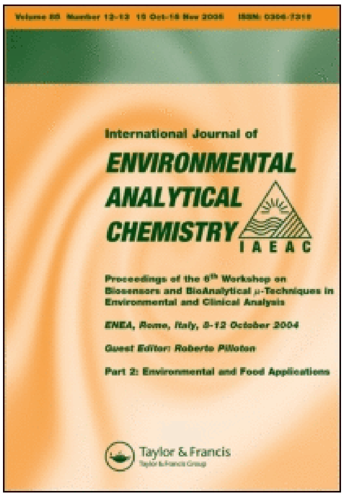

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Sources and Fate of Polycyclic Aromatic Hydrocarbons in Ambient Air of Urban and Rural Croatian Sites

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SOURCES AND FATE OF POLYCYCLIC AROMATIC HYDROCARBONS IN AMBIENT AIR OF URBAN AND RURAL CROATIAN SITES

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Atmospheric concentrations of nineteen polycyclic aromatic hydrocarbons (PAHs) were determined in the particulate and vapour phases of samples collected during 24 hours in winter and summer 1990 from croatian urban, industrial and rural sites.

An analytical procedure is described for a comprehensive determination of polycyclic aromatic hydrocarbons in air samples based on aerosol filtration through glass fiber filters and vapour phase adsorption on XAD-2 resin. Separation, indentification and determination of PAHs were performed by TLC, GC and GC-MS.

Total concentration of PAHs in Kosnica (winter) was about three to four times (summer) higher than concentration of PAHs in Zavižan. The aerosol composition in Kosnica can be attributed to very high traffic near the sampling site. Concentrations of SO_2 and NO_2 and granulometric distribution of particulate matter were also measured.

KEY WORDS: Polycyclic aromatic hydrocarbons, Zavižan, Kosnica, seasonal variations

INTRODUCTION

The occurence and fate of polycyclic aromatic hydrocarbons (PAH) in the environment has been studied with great interest because many of them and their analogs are potent carcinogens and/or mutagens[1–4]. Atmospheric aerosol has been recognized as an important source of these compounds[5–7]. PAH and their derivatives are generated from

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incomplete combustion of fossil fuels[8,9] in forest fires in a large variety of industrial processes, domestic heating or from natural sources. Residential heating and traffic were estimated to be the main source of ambient PAHs in urban areas. Meat cooking operations are a non negligible source of organic aerosol emissions into the urban atmosphere. Gasoline and diesel-powered vehicles are known to contribute appreciable amounts of inhalable fine particulate matter to the atmosphere in urban areas. PAHs can be transported at long-range distances[10–13] and consequently deposited far from their sources.

PAHs in the air are associated both with the vapour phase and the particulate matter[14]. Sorbed PAHs and other volatile organic compounds can be desorbed and achieve the equilibrium distribution between the gas and particulate phases in the atmosphere. The gas/particle distribution of PAHs and other organic compounds have been extensively investigated[15–19]. A better knowledge of the physical nature of gas/particle PAHs partitioning will provide an improved foundation upon which to build a model of long-range atmospheric transport, deposition and washout processes, and reaction kinetics on/in particles[20] and, thus, a better understanding of their behavior in the atmosphere. Only minor quantities of PAHs are present in the vapour phase (those with a small number of rings) while the rest are adsorbed on solid matter. Many authors tried to prove that more than 75% of solid matter on which PAHs are adsorbed is smaller than 2.5 μm in diameter; particles of that size are able to enter the respiratory tract[21].

Concentrations of PAHs vary according to the season, being during winter 8–20 times higher than during summer[22–24]. Mean concentrations of PAHs range from 0.01 ngm^{-3} in unpolluted areas to 60 ngm^{-3} in towns and near industrialized places.

A large number of extensive studies have been performed on PAHs in the particulate phase of ambient air[25–29]. Although many recent studies have characterized the atmospheric concentration of a large number of PAHs, these studies are not readily comparable because of different analytical and sampling techniques and due to the selection of particular PAH for quantification[30–32]. Laboratory and field sampling experiments have been conducted in order to determine the phase distribution of PAHs in the ambient atmosphere, and to determine the potential for artifact formation due to volatilization and ozone reaction during normal sampling conditions[33]. For achieving optimal sampling conditions, it is particularly important to take chemical and photochemical reactions of PAH into consideration because they may modify the isomeric composition of the samples, e.g. benzo(e)pyrene/benzo(a)pyrene + benzo(e)pyrene ratios.

The compounds of interest must be adequately separated from related substances in the complex mixtures often encountered. High sensitivity of detection is required to analyze small samples collected over a relatively short period of time. Analyses of PAH mixtures have typically entailed various partitioning sequences followed by column, paper or thin layer chromatography TLC, prior to detection by luminescence or absorption techniques[34–37], GC techniques[38,39] or GC-MS techniques[40–43].

In the present paper an analytical procedure for determination of PAHs in ambient air of urban and rural sites is described. This study contributes to the understanding of PAHs distribution in the atmosphere between the littoral and the continental part of Croatia.

EXPERIMENTAL

Sampling

Concentrations of PAHs have been measured at two different locations: at Kosnica, on the motorway southeast of Zagreb and on Zavižan on the Velebit mountain. Figure 1

Figure 1 Location of two sampling sites in Croatia, Zavižan on the Velebit and Kosnica southeast of Zagreb.

shows the location of the two sampling sites. Zagreb is a big urban center (approx. 1,000,000 inhabitants) representing a typical town with heavy traffic, central heating and a few major industrial emission sources. In the small housing areas there are also several thousands of residential furnaces, where oil, peat and wood are burned during winter. North of the city there is the mountain Medvednica with its peak Sljeme (1035 m above see level). Zavižan is situated 1594 m above sea level and is included in the EMEP and MEDPOL network. It is far from the direct sources of pollution and it is mainly influenced by long-range transport from distant sources.

