



TNA User Report

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Project title	<i>Detailed molecular characterization of organic aerosols from Domestic Solid Fuel (DSF) Burning</i>
Name of the accessed calibration center	OGTAC CC (Calibration center for organic tracer and aerosol constituents)- TROPOS
Number of users in the project	2
Project objectives (max 100 words)	The scientific objectives were: 1) Identify and quantify (if standards available) well-known combustion markers in ambient and domestic solid fuel (DSF) burning samples. 2) Identify new combustion markers for different fuel types to support efforts in separating the contribution of coal, peat and wood burning to the organic fraction of ambient PM _{2.5} .
Description of work (max 100 words):	Complementary analytical techniques (HPLC/ESI-TOFMS, HPAEC-PAD, GC/MS) were used to identify key combustion markers in PM _{2.5} resulting from DSF combustion. We quantified as many chemical compounds as possible using the standards available and for which there are analytically validated and calibrated methodologies. Ten filters in total were analysed - three ambient samples, six chimney exhaust combustion samples and a blank. These filters were previously analysed using Ultra High Resolution/MS-Orbitrap. The analysis performed during this TNA was very helpful in confirming the identity of many of the species suggested by the Orbitrap technique.

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¹ Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

² UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

³ UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.

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Trans-National Access (TNA) Scientific Report

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Name of the PI: Elena Gomez Alvarez

Calibration center's name and location: OCTAG CC-TROPOS

Campaign name and period: Detailed molecular characterization of organic aerosols from Domestic Solid Fuel (DSF) burning

Introduction and Motivation

Field measurement campaigns were conducted in three rural towns (Killarney, Enniscorthy and Birr) in Ireland where domestic solid fuel (DSF) is the preferential choice for domestic space heating. The field campaigns took place for two months during the period 2014-2016 to assess the contribution of burning to ambient levels of air pollution during winter months. During these campaigns, PM_{2.5} was collected onto filters every six hours. A series of combustion experiments was also carried out to obtain "reference" filter samples (fingerprints of emissions) of Particulate Matter (PM) generated by the different solid fuels (wood, peat, turf, coal and smokeless coal) used in these towns. These samples were previously analysed by direct infusion-nanoESI high resolution mass spectrometry (Orbitrap, University of Cambridge) in order to characterise the chemical composition and assess the impact of DSF burning on the Organic Carbon(OC) fraction of PM_{2.5} in ambient samples. Further chemical analysis, using complementary hyphenated analytical techniques was required to identify (and if possible, quantify) the key combustion markers.

Scientific Objectives

- 1) Identify and quantify (with available standards) chemical components present in PM_{2.5} in our DSF field samples (chimney and ambient) that can help to establish the influence of DSF burning to the OC of PM_{2.5}.
- 2) Identify and quantify known and ideally new combustion markers for the different fuel types to support to differentiate the contribution of the different DSF to ambient levels of PM.
- 3) Establish fingerprints of individual DSF through the use of certain molecular species that can help the source apportionment ambient emissions.
- 4) Obtain as much information as possible about the chemical composition of PM_{2.5} of ambient samples in these rural towns.
- 5) Assess the influence of DSF burning to PM_{2.5} in rural towns in Ireland that use DSF burning as preferential means for domestic heating.

Reason for choosing the calibration centre

One of the greatest strength of TROPOS is the development and improvement of analytical methods for the detection and quantification of organic compounds in the gas and particle phase.

TROPOS is the only calibration centre for the analysis of aerosols in the world. They have an excellent infrastructure and provide a suite of well characterized analytical methodologies for the analysis of most typical aerosol components.

In addition, we highly valued TROPOS' expertise in characterization of biomass burning markers. One of the most important aspects that determined this choice is the particularly well prepared technical and scientific staff. They always provide an opportunity for discussing the results, suggest new ideas for the future or alternative ideas if a particular problem is encountered in the analysis.

TROPOS has carried out thorough analytical characterization of these methodologies (calibration, determination of analytical parameters such as range of linearity, LOD, LOQ, determination of uncertainty) and use a range of standards in order to ensure that they are quantitative.

