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## PAHs LEVELS IN GAS AND PARTICLE-BOUND PHASE IN SCHOOLS AT DIFFERENT LOCATIONS IN SERBIA

### Article Highlights

- Significant seasonal variations of gas and particle-bound phase were observed
- Sum of PAH concentrations in gas phase were much higher
- Traffic emissions and coal combustion were the major source of PAHs
- Diesel engines were the dominant source of PAHs at the industrial site

### Abstract

*This study investigated seasonal variation of PAHs and their partition between gas and particulate-bounded phases in indoor and outdoor air in 4 schools in Serbia located at different locations. The sampling campaigns were conducted during one workweek at each school successively. Campaigns were conducted in schools during heating and non-heating seasons in December 2011 and June 2012. Seasonal variations of gas and particle-bounded PAHs concentrations were observed with higher levels during heating season. The highest total PAH values were associated with the gas phase in both sampling periods. The total PAHs concentration at indoor and at the outdoor sites, during heating season, ranged from 88.45 to 447.72 ng/m<sup>3</sup> and 201.69 to 1017.15 ng/m<sup>3</sup>, respectively. During non-heating season, the total PAHs concentration ranged from 36.91 to 271.57 ng/m<sup>3</sup> in indoor environment and 27.00 to 132.32 ng/m<sup>3</sup> in outdoor environment. Most of the I/O ratios were less than 1, which indicated that the indoor PAHs were mostly from outdoor sources. The use of diagnostic ratio showed that traffic emission and coal combustion are the major sources of PAHs. Only the diagnostic ratios for the school located near the industrial area showed significant deviation compared to other schools.*

*Keywords: PAHs, schools, seasonal variation, I/O ratio, diagnostic ratio.*

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants produced by incomplete combustion processes of organic material, such as biomass and fossil combustion, vehicular emissions, industrial processes, etc. PAHs consist of two or more fused benzene rings containing only carbon and hydrogen. Most PAHs are carcinogenic and mutagenic to human and cause serious damage to human health. The list of priority PAHs varies in different countries, but the US EPA list of 16 priority PAHs is often used as a standard [1].

PAHs exist in the atmosphere in gas and particle-bound phase, and they are distributed between these phases. Most of two- and three-ring PAHs exist in the gas phase, while five- and six-ring PAHs exist mostly in the particulate phase. PAHs with four rings are partitioned between the gas phase and particle phase. Phase distribution of PAHs depends on the vapour pressure, the atmospheric temperature, the PAH concentration and the affinity for suspended particles [1,2]. During the non-heating season, more PAHs get transferred to the gas phase, while the reverse process has been observed in the heating season [3].

Although ambient air pollution contributes to adverse health effects, exposure to the highest concentrations of many air contaminants occurs in other microenvironments (offices, classrooms, houses, pub-

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lic buildings). PAHs are important hazardous pollutants because of their carcinogenicity and mutagenicity. Indoor PAHs may affect the health of the people more than outdoor PAHs, because people spend more than 80% of their time indoors [4]. Typically, outdoor PAHs can enter the indoor environment through infiltration or ventilation systems, and result to indoor exposure of PAHs [5]. The sources of PAHs may also originate indoors from food cooking, candle burning or smoking [5,6]. As children are more susceptible to adverse health effects from air pollution than adults, potentially high pollutant exposures in schools are a concern. Therefore, indoor air quality in schools has attracted increasing attention in recent years [7-10].

While many studies in Europe investigated concentrations, gas/particle partitioning, seasonal variation, source identification and relationship between indoor/outdoor concentrations of PAHs [11-13], measurements of PAHs and related studies in the Republic of Serbia are scarce and limited to only PAHs in ambient air [14-17]. In Serbia, monitoring of particulate matters less than 10 microns began in 2003 [18]. Since then, the Serbian scientific community has published many papers on that issue [19-22].

The aim of this paper was to investigate the seasonal variation of PAHs, their partition between gas and particle-bound phases and identification of pollution sources, using PAHs diagnostic ratios in

indoor and outdoor air, in 4 schools located at different areas in Serbia.