Air sampling was performed at both locations in winter (February) and summer (August) 1990, in order to show differences of atmospheric pollution between these two seasons.

Particulate matter samples were collected with a high volume Sartorius Dust sampler EM 100 Type SM 26734 on Sartorius glass fiber filters SM 13400 (ø = 257 mm) and Gelman AE glass fiber filters (ø = 257 mm). The samplers were all calibrated with the same flowmeter (Digital anemometer, type DA 4000). The mean linear air speed through the filter was 0.520–0.545 ms^{-1}. The flow rate was approximately 70 m^3h^{-1}. The total volume sampled was 1325-2230 m^3. The sampling time was about 24h.

The PAHs present in the vapour phase were adsorbed on XAD-2 resin. The XAD-2 plugs were positioned downstream of the glass fiber filters. A cylindrical ampoule with 80 g of prewashed adsorption resin was connected to the sampler behind the glass fiber filter[37]. The breakthrough volume for the XAD-2 cartridge was about 2500 m^3 at temperature below 25°C, and 2800 m^3 at temperature below 10°C.

The samplers were lifted to a height of 1.5–2.0 m above the ground. The height of filter at Kosnica sampling site was above average height of personal vehicles (1.5–2 m). After sampling, the filter was protected in a standard aluminum shelter.

When the filters could not be analyzed immediately after sampling, they were extracted and the extracts were stored. Cyclohexane extracts with no change of concentration were observed after 1 year of storage at 4°C in a dark place.

Extraction and fractionation of the organic material

The fiber filters were Soxhlet extracted with 500 mL of cyclohexane for 16 hours. The cycling rate for the extraction was 30 min/cycle. The extract was concentrated to 1 mL under vacuum on a rotary evaporator at + 35°C. The optimum time of extraction has been determined on a reference sample.

The XAD-2 resins were extracted with 350 mL of cyclohexane for 16 h. The cycling rate for the extraction was 30 min/cycle. The extract was concentrated to 1 mL under vacuum on a rotary evaporator at +35°C.

In all analytical work, appropriate blanks were run and were subtracted from the analytical data as required. An empty filter and XAD-2 resin (blank-without sample) was extracted for 12 h and the extract was afterwards carried through entire procedure which will be later described. The final gas chromatogram did not display any peaks interfering with the compounds of interest. Before extraction, an internal standard solution of benzo(b)chrysene was added to the filter and XAD-2 samples. The recovery of the internal standard was 94%.

Interfering substances in the cyclohexane extracts were removed using thin-layer chromatography (TLC) on silica gel G (Merck) plates (layer thickness 0.3 mm). 0.3 mL of the extract were applied to each plate and a PAH standard mixture was added separately. TLC plates were developed using a mixture of cyclohexane-benzene (12: 8, v/v) as a mobile phase. All PAHs were found in a thin spot with Rf value between 0.6–0.8. Ahead of the PAH spot, aliphatic compounds were present while at the back polar heterocyclic nitrogen-, oxygen- and sulphur compounds. The spot with the PAHs was quantitatively scraped from the plate and extracted with cyclohexane 5 times in an ultrasonic bath. The volume of collected extracts was reduced by evaporation below 35°C and further concentration was performed by careful evaporation under a slow stream of dry nitrogen to 1 mL.

Analysis by thin-layer chromatography (TLC)

For separation and identification of PAHs in the cyclohexane extracts a two-step thin layer chromatographic separation process was used.

Stationary phases for TLC plates were prepared by standardized procedures. Adsorbents used for plate preparation were acetylated cellulose MN 300 Ac-40, (Macherey Nagel Co.), silica gel G, (Merck), alumina G Type E, (Merck). Plates (20 × 20 cm) have been prepared, with acetylated cellulose—silica gel G—alumina (0.277: 0.277: 0.444) (layer thickness 0.3 mm). The concentrated extract containing PAHs was spotted at the corner of the layer and developed using a mixture of hexane-diethylether (19: 1, v/v) as a mobile phase, along one edge of the plate. The solvent was then evaporated, the plate rotated 90°C, and developed in the orthogonal direction using a mixture of ethanol—dichloromethane—water (0.645: 0.322: 0.322, v/v/v) as a mobile phase.

The position of the spot was detected by UV light at 254 nm and 365 nm. The area identified by the spot (adsorbent with PAHs) was quantitatively scraped from the plate and extracted with cyclohexane in ultrasonic bath for 6 min and filtered to remove suspended material. The extract was evaporated to dryness under a stream of nitrogen, the residues were dissolved in a small volume of spectrograde pentane (2.0 mL) for fluorescence analysis[44]. Pure PAH standards were chromatographed under identical conditions as the sample in this two step TLC separation.

Analysis of pentane solution of samples and standards was conducted by recording the fluorescence excitation and emission spectra with a Farrand MK 1 spectrophotometer, using spectral data[36]. The method was calibrated by preparing curves of fluorescence emission at maximum excitation wavelength for each standard PAH in the concentration range 0.05–0.50 mg L^{-1}. Beer's law is obeyed in this concentration range.

By this procedure, the following percentage recoveries were obtained: acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene: 80.3–83.2%; benzo(a)anthracene, dibenzo(ac/ah)anthracenc, chrysene, coronene: 87.5–89.2%; benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene: 91.3–92.6%. Reproducibility of these recoveries ranged from about ± 4 up to ± 6%. The detection limits for the ambient air samples were 0.1 ngm^{-3}. Recoveries for the whole method were in the range of 86.7–90.5%. These results correspond to those described in the literature[23].

