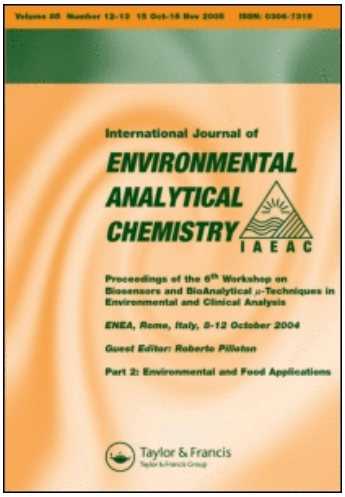

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Biomonitoring of traffic originated PAHs in the air

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Biomonitoring of traffic originated PAHs in the air

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This article sets out the results of air quality biomonitoring along a transect bordering on the A32 Turin–Bardonecchia motorway (Italy). The results were obtained using aeroponic sampling units, an innovation insofar as the plants acting as monitor live and grow in these units above ground, assuring that atmospheric pollutants are absorbed only through the leaves. The accumulation of 15 polynuclear aromatic hydrocarbons (PAHs) on the leaves of *Brassica oleracea* var. *Acephala*, used as biosampler, was determined on samples taken in the months of February, July and October 2002, in each case after two months' exposure. The results highlight: (i) the influence of the seasons on the accumulation of pollutants, (ii) that phenanthrene, fluoranthene, pyrene and chrysene generally account for more than 80% of total PAHs, (iii) that the data may be considered representative of both volatile and non-volatile compounds. Comparison with other sampling methods are supplied and discussed.

Keywords: Biomonitoring; Aeroponic culture; PAH; *Brassica oleracea*; Motorway

1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous atmospheric pollutants. Most of them are released into the environment from diesel engines, vehicle exhausts, and other combustion sources [1–4]. These organic compounds are produced by high-temperature reactions such as incomplete combustion and pyrolysis of fossil fuels and other organic materials [5]. They have been of scientific interest for several decades due to their carcinogenic and mutagenic properties.

Motorway traffic, which has increased considerably in the last 40 years, might be a major source of PAHs in the surrounding atmosphere, in the gaseous and/or the particle-bound phase depending on the vapour pressure of the specific PAH and the prevailing temperature; their determination with high spatial and temporal resolution

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is thus desirable. However, this might entail severe implementation problems due to the high cost associated with conventional monitoring systems using high-volume air samplers. Biomonitoring methods, developed over the last few years, have proven their value as a tool supplementing the more traditional chemical and physical environmental control techniques, especially in terms of high spatial resolution and time–average data series [6].

The monitors used differ considerably, from plants such as *Brassicacee*, ferns, taraxacum, pines and cherry laurel, to other species such as lichens, mosses and some species of mushrooms [6–10].

This article concerns the impact of the approximately 70 km long A32 motorway that connects the city of Turin (Piedmont, Italy) with the transalpine Frejus tunnel. It crosses highly varied territory, stretching from the flood plain close to Turin, crossed by the Dora Riparia river, to the Upper Susa Valley in the Western Alps. Traffic, estimated from current transit data, amounts to around 40,000 vehicles a day, consisting of 90% cars and 10% heavy vehicles. Taking into account the natural features of the area through which the motorway passes, since 1990, SITAF S.p.A. (Società Italiana Traforo Autostradale del Frejus), which manages the motorway, in cooperation with the inter-university consortium "Centro", has undertaken systematic monitoring of the environmental impact of the motorway. An approximate of 3 ha pilot area at Messa Vecchia (Avigliana – Turin) was set up to test different plant species in order to assess their ability to accumulate the main pollutants deriving from automobiles and other motor vehicles.

This monitoring program, extended to the entire motorway route, employed an innovative method based on the aeroponic cultivation, in specific bio-stations, of plant species used as bio-accumulators of traces of pollutants. The plant species used was *Brassica oleracea* var. *Acephala* [7] and the PAHs investigated were those of US EPA Method 610 (excluding naphthalene): acenaphthylene (ACE), acenaphthene (APT), fluorene (FOR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h) anthracene (DBA), indeno(1,2,3-cd)pyrene (INP) and benzo(g,h,i)perylene (BPE).

2 Experimental

2.1 *Monitoring plane*

The monitoring sites at which the bio-stations were installed along the route of the motorway were selected taking into account different topographical and weather conditions. In particular, 18 sampling sites were considered. Seven were located along the motorway route at the following sites: Avigliana Barriera (Mw1), Borgone (Mw2), Ramats (Mw3), Gad (Mw4), Vezzani (Mw5), Prerichard (V1) and Frejus (T1/2), all located at weather stations. Vezzani is a bio-station situated at high altitude, above the motorway level, used mainly for checking the functioning of the system, consists of a plant biosensor and the aeroponic module, in unfavourable climatic conditions. Many of them are put in proximity of weather stations. Seven aeroponic units were positioned in the pilot area of Messa Vecchia (A0–A6) perpendicular to the axis of the motorway at distances of 18.3 (A0), 28.7 (A1), 38.4 (A2), 49.0 (A3),

58.1 (A4), 71.1 (A5) and 82.1 (A6) meters, to assess the fallout of pollutants by distance from the motorway.

Three city stations were also set up: Turin (TO), in a zone of considerable traffic pollution; this station also served to verify the absence of saturation phenomena in the determinations made in the Susa Valley; Avigliana Vigili (AVVI), located near the municipal police station in Avigliana, a town of about 10 000 inhabitants; Bardonecchia (BAR), located in the centre of the tourist resort. These three town stations enable motorway pollution data to be compared with those of urban areas, which include different sources of pollutants such as domestic heating systems and various types of road traffic. Figure 1 shows the diagram of sampling sites.

