Supplementary Material for: Chemical characterization and stable carbon isotopic composition of particulate Polycyclic Aromatic Hydrocarbons issued from combustion of 10 Mediterranean woods

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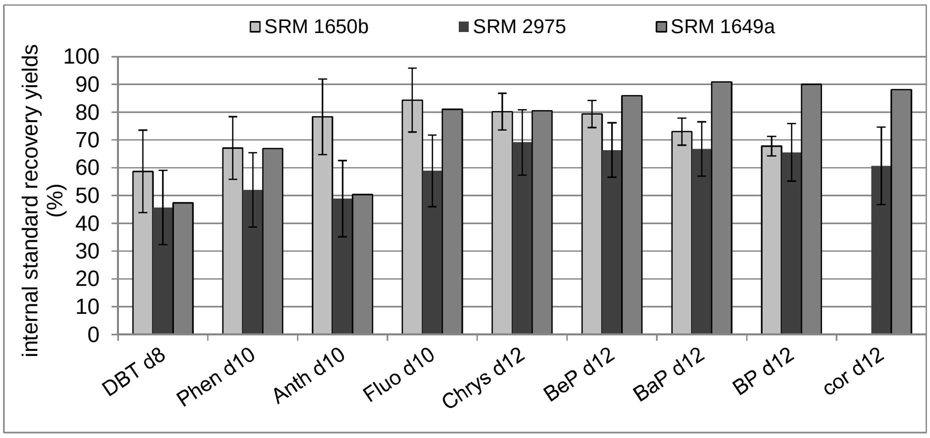
Appendix S1: Validation of analytical procedure

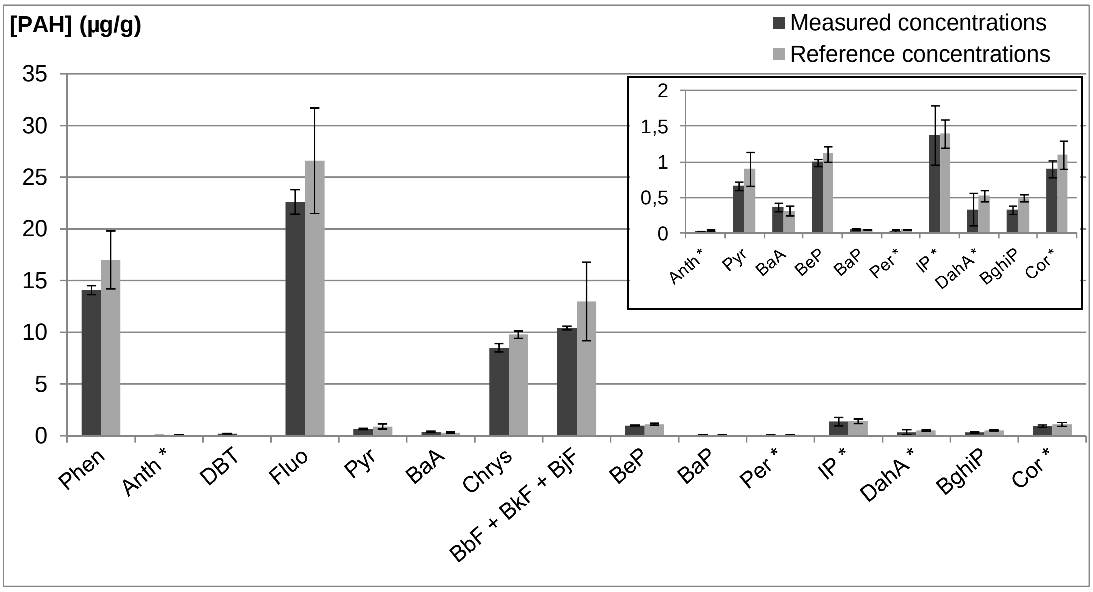
Firstly, SRM 2975 was extracted and particulate-PAHs were quantified with the GC/MS method used for the validation of HPLC fractionation (HP-5MS column). The aims of the extraction and analysis of particulate-PAHs from SRM 2975 were to confirm the good internal standard recovery yields in these analytical conditions and to validate the chromatographic analysis on ambient or atmospheric samples. Internal standard recovery yields obtained in this work allow performing a quantification of PAHs (Fig. A1): they range between (46 ± 13) % and (69 ± 12) % for SRM 2975. Uncertainties range from 10 to 15%, traducing the complexity of natural particle composition.

Figure S1 : Internal standard recovery yields for pressurised fluid extraction of PAHs from SRM 1650b, SRM 2975 and SRM 1649a



In this case of study, measured particulate-PAH concentrations (Fig. A2) are in good agreement with PAH-certified values whatever the compounds and the concentration values.

Figure S2: Concentrations of PAHs measured in particles of SRM 2975



* PAH concentrations are not certified but only given as reference concentrations by NIST.

Note that uncertainties are low enough to precisely quantify the concentrations of PAHs adsorbed on natural particles.

Therefore, in order to validate the analysis on the second chromatographic column (Rxi-17®), quantification of PAHs adsorbed on particles of SRM 1650b and SRM 1649a were performed in the same conditions of extraction and purification. The aims of these analyses were to validate the analytical procedure (SRM1650b) and the sequence of extraction (SRM 1649a) used for the particles sampled during wood combustion and extracted for the determination of PAH isotopic compositions. Internal standard recovery yields allow to perform quantitative measurements in accurate conditions (Fig. A1). They ranged between (59 ± 15) % and (84 ± 12) % for SRM 1650b and from 47 % to 91 % for SRM 1649a. Note that no uncertainties are presented for SRM 1649a because only one replicate was quantified by adding this SRM with the sequence of samples extraction in order to validate this series of extraction and purification. Error bars obtained for SRM 1650b are between 5 and 15 % traducing the complexity of natural particles, already quoted for SRM 2975. Measured concentrations of SRM 1650b are in good agreement with certified and reference values (Table A1).

