Electronic Supplementary Material (ESI) for Analytical Methods.

SUPPORTING INFORMATION

Derivatization and analysis of levoglucosan in ambient air particulate matter by moderate temperature thermal desorption coupled with GS/MS.

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The additional material herein supplied consists of a GC-MS chromatogram (Figure S1), the mathematical relationships calculated between ambient air filter concentrations of levoglucosan and PAHs and between concentrations of levoglucosan and total carbon (Figure S2), amounts detected in ambient air filter samples (Table S1), discussion on the determinations on $PM_{2.5}$ filter samples from a semirural background area (section 3.4 extension), Limits of detection and quantification for the analysed compounds (Table S2) and corresponding sampling volumes for the considered sections of filters.

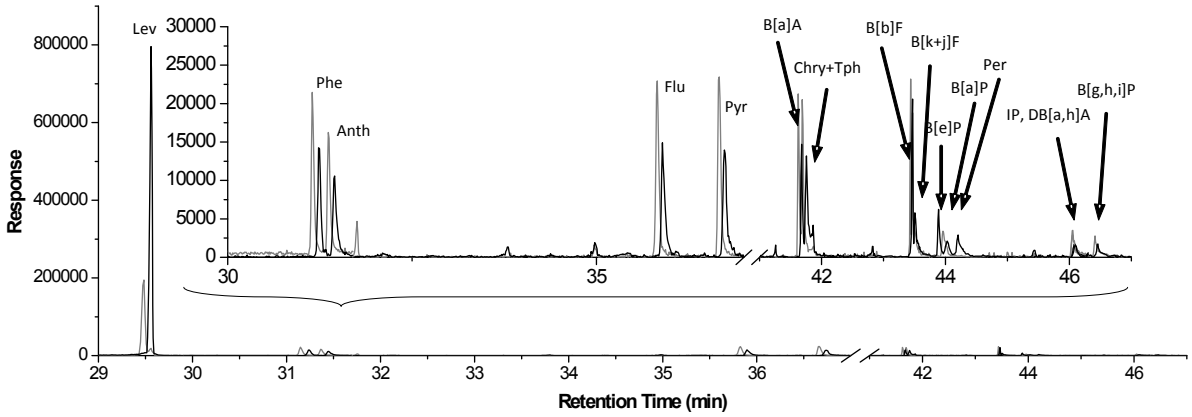

Figure S1 – GC-MS chromatogram SIM mode (black line: target compound peaks; grey line: deuterated compound peaks).

3.4 Determinations on $PM_{2.5}$ filter samples from a semirural background area

[extension of section 3.4]

Levoglucosan concentrations were comprised between 85 and 719 ng/m^3 (10 – 154 ng injected), while those of B[a]P were comprised between 139 and 1401 pg/m^3 (19 – 300 pg injected). These concentrations are in line with previously reported values for this sampling site[17,19]. Figure S2 reports the trends for levoglucosan and the sum of the heavier PAHs with EC, OC and the minimum temperature at the time of the sampling. The organic compound concentrations show comparable trends, opposite to the temperature trend registered for those days. As a consequence, good correlations were found between levoglucosan and the heavier PAH concentrations (linear correlation $R^2 = 0.897$ - Figure S2) as well as between levoglucosan and TC (power correlation $R^2 = 0.830$ - Figure S3).

These observations could be easily explained by the start up of residential heating in the cold days at the time of the sampling. The studied site is a rural area where biomass burning is largely used for heating, constituting a significant source of PM emissions. Previous studies[17] indicated that the most important carbonaceous aerosol source in Ispra is biomass burning, representing 41% of the total mass of carbon emitted during the whole year, with highest contribution in the coldest months. Moreover, PAH emissions were found to be related to wood combustion: PAHs peak concentrations are concomitant with the higher levoglucosan emissions during the cold period (November - January), when the contribution of wood combustion is of the same order as that of traffic emissions[19].

