Characterisation of Hydrocarbons in Atmospheric Aerosols from Different European Sites

C. A. Alves, A. Vicente, M. Evtyugina, C. A. Pio, A. Hoffer, G. Kiss, S. Decesari, R. Hillamo, and E. Swietlicki

Abstract—The concentrations of aliphatic and polycyclic aromatic hydrocarbons (PAH) were determined in atmospheric aerosol samples collected at a rural site in Hungary (K-puszta, summer 2008), a boreal forest (Hyytiälä, April 2007) and a polluted rural area in Italy (San Pietro Capofiume, Po Valley, April 2008). A clear distinction between "clean" and "polluted" periods was observed. Concentrations obtained for Hyytiälä are significantly lower than those for the other two sites. Source reconciliation was performed using diagnostic parameters, such as the carbon preference index and ratios between PAH. The presence of an unresolved complex mixture of hydrocarbons, especially for the Finnish and Italian samples, is indicative of petrogenic inputs. In K-puszta, the aliphatic hydrocarbons are dominated by leaf wax *n*-alkanes. The long range transport of anthropogenic pollution contributed to the Finnish aerosol. Industrial activities and vehicular emissions represent major sources in San Pietro Capofiume. PAH in K-puszta consist of both pyrogenic and petrogenic compounds.

Keywords—Particulate matter, *n*-alkanes, PAH, BaPE, rural sites, source reconciliation.

I. INTRODUCTION

AEROSOL particles are ubiquitous, but a highly variable component, in the troposphere. It is now recognised that atmospheric aerosols play a far more complex role in the climate system than previously thought [1]. Exposure to fine-particulate air pollution has also been associated with increased morbidity and mortality [2].

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Although organic compounds are generally the most important constituents of atmospheric aerosols, their inventory is far from being comprehensive. Hydrocarbons constitute an important group among them. Natural aliphatic and aromatic hydrocarbons are produced by continental and marine plants, with typical components or distributions revealing their origin. Anthropogenic hydrocarbons are widely spread, deriving from the combustion of fuels, like crude or refined petroleum derivatives, coal, wood, etc. Aliphatic hydrocarbons are present in all atmospheric aerosol types regardless of whether they are from urban, rural or marine environments [3]. In spite of representing a small fraction of the total organic matter in aerosols, they are regarded as good candidates for source apportionment studies [4]. Polycyclic aromatic hydrocarbons (PAH) derive almost exclusively from incomplete combustion processes, and are also useful organic indicator species, especially for vehicular emissions [5-7]. Some of them are among the strongest recognised carcinogens [8-11]. Atmospheric PAH are partitioned between the gaseous and the particulate phases, but the carcinogenic 5- and 6-ring constituents are chiefly linked to particles [12,13]. The European Directive 2008/50/EC stipulates several air pollutants to be taken into consideration in the assessment and management of ambient air quality, defining a target concentration for benzo(a)pyrene, which is used as a marker substance for PAH generally.

This study was performed within the European Integrated Project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI), which aims to reduce the current uncertainty of the impact of aerosol particles on climate and to improve our ability to accurately apportion the European aerosol to its various sources. Accurate aerosol source apportionment is a pre-requisite for cost-efficient abatement strategies to mitigate the negative effects of atmospheric particulate matter on human health and to model aerosol climate forcing. The main objectives are to characterise and trace the origin of aliphatic and aromatic hydrocarbons in atmospheric aerosol particles from three non-urban sites throughout Europe and to reveal the relative share of biogenic *versus* anthropogenic sources for these compounds.

II. EXPERIMENTAL

A. Sampling Details

One of the sampling sites was located in Hyytiälä (61°51' N, 24°17' E, 181 m above sea level), at the Finnish Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II). The terrain around the station is representative of the boreal coniferous forest. The 40-year old Scots pine *(Pinus sylvestris L.)* dominated stand is homogenous for about 200 m in all directions, extending to the north for about 1.2 km. The largest city near the station is Tampere, approximately 60 km S-SW of the measurement site. The terrain is subject to modest height variation. The annual mean temperature is 3ºC and precipitation is 700 mm. The daily sampling program, in 2007, occurred from April 5 to 15 under "clean" atmospheric conditions. In the period 15-17 of April, the sampling site was under the influence of long range transport of atmospheric pollution. High volume equipment running at 850 L min^{-1} was used to collect particles with aerodynamic diameter < 2.5 μm (PM$_{2.5}$).