Analysis by GC and GC-MS

Confirmatory identification of PAHs in the extracts was obtained with a Hewlett Packard 5890 gas chromatograph equipped with a split/splitles injector, a SPB-5 fused silica capillary column (40 m × 0.31 mm I.D., film thickness 0.35 µm) and a FID detector. The injector and detector were maintained at 295°C and 315°C, respectively. Column temperature programming consisted of the following steps; injection at 60°C, isothermal hold at 60°C for 3 min, temperature ramp of 10°C min^{-1} to 160°C and 3°min^{-1} to 285°C, and isothermal hold at 285°C for another 10 min. Using internal standards (D_{10}-Phenanthrene, 1-n-butylpyrene, D_{12}-Perylene) was routinely monitored.

The GC-MS analyses were carried out with a Hewlett-Packard GC-MS, system consisting of a Model 5890 gas chromatograph and Model 5971 A mass spectrometer. The chromatographic conditions were identical to those used for the GC analyses. The GC-MS analyses were performed by electron impact ionization with an electron energy of 70 eV. The mass spectrometer was manually tuned to maximize thc ion intensity of the m/z 219 peak for perfluorotributylamine. The interface temperature was 250°C. The MS was scanned from about 100 to 400 amu at 1.4 s/scan. The injection volume was 1 µL in splitless condition.

The mass spectrometer was calibrated by injecting various ratios of deuterated PAHs (D_{10}-Phenanthrene, D_{10}-Pyrene, D_{12}-Chrysene, D_{12}-Perylene).

The concentrations of individual PAHs were obtained by comparison of the intensities of the molecular ions of the compounds present in the samples with those of external standards. Thus, a standard of phenanthrene (m/z 178) was used to calculate the concentrations of phenanthrene and anthracene, a standard of fluoranthene (m/z 202) for fluoranthene and pyrene; chrysene (m/z 228) for chrysene and benzo(a)anthracene, Benzo(a)pyrene (m/ż 232) for the benzo-fluoranthenes, benzo(e)pyrene and benzo(a)pyrene and benzo(ghi)perylene (m/z 276) for benzo(ghi)perylene and indeno (1, 2, 3cd)pyrene.

Quantification and compound confirmation was achieved by using the following standard mixture: naphthalene, 2-methyl naphthalene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1, 2, 3-cd)pyrene, dibenzo(ac/ah)anthracene, benzo(ghi)perylene and coronene.

The PAH compounds were identified by comparing the chromatograms with those of PAH standards and with their mass spectra with the NBS library. The amounts were determined comparing the electronically integrated area of each peak with those of the internal standards. Standards of PAHs were purchased from Supelco, Aldrich-Chemie and Fluka. The level of determination was about 0.1 ngm^{-3} for each individual PAH component.

Particle size distribution

Sampling of the particulate matter in ambient air at Kosnica and on Zavižan was conducted using glass fiber filters, Gelman AIE 81736, diam. 127 mm. Approximately 1000 m^3 was pumped through the filter during a period of 72 h. The particulate matter was extracted from filters in an ultrasonic bath. The particle size distribution of samples has been measured by Coulter counter model ZB Industrial. The experimental conditions were: orifice tube; 30 μm, electrolyte; 5% w/v trisodium orthophosphate.

RESULTS AND DISCUSSION

This study intends to contribute to the understanding of atmospheric concentrations of PAHs in the particulate and gaseous phase, of two different locations, Zavižan and Kosnica, representing urban-industrial and rural sites. Beside PAHs, concentrations of sulphur dioxide were determined. Results obtained should give information about the influence of traffic, proximity of an urban-industrial zone and different distant sources of pollution, by transport through the atmosphere during winter and summer. The ratio benzo(e)pyrene/benzo(a)pyrene + benzo(e)pyrene has been taken into consideration. It could be of interest for assessing sources of emission or long-range transport.

Meteorological conditions

The sampling periods, meteorological parameters and the concentration of sulphur dioxide are presented in Table 1. Climate is influenced in this particular case by the position of an orographic obstacle (Velebit mountain) and the prevailing wind circulation and the distance from the sea. The Velebit mountain is the longest mountain chain in

Table 1 Meteorological parameters during two sampling periods, February and August 1990, in Zavižan and Kosnica.

Sampling periods (1990 Z = Zavižan K = Kosnica		*Sampling rate* (m^3h^{-1})	*Sample volume* $(m)^3$	*Mean temp. °C in 10 days*	*Mean rel. humidity (%) in 10 days*	*Mean rainfalls (mm) in 10 days*	*Cloudness mean val. in 10 days*	*Prominent wind direc. in 30 days*		*Mean wind speed* (ms^{-1}) *in 30 days*	*Concentration* SO_2 *in* $\mu g\ m^{-3}$	*Concentration* NO_2 *in* $\mu g\ m^{-3}$
01–02/2	Z_1	71.7	1937	+1.2	66	2.9	5.3	C	7	–	< d.l.	<d.l.
05–06/2		66.2	1854					N	1	0.8	< d.l.	22
08–09/2		66.5	1930					NE	–	–	< d.l.	27
12–13/2	Z_2	57.9	1623	–0.6	80	2.2	6.2	E	21	6.6	< d.l.	< d.l.
15–16/2		56.6	1585					SE	3	2.3	< d.l.	< d.l.
19–20/2		61.0	1710					S	1	18.9	< d.l.	< d.l.
22–23/2	Z_3	68.4	2053	+ 2.9	55	0	3.0	SW	10	4.9	< d.l.	23
26–27/2		69.5	2085					W	6	6.3	< d.l.	28
01–02/3		65.9	1977					NW	5	2.3	< d.l.	< d.l.
02–03/8	Z_4	69.3	2080	+ 11.7	76	4.0	3.2	C	14	–	11.2	32
06–07/8		66.6	2000					N	–	–	< d.l.	28
09–10/8		70.0	2100					NE	–	–	11.5	27
13–14/8	Z_5	65.8	1975	+ 12.9	73	0.8	3.7	E	50	7.2	< d.l.	28
16–17/8		64.1	1924					SE	–	–	< d.l.	23
20–21/8		60.3	1810					S	3	4.2	< d.l.	21
23–24/8	Z_6	66.0	1980	+ 13.5	84	1.2	4.5	SW	2	3.8	< d.l.	22
27–28/8		63.0	1895					W	21	3.0	< d.l.	23
30–31/8		74.0	2230					NW	3	2.2	< d.l.	25
01–02/2	K_1	66.0	2000	+ 8.0	67	0.5	3.8	C	22	–	10.2	28
05–06/2		66.0	1980					N	12	1.6	8.5	45
08–09/2		71.9	2230					NE	10	1.5	35.0	25
12–13/2	K_2	69.3	2080	+ 7.2	64	1.5	4.9	E	3	1.3	30.2	65
15–16/2		66.0	1980					SE	3	1.3	22.0	85
19–20/2		71.1	2205					S	7	2.2	75.0	82
22–23/2	K_3	61.2	1900	+ 8.8	46	0.6	1.9	SW	6	3.1	16.0	42
26–27/2		67.0	2080					W	16	3.1	14.7	7
01–02/3		65.3	2025					NW	5	2.1	5.0	15
02–03/8	K_4	62.6	1880	+ 22.5	50	1.0	3.1	C	20	–	< d.l.	< d.l.
06–07/8		55.1	1325					N	15	1.6	< d.l.	< d.l.
09–10/8		58.6	1760					NE	23	2.5	< d.l.	< d.l.
13–14/8	K_5	66.0	2000	+ 22.2	58	0.3	3.2	E	3	2.8	< d.l.	< d.l.
16–17/8		64.3	1730					SE	7	1.7	< d.l.	< d.l.
20–21/8		62.9	1950					S	14	1.7	< d.l.	< d.l.
23–24/8	K_6	65.4	2030	+ 24.0	60	0.1	5.2	SW	6	1.5	< d.l.	< d.l.
27–28/8		63.6	1910					W	5	1.4	< d.l.	19
30–31/8		66.9	2075					NW	–	–	8.2	2