Samples were taken at each station in February, July, and October 2002. Samples of air and particulates were also taken at Messa Vecchia, close to bio-station A5, and in the city of Turin, in the period between June and July.

The air samples were taken by aspirating 50 m^3 of air, with an aspiration velocity of 18 l min^{-1}, in XAD-2 sorbent tubes manufactured by SKC Inc. The sampling was carried out in stable weather conditions. The powders were collected on PTFE (polytetrafluoroethylene) filters with a diameter of 37 mm and pore size of 2.0 μm, provided by Omega Speciality Instruments Co [11].

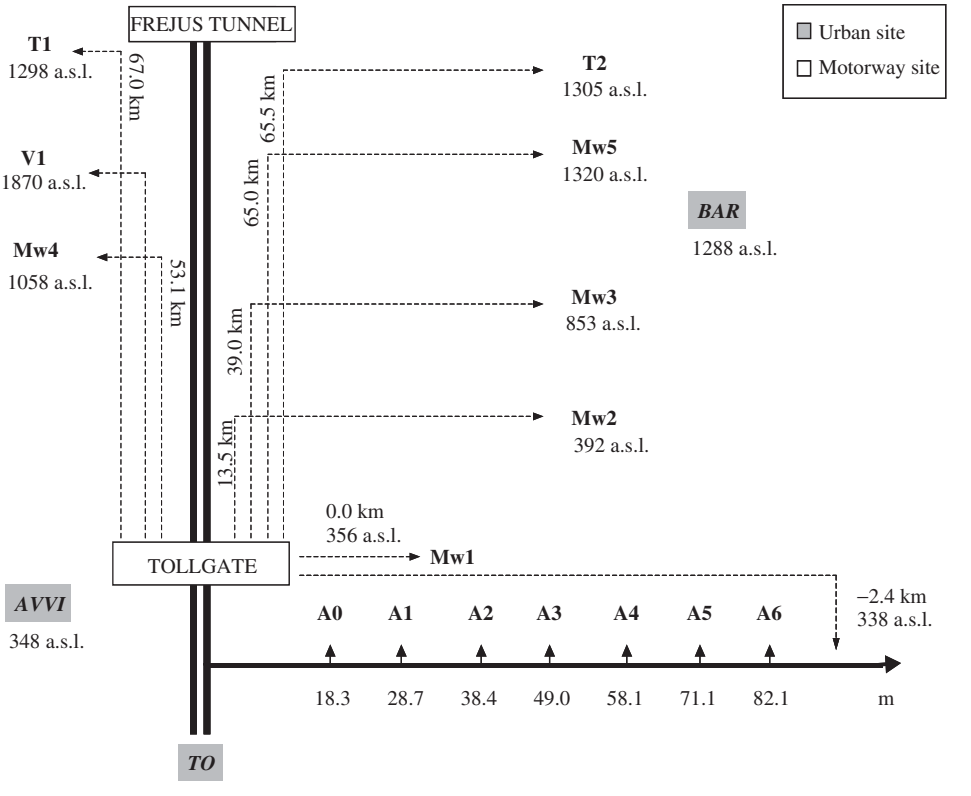

Figure 1. Biomonitoring network along the A32 Turin–Bardonecchia motorway. Urban sampling sites: TO: Turin, AVVI: Avigliana Vigili, BAR: Bardonecchia. Motorway sampling sites: A*n*: Messa Vecchia sites, Mw1: Avigliana Barriera, Mw2: Borgone, Mw3: Ramats, Mw4: Gad, Mw5: Prerichard, T1/2: Frejus. Reference sampling site: V1: Vezzani.

2.2 *Aeroponic bio-control units*

Aeroponic bio-control units allow the biosensors to be grown in optimal conditions and that exclude the possibility that pollutants are absorbed via the root system, so that air pollutants alone accumulate. Figure 2 shows a diagram of the aeroponic control unit, comprising a tank containing nutrient solution (fed by ion-exchange resins with a cation–anion ratio of 1 : 2 and an exchange capacity of 150 meq/100 g), and a system of spray jets to spray the plant roots with nutrient solution. The functioning of the stations is monitored by a series of sensors that measure: (i) internal and external air temperature; (ii) the thermostatically controlled temperature of the nutrient solution; (iii) nutrient solution level; (iv) pressure of the spray jets. Each individual control station has a remote control system (via GSM network) enabling remote collection and monitoring of all the technical parameters and providing periodic reports on the state of functioning.

2.3 *Preparing the bio-control stations*

The bio-control station was prepared by inserting the plants into the support, taking care that the root system was positioned correctly inside the panel. The plants were

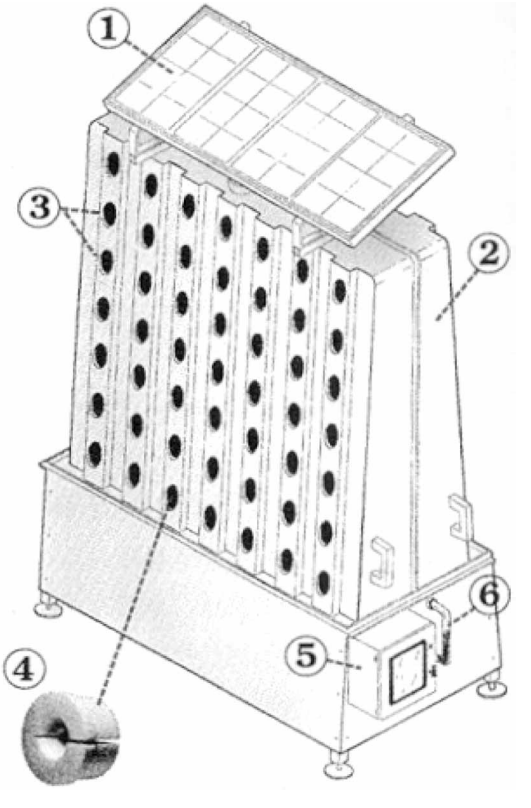

Figure 2. Aeroponic bio-station.

taken from a nursery. Some plants of the same lot were analysed to verify the absence of analytes. For each bio-station, the number of plants, which remain exposed for 2 months, varied between a minimum of 30 and a maximum of 80. After each sampling operation, fresh *Brassica* plants were repositioned on the mechanical supports.

