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LEVELS AND PROFILES OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE ZAGREB AIR IN THE HEATING SEASON

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Samples of suspended particulate matter, collected at four sites in Zagreb during the heating season were analysed for the content of polycyclic aromatic hydrocarbons. Data were analysed with special reference to indicators of car traffic contribution the BghiPer/BaP and Cor/BaP ratios. Taking 1.5 as a borderline value for the BghiPer/BaP ratio, a significant influence of car traffic on air pollution by polycyclic aromatic hydrocarbons was noticed at a site close to a petrol station. Our data were compared with the BghiPer/BaP and Cor/BaP ratios from other countries. A similar relationship of the ratios between urban and traffic near sites was obtained.

Key terms: air pollution, airborne particles, benzo-a-pyrene, car traffic, petrol station, source identification, urban area

Polycyclic aromatic hydrocarbons (PAH) are products of thermal degradation of organic matter. Usually, they are due to incomplete combustion of fossil fuels. Their presence has been detected in the air, water, soil and food.

The PAH concentration levels in the air depend on heating practice, traffic density and type of industrial emissions. They tend to vary with season and to fluctuate with meteorological conditions. The recorded concentrations have been reported to range from 0.01 ng/m^3 in rural areas to 10 ng/m^3 in urban areas reaching 40 ng/m^3 around some industries (1).

Tetracyclic and larger PAH are bound to respirable particles and therefore can be determined in samples of suspended particulate matter (SPM).

About 200 PAH have been identified in the air, but in practice only up to 20 are measured. Quite often only benzo-a-pyrene (BaP) is measured and taken as an index of PAH pollution, being the most widely investigated PAH and a proven carcinogen.

In this paper results are presented for eight PAH measured in SPM samples, collected at four stations of the Zagreb network in the heating season. The PAH/BaP ratios (PAH profiles) were analysed with special reference to benzo-ghi-perylene/benzo-a-pyrene (BghiPer/BaP) and coronene/benzo-a-pyrene (Cor/BaP) ratios which are indicators of traffic contribution to air pollution by PAH.

EXPERIMENTAL

Sampling locations

Samples were collected at four locations: (A_1) low-housing residential area with individual heating and low traffic density, (A_2) business and residential city centre with individual and central heating and dense traffic, (A_3) central square with no traffic but surrounded with busy streets, (A_4) city centre close to a busy petrol station.

At sites A_1, A_2 and A_3 samples were collected at the height of about four metres above the ground. At site A_4 sampling was done at the pedestrian level (1.5 m above the ground).

Collection of samples

All samples were collected over a 24-hour period. At the first three stations samples were collected by high-volume (HV) samplers on 20x25 cm glass fibre filters from about 1 800 m^3 of air. At the fourth station samples were collected by low volume (LV) samplers on glass fibre filters with a 2.5 cm diameter sampling surface from about 2 m^3 of air. Before and after sampling HV filters were conditioned to a constant humidity and weighed. All samples were kept in a freezer at –18 °C, wrapped in Al foil, until analysed.

Sample analysis

High-volume samples. PAH were extracted from SPM samples with cyclohexane in a Soxhlet apparatus for eight hours. The extracts were evaporated to a small volume, cleaned up from interfering substances by passing the concentrated extract through a silicagel column, and evaporated to dryness. The residue was dissolved in acetonitrile and injected in a high performance liquid chromatograph (HPLC) coupled to a fluorescence detector.

Low-volume samples. PAH were extracted with cyclohexane in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation and evaporated to dryness. They were redissolved in acetonitrile and analysed in the same way as the HV samples.

A detailed procedure for the preparation and analysis of samples has been described elsewhere (2). The following PAH were measured: fluoranthene (Flu), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP), benzo-ghi-perylene (BghiPer), anthanthrene (Ant) and coronene (Cor). In addition pyrene (Pyr) was measured in HV samples.

RESULTS AND DISCUSSION

Table 1 shows average concentrations and the range of measured compounds for the four sampling locations. The unusually high SPM levels at location A_3 were due to the nearby building activities, but they were not followed by correspondingly high PAH levels. Generally, the lowest PAH concentrations were observed in the low-housing residential area (A_1) and highest near a petrol station (A_4). In order to estimate whether this should be attributed to a generally higher pollution at the pedestrian level at site A_4 or to motor car exhausts, the PAH profiles (PAH/BaP ratios) were analysed with special reference to the BghiPer/BaP ratio, which is an indicator of PAH coming from incompletely burned petrol. The PAH profiles are shown in Figure 1.