Croatia parallel to the coast (see Figure 1). It is the most important orographic obstacle and contributes to the formation of weather conditions and climate characteristics of the mediteranian and continental part of the country.

Zavižan has a very characteristic wind rose, showing the presence of strong channel effects. The prevailing wind blows from East and West. Close to Zavižan, there are no local sources of pollution, there are no large industrial or urban centers. This also confirms the fact that Zavižan is mainly under the influence of pollution from distant sources transported through the atmosphere. The sampling period averaged: relative humidity 67%, rainfall 1.7 mm, temperature range from –0.6°C to + 2.9°C (February), relative humidity 77%, rainfall 2.0 mm, temperature range from 11.7°C to 13.5°C (August); and enabled stable sampling of particulate matter and vapour. Wind velocity was changing from complete calm to 18.9 ms^{-1} (February) and complete calm to 7.2 ms^{-1} (August).

Kosnica is situated 5 km away from the Zagreb industrial and urban area, so that PAHs are transported to the sampling site also through the atmosphere. The urban center and the industrial zones at the southeast of Zagreb have considerable influence on air pollution at Kosnica. The thermal effect (rise of temperature), due to the presence of a big city (Zagreb) causes formation of anomalies in regional temperature range: the center of the town is much warmer than the suburbs. The consequences of such a temperature distribution are specific streams that lift up pollutants in the air from the town and transport them to town surroundings. The mountain Medvednica strongly influences the macro streams in the investigated zone. The mountain, considered as an obstacle, causes north flux of the air above the town. This helps transporting of pollutants to Kosnica and at the same time cleans the atmosphere of the town[45]. The influence of the Sava river is stronger during winter, when the valley is mostly foggy. Traffic also increases the concentration of the pollutants at Kosnica. During the sampling periods, a considerable influence of traffic was noted.

Air at Kosnica averaged: relative humidity 59%, rainfall 0.67 mm, temperature range from +7.2°C to +8.8°C (February); relative humidity 56%, rainfall 0.46 mm, temperature range from +22.2 to +24°C (August).

PAH distribution

Particulate matter can be transported through the environment by several mechanisms. We can assume that PAHs absorbed on smaller particles were transported to sampling sites Zavižan or Kosnica. The particle size distribution of aerosol samples from these sites is shown in Table 2. Results obtained are the mean value in winter and summer. About 85% of particles collected on Zavižan and about 80% at Kosnica were smaller than 1.8 μm; which are less efficiently removed by wet and dry deposition processes. Their atmospheric residence time is longer and therefore they can be deposited far from their sources.

Concentrations of PAHs determined in winter and summer are reported in Tables 3 and 4. Mean values are estimated for ten days sampling periods (Table 1).

Separation, identification and quantification of PAHs were performed by TLC, GC and GC-MS. Results obtained by TLC of PAHs were reliable and reproducible. The loss of each PAH during the analytical procedure was found to be between 8.05% for benzo(ghi)perilene to 18.25% for phenanthrene. GC and GC-MS were used as standard methods and the quantitive determination is reported in Tables 3 and 4.

Table 2 Particle size distribution of samples collected in Zavižan and Kosnica.

Particle size µm	*Cumulative weight undersize %*			
	Sampling site Zavižan		*Sampling site Kosnica*	
	Sampling period		*Sampling period*	
	Z_1, Z_2, Z_3	Z_4, Z_5, Z_6	K_1, K_2, K_3	K_4, K_5, K_6
2.40	94.8	94.6	93.2	94.0
1.90	90.2	91.0	86.8	87.2
1.80	85.2	84.8	80.0	79.8
1.51	71.3	72.0	47.2	46.8
1.20	50.0	51.0	26.0	25.4
0.95	32.3	33.0	13.2	13.6
0.76	18.9	18.7	6.9	7.3
0.60	6.5	6.3	1.7	1.9

*Z_1, Z_2... K_1, K_2... Sampling periods in Zavižan (Z) and Kosnica (K) (see Table 1).