2.4 *Sampling method*

Sampling was done throughout the monitoring system in the shortest time possible, within a maximum of 7 days, during a period of high pressure and some days after prolonged or heavy rainfall. Samples of the leaves were taken following a standard procedure: two diagonals forming four sectors were traced on each rectangular panel of the bio-station and the leaves were taken from the centre of the sectors. At least 25–30 g of leaves were collected for each analysis.

2.5 *Sample extraction*

In the laboratory the leaves were cut into small regular-sized pieces. Approximately 20 g of each sample were placed in a centrifuge tube with 80 μL of an internal standard of deuterated compounds (benzo(a)pyrene, anthracene, fluoranthene, supplied by Cambridge Isotope Laboratories Inc.) and extracted with hexane (pesticide grade) in three successive extractions (60 mL in all), with ultrasonic means (Grant Ultrasonic Bath XB6) at room temperature [12, 13]. The residues were dried at 80°C until constant weight, and weighed to determine the dry weight. Each extract was washed with 40 mL of 1% w/v KOH solution in a separator funnel. The organic phase, after anhydrification with sodium sulphate, was concentrated *via* Rotovapor (Büchi 461 Water Bath) at 70°C up to a final volume of 3 mL [7, 14].

Both filters and sorbent tubes were extracted with 6 mL of methylene chloride (pesticide grade) in three successive extractions, with ultrasonic means. The extract was concentrated to 1 mL by nitrogen stream.

2.6 *Instrumental analysis*

The PAHs were determined using GC–MS (gas chromatography–mass spectroscopy, quadropole MQDS 1000, Carlo Erba). Analyses of 14 PAHs was performed in SIM-mode. A Supelco SPB5 column, 30 m × 0.25 mm i.d. with 0.25 μm film thickness was used. The GC temperature program conditions were 50°C isothermal for 2 min, ramped at 25°C min^{-1} to 160°C, ramped at 10°C min^{-1} to 300°C, ramped at 1.5°C min^{-1} to 320°C, and then isothermal for 1 min. The mass spectrometer was operated in EI-mode at an electron energy of 70 eV. The ion source temperature was 280°C. PAHs were identified by matching the retention time of each substance with the retention times of an external standard mix (SS TCL PAHs standard mix provided by Supelco). Analyte concentrations were calculated from the external and internal standard. To estimate the matrix effect and possible loss of analytes during sample treatment, standard addition method has been applied on five samples. The ratio between the slope of the external calibration curve and that of the standard addition curve enabled to evaluate signal loss, which was between 18 and 7% depending on the compound's volatility.

To assess repeatability, extractions were performed on three sub-samples in parallel. The repeatability, expressed as relative standard deviation, was between 3%, for benzo(a)pyrene, and 10%, for fluorene. As chromatographic resolution of benzo(b)- and benzo(k)-fluoranthene was low, they were quantified as a single compound, indicated as benzo(b + k)fluoranthene (BbkF).

3. Results and discussion

3.1 *Variations in total PAHs with seasons and distance*

In general, seasonal variations in PAH content observed at different locations were significant. Figure 3 shows the total concentrations of PAHs for the different sampling sites, expressed in ng *per* g of dry sample, for the months of February, July and October 2002. Table 1 gives the PAH concentration values measured in each sampling period, and for all sampling sites. In July, the total PAH concentration was in general low; for stations Mw2, Mw4, A0, A1 and A2 the values were below $100\,ng\,g^{-1}$. The PAH concentration increased strongly in the cold season (February), with about $2800\,ng\,g^{-1}$ (off-the-scale in the graph) at Turin and about $1300\,ng\,g^{-1}$ at A4. The high value measured in Turin and AVV1 is due to several sources of pollution, such as domestic heating and the different driving style typical of city traffic.

In general, PAH concentrations tend to be about one order of magnitude higher in winter than in summer. The main reason for these variations are: (i) meteorological factors, such as increased atmospheric stability in winter; (ii) higher emissions from

