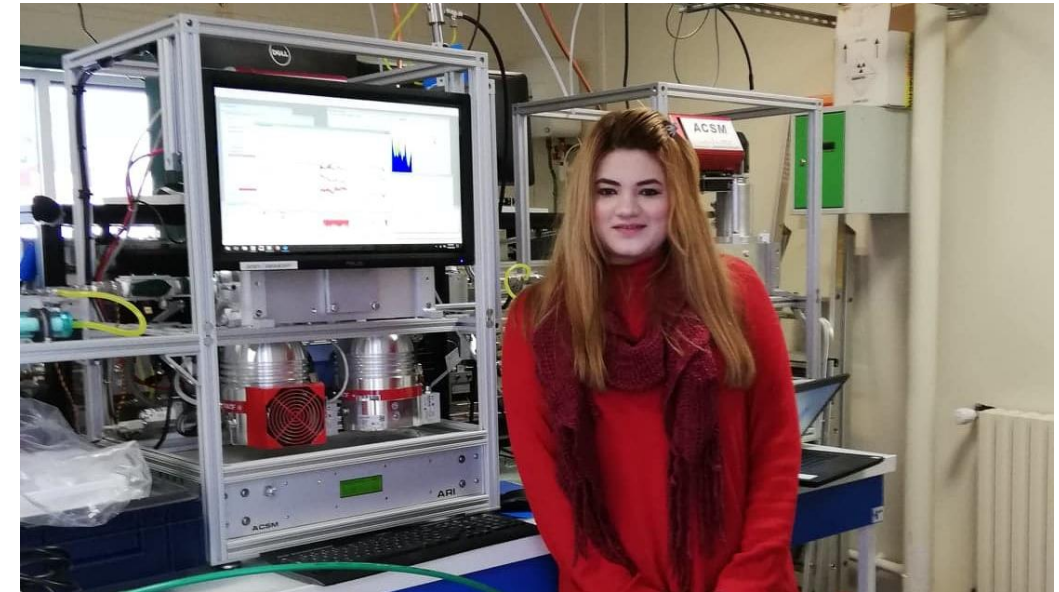
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The person who did the actual work

- Zainab Bibi (pictured)
- Paper currently in review at ACP:
<https://acp.copernicus.org/preprints/acp-2020-890/>
- Due to submit thesis in the coming year



BC apportionment/attribution

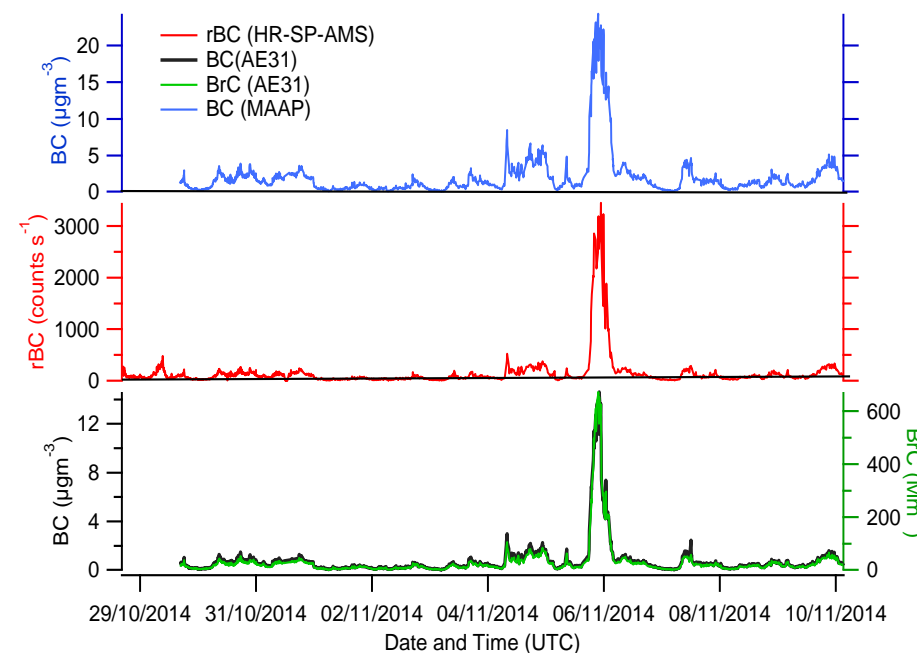
- Methods for BC source apportionment include:
 - Optical (e.g. Aethalometer, PAS)
 - Use of tracers (e.g. levoglucosan, potassium, fossil fuel tracers)
 - Isotopic analysis, principally ^{14}C
- Existing established methods typically split BC into two sources, e.g.:
 - Black vs brown carbon
 - Traffic vs wood burning
 - Modern vs fossil carbon
- The SP-AMS delivers mass spectral data. Can we do better by applying PMF?