Methods and Experimental set-up

Three analytical techniques were used to analyse the samples, as described below. One week was allocated to each technique to incorporate filter extraction (1 day), chemical analysis (2 days) and initial data treatment (2 days). The data analysis was continued on return to the scientists' home institution.

- *High Performance Liquid Chromatography Electrospray Ionisation Time of Flight Mass Spectrometry (HPLC/ESI-TOFMS)*

This technique was used for analysis of methoxy- and hydroxy-substituted phenols (10 standards available) and nitro-substituted phenols (9 standards available) using methods described in the literature ([Hoffmann et al., 2007](#)). Terpene-derived SOA compounds (7 standards available) were also analysed using documented methods ([Mutzel et al., 2016](#)).

- *High Performance Anion Exchange Chromatography with Pulsed Amperometry Detection (HPAEC-PAD)*

This technique was applied to obtain qualitative and quantitative information on sugar alcohols, mono-saccharides, and mono-saccharide anhydrides (11 standards available) ([Iinuma et al., 2009](#)).

- *Curie-Point Pyrolysis Gas Chromatography Mass spectrometry (CPP-GC/MS)*

This technique allowed determination of alkanes (17 standards available), polycyclic aromatic hydrocarbons (PAHs) (19 standards available), oxygenated PAHs (3 standards available) and hopanes (9 standards available) ([Plewka et al., 2004](#)).

Preliminary results and conclusions

HPAEC-PAD

The analysis by HPLC/ESI-TOFMS enabled identification and quantification of the following species in the samples: arabitol, erytritol, galactose, galactosan, glucose, levoglucosan mannosan and mannitol.

	Levoglucosan ($\mu\text{g}\cdot\text{m}^{-3}$)
Wood	31.96 \pm 1.02
Turf	24.54 \pm 0.78
Peat	6.75 \pm 0.21
Coal	0.38 \pm 0.01
SLC	1.85 \pm 0.06
Wet Wood	95.15 \pm 3.02
Birr	5.22 \pm 0.17
Enniscorthy	4.68 \pm 0.15
Killarney	3.02 \pm 0.10

Table 1: Concentrations of levoglucosan determined in the nine samples analysed

Among the ambient samples, the highest value of levoglucosan was found for Birr (5.22 \pm 0.17 $\mu\text{g}/\text{m}^3$). This is consistent with the statistical data available from the national census in 2016 (www.cso.ie) in which higher use of wood, peat and turf were registered in Birr whereas coal was preferentially used in Enniscorthy.

The concentrations determined in the ambient samples are very high. A previous study carried out in Cork (Ireland) during winter determined an average concentration of 298 ng/m^3 for levoglucosan, with minima and maxima of 14.1-1421 ng/m^3 respectively ([Kourtchev et al., 2011](#)). The values reported here are 3 to 5 times higher, likely because the sampling was conducted in residential areas where extensive solid fuel burning activities were taking place. The topography of these locations, especially Enniscorthy, which is set in a valley) also favours the accumulation of combustion products.

HPLC/ESI-TOFMS

Nitroaromatics	Lignin-pyrolysis derived compounds
4-nitrophenol	homovanillic acid
2-methyl-4-nitrophenol	coniferyl aldehyde
nitrocatechol	syringaldehyde
2,4-dinitrophenol	vanillic acid
3-methyl-4-nitrophenol	3,5-dimethoxy-4-hydroxy acetophenone
2-methyl-4,6-dinitrophenol	syringic acid
2,6-dimethyl-4-nitrophenol	

Table 2: List of nitroaromatics and lignin pyrolysis derived compounds quantified with standards

The list of nitroaromatics and lignin pyrolysis products quantified by HPLC/ESI-TOFMS is provided in Table 2.

An important aspect that emerged from this analysis is the possibility that we may have found molecular tracers for different solid fuel types. In particular 2,4-dinitrophenol and 2,6-dimethyl-4-nitrophenol could be valid tracers for coal since they were only detected in PM samples from this fuel type. These nitrophenols were also detected in the three ambient samples. On the other hand, 3,5-dimethoxy-4-hydroxy acetophenone was detected only

in peat and turf, and is therefore a potential specific tracer of these two very similar type of solid fuels (peat is compressed turf). Further tests to confirm and validate this compound as a tracer for turf and peat should be performed.