The Italian sampling site was located in San Pietro Capofiume (44°39'17'' N, 11°37'25''E, 11 m above sea level), in a flat rural area in the north-eastern part of the Po Valley, northern Italy, between the cities of Bologna and Ferrara (roughly 40 km from both cities). The Po Valley has an area of approximately 60,000 km^2 with a high population density (roughly 40% of the Italian population live here), characterised by intensive industrial, trading and agricultural activities. High levels of pollution are therefore reported for this region. According to EMEP (European Monitoring and Evaluation Programme under the Convention on Long-range Transboundary Air Pollution), San Pietro Capofiume is a background urban site. The sampling campaign took place between April 8th and 14th, 2008. A high volume (300 L min^{-1}) dichotomous sampler was employed to collect nocturnal and diurnal samples. The submicron fraction (PM$_1$, particles with aerodynamic diameter <1 μm) was used for the organic characterisation.

Aerosols from K-puszta (46°58'N, 19°35'E) were collected at the station run by the Hungarian Meteorological Service and the University of Pannonia, as part of the EMEP network. The site is in the middle of the Hungarian Plain, 60 km southeast from Budapest (1.9 million inhabitants). The largest nearby town (Kecskemét, 110,000 inhabitants) is located 15 km southeast from the station. The sampling site is surrounded by forests (62% coniferous trees) interspersed with clearings. Aerosol was sampled at a flow rate of 32 m^3 h^{-1} on quartz fibre filters (Whatman QM-A) of 14 cm diameter (exposed area). The sampler was located at 7 m above ground and was configured to remove particles larger than 2.5 μm. Daily sampling was carried out from May 5th to June 4th and from July 1st and July 12th, in 2008.

Additional particulate, air quality and meteorological measurements carried out by different EUCAARI teams enabled classifying the sampling periods as "clean" or "polluted".

B. Analytical Methodologies

After sampling, the filters were split into several parts and distributed to other EUCAARI partners for posterior analysis of organic and elemental carbon, ^{14}C by accelerator mass spectrometry, elemental composition by particle induced x-ray emission and spectral fingerprints by proton nuclear magnetic resonance. The portion devoted to organic speciation represented 20-30% of the total filter area. In some cases, parts of the quartz fibre filters from consecutive days were combined to meet the limits of detection from speciated organic compounds. Pieces of the filters were extracted by refluxing dichloromethane for 24 h. The total organic extract was vacuum concentrated and dried under a gentle ultra pure nitrogen stream. Aliphatic compounds and PAH were separated from this total extract by flash chromatography with silica gel (230-400 mesh, 60 Å Merck Grade 9385) using, respectively, 15 mL of *n*-hexane and 15 mL of toluene–*n*-hexane (5.6:9.4) (Merck SupraSolv®). After each elution, the different fractions were vacuum concentrated (25-30ºC under reduced pressure) and evaporated under a nitrogen stream. Hydrocarbons were analysed by gas chromatography–mass spectrometry (GC-MS). The quadrupolar analytical equipment was from Hewlett-Packard (GC 9890 and MS 7883), operating with a TRB-5MS 60 m × 0.25 mm × 0.25 μm column. Data were acquired in the electron impact (EI) mode (70 eV). The oven temperature program was as follows: 60ºC (1 min); 60-150ºC (10ºC min^{-1}), 150-290ºC (5ºC min^{-1}), 290ºC (30 min) and using helium as carrier gas at 1.2 mL min^{-1}. Calibration for GC-MS analysis was based on a total of about 70 standards (Sigma-Aldrich, TSI and Chiron) in five different concentration levels with relative response factors determined individually to the majority of compounds. For those with no authentic standards available, relative response factors were calculated as an average of the relative response factors from the overall homologous series or from compounds of similar chemical structure and retention time. Aliphatic standards and samples were both co-injected with chlorohexadecane (Merck 802339) as an internal standard. In the case of PAHs, a mixture of deuterated internal standards was used: 1,4-dichlorobenzene-D4, naphtalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12 (Sigma-Aldrich). The aliphatic fraction was analysed in the scan mode, whereas aromatic compounds were acquired in both the selected ion monitoring (SIM) and scan modes. Compound identification was based on comparison of the resulting mass spectra with the Wiley spectral library, co-injection with authentic standards and analysis of fragmentation patterns. A detailed description of the analytical methodology, including recovery efficiency tests for several compounds, can be found in Alves and Pio [14] and Oliveira *et al.* [15]. This methodology was previously tested in our laboratory [16, 17] and elsewhere [18].