Fullerenes

- The C_x peaks can be grouped into 'low' (C_{1-5}), 'mid' (C_{6-31}) and 'high' ($C_{>31}$) m/z ranges (Onasch et al., 2012)
- The 'low' C_x peaks do not show enough variation and the 'mid' C_x peaks get lost amongst organics in ambient spectra. Can we get better PMF factorisation through inclusion of 'high' C_x peaks in the mass spectral matrix?
- Previous studies have reported fullerenes in the high C_x range from certain soot sources in the SP-AMS (Fortner et al., 2012)
 - Not sure whether they are produced in the flame or the instrument
 - Some 'weird' behaviour has been noted, so must be taken with a pinch of salt

The case study

- Bonfire night, an annual festival on or around the 5th of November celebrating the gunpowder plot in 1605
- In 2014 we ran a suite of instruments at the lab in Manchester for that night and a week either side of it
- Fortuitously, that year a strong nocturnal inversion formed, presenting a very good case study of biomass burning and fireworks against typical wintertime UK urban background
- The subject of four papers involving the AMS/Aethalometer (Reyes Villegas et al., 2018), TOF-CIMS (Priestley et al., 2018), SP2 (Liu et al., 2017) and now SP-AMS (Bibi et al., in review)

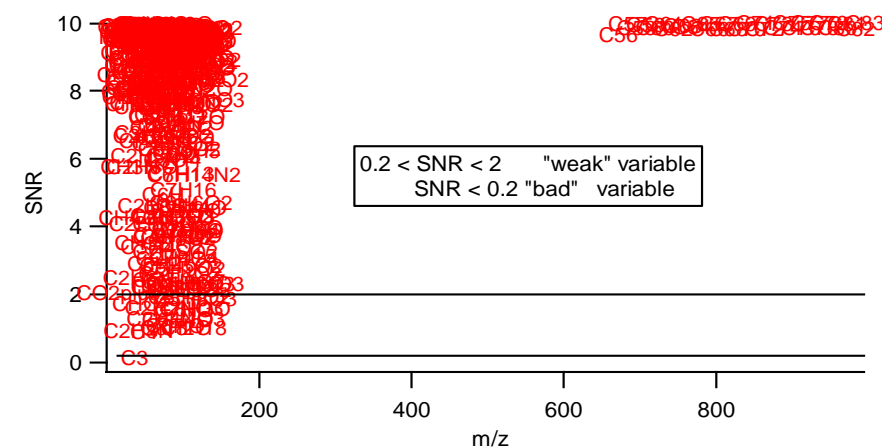
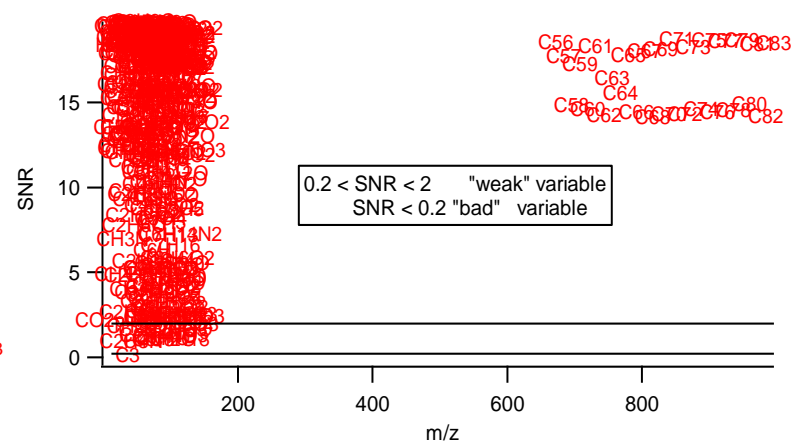
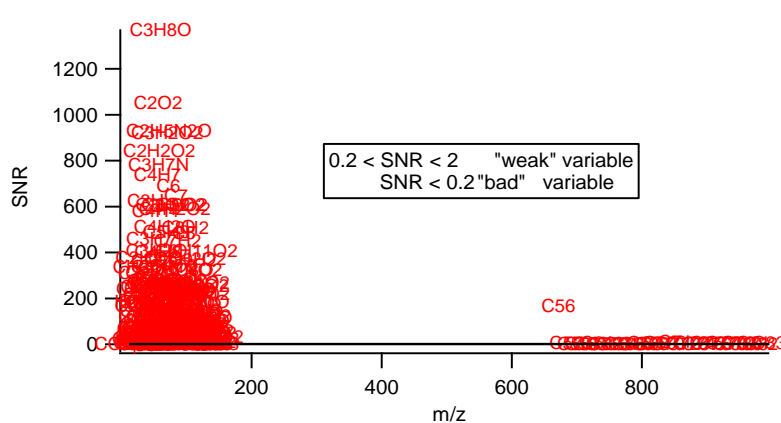