## EXPERIMENTAL

In Serbia, almost all schools are naturally ventilated. Samples were collected from three classrooms in each school, and at the same time, in outdoor air in front of the windows on the terrace, during December 2011 and Jun 2012. Four schools were selected to match four types of representative locations (Figure 1):

- The urban school (U) is in Belgrade ( $44^{\circ}49'N$ ,  $20^{\circ}28'E$ ), located in the middle of a densely populated residential area, 600 m away from a main road. The area is heated by the district heating system, surrounded by greenery, buildings and parking spaces. The school consists of two buildings: a smaller one that has 2 floors, and a bigger one that consists of 3 floors. The buildings are connected with a corridor, making one unit. The outdoor air sampler was placed on the terrace above the school yard, at about 5 m above ground level. Near the school, the frequency of traffic is low. Indoor samples were collected in classrooms on the first floor. The school has a kitchen and a canteen on the ground floor.

- The urban/traffic school (U/T) is in Zaječar ( $43^{\circ}55'N$ ,  $22^{\circ}18'E$ ), located next to a highly dense traffic street in the city centre. The terrace with the

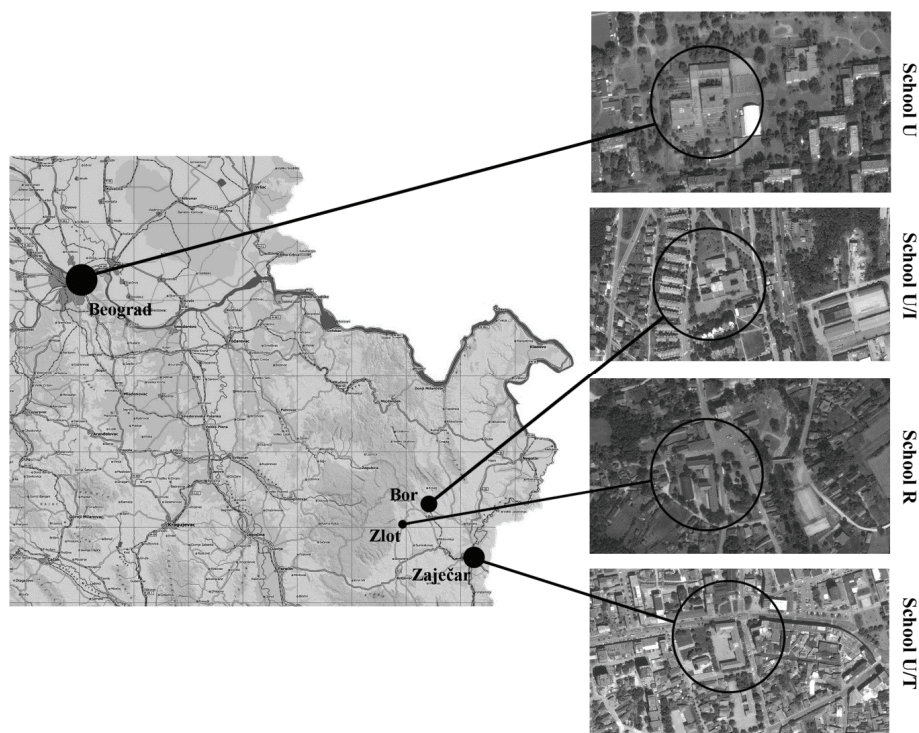


Figure 1. Map of the Republic of Serbia with marked sampling sites.

outdoor air sampler, was located directly above the street with the most frequent traffic in town, at a distance of about 2 m, and at about 3 m above ground level. The location is directly influenced by traffic emissions. There is a large number of coal combustion boilers for domestic heating, which contributes to air pollution level in the winter. The school has a canteen, but the food was not prepared in the school.

- The urban/industrial school (U/I) is in Bor (44°05'N, 22°06'E), located at about 1 km west from the Copper Smelter Complex. Outdoor air sampler was situated on the balcony, which is 8 m above the ground level, and at about 200 m away from a main road. School has a kitchen with a canteen. This location is close to the residential area. Almost the entire town is heated by the district heating system.

- The rural school (R) is in Zlot (44°00'N, 21°59'E), located in a low population density area. The school is located in the village centre, about 5 m from the main crossroad. In the village there is no district heating system and all households are heated by burning coal and wood. The school has a canteen.