III. Results and Discussion

The aliphatic fraction of particulate matter comprised *n*-alkanes (Fig. 1), *n*-alkenes with a carbon chain length between C_{13} and C_{23}, the unresolved complex mixture of cyclic branched and unsaturated hydrocarbons and acyclic isoprenoids (pristane and phytane). *n*-Alkanes represented the most abundant group among the identified compounds. In general, the *n*-alkanes from C_{19} to C_{32} from fossil fuel are dominated by the C_{20} and C_{25} homologues for gasoline vehicles and by the C_{20} for heavy [19] and medium [20] duty diesel trucks. Unburned heating oil is another source for *n*-alkanes with carbon number between 14 and 25, presenting maximum concentrations for the C_{19}-C_{25} homologues [21]. While the *n*-alkanes with a carbon number around C_{20} mostly derive from unburned fuel [22], the homologues around C_{25} are largely originated from lubricating oil [23]. *n*-Alkanes from these anthropogenic sources show no significant odd or even carbon number predominance. Other important sources of atmospheric *n*-alkanes are higher plant waxes, which are released due to abrasion from leaves [24] or as products of incomplete biomass combustion [25]. These inputs contribute with homologues in the C_{24}-C_{35} range, maximising at C_{27}, C_{29} or C_{31}. The carbon preference index (CPI), which is defined as the sum of the concentrations of the odd carbon number *n*-alkanes divided by the sum of the concentrations of the even carbon number *n*-alkanes, can be used as a qualitative tool to assess the influence of biogenic and anthropogenic inputs [3].
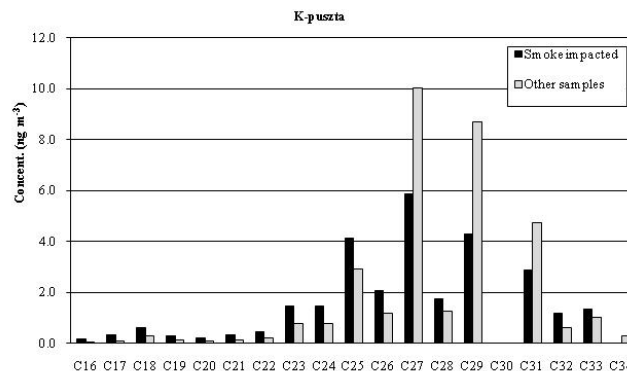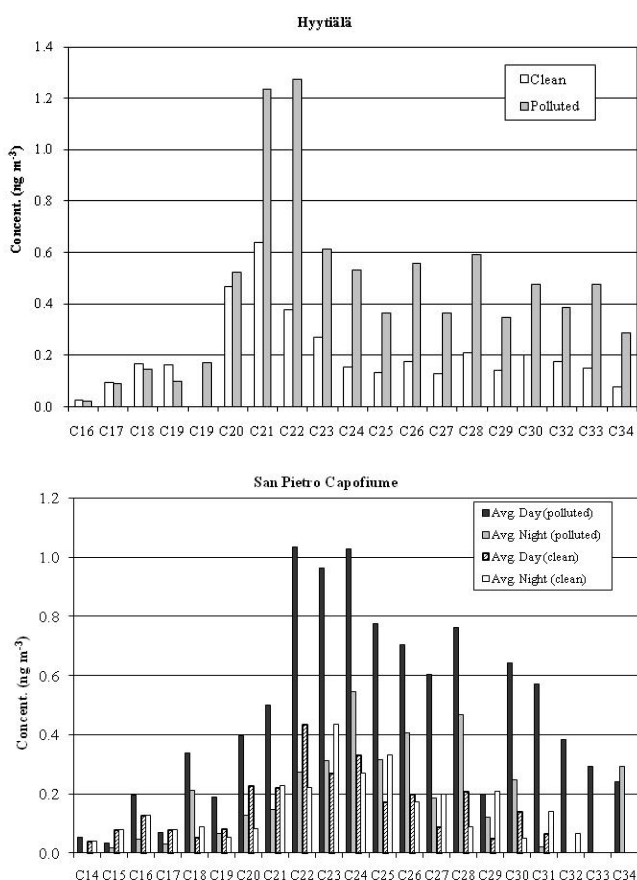

Fig. 1 *n*-Alkanes distribution in aerosols from the 3 EUCAARI sites

The CPI typically ranges from 1.1 to 2.0 in urban environments, while a CPI higher than 2.0 is characteristic of rural environments, where the biogenic influence is more important.