SP-AMS configuration

- The SP-AMS alternated between the standard 'V' and 'W' modes, with an extra 'fullerene' modes, which was 'V' mode with a much lower pulsing frequency (allowing the study of m/z 's of 1000s)
 - 'W' mode proved unusable
 - The lower m/z channels were analysed with PIKA, whereas UMR was used to provide the fullerene data
- Was not calibrated for rBC (didn't have a protocol at the time) – all data is presented in counts per s
- Also alternated with a catalytic stripper, not presented here (that can wait for another time...)

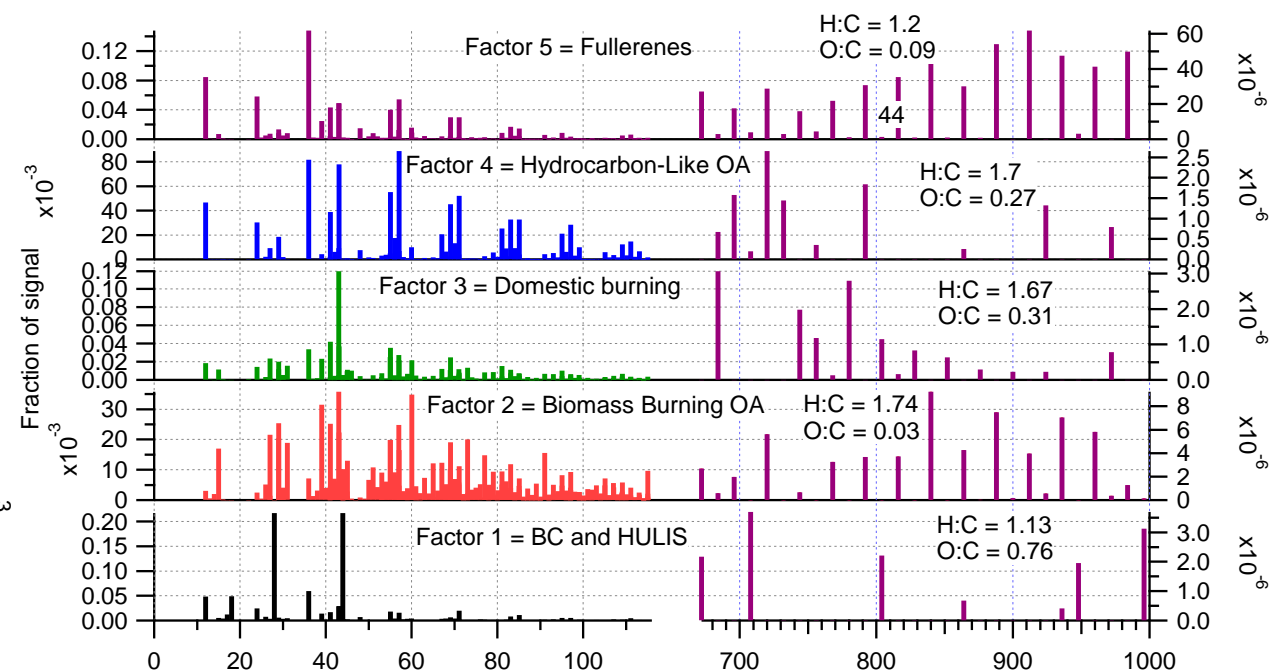
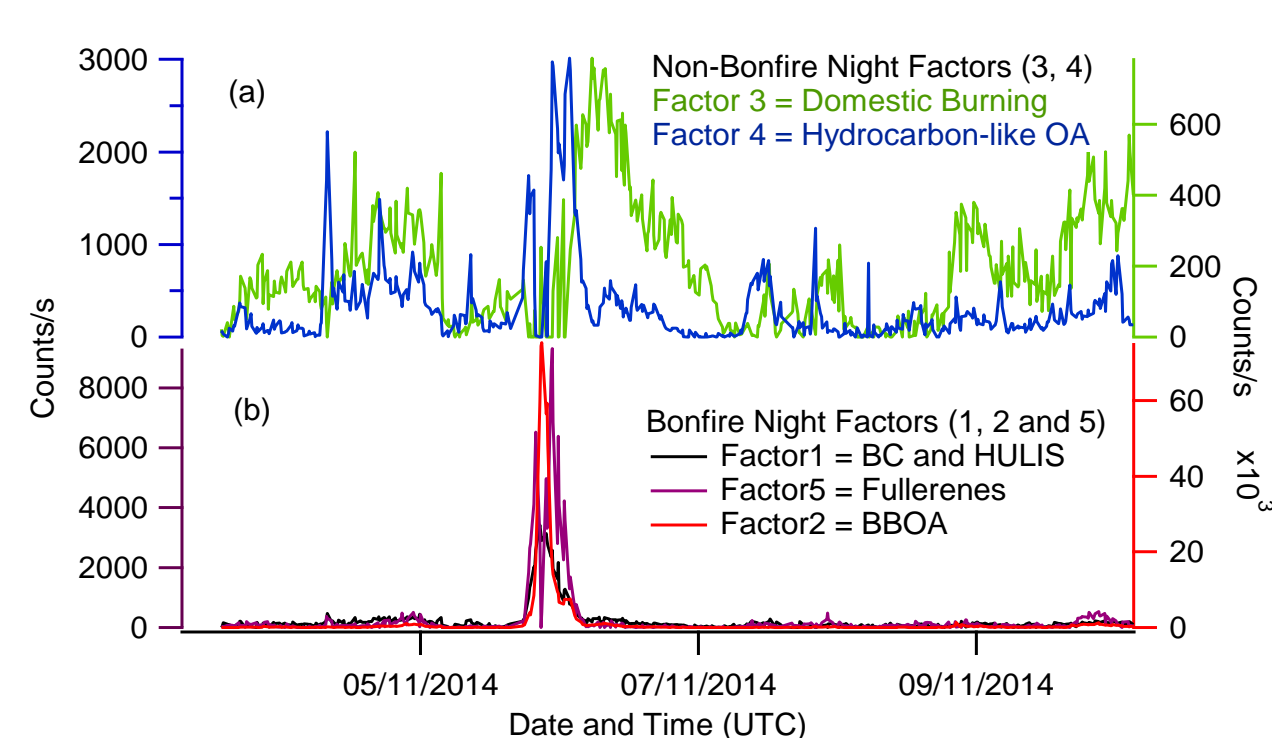
Error treatment