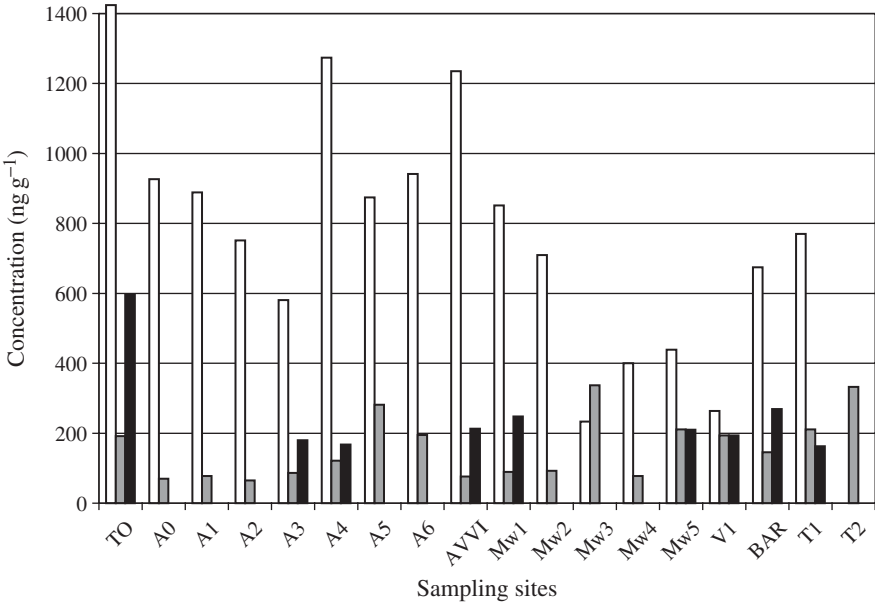

Figure 3. Total concentrations ($ng\,g^{-1}$) of PAHs in *Brassica* from different sampling sites, for the months of February, July and October 2002. (i) white bar: February; (ii) grey bar: July; (iii) black bar: October. The sampling sites are reported in order of motorway run. The off-the-scale value for the Turin station (TO) (February 2002) is 2834 ($ng\,g^{-1}$).

Table 1. Concentration values ($ng\,g^{-1}$) of PAHs for three sampling periods and all sampling sites. Relative standard deviation was between 3%, for benzo(a)pyrene, and 10%, for fluorene.

PAH concentrations ($ng\,g^{-1}$) – 2002																		
		Sampling sites																
PAH	Months	TO	A0	A1	A2	A3	A4	A5	A6	Mw1	AVVI	Mw2	Mw3	Mw4	V1	Mw5	BAR	T1	T2
ACE	February	23.2	26.2	15.4	14.4	17.0	11.3	18.5	20.6	28.8	28.9	17.3	12.8	7.1	15.4	123.0	14.2	14.7	–
	July	23.5	6.8	4.7	5.1	4.5	3.9	12.2	18.0	2.8	2.7	3.6	9.0	4.7	12.5	23.0	8.9	15.2	16.2
	October	11.9	–	–	–	7.2	10.0	–	–	13.5	4.5	–	–	–	6.2	7.1	7.8	5.7	–
APT	February	16.0	5.0	5.4	4.0	3.9	3.0	5.9	5.5	8.0	12.4	5.3	0.0	6.3	12.0	15.7	12.0	2.7	–
	July	9.6	3.1	3.4	2.8	3.7	6.6	31.7	11.4	3.3	4.7	3.9	6.6	3.6	8.8	13.1	3.7	8.2	8.0
	October	11.5	–	–	–	9.9	17.0	–	–	21.3	13.0	–	–	–	12.4	10.7	25.7	15.6	–
FOR	February	18.6	29.5	7.3	9.0	10.9	13.9	20.9	13.4	17.1	28.4	2.0	9.5	0.5	13.2	8.5	9.3	8.3	–
	July	15.2	4.2	4.8	3.0	3.7	5.4	14.4	10.6	3.3	3.4	3.5	9.2	3.8	8.4	16.9	4.3	16.1	16.7
	October	21.7	–	–	–	11.7	9.2	–	–	30.3	8.1	–	–	–	18.2	23.8	14.3	28.3	–
PHE	February	225.0	159.0	144.0	167.0	133.0	135.0	144.0	175.0	193.0	207.0	107.0	54.1	110.0	80.2	102.0	232.0	110.0	–
	July	59.5	21.5	23.7	15.6	22.8	25.2	72.7	61.2	21.2	15.8	14.7	33.2	21.0	53.1	92.2	18.4	77.4	86.7
	October	72.5	–	–	–	61.0	44.4	–	–	56.5	45.7	–	–	–	68.8	52.1	86.2	40.8	–
ANT	February	24.9	11.9	10.5	8.5	6.9	8.9	8.3	14.3	8.6	12.8	8.0	5.1	12.1	8.5	7.8	11.7	9.1	–
	July	4.0	1.6	2.0	1.4	1.6	2.2	4.1	4.3	1.5	1.3	1.3	2.4	1.0	4.9	3.7	2.3	3.0	7.1
	October	24.1	–	–	–	5.7	5.4	–	–	7.1	5.5	–	–	–	7.1	7.7	7.9	4.8	–
FLU	February	566.0	270.0	244.0	215.0	149.0	313.0	268.0	260.0	183.0	394.0	225.0	50.4	115.0	64.0	88.3	199.0	109.0	–
	July	27.2	10.3	11.9	8.6	13.4	19.5	27.2	24.7	11.5	12.3	12.5	18.2	10.1	13.2	22.1	11.5	18.0	47.9
	October	111.0	–	–	–	26.4	22.0	–	–	24.4	33.9	–	–	–	22.4	28.3	52.5	20.7	–
PYR	February	595.0	199.0	188.0	149.0	119.0	286.0	194.0	183.0	117.0	316.0	158.0	41.5	71.4	33.8	52.7	133.0	92.7	–
	July	24.5	8.7	13.4	7.9	14.8	18.3	33.9	34.0	9.9	12.0	10.0	26.3	8.1	15.0	26.8	12.6	20.3	69.3
	October	99.7	–	–	–	27.3	28.4	–	–	35.5	31.1	–	–	–	26.4	27.2	45.6	21.2	–
BaA	February	299.0	51.1	53.5	45.0	28.7	129.0	50.5	78.9	61.2	54.3	40.8	17.3	19.0	26.9	25.9	24.6	94.3	–
	July	3.2	1.5	1.6	2.0	5.1	4.8	25.3	6.1	3.1	2.7	6.2	70.7	1.9	15.1	3.1	4.9	3.5	10.3
	October	105.0	–	–	–	11.9	23.7	–	–	24.0	22.0	–	–	–	14.0	9.5	12.4	6.3	–
CHR	February	696.0	137.0	192.0	121.0	108.0	308.0	168.0	159.0	161.0	188.0	138.0	52.0	51.1	27.2	36.6	50.0	133.0	–
	July	9.1	2.1	2.6	2.8	3.8	7.7	28.2	10.5	4.6	5.8	7.6	69.4	3.1	14.7	5.0	5.7	5.8	25.2
	October	129.0	–	–	–	19.2	8.1	–	–	39.5	41.1	–	–	–	18.1	43.1	16.5	20.0	–
BbF	February	156.0	33.0	21.5	31.6	18.9	83.0	12.5	50.5	47.9	15.7	15.4	nd	6.4	4.0	2.6	10.1	81.8	–
	July	5.5	3.8	4.0	3.2	4.0	11.8	9.6	4.1	10.7	5.3	9.9	28.7	8.7	6.7	0.9	13.3	13.6	6.7
	October	9.4	–	–	–	nd	nd	–	–	nd	3.7	–	–	–	nd	nd	nd	nd	–