Total concentrations of *n*-alkanes in the Finnish samples (3.6-8.2 ng m^{-3}) were of the same order as those previously reported for the same site, which in turn were 10 to 100 times lower than in particulate matter samples collected in the city of Helsinki in July 2002 with the same sampler [26]. The CPI values in our study (Table I) are lower than values for other forest environments [32, 33]. According to Anttila *et al.* [26], this may be partially due to the weak emission of plant waxes at the low temperatures prevailing in boreal forests. As observed for *n*-alkanes, the envelope of unresolved hydrocarbons was twice higher for the polluted episode than the corresponding hump for the clean period. Ratios between the unresolved and the chromatographically resolved aliphatics (U/R) much higher than 1 and the FLEXTRA back trajectories (Fig. 2) highlight the impact in forest aerosol of long-range transport of anthropogenic pollution from western and central Europe.
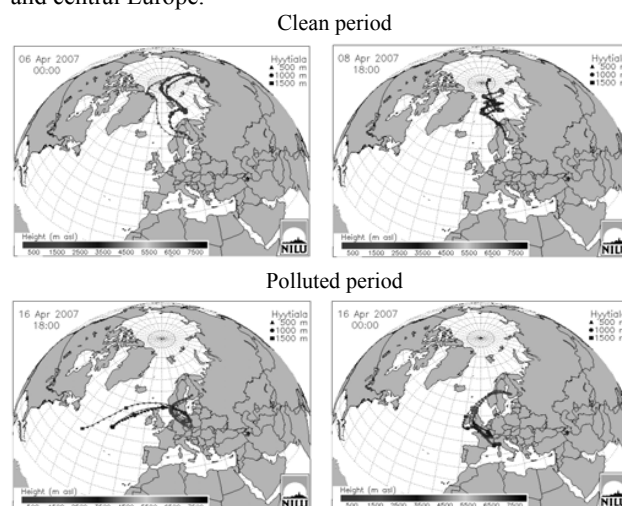
Clean period

Polluted period

Fig. 2 Air mass back trajectories arriving at Hyytiälä calculated by FLEXTRA model from the Norwegian Institute of Air Research (http://www.nilu.no/trajectories/index.cfm). Clean period – Artic air masses; Polluted period – air masses from Western/Central Europe

Besides the CPI and the U/R ratios, the carbon number of the most abundant n-alkanes (C_{max}) and a low biogenic contribution of wax n-alkanes from plants (WNA=C_n-[C_{n+1}+C_{n-1})/2]) are indicative of a petrogenic signature.

Total levels of n-alkanes in $PM_{2.5}$ from K-puszta varied between 7.3 and 83 ng m^{-3}. The predominant n-alkane congeners (C_{27} and C_{29}) reflect a significant incorporation of higher plant waxes. This biogenic origin is also pointed out by an average CPI of 6.7, which is in the range of values reported for other rural areas (Table I).

In San Pietro Capofiume, the total n-alkane levels ranged from 2.6 to 18 ng m^{-3}, showing a diurnal pattern with highest values in the daytime and lowest during the night. This may be due to the reduction in the traffic flow rate at night and unfavorable dispersion conditions. A substantial decrease in global concentrations during the "clean" period was observed. The diagnostic ratios (Table I) indicate a strong influence of anthropogenic emissions.

concentrations obtained during the "clean" periods in Hyytiälä and San Pietro Capofiume are significantly lower than during the "polluted" events (Table II). The atmospheric concentrations of PAH depend greatly on the meteorological conditions under which emissions are released. The gas/particle partitioning is influenced by the ambient temperature, whereas photo-degradation is affected by solar radiation. PAH, such as fluoranthene and benzo(a)anthracene, decay rapidly upon exposure to sunlight [37]. This might partly explain the higher nighttime concentrations observed for some PAH in San Pietro Capofiume. It should be stated that, during the campaign, the polluted conditions were due to emission sources within the Po Valley. Possible sources of particulates in an area of ca. 70-100 km of radius around San Pietro Capofiume are the intense traffic, power plants and other industries. Other potential source includes the maritime traffic in the Adriatic Sea [34].