The PAHs ranging from naphthalene to coronene were the primary components. In the particulate and vapour phase in air on Zavižan and at Kosnica acenaphtene, fluorene, phenanthrene and fluoranthene were predominant. The total concentration of these PAHs at Kosnica is 1.32 times (winter) and 2.55 (summer) times higher than the concentration on Zavižan. In general, the lower molecular weight PAHs, including phenanthrene, anthracene, fluoranthene, benzo(a)anthracene and chrysene, displayed similar tendency for volatilization and artifact formation during both the winter and summer sampling periods. The sum of concentrations of nine major nonalkylated PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzofluoranthene, benzo(a)pyrene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perilene), which is expressed as Σ COMB, has often been used as an indicator of PAHs from combustion. The winter and summer Σ COMB in Zavižan (101.40 ng m^{-3}) is about 5.7 times lower than Σ COMB in Kosnica (573 ngm^{-3}). Σ COMB in Zavižan (winter) (70.25 ng m^{-3}) is about 4.8 times lower than Σ COMB in Kosnica (338.75 ng m^{-3}) whereas in summer is about 7, 5 times lower. This difference shows that Kosnica (urban sites) is significantly more exposed to direct pollution than Zavižan (rural site). The proportion of fluoranthene + pyrene within Σ COMB in Zavižan is 57.7% and in Kosnica 39.5%. This ratio indicates that the concentration of PAHs in the air is mainly influenced by traffic and combustion products in stationary sources.

The long-range transport of the PAHs through the atmosphere can be investigated via the ratios presented in Table 5. Some ratios from the present study and others have been compared together with the wind direction conditions during sampling[12,45–47] and the source of PAHs. As it can be seen in Table 5, there are only slight differences between the summer and winter ratios of the different compounds in both locations.

The phenanthrene/anthracene, fluoranthene/pyrene, benzo(ghi)perylene/benzo(e) pyrene and other ratios indicate mixed pyrolitic sources, originated in traffic and domestic emissions. The benzo(e)pyrene/ benzo(a)pyrene + benzo(e)pyrene ratios are also similar to those of gasoline car emissions whereas the indeno(1,2,3-cd)pyrene/benzo(ghi)perylene ratio may indicate some contribution from diesel and vehicle exhausts[48]. More recently[49]it was also suggested that a larger abundance of alkylated phenanthrenes in aerosols is indicative of diesel oil combustion sources. Diesel

Table 3 Concentration levels (in ngm^{-3}) of polycyclic aromatic hydrocarbons in Zavižan from particulate (P) and vapour (V) phases.

Component	*Location ZAVIŽAN*													
	Sampling periods							*Sampling periods*						
	Z_1		Z_2		Z_3			Z_4		Z_5		Z_6		
	P	*V*	*P*	*V*	*P*	*V*	*Mean value*	*P*	*V*	*P*	*V*	*P*	*V*	*Mean value*
Naphthalene	–	–	< 0.1	–	< 0.1	–	–	–	–	–	–	–	–	–
2-Methyl naphthalene	–	–	< 0.1	–	< 0.1	–	–	–	–	–	–	–	–	–
1-Methyl naphthalene	–	–	< 0.1	–	< 0.1	–	–	–	–	–	–	–	–	–
Acenaphthene	–	10.0	–	8.5	–	19.2	12.5	–	0.6	–	0.7	–	0.4	0.5
Fluorene	0.1	30.5	3.5	15.5	1.2	27.3	13.0	< 0.1	8.3	–	2.6	–	11.5	7.5
Phenanthrene	0.35	23.0	0.25	18.0	0.3	26.0	11.3	< 0.1	13	0.15	9	0.2	21	7.24
Anthracene	0.8	0.8	0.45	0.35	0.3	0.75	0.58	0.4	0.35	0.25	0.15	0.4	0.26	0.30
1-Methyl phenanthrene	< 0.1	0.1	< 0.1	0.1	< 0.1	< 0.1	0.05	–	–	< 0.1	0.1	< 0.1	0.1	0.05
Fluoranthene	0.8	2.5	0.7	12.0	0.7	21.0	6.2	0.3	7.5	0.3	7.0	0.5	9.5	3.1
Pyrene	0.2	0.25	0.3	0.45	< 0.1	0.4	0.28	< 0.1	–	< 0.1	0.15	0.15	< 0.1	0.08
Benzo(a)anthracene	1.4	0.15	1.0	0.3	1.2	0.15	1.43	1.3	0.2	0.82	< 0.1	0.65	–	0.60
Chrysene	2.5	0.25	2.6	0.15	2.3	0.25	1.33	1.8	0.15	1.35	0.2	1.15	0.2	0.81
Benzo(j/k/b)fluoranthene	1.3	0.35	7.3	2.15	1.1	0.3	2.08	0.4	< 0.1	0.15	< 0.1	0.25	0.15	0.18
Benzo(e)pyrene	0.45	–	0.55	–	0.35	–	0.45	0.2	–	0.15	–	0.2	–	0.18
Benzo(a)pyrene	0.3	–	0.45	–	0.25	–	0.42	0.15	–	0.1	–	0.15	–	0.13
Indeno(1,2,3-cd)pyrene	1.15	0.1	0.1	< 0.1	1.0	< 0.1	0.43	0.15	–	0.4	0.3	0.75	–	0.40
Dibenzo(ac/ah)anthracene	< 0.1	< 0.1	1.2	–	0.15	–	0.07	0.2	< 0.1	0.1	–	< 0.1	–	0.10
Benzo(ghi)perylene	0.3	0.1	0.3	< 0.1	0.2	0.1	0.17	0.15	–	0.15	< 0.1	0.2	< 0.1	0.10
Coronene	–	–	–	–	< 0.1	–	–	–	–	–	–	–	–	–

Z_1, Z_2... Sampling periods. (see Table 1).