Table 1. *Arithmetic means (X) and ranges of suspended particulate matter (SPM) ($\mu g/m^3$) polycyclic aromatic hydrocarbons (ng/m^3) in the city of Zagreb, recorded at four sites (A_1–A_4)*

Measured component	A_1			A_2			A_3			A_4		
	n	$\bar{X}$	range	n	$\bar{X}$	range	n	$\bar{X}$	range	n	$\bar{X}$	range
SPM	14	136	70–268	7	179	118–275	20	269	60–809			
Flu	14	33.8	11.7–128.1	7	65.7	8.4–176.3	20	44.5	9.1–121.3	15	63.5	6.5–165.5
BbF	14	12.1	6.8–28.5	7	17.8	6.6–50.7	20	14.4	2.8–37.8	15	27.1	7.9–66.2
BkF	14	4.8	0.8–11.4	7	6.2	2.5–16.1	20	2.6	0.5–7.6	15	9.7	2.9–21.1
BaP	14	10.3	4.4–28.9	7	13.1	4.3–40.8	20	8.1	1.4–23.6	15	23.0	3.7–52.6
BghiPer	14	9.3	4.4–21.8	7	14.5	4.8–41.2	20	10.9	1.7–31.8	15	56.8	11.8–197.9
Ant	14	9.3	3.9–24.3	7	5.4	1.1–17.9	20	3.3	0.4–21.6	15	11.8	2.7–22.8
Cor	12	3.5	2.0–7.7	1	–	n.d.–13.6	7	2.7	n.d.–20.7	15	12.9	7.1–32.6
Pyr	14	32.9	13.5–105.3	7	78.8	12.0–208.6	19	59.4	4.2–138.7			

n = number of samples
n.d. – not detectable

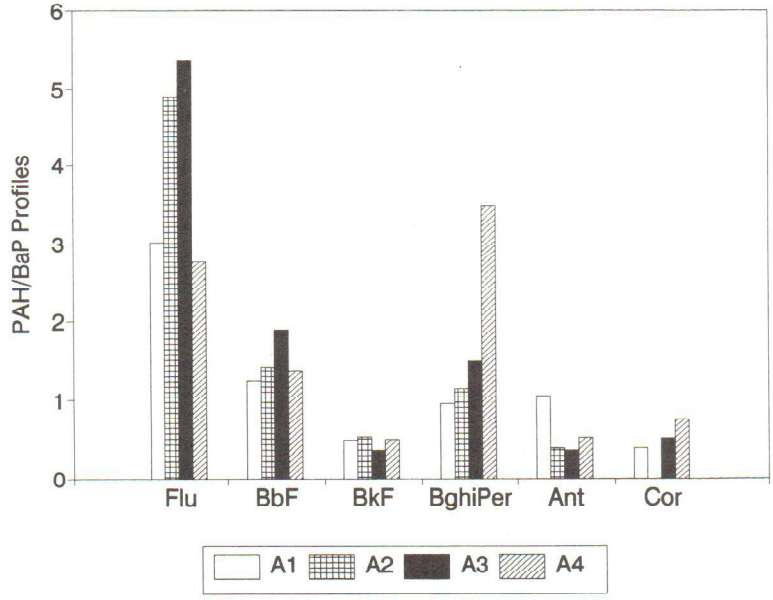

Figure. *PAH profiles for the four sampling locations*

Due to a large variability of the results and a relatively small number of samples, a non-parametric test seemed to be more suitable for testing the significance of difference between BghiPer/BaP ratios at the four sampling sites. After inspecting the results the ratios were divided into those higher and those lower than 1.5 (Table 2). Statistical analysis

proved a significant difference in the frequency of BghiPer/BaP ratios higher or lower than 1.5 at the four locations (χ^2=21.5, P<0.005), which indicates a dominant contribution of car traffic to air pollution at site A_4.