- The use of a combination of large and small signals ensured factors were dominated by splits in the large signals, overcome by application of the 'model error' parameter
- Through trial and error, a value of 0.1 was settled on as giving the 'best' PMF outputs
- A more rigorous approach such as Corbin et al. (2015) was not possible due to the combination of PIKA and UMR data



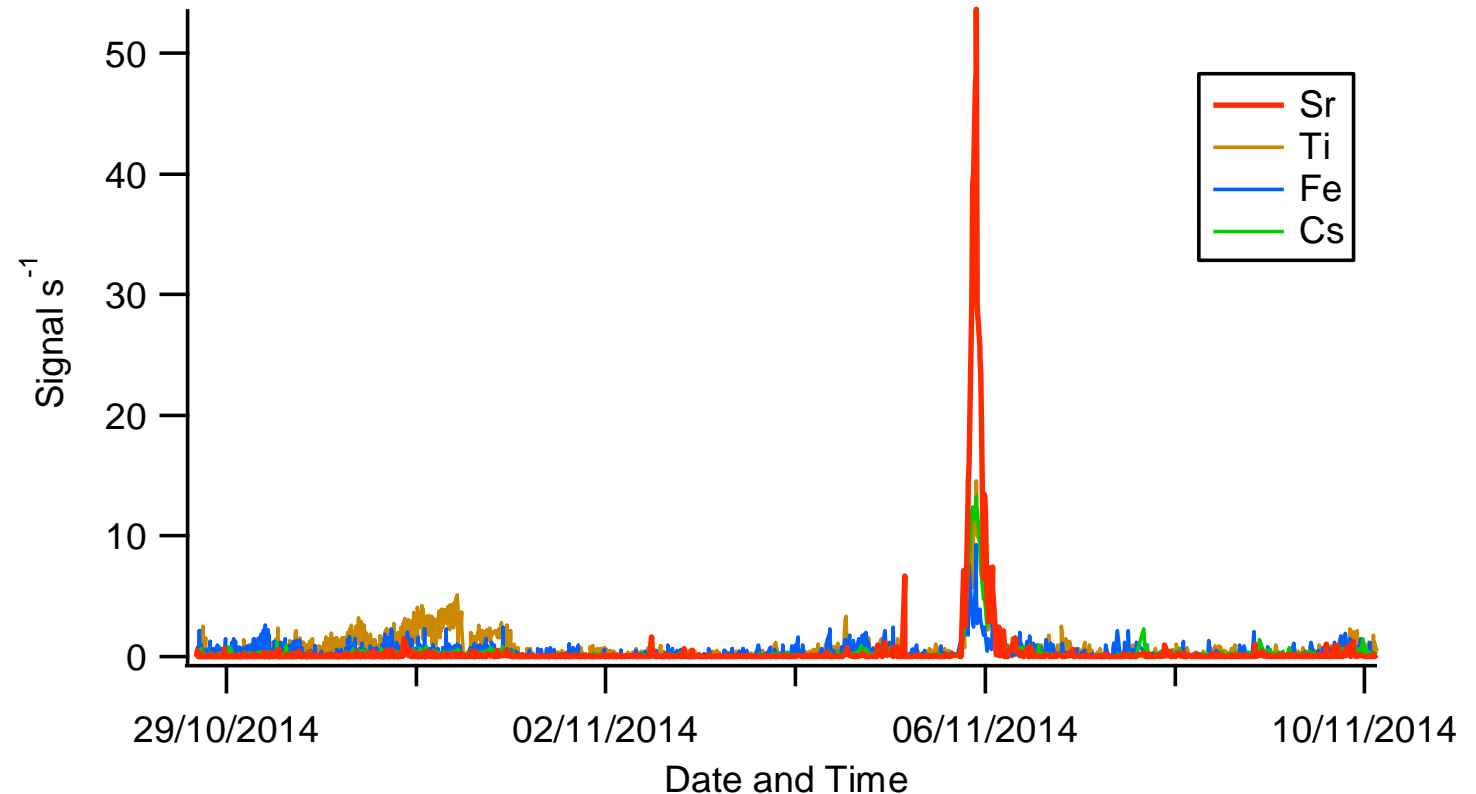
5 factor solution

- Fullerenes present in 2 factors, both associated with bonfire emissions
- Fullerenes not present in traffic or domestic BBOA
- Only one ambiguous factor, one with HULIS (associated with both bonfire and other sources)