(*Continued*)

Table 1. Continued.

PAH concentrations ($ng\,g^{-1}$) – 2002																		
		Sampling sites																
PAH	Months	TO	A0	A1	A2	A3	A4	A5	A6	Mw1	AVVI	Mw2	Mw3	Mw4	V1	Mw5	BAR	T1	T2
BaP	February	2.5	1.8	0.9	nd	0.9	1.2	0.9	1.0	0.7	1.5	nd	nd	nd	nd	nd	1.8	0.9	
	July	2.9	nd	nd	1.9	1.2	nd	nd	1.2	nd	nd	nd	nd	nd	nd	nd	11.7	nd	7.2
	October	nd	–	–	–	nd	nd	–	–	nd	nd	–	–	–	nd	nd	nd	nd	–
DBA	February	34.7	nd	nd	nd	nd	nd	nd	nd	14.9	nd	nd	nd	nd	nd	nd	nd	34.4	–
	July	nd	0.8	0.4	2.2	1.3	nd	5.3	0.9	5.2	5.3	nd	12.9	nd	5.6	nd	10.4	nd	1.9
	October	nd	–	–	–	nd	nd	–	–	nd	nd	–	–	–	nd	nd	nd	nd	–
BPE	February	92.7	20.5	11.1	nd	nd	nd	6.4	nd	20.0	11.8	nd	nd	4.2	3.6	nd	nd	49.7	–
	July	5.1	3.2	3.5	4.7	4.3	10.6	11.8	5.7	10.3	2.9	12.4	27.8	8.9	27.4	4.0	22.6	20.2	20.5
	October	nd	–	–	–	nd	nd	–	–	nd	nd	–	–	–	nd	nd	nd	nd	–
INP	February	84.0	18.8	8.7	nd	nd	nd	4.4	nd	15.8	6.8	nd	nd	3.7	nd	nd	nd	41.5	–
	July	2.5	2.1	1.6	4.0	2.3	5.4	4.9	2.4	2.1	2.4	6.9	22.6	2.8	8.6	nd	15.7	9.7	9.1
	October	nd	–	–	–	nd	nd	–	–	nd	nd	–	–	–	nd	nd	nd	nd	–
Total conc.	February	2833.6	962.8	902.3	764.5	596.2	1292.3	902.3	961.2	877.0	1277.6	716.8	242.7	406.8	288.8	463.1	697.7	782.1	–
	July	291.5	69.7	77.6	65.2	113.8	149.8	281.3	195.1	125.0	107.7	92.5	337.0	77.7	220.4	238.0	191.6	232.2	332.8
	October	595.8	–	–	–	180.3	168.2	–	–	252.1	208.6	–	–	–	193.6	209.5	268.9	163.4	–

nd, not detected.
–, not available samples.

domestic heating systems, and reduced atmospheric reactivity of PAH compounds, e.g. reduced degradation by photo-oxidation and reaction with OH-radicals, in winter [15].

The results also reveal that, for the A0–A6 stations, the concentrations tend to decrease with increased distance from the motorway as far as station A3, after which the values start to increase again. This trend, already encountered in previous surveys, is not interpretable easily. It can be attributed to a process of diffusion of the pollutants comparable to the so-called chimney effect, defined by IUPAC as "a vertical movement of a localized mass of air or other gases which occurs due to local temperature differences" [16]. In this case, vehicle exhausts, which are at a high temperature, tend to rise and then fall again at a certain distance from the source. This is in accordance with the data in the Report 4/2000 in *Environmental Monitoring European Program* [15].

3.2 *The PAH profiles*

The original PAH composition can change significantly during their dispersion. For example, reactions of degradation and changes of state can occur, depending on the ambient temperature [17–21]. Even so, numerous studies have proposed a variety of PAH profiles for various origins of PAHs [19, 22–24].