TABLE I
COMPARISON OF DIAGNOSTIC RATIOS FOR THE AEROSOL ALIPHATIC FRACTION FROM DIFFERENT ENVIRONMENTS

Location	Period	Particles	C_{max}	CPI	U/R	%WNA	Ref.
Hyytiälä, Finland	Apr 2007	$PM_{2.5}$	C_{22}, C_{23}	1.18±0.029	8.98±5.36	14.5±3.64	This study
K-puszta, Hungary	Spring/Summer 2008	$PM_{2.5}$	C_{27}, C_{29}	6.65±2.23	1.40±0.72	66.3±21.0	This study
San Pietro Capofiume, Italy	Apr 2008	PM_1	C_{22}, C_{24}	0.54±0.41	9.41±4.79	27.5±12.3	This study
Terceira island, Azores, Portugal	Jul 2002-Sept 2003 (Summer-Winter averages)	$PM_{2.5}$	C_{27}, C_{29}, C_{31}	5.1-2.5	1.0-1.7	57.8-42.8	[15]
Aveiro, coastal rural, Portugal	Jul 2002-Sept 2003 (Summer-Winter averages)	$PM_{2.5}$	C_{22}, C_{27}, C_{29}, C_{31}	2.5-1.5	2.9-7.8	44.8-22.5	[15]
Puy de Dôme, rural highlands, France	Jul 2002-Sept 2003 (Summer-Winter averages)	PM_{10}	C_{21}, C_{27}, C_{29}, C_{31}	5.5-2.2	1.2-2.1	66.2-36.9	[15]
Schauinsland, forested highlands, Germany	Jul 2002-Sept 2003 (Summer-Winter averages)	PM_{10}	C_{24}, C_{25}, C_{27}, C_{29}, C_{31}	8.2-2.1	0.9-2.4	71.5-31.0	[15]
Sonnblick, mountain, Austria	Jul 2002-Sept 2003 (Summer-Winter averages)	$PM_{2.5}$	C_{27}, C_{29}, C_{31}	3.2-1.5	5.0-3.8	46.8-18.8	[15]
Athens, roadside, Greece	Aug 2003	$PM_{2.5}$	C_{27}	1.84	25.25	25.15	[27]
Nanjing, urban, China	2001-2002	$PM_{2.5}$	C_{23}, C_{25}, C_{27}, C_{29}, C_{31}	1.29-1.54		10.8-15.6	[28]
Vienna, urban, Austria	Jan-Dec 2004	PM_{10}	C_{27}, C_{29}, C_{31}	1.23		13.1	[29]
Chapinería, rural, Spain	Apr 2004 – Apr 2005	$PM_{2.5}$	C_{25}	1.3		14	[30]
Beijing, China	Aug 2001 – Jul 2002	$PM_{2.5}$	C_{25}	1.6		20.0	[31]

A series of even carbon numbered n-alkanoic acid methyl esters ranging from C_{14} to C_{24} has been detected with global concentrations up to 16 ng m^{-3}, but only in samples from San Pietro Capofiume. Information concerning concentrations and emission sources or formation processes of these particulate constituents is rather sparse. Fine et $al.$ [35] have found methyl alkanoates from C_{17} to C_{27} in emissions from wood combustion. Schenelle-Kreis et $al.$ [36] found n-alkanoic acid methyl esters in the $PM_{2.5}$ fraction of Augsburg, Germany. They attributed the presence of these constituents to variable influences of wood and coal combustion.

PAH concentrations measured at the three sites are lower than those reported for different urban environments throughout Europe [37, 38, and references therein]. A Hungarian sample strongly impacted by biomass burning deserves attention, in view of the fact that its PAH concentrations were 20 to 50-fold higher than levels measured for the other samples. For the most part of PAH,

High pressure conditions and episodes of pollutant accumulation were not registered at the regional scale. Pollution from long-range transport from central and Eastern Europe to the Po Valley occurred in many days, but associated with low (background) concentrations. The so-called "polluted" cases were mainly determined by shallow stratification of the atmosphere due to nocturnal cooling at the surface level.