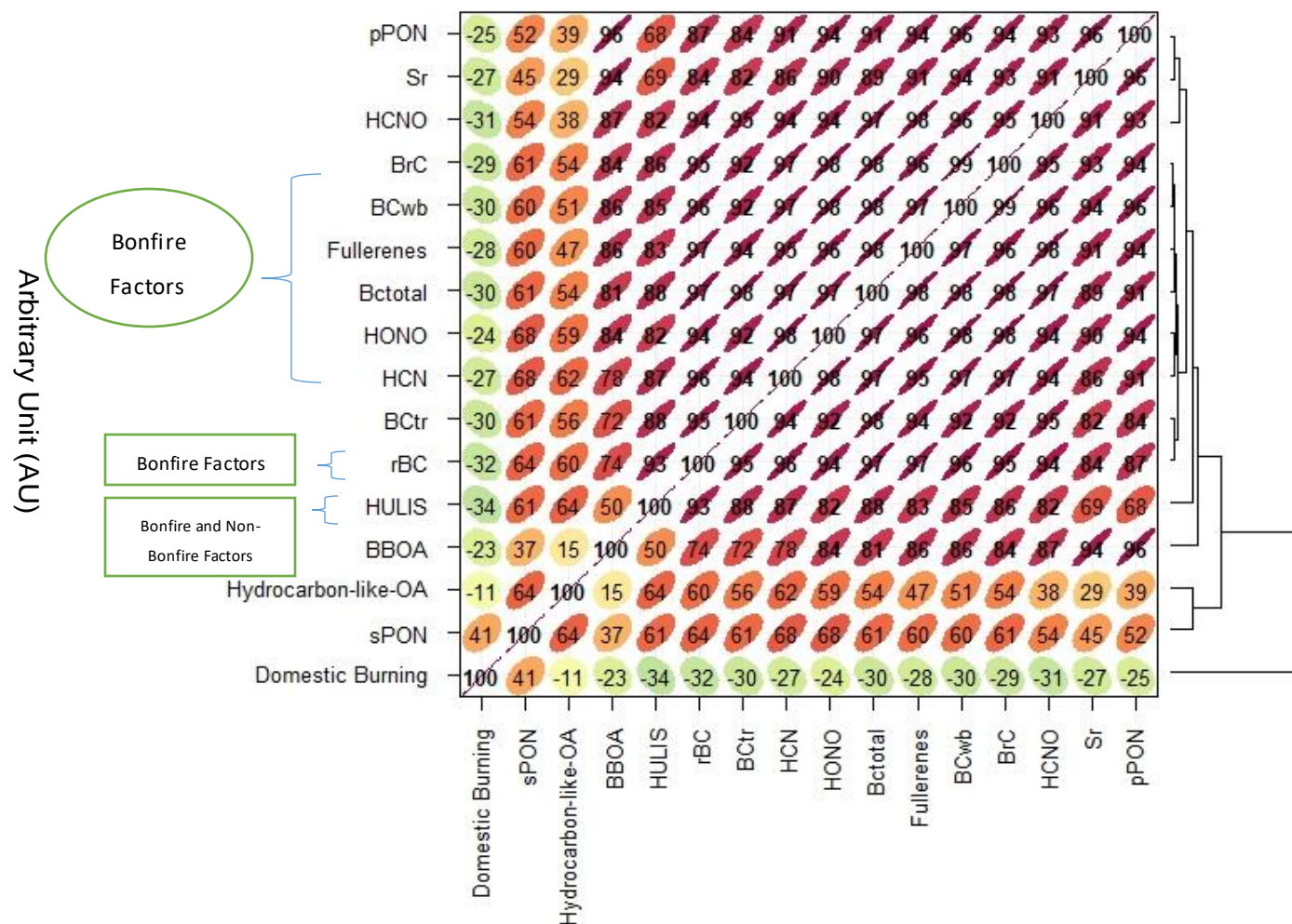