Most of the measured PAH concentration values are lower than those certified or referenced. In this work, PFE extractions were performed at 100°C contrary to several tested conditions (DCM or toluene, 100°C or 200°C) for NIST certification. Nevertheless, our set of values is consistent with NIST concentrations considering reported uncertainties except for four compounds. Indeed, concentrations of acenaphtylene, fluorene, anthracene and dibenzothiophenes are equal or higher than the corresponding certified (or referenced) values. This may be explained by the fact that these compounds were extracted by NIST at only 100°C (as in our study) on the contrary to other PAHs. Different certified values were reported by NIST after 100°C and 200°C PFE traducing the high influence of extraction conditions on PAH concentration values.

Regarding the SRM 1649a, measured values are all in good agreement with the certified values reported by NIST (Table A1). The results obtained on SRM 1650b and SRM 1649a traduce the good reproducibility and repeatability of our analytical procedure. Analyses performed in accurate conditions were validated and consequently, allow the determination of the concentrations of PAHs of generated particles.

Table S1: Measured concentrations (µg/g) of PAHs extracted from SRM 1650b and SRM 1649a

PAHs	**SRM 1650b**		**SRM 1649a**	
	Measured concentrations	**Certified values**	**Measured concentrations**	**Certified values**
Acy *	*0.35 ±0.04*	*0.36 ±0.03*		
Ace *	0.12 ± 0.04	0.223 ± 0.024		
Fl *	*0.83 ±0.10*	*0.77 ±0.04*	0.13	0.23 ± 0.05
Phen	61.63 ± 6.81	69.5 ± 1.9	3.54	4.14 ± 0.37
Anth	*2.16 ±0.39*	*1.58±0.22*	0.53	0.432 ± 0.082
DBT *	*11.39 ±0.94*	*9.18 ±0.43*	0.22	0.18 ± 0.01
Fluo	45.09 ± 1.67	47.3 ± 0.8	5.83	6.45 ± 0.18
Pyr	37.15 ± 3.49	43.4 ± 1.6	4.68	5.29 ± 0.25
BghiF **	11.13 ± 1.34	10.8 ± 1	0.91	0.88 ± 0.02
BcP **	2.79 ± 0.18	2.51 ± 0.29		
BaA	6.20 ± 0.21	6.18 ± 0.3	2.13	2.208 ± 0.073
Chrys	22.67 ± 0.80	22.47 ± 2.04	3.76	4.406 ± 0.104
CcdP *	3.57 ± 0.15	0.35 ± 0.04		
BbF	6.43 ± 0.42	6.77 ± 0.84	5.32	6.45 ± 0.64
BkF	2.16 ± 0.06	2.37 ± 0.21	1.74	1.913 ± 0.031
BjF **	2.77 ± 0.05	3.24 ± 0.42	1.75	1.5 ± 0.4
BaF	0.33 ± 0.03	0.37 ± 0.029	0.55	0.409 ± 0.035
BeP	5.58 ± 0.06	6.3 ± 0.5	3.05	3.09 ± 0.19
BaP	0.76 ± 0.06	1.17 ± 0.09	2.02	2.509 ± 0.087
Per	0.06 ± 0.01	0.165 ± 0.032	0.61	0.646 ± 0.075
DBacA	0.39 ± 0.02	0.438 ± 0.043	0.42	0.2 ± 0.025
IP	2.55 ± 0.18	4.44 ± 0.28	2.53	3.18 ± 0.72
DBahA	0.32 ± 0.01	0.365 ± 0.071	0.34	0.288 ± 0.023
BghiP	3.95 ± 0.35	5.91 ± 0.18	3.88	4.01 ± 0.91
Antha			0.69	0.45 ± 0.067
DBbkF			0.76	0.724 ± 0.076
DalP *			0.07	0.0612 ± 0.007
DaeP			0.50	0.565 ± 0.06
Cor *			3.70	3.59 ± 0.58
DahP			0.11	0.047 ± 0.01

*Concentration values for these PAHs are not certified but only given as reference concentrations by NIST for these two reference materials.

**Concentrations for these PAHs are certified for SRM 1650b but only given as reference values for SRM 1649a

Italic values correspond to concentrations validated by PFE at 100°C only

Appendix S2: Quality insurance

- Extraction blanks

Therefore, PAH concentrations were determined in “extraction blank” corresponding to the application of analytical procedure of preparation applied without any particles or filters. These blank measurements traduce levels of PAHs that could interfere during the protocol of sample preparation. No PAHs were detected except acenaphtene (< 1 ng), phenanthrene (< 2.5 ng), anthracene, DBT, fluoranthene and pyrene (< 0.7 ng). These values are not significant compared to the quantities of PAHs extracted from the ambient samples (at least 10 times higher than blanks levels).

- Blank filters :

Concentrations of PAHs were determined on the blank filters collected prior to any series sampling of wood combustion. In the blanks, internal standard recovery yields are ranging between 50 and 90%, depending on the sample and the PAH. These values allow performing quantification in accurate conditions and levels of PAHs on blank filters were determined following the validated analytical protocol described in previous sections. Most of PAHs were not detected on blank filters except acenaphtylene (< 3 ng/filter), phenanthrene (< 0.5 ng/filter), fluoranthene (< 0.8 ng/filter), pyrene (< 1 ng/filter), benz(a)anthracene and chrysene (both < 0.3 ng/filter). These values were subtracted from the masses of PAHs measured on the punch, corrected with filter surface ratio.