Table 4 Concentration levels (in ngm^{-3}) of polycyclic aromatic hydrocarbons in Kosnica from particulate (P) and vapour (V) phases.

	Location KOSNICA													
Component	*Sampling periods*							*Sampling periods*						
	K_1		K_2		K_3			K_4		K_5		K_6		
	P	*V*	*P*	*V*	*P*	*V*	*Mean value*	*P*	*V*	*P*	*V*	*P*	*V*	*Mean value*
Naphthalene	0.3	–	0.8	–	3.5	–	1.53	0.5	–	< 0.1	–	1.5	–	0.7
2-Methyl naphthalene	0.1	–	0.3	–	1.6	–	0.67	0.3	–	< 0.1	–	0.1	–	0.1
1-Methyl naphthalene	0.1	–	0.2	–	0.8	–	0.37	0.1	–	< 0.1	–	0.1	–	0.07
Acenaphthene	–	40.2	–	37.2	–	43.6	40.33	–	13.0	–	26.0	–	24.0	21.0
Fluorene	2.5	40.5	1.6	28.5	3.5	31.5	18.02	< 0.1	11.3	0.3	16.0	–	8.7	7.3
Phenanthrene	0.15	26	0.9	47.5	0.2	18.5	15.50	0.1	13	0.11	26	0.7	21	10.1
Anthracene	3.5	1.2	2.8	1.15	2.15	0.8	1.93	1.3	0.7	1.95	0.55	1.75	1.1	1.26
1-Methyl phenanthrene	0.1	0.3	0.1	0.2	0.1	–	0.16	0.1	0.6	< 0.1	0.2	< 0.1	0.3	0.22
Fluoranthene	10.2	35.0	13.5	53.0	8.0	4.0	20.62	2.5	35.0	4.0	25.0	14.0	18.0	15.0
Pyrene	0.65	1.3	0.6	2.3	0.4	2.05	1.22	0.3	1.4	0.35	1.35	0.3	1.4	0.85
Benzo(a)anthracene	12.0	0.8	14.5	1.8	11.3	2.5	7.15	8.7	2.0	9.3	1.5	11.5	1.5	5.7
Chrysene	4.5	1.05	12.5	6.5	14.3	2.0	6.80	12.5	3.5	11.0	5.3	8.5	4.5	7.5
Benzo(j/k/b)fluoranthene	6.5	3.2	7.2	3.55	9.3	5.4	5.85	3.5	1.7	1.3	0.7	5.30	3.15	0.08
Benzo(e)pyrene	5.3	–	1.5	–	2.5	–	3.10	2.9	–	2.0	–	0.85	–	1.92
Benzo(a)pyrene	5.5	–	4.2	–	2.1	–	3.93	2.5	–	1.6	–	0.7	–	1.6
Indeno(1,2,3-cd)pyrene	2.4	1.2	1.75	–	3.2	1.15	1.94	0.45	–	3.5	0.3	1.95	0.55	1.35
Dibenzo(ac/ah)anthracene	3.5	0.15	1.05	–	< 0.1	–	1.20	1.5	–	0.5	–	1.1	–	1.03
Benzo(ghi)perylene	12.5	0.9	28.0	0.95	14.5	1.2	9.67	8.7	1.2	6.55	0.15	9.8	0.2	4.43
Coronene	0.1	–	0.15	–	–	–	0.13	< 0.1	–	< 0.1	–	–	–	–

K_1, K_2... Sampling periods (see Table 1).

Table 5 Individual PAH ratios.

	Location Kosnica								*Location Zavižan*							
	Sampling periods								*Sampling periods*							
Ratio of PAH	K_1	K_2	K_3	*Mean value*	K_4	K_5	K_6	*Mean value*	Z_1	Z_2	Z_3	*Mean value*	Z_4	Z_5	Z_6	*Mean value*
Phenanthrene/ (Phenanthrene + Antracene)	0.85	0.92	0.86	0.88	0.87	0.91	0.88	0.89	0.94	0.96	0.96	0.95	0.95	0.96	0.97	0.96
Fluoranthene/ (Fluoranthene + Pyrene)	0.96	0.96	0.83	0.92	0.96	0.94	0.95	0.95	0.88	0.94	0.98	0.93	0.98	0.97	0.98	0.98
Benzo(e)pyrene/ (Benzo(e)pyrene +Benzo(a)pyrene)	0.49	0.26	0.54	0.43	0.54	0.56	0.70	0.60	0.60	0.50	0.58	0.56	0.57	0.6	0.57	0.58
Benzo(a)anthracene/ (Benzo(a)anthracene + Chrysene)	0.49	0.26	0.54	0.43	0.54	0.56	0.57	0.56	0.36	0.32	0.35	0.34	0.44	0.35	0.33	0.37
Indeno(1,2,3-cd)pyrene/ (Indeno(1,2,3cd)pyrene + Benzo(ghi)perylene)	0.20	0.06	0.22	0.16	0.04	0.36	0.20	0.20	0.86	0.33	0.79	0.66	0.50	0.74	0.71	0.65
Pyrene/benzo(b)fluoranthene	0.20	0.27	0.17	0.21	0.33	0.83	0.20	4.36	0.27	0.08	0.36	0.24	0.20	1	0.63	0.61
Benzo(ghi)perylene Benzo(e)pyrene	2.43	6.89	7.47	5.60	3.96	4.16	14.2	7.47	0.89	0.73	0.86	0.83	0.75	1.07	1.5	1.11
Benzo(e)pyrene/Benzo(a)pyrene	0.96	0.36	0.84	0.72	1.16	1.25	0.97	1.13	1.50	1.22	1.40	1.37	1.33	1.50	1.33	1.39

Z_1, Z_2... K_1, K_2... Sampling periods in Zavižan (Z) and Kosnica (K). (see Table 1) oil engines are known to produce larger PAHs than those fueled with gasoline[50]. The ratios flouranthene/pyrene and indeno(1,2,3-cd)pyrene/benzo(ghi)perylene are close to those reported for coal combustion emissions[51].