Table 2. *Contingency table of BghiPer/Bap ratios at the four sampling sites*

Site	<1.5		>1.5		f_{tot}
	f_o	f_{ex}	f_o	f_{ex}	
A_1	14	9.2	–	4.8	14
A_2	7	4.6	–	2.4	7
A_3	12	13.2	8	6.8	20
A_4	4	9.9	11	5.1	15
f_{tot}	37	–	19	–	56

f = frequency, o = observed, ex = expected, tot = total

The other indicator of traffic pollution, coronene, was detected only in 32 out of 56 samples and therefore was not submitted to the same statistical procedure. The Cor/BaP ratios in Figure 1 show, however, the same trend as the BghiPer/BaP ratios. There was also a high correlation between BghiPer and Cor concentrations at all sites (N=32, r=0.882). The average Cor/BaP ratio at site A_4 was 0.75 while at other stations the average ratios were 0.38 (A_1) and 0.50 (A_3).

Comparison of our findings with the data reported earlier by some other authors support such an approach. *Sexton and co-workers* (3) reported BghiPer/BaP and Cor/BaP ratios in a wood burning community in winter to be 1.3 and 0.3 respectively. The same ratios calculated from the winter data of *Masclet and co-workers* (4) amounted to 0.65 and 0.25 for ambient air and to 1.7 and 2.0 for highway at road level. *Greenberg and co-workers* (5) reported BghiPer/BaP and Cor/BaP ratios at three urban locations in New Jersey in winter to have been 1.4 and 0.5 (Newark), 1.9 and 0.9 (Elisabeth), 1.2 and 0.6 (Camden). Higher levels in Elisabeth were attributed to higher emissions from local motor vehicles. In the 1991 annual report of the Regional Institute for Air Pollution Control in North-Rhine Westphalia (Germany) (6) BaP/Cor ratio is used for analysing the contribution of car traffic to air pollution by PAH over years. In order to make those data comparable to our profiles we inverted them to Cor/BaP ratios and calculated also the BghiPer/BaP ratios from their data for 1991 (52 sites).

Owing to the control of coal burning sources, especially after a large coke works in this area was brought to a standstill, in the period 1985–1991 the average Cor/BaP ratios increased from 0.33 to 0.56 indicating that whereas the total PAH emission had been reduced over the years, the relative contribution of car exhaust increased. In 1991 at two high traffic density sites the Cor/BaP ratio amounted to 0.78 and 0.80.

Among 44 German stations representing general urban sites, 95.5% had the BghiPer/BaP ratio below 1.5; at two traffic exposed stations the ratio was 1.57 and 1.64. The fact that the numerical values of the ratios for the German and Zagreb data are practically identical must not, however, be misinterpreted as the German data are annual means and our data are means for the heating season. The mean annual BghiPer/BaP and

Cor/BaP ratios are expected to be higher than those for the heating season since summer ratios tend to be higher not only because of the absence of space heating, but also because of greater stability of BghiPer and Cor than of BaP at higher temperatures (7, 8). But irrespective of absolute figures the given ratios at general urban and close to the traffic sites show a consequent relationship for all sets of data.

CONCLUSION

Analysis of PAH concentrations in the air at four sites in Zagreb during the heating season, with special reference to the contribution from car traffic, has confirmed that BghiPer/BaP and Cor/BaP ratios are suitable indicators of air pollution by car exhausts.

Although the number of our data is rather limited they show the same tendency as the data from urban and traffic sites in other countries.

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Sažetak

RAZINE I PROFILI POLICIKLIČKIH AROMATSKIH UGLJIKOVODIKA U ZRAKU ZAGREBA U SEZONI LOŽENJA

Uzorci lebdećih čestica, sakupljeni na četiri mjerne stanice u Zagrebu u sezoni loženja, analizirani su na sadržaj policikličkih aromatskih ugljikovodika. Podaci su razmatrani s posebnim osvrtom na pokazatelje doprinosa prometa: omjeri BghiPer/BaP i Kor/BaP. Uzevši 1,5 kao graničnu vrijednost za omjer BghiPer/BaP utvrđen je značajan utjecaj prometa na onečišćenje zraka policikličkim aro-

matskim ugljikovodicima na stanici u blizini benzinske crpke. Usporedba naših podataka s omjerima BghiPer/BaP i Kor/BaP u drugim zemljama pokazuje slične odnose između ta dva omjera u općoj atmosferi i u blizini toka prometa.

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Ključne riječi: automobilski promet, benzinska crpka, benzo-a-piren, gradsko područje, identifikacija izvora, lebdeće čestice, onečišćenje zraka