To further assess the different sources of PAH present in the aerosol samples, a comparison was made among diagnostic ratios (Table III). The IcdP/(BghiP+IcdP) and Flu/(Flu+Pyr) ratios for the three sites fell in the range of PAH emitted by diesel vehicles. However, the Flu/(Flu+Pyr) ratio suggests a predominant input from biomass burning in Hyytiälä during the "clean" period. The BghiP/BeP is indicator for traffic, with higher ratios suggesting higher vehicular emissions. This ratio was far below the

TABLE II
PAH Concentrations (pg m^{-3})

| | Hyytiälä | | K-puszta | | San Pietro Capofiume | | | |
	Clean	Polluted	Smoke impacted	Other samples	Polluted/Day	Polluted/Night	Clean/Day	Clean/Night
Fluorene			1.4	0.806				3.28
Phenanthrene	2.16	2.86	98.1	6.94				1.34
Anthracene	2.51	1.53	13.7	3.86			0.707	
Fluoranthene	144	306	2637	192	14.7	17.7		
Pyrene	121	243	1767	208	9.51			32.9
Benzo(a)anthracene			1032	29.1	32.7	43.6	5.12	10.6
Chrysene	28.8	86.9	2264	86	80.2	124	15.4	37.0
Terphenyl			66.4					27.1
Retene	7.41	3.57	4.19	2.14	7.57	2.09	0.795	0.981
Benzo(b)fluoranthene	13.5	52.6	7005	87.2	41.9	89.0		50.2
Benzo(k)fluoranthene	13.5	47.8	2803	60.2	72.7	92.7	207	27.6
Benzo(a)pyrene	2.75	4.78		40.2	49.5	53.4	5.64	14.3
Benzo(e)pyrene	14.7	58.0	3250	78.7	83.7	107	17.5	37.8
Perylene			159	8.75	3.77	8.77		4.57
Indeno(1,2,3-cd)pyrene		55.9	3698	52.3	39.6			274
Benzo(ghi)perylene		51.1	2104	58.1	30.4			
Dibenzo(a,h)anthracene		1.64	1344	0.397	5.64	1.52	0.602	

Note: Cells in white represent non-detected PAH or concentrations below the detection limit.

TABLE III
Concentration Ratios between PAH

| | Hyytiälä | | San Pietro Capofiume | | | | K-puszta | Source/Interpretation |
	Clean	Polluted	Polluted Day	Polluted Night	Clean Day	Clean Night		
RATIOS IcdP/(BghiP+IcdP)	-	0.521	0.566	-	-	-	0.496	~ 0.2 gasoline emissions [3]; 0.35-0.70 diesel cars [28]; 0.51 coal burning [39]; 0.44 biomass burning [40]
BeP/(BeP+BaP)	0.842	0.924	0.651	0.706	0.757	0.725	0.712	0.34 wood; 0.6-0.8 vehicle emissions [3]
Flu/(Flu+Pyr)	0.543	0.557	0.607	-	-	-	0.569	0.26 biomass burning [40]; ~ 0.40 gasoline cars [3]; 0.6-0.70 diesel engines [28]; > 0.50 coal burning [41]
BghiP/BeP	-	0.885	0.360	-	-	-	0.965	2.02 vehicle emissions; 0.80 non-traffic sources [42]
BghiP/BaP	-	11.7	0.614	-	-	-	2.31	0.02–0.06 industrial furnaces; 1.2-2.2 diesel cars; 2.5-3.3 gasoline cars [3];
BFs/BghiP	-	1.96	-	-	-	-	2.16	0.33 gasoline cars; 1.6 diesel cars; 2.18 wood; >4 industrial processes [3]