CPP-GC/MS

Hopanes

The hopanes identified and quantified by CPP-GC/MS are listed in Table 3.

a,a,a 20R- Cholestane	17a(H)-22,29,30- Trisnorhopane	17a(H),21b(H)- 30-Norhopane
17a(H),21b(H)- Hopane	17b(H),21a(H)- Hopane	17b(H),21b(H)- Hopane
17a(H),21b(H)- 22R-Homohopane	17a(H)21b(H)- 22S-Homohopane	Hop-17(21)-ene

Table 3: List of hopanes compounds quantified with standards

The total concentration of hopanes was highest for coal samples (over 500 ng/m³), with values for turf amounting to around 300 ng/m³. The largest concentration of individual hopanes was thus mainly found in coal samples, although in some cases it was turf (such as for hop-17-(21)-ene and 17a(H),21b(H)-22-R-Homohopane). The hopanes detected in the

ambient samples also reflected the main type of solid fuel used in the town. Thus, levels of hopanes for which coal was the main contributor were higher in Enniscorthy (in line with their preferential use of coal). Conversely, for hopanes mainly produced by peat or turf, the concentration levels were higher in Birr (high usage of peat and turf). Overall, the total concentration of hopanes in the ambient locations was the highest in Birr (just over 100 ng/m³) closely followed by Enniscorthy. In Killarney, the total amount of hopanes was a factor of two smaller.

Alkanes

Very high concentrations of the 17 alkanes identified were determined in all samples analysed. The fuels that mostly contributed to these high concentrations of alkanes were coal, turf and peat. Smokeless coal (SLC) contributes only a small percentage and the contribution from wood was negligible. The ambient concentrations were also high (of up to 4 µg.m⁻³) in Enniscorthy as a clear result of the widespread use of coal. The total amount of alkanes in coal was calculated to be 25 µg/m³ which is an extremely high value.

As for hopanes, the ambient concentrations of individual alkanes were a direct reflection of the most widely used fuel type in the town. Thus, the alkanes predominantly produced by turf, such as

titriacontane reached the highest levels in Birr and those more widely emitted by coal, reached higher concentration values in Enniscorthy.

PAHs

Total levels of PAHs in ambient samples were close to $2 \mu\text{g}/\text{m}^3$ in Enniscorthy and over $1 \mu\text{g}/\text{m}^3$ in Killarney. These results are again consistent with the statistical values available from the census. These levels are three times higher than the highest value reported in Shanxi (North China) ranging between $432\text{--}700 \text{ ng m}^{-3}$ in a study carried out to investigate spatial distribution and sources of 15 PAHs in North China with passive sampling in 90 gridded sites (*Zhang et al., 2016*).

The results obtained for PAHs are graphically presented in Figure 1. The highest levels of PAHs were detected in coal and smokeless coal (SLC) samples. Given the toxic nature of these compounds, this clearly indicates that coal burning could have a large negative effect on human health.

Conclusions and future

- Very high levels of levoglucosan were detected in the three small towns, indicating a large contribution of domestic solid fuel burning to $\text{PM}_{2.5}$ at these locations.
- Levels of alkanes, hopanes and especially PAHs were also very high, indicating that these solid fuel burning particles represent a significant threat to human health.
- Some potential new molecular markers have been identified for coal and peat/turf.
- The availability of standards allowed confirmation of numerous compounds by each analytical technique used. However, the analysis also indicated that many other compounds are present in the samples. Analysis by CP/GC-MS in particular, produced very crowded chromatograms with many high intensity, clearly defined peaks - certain fatty acids and alkenes could be tentatively identified.

Outcome and future studies

The combined use of these three powerful analytical techniques has allowed us to positively identify, and in many cases quantify, numerous chemical species that were tentatively proposed following bulk analysis by Orbitrap-MS. The results will be presented at two international conferences (EGU Assembly, Vienna, April 2019 and EAC, Gothenburg, August 2019). Several journal publications are planned.