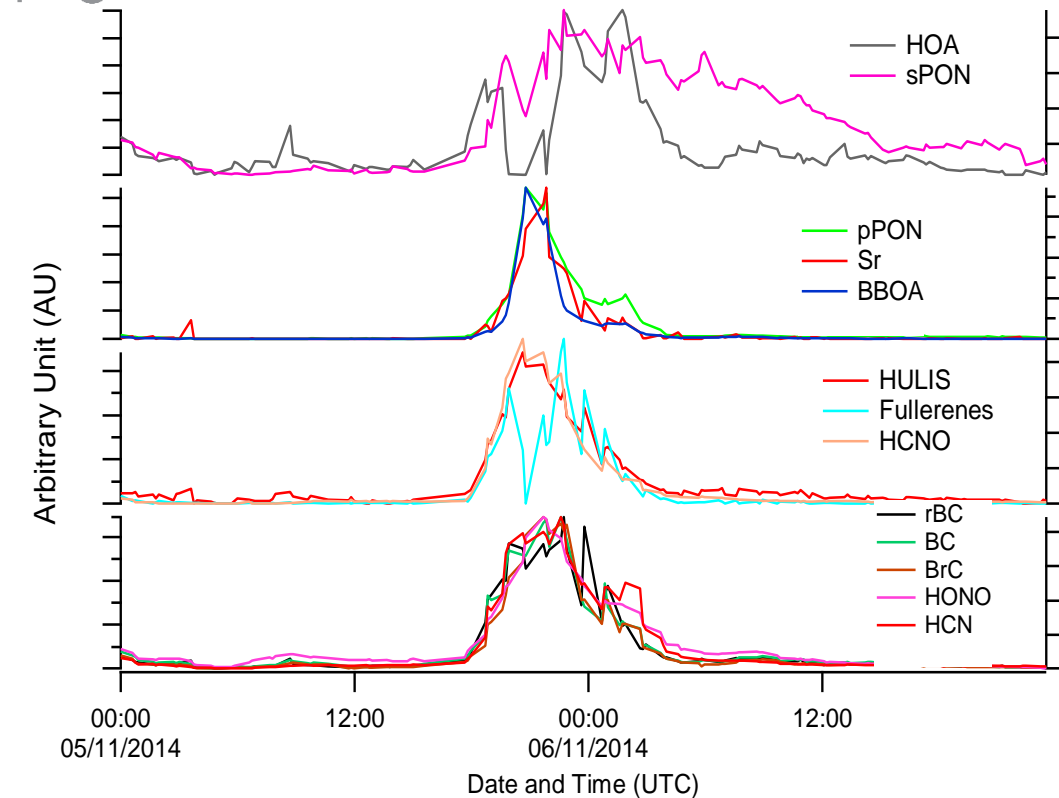
What about fireworks?