The sampling campaigns were conducted simultaneously indoor and outdoor during one workweek, successively in each school in both heating and non-heating seasons. All samples were collected using the low volume reference sampler, Sven/Leckel (LVS), over a 24 h period. Three samplers were placed in classrooms and one was placed outdoor in each school. The air was drawn by LVS reference sampler through a quartz filter (Whatman QMA, 47 mm), to collect total suspended particles (TSP) and then through polyurethane foam (PUF) to collect gas phase of pollutants. The sampling flow rate was 2.3 m<sup>3</sup>/h (38 l/min). Before sampling, PUF plugs were cleaned by extracting them in a Soxhlet extractor with acetone (8 h) and 1:5 mixture of diethylether/hexane (16 h). The filters were baked at 900 °C for 4 h so that organic compounds could be removed and blank values reduced. The filters were weighed before and after sampling, to determine the amount of particles captured. Air volume drawn by the sampler was used to calculate the mass concentrations of TSP and PAHs.

After sampling, PUFs were extracted by acetone and hexane (1:1) for 8 h at 90 °C using Soxhlet extraction. Exposed filters were extracted in microwave with mixture of solvents hexane:acetone (12.5 ml *n*-hexane:12.5 ml acetone) according to EPA 3546. After extraction, solvent volume was reduced by rotary evaporation under reduced pressure (55.6 kPa and with 0.2 ml isooctane as a keeper) to 1 ml. Afterwards, *n*-hexane solution was reduced to 0.25 ml under nitrogen stream at room temperature to 0.5 ml

and analyzed using gas chromatography. Known quantities of internal standard were added to estimate the method recovery. PAHs were analyzed using gas chromatography coupled with mass selective detector (Agilent GC 6890/5973 MSD) according to EPA Compendium Method TO-13A [23] with a DB-5 MS capillary column (30 m×0.25 mm×25 μm). The oven temperature program started at 70 °C (held 4 minutes) followed by ramping up at a rate of 8 °C/min to 310 °C (held 5 min). The solvent delay was 5 min and time of run was 46 min. Sixteen US EPA priority PAHs were determined: naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ane), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DbA), benzo[g,h,i]perylene (BgP) and indeno[1,2,3-*cd*]pyrene (InP).

The calibration curves for all 16 PAHs were obtained by spiking the seven known quantities of substances, all with an  $R^2$  of the calibration curve above 0.995. Method quantification limit for all PAHs was 0.02 ng/m<sup>3</sup>.

## RESULTS AND DISCUSSION

PAHs exist in the atmosphere in both gas (G) and particle-bound (PB) phase, which is why we observed the sum of median values of gas and particle-bound phase PAHs (G+PB PAHs). These values for heating and non-heating season at all sampling sites are given in Tables 1 and 2, respectively. Significant seasonal variations of PAH concentrations were observed with higher levels during heating season, at all locations. Levels of total PAH, expressed as the sum of median value of PAHs ( $\Sigma$ PAH), were highest during heating season at school U/T, both indoor and outdoor. The median values of individual PAHs at school U/T during heating season were higher than in the other schools, mainly due to the high emissions from the traffic and coal-burning boilers for individual heating of dwellings. Especially interesting were high outdoor values for naphthalene, acenaphthylene and phenanthrene, with concentrations of 205.05, 232.88 and 207.26 ng/m<sup>3</sup>, respectively. Emissions from petroleum refining and coal tar distillation are major contributors of acenaphthylene to the environment. A variety of coal tar products contain acenaphthylene, as well as many others, which might be released to the environment via manufacturing effluents and the disposal of manufacturing waste byproducts. During its production, which is a

Table 1. The median values of G+PB PAHs (ng/m<sup>3</sup>) and average values of temperatures and relative humidities in indoor and outdoor environments at four sampling sites during heating season (n = 5)