Figure 4 shows the percentage composition of the most abundant PAHs determined in this study for the three periods. The percentage values are calculated on the sum

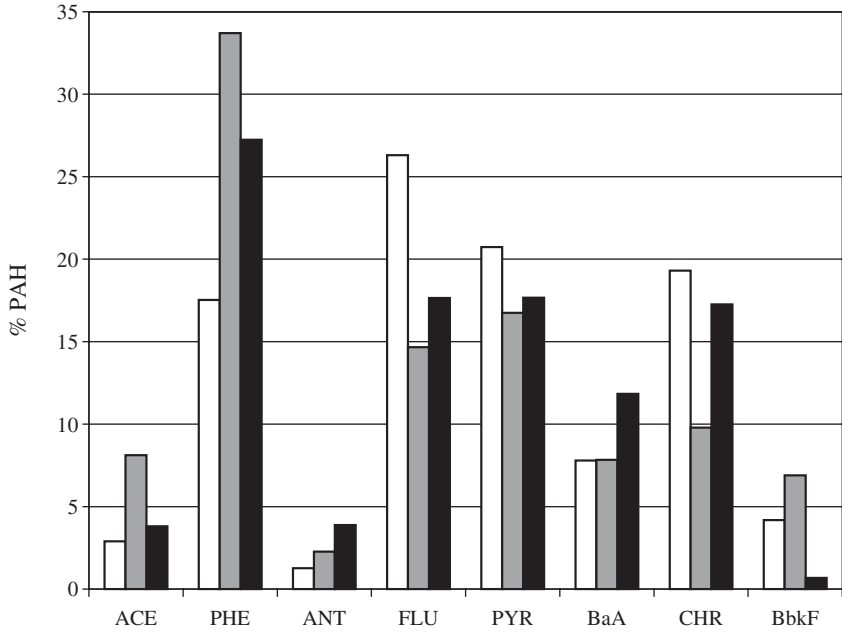

Figure 4. Percentage of most abundant PAHs in the different sampling periods. The percentage values were obtained for each PAH from the sum of the concentrations recorded, for each period, at all the biomonitoring stations. (i) white bar: February; (ii) grey bar: July; (iii) black bar: October. (For PAH abbreviations see section 1.) Benzo(b + k)fluoranthene percentages correspond to the sum of benzo(b)- and benzo(k)fluoranthene concentration values.

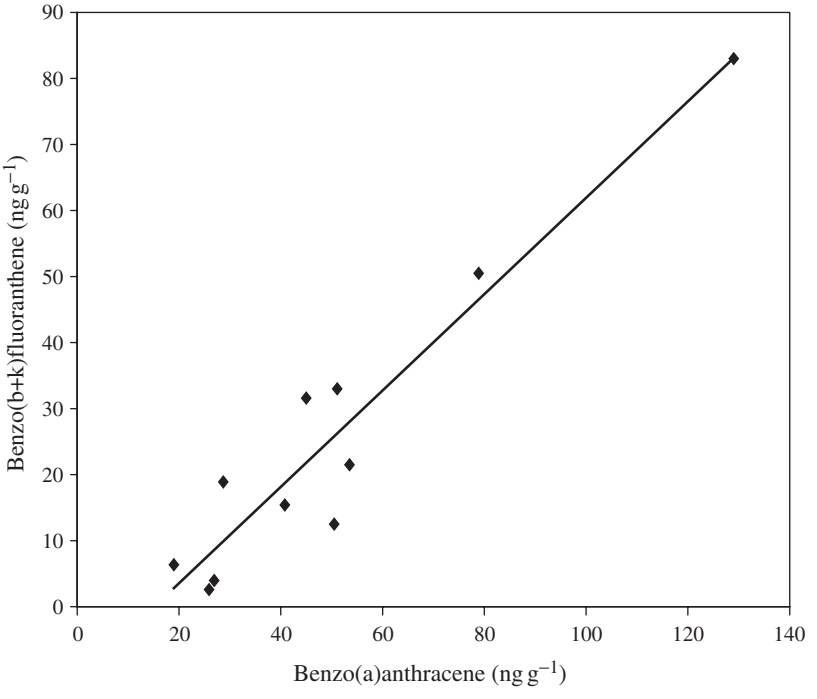

Figure 5. Correlation between concentration values (ng g^{-1}) of benzo(a)anthracene and benzo(b + k) fluoranthene in samples of *Brassica* in February 2002. Benzo(b + k)fluoranthene percentages correspond to the sum of benzo(b)- and benzo(k)fluoranthene concentration values.

of concentrations recorded at all bio-stations. Analysis of the data highlights that, in July and October, the most abundant hydrocarbon was phenanthrene which, in the month of July, rose to above 30% of the total, whereas fluoranthene is the most abundant in February. These two PAHs, together with pyrene and chrysene account for 80% of the total. Other hydrocarbons, such as anthracene, acenaphthylene and benzo(b + k)fluoranthene, do not individually exceed 5% of total PAHs, except for the last two in the month of July.

Correlation between the concentrations of some PAHs is good; the graph in figure 5 shows the similarity in concentration trends of benzo(a)anthracene and benzo(b + k) fluoranthene in the month of February. The straight line representing the concentrations of the two hydrocarbons in the various samples has a slope of approximately 0.7, and a correlation coefficient $R = 0.95$. A close correlation was also found between fluoranthene and pyrene ($R = 0.93$; slope approximately 1).

Considering the TO and A0 stations, as representatives of urban and motorway pollution respectively, it emerges (table 2) that, in February, anthracene, fluoranthene and pyrene were present at both stations in comparable percentages. A0 had percentages of acenaphthylene and phenanthrene that were respectively approximately triple and approximately double those of TO, which had percentages of benzo(a) anthracene and benzo(b + k)fluoranthene approximately double those of A0. These two pairs of hydrocarbons may be considered indicative of motorway pollution and city pollution, respectively.

Table 2. Percentage composition of some PAHs in the February samples for TO and A0 stations. The values correspond to the percentage of each PAH on the total PAH concentration.