The ratios of specific indicators in Zavižan are close to those found in the western Mediterranean[12,13], while in Kosnica they are strongly influenced by the vicinity of an urban center as well as by meteorological conditions at the time of sampling. If atmospheric reactivity was a significant determinant of PAH levels, then one would have anticipated reactive PAH/unreactive PAH ratios to be lower for the more aged (long-range transported) aerosol as well as for the samples collected during summer, and this is apparent from the data in Table 5.

Detectable amounts of PAHs require a long sampling time, which may also give rise to changes in concentration and content compared to the original air mass. Thus blow-off and/or chemical and photochemical degradation can lead to an underestimation of the PAH concentration in the atmosphere. Degradation of PAHs absorbed on particulate matter by nitrogen dioxide and ozone should also be considered[52]. During sampling typical carcinogenic compounds such as benzo(a)anthracene or benzo(a)pyrene can be oxidized when absorbed on glass fiber filter while phenanthrene and chrysene are more refractory[53].

PAH concentrations

In general, the concentrations of PAHs in the studied air samples were low at both locations, Zavižan (rural) and Kosnica (urban). Total mass concentrations of PAHs in Zavižan were 259.15 ngm^{-3} (mean value 3.36) in winter and 100.96 ngm^{-3} (mean value 1.42) in summer, while in Kosnica were 686.25 ngm^{-3} (mean value 7.31) in winter and 410.01 ngm^{-3} (mean value 1.42) in summer.

Total concentrations of PAHs in Kosnica were from about three to four times higher than concentrations of PAHs in Zavižan and they do not yet show a very polluted atmosphere (Table 6). The great difference between winter and summer periods can be attributed to local pollutant sources. Measurement of free SO_2 concentrations in air contributes to assess the general pollution in Zavižan and Kosnica. Concentrations of SO_2 (Table 1) in Zavižan in February were below the detection limit and in August two smaller incidents (11 μgm^{-3}) happened. The mean concentration value of SO_2 determined in February in Kosnica was 24 μgm^{-3} with a maximal concentration of 75 μgm^{-3} while in August it was below the detection limit except in August 30/31st when it was 8 μgm^{-3}. The big difference between Zavižan and Kosnica is due to the wind direction from the industrial and domestic emission sources (urban site). Incidents like these can be caused by uncontrolled burning of organic matter near the sampling site although during that period there was no domestic heating.

Concentrations of SO_2 are not dependent on total concentration of PAHs, although in February, the highest concentration of SO_2 at Kosnica ranged from 8.5 to 75 μgm^{-3}. The concentration of oxidizing agents as well as NO_2 were determined in winter and summer in Zavižan and Kosnica (Table 1). On both locations the determination was performed four times in winter and nine in summer. The concentrations determined indicated low levels of photochemical agents. Transformation processes of PAHs in air due to the presence of these compounds will result in lower concentration of parent compounds. Depending on the relative humidity, temperature, residence time of PAHs in air, and the concentration of SO_2, NO_2, the importance of these transformation processes will

Table 6 Seasonal average concentration of carcinogenic PAH in air (particulate and vapour phase) in ngm^{-3}.

	Location ZAVIŽAN				*Location KOSNICA*			
	Sampling periods				*Sampling periods*			
	Winter $Z_1\,Z_2\,Z_3$		*Summer $Z_4\,Z_5\,Z_6$*		*Winter $K_1\,K_2\,K_3$*		*Summer $K_4\,K_5\,K_6$*	
PAH	*P*	*V*	*P*	*V*	*P*	*V*	*P*	*V*
Phenanthrene	0.25–0.35	18.0–26.0	< 0.1–0.2	9.0–2.1	0.15–0.9	18.5–26	0.1–0.7	13–26
Benzo(a)anthracene	1.0–1.4	0.15–0.3	0.65–1.3	0–0.2	11.3–14.5	0.8–2.5	8.7–11.5	1.5–2.0
Chrysene	2.3–2.6	0.15–0.25	1.15–1.8	0.15–0.2	4.5–14.3	1.05–2.0	8.5–12.5	3.5–5.3
Benzo(j/k/b)fluoranthene	1.1–7.3	0.3–2.15	0.15–0.4	< 0.1–0.15	6.5–7.2	3.2–5.4	1.3–5.3	0.7–3.15
Benzo(a)perylene	0.25–0.45	–	0.1–0.15	–	2.1–5.5	–	0.7–2.5	–
Indeno(1,2,3-cd)pyrene	0.1–1.15	0.1–0.1	0.15–0.75	0–0.3	1.75–3.2	0–1.2	0.3–1.95	0–0.55
Dibenzo(ac/ah)anthracene	< 0.1–0.15	0–< 0.1	< 0.1–0.2	0–< 0.1	< 0.1–3.5	0–0.15	0.5–1.5	–

Z_1, Z_2... K_1, K_2... Sampling periods in Zavižan (Z) and Kosnica (K) (see Table 1).

naturally be different in different areas of sampling[54]. The total concentrations of PAHs determined in Zavižan as a reference place (1954 m a.s.l.) were lower than the concentrations measured in the air of Kokkola a town located on the coast of the Gulf of Bothnia, in central Finland, and in the Rijnmond[3] area in the western part of The Netherlands, near the coast, and Alfabia ridge (~ 1100 m Mallorca Island)[13].

Concentrations of PAHs during periods of air low temperatures, ranging from –0.6°C to + 2.9°C (Zavižan) and from + 8°C to + 8.8°C (Kosnica), were three times higher compared to the concentrations determined in the temperature range from +11.7°C to +13.5°C (Zavižan) and from +22.2°C to + 24°C (Kosnica). This is due to the amount of organic fuel consumption in winter and summer. Concentrations of PAHs were not influenced by rainfalls since they were minor (from 0 to 4 mm), although it was cloudy during the sampling periods. Total concentration of PAHs during calm periods without wind was up to two times higher than the average concentration measured when the wind speed was higher than 1.5 ms^{-1}.