Ambient concentrations of levoglucosan, alkanes, hopanes and PAHs were very high, thus confirming that solid fuel burning is a major source of $\text{PM}_{2.5}$ in the three small towns. The very high concentrations of PAHs is of serious concern and additional samples from the field measurement campaigns will be analysed in the future. Additional future work will be directed towards identification of the many compounds in the chromatograms, with an emphasis on nitroaromatics, alkenes and fatty acids.

References

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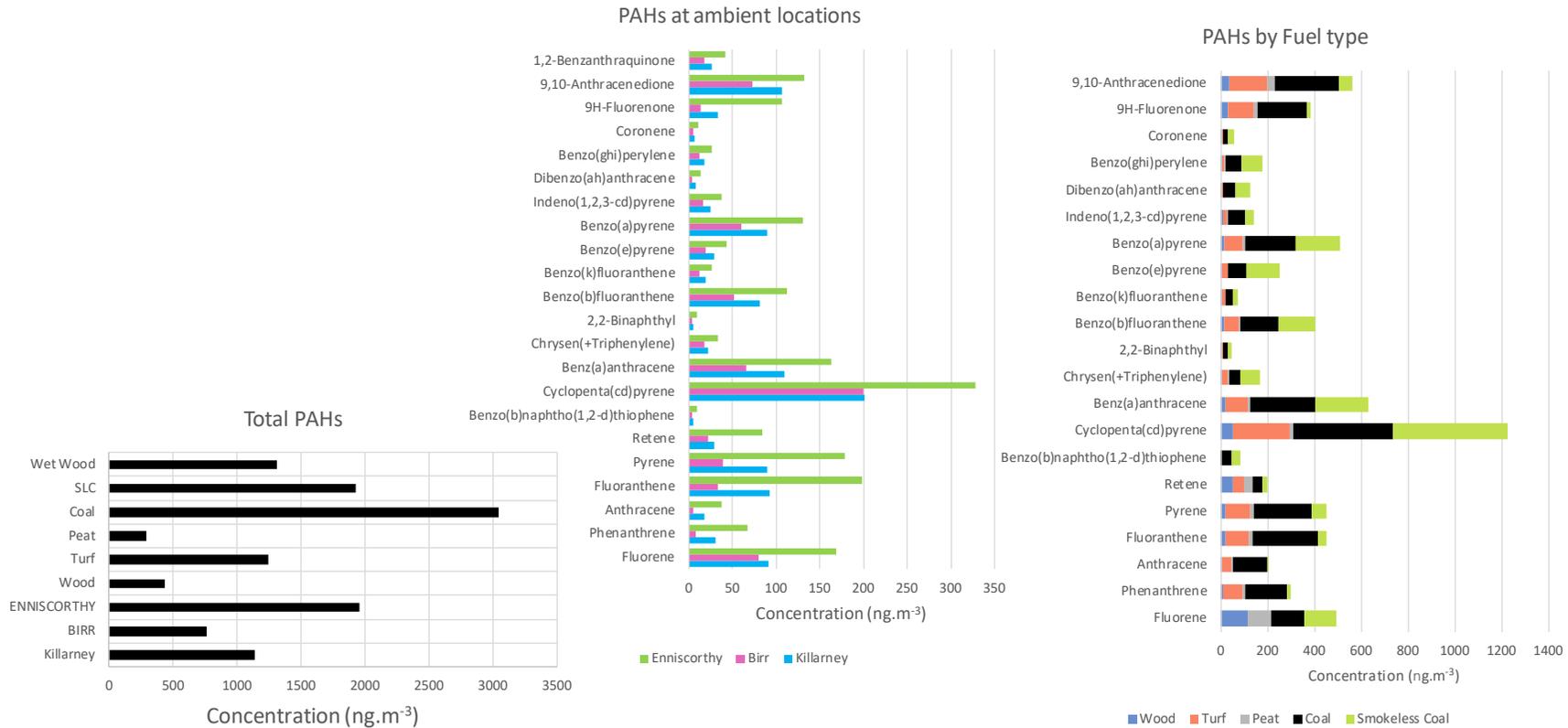


Figure 1: Concentrations of PAHs by fuel type and distribution in the three rural towns (Birr, Enniscorthy and Killarney).