	Bio-station	
Substances	TO (%)	A0 (%)
Acenaphthylene	1.2	3.5
Phenanthrene	11.9	21.2
Anthracene	1.3	1.6
Fluoranthene	30.0	36.0
Pyrene	31.5	26.5
Benzo(a)anthracene	15.8	6.8
Benzo(b + k)fluoranthene[a]	8.2	4.4

[a]Benzo(b + k)fluoranthene percentages correspond to the sum of benzo(b)- and benzo(k)-fluoranthene concentration values.

The extent to which a PAH molecule will reside in the gas phase or the particle phase is determined by its vapour pressure and the ambient temperature. It has been shown to a first approximation, for urban air particulate matter, that compounds with vapour pressures above 1×10^{-3} Pa should occur predominantly in the gas phase, whereas those with vapour pressured below 1×10^{-6} Pa should exist exclusively in the particle phase. Any compound with a vapour pressure between these two limits may be expected to occur in both the vapour and the particulate phases [25]. Vapour pressure data (at 25°C) for some PAHs have been reported [26], and from these it is possible to determine which phase the compound should be found in. Acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene should be found primarily in the vapour phase; fluoranthene, pyrene, benzo(a)anthracene and chrysene should occur in both phases, and benzo(b + k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene should occur exclusively in the particle phase.

In the light of these predictions it is interesting to compare the results obtained from the *Brassica* samples and the more traditional type obtained through air aspiration. For this purpose, data from the biosensor for the month of July and the average of four air samples taken in the same period were processed. Figures 6 and 7 show the percentage compositions of the groups of PAHs determined in *Brassica*, in air filtered at 2.0 μm and in the particulate that accumulated in the filter, at the A5 and TO stations. In summer, in the TO station, the total average concentration of PAHs in air and particulate samples were 71.4 and 7.6 ng m^{-3}, respectively and in A5 station they were found to be 37.9 and 2.2 ng m^{-3}. The two graphs reveal the same trend: the set of air samples, taken by aspiration, discriminate entrapment of the hydrocarbons, favouring the three-ring PAHs. The four-ring PAHs were found to be distributed between the particle and vapour phases, and the five- and six-ring PAHs were found exclusively in the particle phase. On the other hand, the *Brassica* data show the plants to have an accumulation capacity for the whole set of hydrocarbons. Figure 8 highlights the trapping capability of each sampling method for each individual PAH; it was constructed from figure 7 as follows: the triad of data reported on the ordinate for each substance in figure 7 have been added and expressed as percentages. The resulting graph clearly reveals *Brassica*'s greater ability to capture PAHs with intermediate molecular weight. Data from the A5 station confirmed this finding.

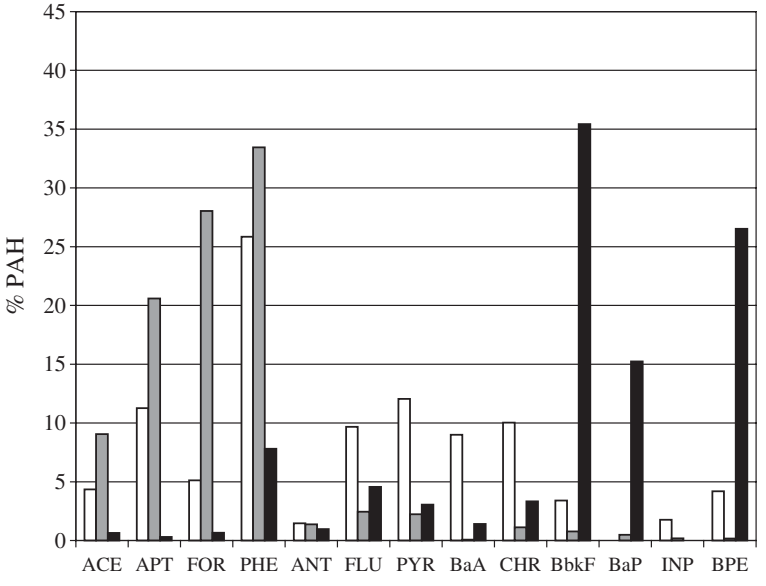

Figure 6. Percentage compositions of PAHs relating to the various samples taken in July at the A5 station. The percentage values for each analyte were calculated on the total PAH concentration for each sampling method. (i) white bar: *Brassica oleracea* samples; (ii) grey bar: filtered air samples; (iii) black bar: particulate samples. (For PAH abbreviations see section 1.) The analytes are listed in order of weight. Benzo(b + k)fluoranthene percentages correspond to the sum of benzo(b)- and benzo(k)fluoranthene concentration values.