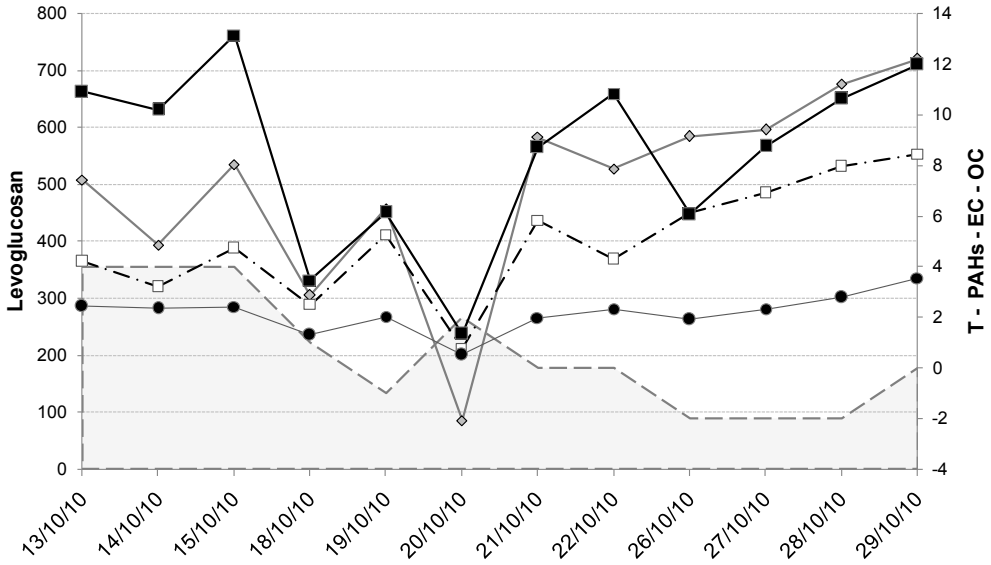

Figure S2. Trends of levoglucosan (—◇—), of the sum of PAHs from B[b]F to B[ghi]P (- -□- -), of elemental carbon (—●—), organic carbon (—■—) and of the minimum temperature (▭) registered during the sampling period.

It is noted that the 20th of October 2010 was a peculiar day, with suddenly low concentrations registered for all the pollutants. This day was characterized by a drop of the relative humidity and slight increase in the temperature due to the north Föhn wind, which contributed significantly to the abatement of PM concentrations. This represented just a dilution effect and not a qualitative change in the emission ratios in the area, as was shown in a previous study[52].

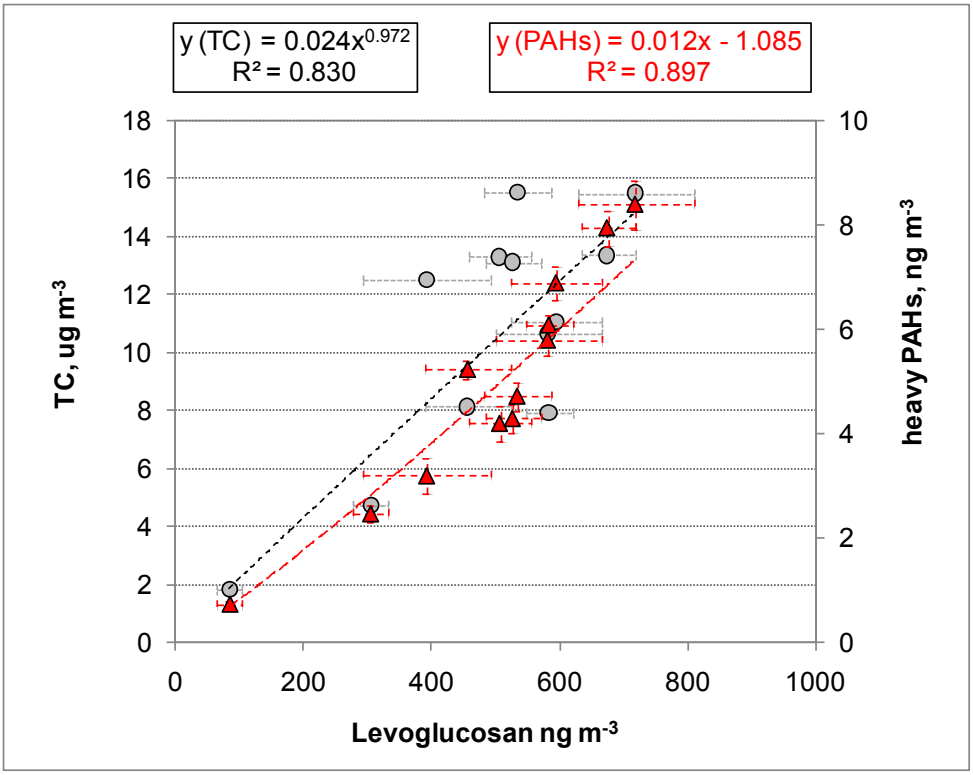

Figure S3 – Relationships between levoglucosan and PAH (from B[b]F to B[ghi]P, which concentrations in air are mainly in the particulate phase) concentrations (▲) and between levoglucosan and TC concentrations (●).