Kosnica sampling site was mostly loaded by vehicle pollution during the sampling periods. This is confirmed by the occurance of lead in all samples.The average concentration of lead during winter period at Kosnica was 0.06 μgm^{-3} (0.02–0.11) and during summer 0.05 μgm^{-3} (0.01–0.09). Lead was due to car gasses since there was circulation in the atmosphere, concentrations remained quite low. The lead concentrations and fluxes, between the two seasonal periods and the constant automobile traffic intensity throughout the winter and summer season support the earlier stated theory that the PAH flux and concentration differences between the two periods were to a great deal dependent upon the additional load from domestic heating and central heating boilers during the winter.

The distribution of seven PAHs: phenanthrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and dibenzo(ac/ah) anthracene, absorbed on particulate matter, and in vapour phase, is presented in Table 6. The ratio of noncarcinogenic PAHs (phenanthrene and chrysene) to the total sum of concentrations of all seven PAHs is found to be higher in winter (Zavižan: 1.3 times in winter and 1.1 in summer; Kosnica:1.7 times in winter and 1.6 in summer).

Benzo(a)pyrene is one of the most important PAHs because of its carcinogenic properties[55,56]. Concentration levels of benzo(a)pyrene in ambient air have been many times reported and benzo(a)pyrene is commonly used as an indicator of PAHs. In this work benzo(a)pyrene was found at both sampling sites only in the particulate phase. Measured concentrations of benzo(a)pyrene in Zavižan can be compared with those in Kokkola[41] (remote station in a rural area) and it can be concluded that the atmosphere of the referent location is low polluted. Mean concentration of benzo(a)pyrene at Kosnica during winter was 11.8 ngm^{-3} (2.1–5.5 ngm^{-3}) which was lower than in other cities from the region, namely Zagreb in Croatia[57] and Ljubljana in Slovenia[58]. The concentration of benzo(a)pyrene dropped to 4.8 ngm^{-3} at Kosnica during summer, and it was assumed that the average concentration of pollution was affected by the traffic. Figure 2 presents the distribution of benzo(a)pyrene concentrations and the air temperature in winter and summer sampling periods, in Zavižan and Kosnica. The histogram shows that higher concentration of benzo(a)pyrene appear on cooler days at both locations; on warmer days, it decreases. It is preassumed that an increase of temperature originate a decrease of benzo(a)pyrene concentration in the particulate.

Mean concentration of PAHs measured in Zavižan can be compared to mean concentration of PAHs in Rijnmond rural area[3] (OOstvoorne). Values for PAH concentrations obtained from the aerosol collected at Mallorca[13] are lower then those measured in Zavižan.

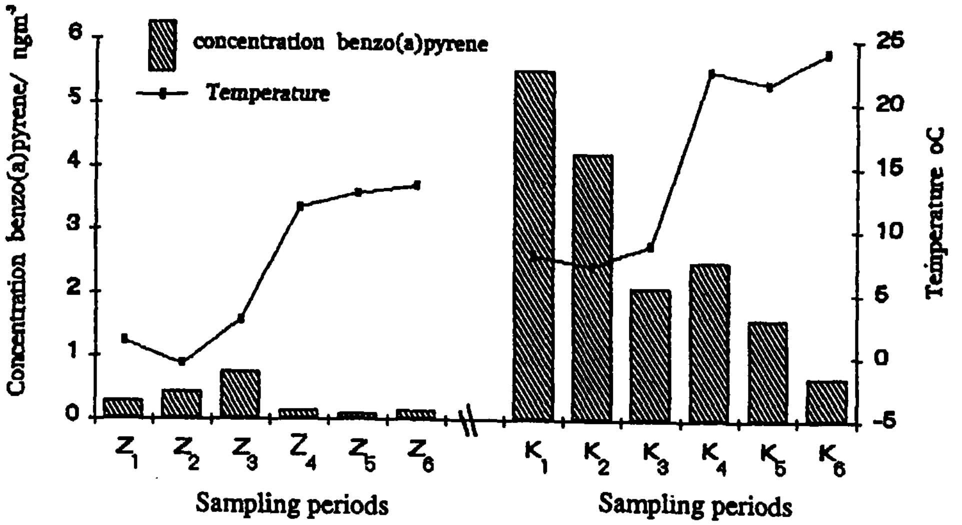

Figure 2 Distribution of the benzo(a)pyrene concentration in air (particulate phase) in ngm^{-3} and temperature in the sampling periods, winter and summer 1990, in Zavižan (Z) and Kosnica (K).

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*Z_1, Z_2... K_1, K_2... Sampling periods in Zavižan (Z) and Kosnica (K) (see Table 1).

CONCLUSION

Concentrations of PAHs, oxidizing agents NO_2 and SO_2 were determined in the air of two sampling sites, Zavižan and Kosnica, Republic of Croatia. Concentrations of PAHs and other pollutants measured in these sites originate from combustion. The main source of pollution is local automobile exhausts but it can be assumed that long-range transport through the atmosphere also contributes to it. Nineteen PAHs were measured, six of them carcinogenic. Values obtained for PAHs in Kosnica (urban) in winter were about three times higher than in Zavižan (rural),while during summer they were about four times higher.

The distribution of benzo(a)pyrene enabled us to consider the sites of Zavižan and Kosnica as low polluted compared to the industrial and urban centers of Zagreb, in Croatia,[56] and Ljubljana, in Slovenia[57]. Meteorological conditions influence the concentrations of PAHs; wind, higher temperatures, rain and snow decrease the values while calm without wind, lower temperature and cloudiness increase them. The vapor/particulate phase partitioning is also influenced by ambient temperature.

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