IcdP – Indeno(1,2,3-cd)pyrene; BghiP – Benzo(ghi)perylene; BeP – Benzo(e)pyrene; BaP – Benzo(a)pyrene; Flu – Fluoranthene; Pyr – Pyrene; BFs = Benzofluoranthenes

characteristic value for traffic emission, but more close to that of non-traffic sources. The BeP/(BeP+BaP) ratio is affected by the strong reactivity in the atmosphere since BaP is easily decomposed by light and oxidants. Most of the fresh exhausts have similar contents of BeP and BaP, thus the increasing of the ratio can be regarded as an index of the aging of particles. This diagnosis ratio suggests that vehicular emissions are the major source of the particulate PAH in San Pietro Capofiume and K-puszta, while a more aged aerosol was collected in Hyytiälä. The high Bghi/BaP ratio obtained for the boreal forest reflects, once again, some atmospheric processing of aerosol, suggesting the occurrence of decomposition of BaP during air mass transport. The average Bghi/BaP ratio for the Hungarian samples is in the range of values reported for vehicular emissions. The low values found for San Pietro Capofiume in the polluted period reveal a mixed influence associated with both traffic and industrial processes. The BFs/BghiP ratios suggest again impact of biomass burning in K-puszta and a mixed input from both wood combustion and vehicular emissions in Hyytiälä.

Benzo(a)pyrene is considered a classical carcinogen and one of the most powerful mutagens. The benzo(a)pyrene equivalent concentration (BaPE) has been introduced instead of the sole benzo(a)pyrene since the later is easily decomposed in reactive air. It tries to parameterise the health risk for humans related to ambient PAH exposure and is calculated by adding weighted concentrations of each carcinogenic congener. According to the European Union air quality standards, the maximum permissible risk level is 1 ng m^{-3} (annual average). The average BaPE concentrations obtained for every EUCAARI sites (Fig. 3) are much lower than those in urban areas around the world, where the target

value is frequently exceeded [28]. Benzo(a)pyrene is the highest carcinogenic contributor in San Pietro Capofiume, while benzofluoranthenes and dibenzo(a,h)anthracene predominate in K-puzsta. Concentrations of carcinogenic compounds represented 2.5%, 6.5% and 27% of total PAH in Hyytiälä, K-puszta and San Pietro Capofiume, respectively.
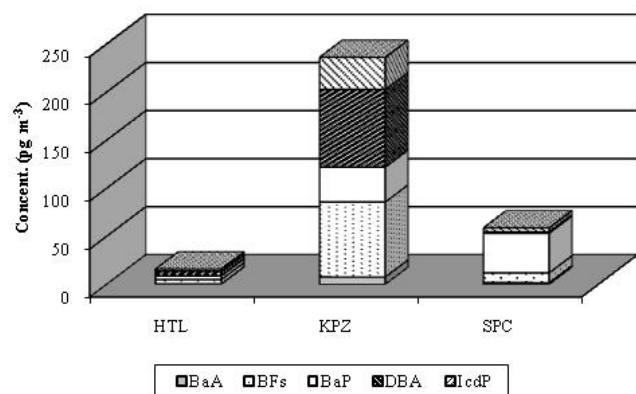

Fig. 3 Average benzo(a)pyrene equivalent concentrations (BaPE=BaA×0.06 + BFs×0.07 + BaP + DBA×0.6 + IcdP×0.08; BaA – Benzo(a)anthracene; DBA= Dibenzo(a.h)anthracene)

IV. CONCLUSION

n-Alkanes and PAH in atmospheric aerosols from three rural European sites were chemically characterised, along with source reconciliation based on CPI, U/R, %WNA and diagnostic ratios of PAH. The presence of petroleum residues was confirmed by the low CPI values and high ratio of resolved to unresolved aliphatic components, particularly in Hyytiälä and San Pietro Capofiume. The input of biogenic sources was significant in K-puszta, where 60% of the total n-alkanes were attributable to plant waxes. This biogenic contribution represented only 15 and 23% of the total n-alkanes found in the boreal and Mediterranean aerosol, respectively. Diagnostic ratios between PAH suggest that vehicular emissions and biomass burning also influence the aerosol constitution in the Hungarian site. Long range transport of air masses contributed with anthropogenic components to the atmospheric aerosol in the boreal forest. In spite of transboundary pollution, Hyytiälä registered the lowest hydrocarbon levels among all locations. Aliphatic and aromatic hydrocarbons in samples from San Pietro Capofiume reveal that both vehicular and industrial emissions are major sources influencing the diel pattern of concentrations. The average BaPE concentrations obtained for every EUCAARI sites were far lower than the mandatory limit value (1 ng m^{-3}).

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