- Many metals were found associated with fireworks, with Sr (red colorant) was found to be most specific
- Was not part of any factors, even when forced by artificial upweighting, suggesting fireworks did not influence the rest of the data



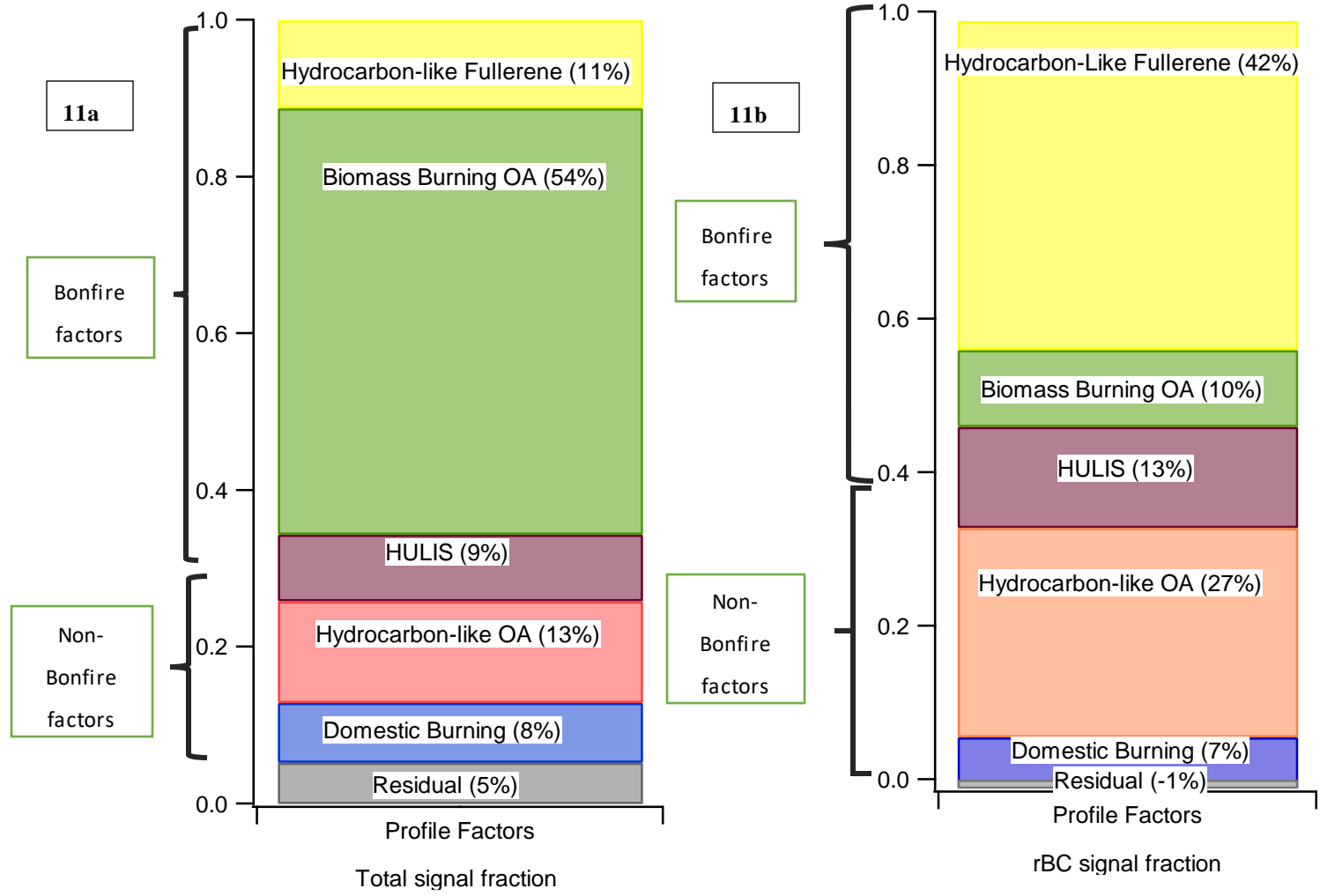
Comparisons with other data (Reyes Villegas et al. 2018)

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Budgeting BC

- The contribution of the factors to the overall signal and the rBC (C_x) signals can be calculated
- This can be applied to another BC measure (e.g. AE31) to apportion the BC



Conclusions

- This case showed that we can use the SP-AMS, incorporating fullerene signals, to resolve more than two BC sources and budget for BC
- It is not vital to quantitatively calibrate the SP-AMS providing a collocated measure of BC is present (e.g. Aethalometer)
- The SP-AMS can also detect firework signals in the form of metals, with strontium proving the best tracer
- Would be interesting to repeat this in other BC-rich environments