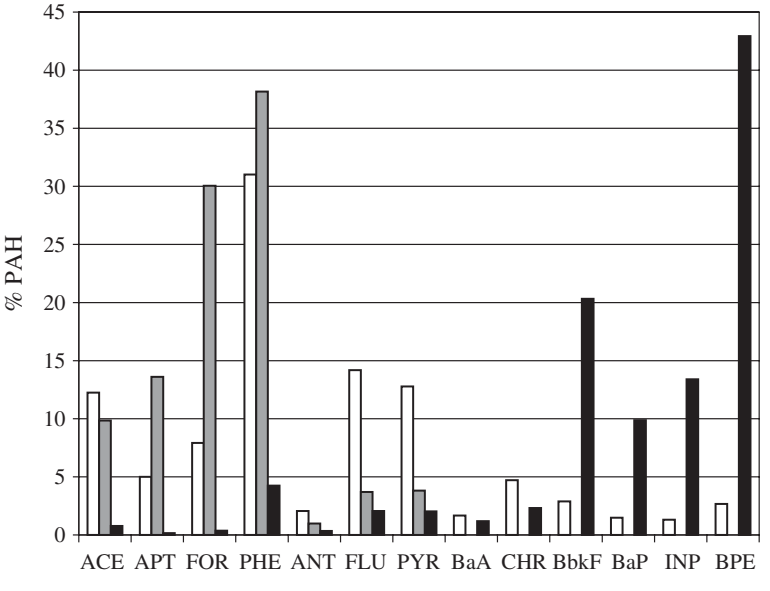

Figure 7. Percentage compositions of PAHs relating to the various samples taken in July at the Turin station. The percentage values for each analyte were calculated on the total PAH concentration for each sampling method. (i) white bar: *Brassica oleracea* samples; (ii) grey bar: filtered air samples; (iii) black bar: particulate samples. (For PAH abbreviations see section 1.) The analytes are listed in order of weight. Benzo(b + k)fluoranthene percentages correspond to the sum of benzo(b)- and benzo(k)fluoranthene concentration values.

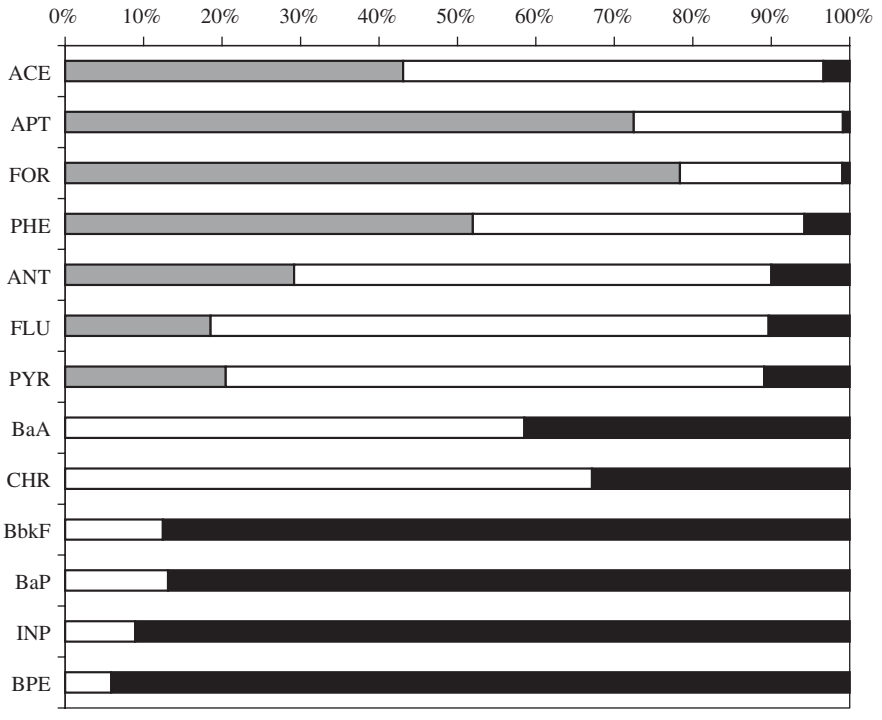

Figure 8. Trapping ability diagram. The percentage values for each analyte, calculated on the total PAH concentration for each sampling method (data on the ordinate of figure 7), have been added for each substance and expressed as percentage (see section 3.2). (i) white bar: *Brassica Oleracea* samples; (ii) grey bar: filtered air samples; (iii) black bar: particulate samples. (For PAH abbreviations see section 1.) The analytes are listed in order of molecular weight. Benzo(b + k)fluoranthene percentages correspond to the sum of benzo(b)- and benzo(k)fluoranthene concentration values.

The literature reports that PAHs in the vapour phase can penetrate directly into the leaves of *Brassica*, diffusing through the wax and cuticular membrane [27, 28]. Particle-bound PAHs accumulate on the leaf surface, where a portion is probably quickly removed by wind abrasion. The residual particle-bound PAHs, however, are adsorbed onto the leaf surface and incorporated in the leaf.

4. Conclusions

Brassica oleracea var. *Acephala* leaves are suitable active samplers and good accumulators of PAHs over time, providing reliable time-integrated pollution records. The plant is also particularly suitable for this type of use in view of its resistance to climatic factors. The use of aeroponic units assures optimal conditions of growth for the plants and guarantees that pollutants only accumulate through the aerial parts and not through the roots. The PAH distribution is dominated by phenanthrene, fluoranthene and pyrene, as observed in several other studies, and a good correlation exists between some of the individual PAHs.

It is interesting that *Brassica* sampling may be considered representative of both volatile and non-volatile compounds. Other classic sampling methods show

higher selectivity, favouring the capture of light (air fraction) or heavy (particle fraction) PAHs. The picture of PAH atmospheric pollution obtained by means of *Brassica*-based sampling criterion may thus be considered reliable. *Brassica* sampling is an effective method to monitor variations in PAH distribution as a function of time, and is effective in determining both environmental and traffic changes. This result is of great practical significance in assessing environmental impact, which must also take into account the different properties of individual pollutants, as in this specific case, where the less volatile compounds are highly toxic.

The results relating to distance from the motorway permit quantitative assessment of accumulation in vegetables that may enter the food chain. Assuming the store of PAHs in the *Brassica* as representative of local aerial biomass, it is possible to estimate the total PAH burden for the considered area vegetation as reported by Wild and Jones for UK vegetation [29]. It is also useful to consider that soil and vegetation degradation rates are lower, leading to a higher content and slower rate of clearance from these media compared to air [15]. Furthermore, the results stress the different composition of the mix of pollutants between the urban atmosphere, where the heavier hydrocarbons tend to dominate, and that of the motorway.

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