Table S1 – Average amounts of levoglucosan (ng) and PAHs (pg) found in ambient air filters (F) at Ispra site with standard deviation (SD) and relative standard deviation (RSD).

		Levo	Phe	Anth	Flu	Pyr	B[a]A	Chry +Tph	B[k+j] F	B[b]F	B[e]P	B[a]P	Per	IP	DB[ah]A	B[ghi]P
F 1	Mean	109	252	<DL	104	94	50	66	269	82	113	143	23	118	26	128
	SD	11	33		16	17	9	9	65	14	23	20	4	12	3	9
	RSD	10	13		15	18	18	14	24	16	20	14	17	10	13	7
F2	Mean	10	188	<DL	89	67	27	23	38	<DL	<DL	17	<DL	16	<DL	13
	SD	3	34		31	20	5	3	6			3		5		3
	RSD	26	18		11	12	18	15	15			18		30		23
F 3	Mean	114	225	46	138	126	54	68	300	87	122	140	24	198	47	96
	SD	12	25	4	4	5	13	9	30	17	36	21	1	19	7	1
	RSD	10	11	8	3	4	24	14	10	20	30	15	5	10	14	1
F 4	Mean	65	272	55	108	112	51	74	142	70	83	96	16	50	22	52
	SD	6	60	15	7	10	9	8	14	18	20	15	1	1	1	2
	RSD	9	22	27	7	9	18	11	9	26	24	16	4	3	7	3
F 5	Mean	98	336	<DL	114	118	54	79	379	107	152	173	33	130	25	125
	SD	14	54		13	5	12	7	5	7	8	21	5	27	4	5
	RSD	15	16		11	4	23	9	1	6	5	12	15	21	14	4
F 6	Mean	18	282	<DL	89	76	30	31	54	<DL	24	30	<DL	26	<DL	27
	SD	4	57		14	12	3	0	12		2	4		4		2
	RSD	24	20		16	16	11	2	21		9	13		15		6
F 7	Mean	125	168	<DL	114	127	70	106	274	119	177	207	32	207	42	186
	SD	18	45		16	24	14	15	49	15	3	5	3	37	11	17
	RSD	14	27		14	19	20	14	18	12	2	2	9	18	25	9
F 8	Mean	113	195	50	107	105	54	75	295	75	121	157	20	129	30	114
	SD	9	9	7	11	12	3	11	42	12	32	27	3	6	3	3
	RSD	8	5	14	10	12	5	14	14	16	26	17	17	4	11	2
F 9	Mean	125	174	49	126	124	76	102	364	99	196	236	36	178	36	162
	SD	8	0	6	10	12	4	4	1	13	30	9	2	13	5	22
	RSD	6	19	11	8	10	5	4	0	13	15	4	6	8	14	13
F 10	Mean	127	165	<DL	138	141	90	131	466	116	228	216	39	189	41	183
	SD	15	6		15	23	10	12	42	19	30	15	5	25	1	22
	RSD	12	4		11	16	11	9	9	16	13	7	12	13	1	12
F 11	Mean	145	148	<DL	129	124	107	142	435	140	269	265	43	246	55	251
	SD	9	25		15	10	20	19	41	20	44	11	7	27	11	21
	RSD	6	17		12	8	19	14	9	14	16	4	17	11	20	8
F 12	Mean	154	173	47	138	137	98	150	509	103	263	330	52	249	56	240
	SD	19	1	2	23	28	9	2	76	11	54	29	5	29	10	32
	RSD	13	0	5	17	20	9	1	15	10	20	9	10	12	18	14

Table S2 - Limits of detection and quantification and linearity of the calibration curves for the investigated compounds. Limits of detections and quantification correspond to 3 and 10 times the UCL of blank signals, respectively.

	LOD (pg)	LOQ (pg)	R^2
Levo	10000	34000	0.988
Phe	46	154	0.999
Anth	76	252	0.999
Flu	55	184	0.999
Pyr	24	79	0.999
B[a]A	20	66	0.999
Chry+Tph	28	93	0.992
B[k+j]F	40	132	0.985
B[b]F	19	62	0.997
B[e]P	5	17	0.999
B[a]P	17	56	0.998
Per	10	33	0.999
IP	10	32	0.988
DB[ah]A	6	20	0.985
B[ghi]P	9	31	0.990

Table S3 - Corresonding sampling volume for the analyzed sections of filters

Filter section ~ diameter, mm	weight, mg	Sampled volume, m^3
39	101.91 ± 0.15	50
12.9	11.31 ± 0.15	5.47
5.45	2.272 ± 0.035	1.114
2.15	0.377 ± 0.025	0.194