PAHs	School U		School U/I		School U/T		School R	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Nap	18.89	50.04	19.76	139.59	56.11	205.05	47.94	104.84
Ace	7.15	26.95	13.03	9.31	72.02	232.88	18.63	64.54
Ane	4.19	6.66	6.12	2.38	14.82	30.45	18.06	11.71
Flu	16.81	15.88	11.00	10.76	55.31	98.32	33.86	33.35
Phe	30.75	43.93	18.71	27.49	95.52	207.26	65.32	93.28
Ant	1.00	3.29	1.24	2.80	15.83	42.45	3.66	17.68
Fla	6.01	12.58	4.47	8.56	22.47	56.32	23.39	32.30
Pyr	5.78	10.29	4.06	6.17	22.19	49.27	13.71	27.96
BaA	2.04	4.57	1.12	1.76	12.63	19.58	3.81	9.89
Chy	3.19	6.97	2.16	4.12	14.36	21.97	5.37	13.60
BbF	2.73	4.78	1.72	3.36	9.11	13.68	4.05	7.96
BkF	3.44	4.55	1.39	2.95	6.82	9.90	4.74	7.69
BaP	3.03	4.32	1.20	1.83	9.84	12.24	5.07	7.56
InP	2.03	2.71	0.91	1.44	6.25	7.55	3.09	4.89
DbA	0.69	0.79	0.21	0.40	1.91	2.26	0.96	1.47
BgP	2.71	3.38	1.34	2.02	6.75	7.97	3.62	6.00
ΣPAH	110.44	201.69	88.45	224.93	421.94	1017.15	255.28	444.72
t/ °C	21.4	8.6	14.6	-13.6	21.2	1.9	15.2	0.7
RHI %	32.2	56.6	27.5	77.9	33.3	80.1	49.4	70.1

Table 2. The median values of G+PB PAHs (ng/m<sup>3</sup>) and average values of temperature and relative humidities in indoor and outdoor environments at four sampling sites during non-heating season (n = 5)

PAHs	School U		School U/I		School U/T		School R	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Nap	1.99	2.85	4.21	3.72	17.77	24.50	22.45	24.57
Ace	0.70	1.78	1.32	2.55	5.61	6.32	8.92	13.82
Ane	4.17	2.96	3.37	0.74	6.07	6.98	13.75	4.04
Flu	11.68	4.60	9.50	3.74	23.54	11.09	35.23	11.62
Phe	13.98	7.86	16.51	10.44	44.52	24.98	118.71	40.99
Ant	0.45	0.04	0.63	1.05	1.02	1.49	2.93	4.55
Fla	1.77	2.31	1.72	2.70	6.08	5.07	44.91	11.76
Pyr	1.33	1.96	1.57	2.01	4.42	4.69	20.12	10.42
BaA	0.04	0.49	0.08	0.06	0.57	0.90	0.10	1.60
Chy	0.11	0.68	0.08	0.11	0.75	1.44	0.21	1.60
BbF	0.15	0.36	0.31	0.31	0.40	0.94	0.57	1.49
BkF	0.09	0.27	0.24	0.27	0.30	0.55	0.46	1.17
BaP	0.11	0.23	0.29	0.16	0.43	0.60	0.78	1.15
InP	0.16	0.24	0.46	0.25	0.58	0.87	0.91	1.33
DbA	0.03	0.04	0.08	0.05	0.16	0.22	0.25	0.39
BgP	0.14	0.32	0.43	0.29	0.63	1.37	1.27	1.81
ΣPAH	36.91	27.00	40.79	28.46	112.84	92.03	271.57	132.32
t/ °C	23.1	20.7	19.6	12.9	25.2	19.4	21.3	18.7
RHI %	57.5	65.4	54.8	72.8	44.9	57.8	69.6	71.5

result of incomplete combustion of organic materials, phenanthrene is released to the environment through various waste streams. Phenanthrene is found in fossil fuels and plants [24]. Naphthalene is a toxic air pollutant widely found in ambient and indoor air due to emissions from the chemical and primary metal industries, biomass burning, gasoline and oil combustion, tobacco smoking, the use of mothballs, fumigants and deodorizers, and many other sources [25]. Therefore, at school U/I, higher concentration of this compound was observed. During non-heating period higher levels of these PAHs were observed outdoor at school R, probably due to the combustion of biomass during agricultural activities and usage of farm machinery using oil as fuel.

The lowest median values of PAH during both seasons were in school U. This is the opposite compared with values from available literature data, where the PAH values were lower in rural areas than in urban areas [26–29]. This can be explained by the fact that the school U is located in a residential area, with a low traffic density and without any coal-burning boilers for individual heating in vicinity, which are important sources of PAHs in urban areas. On the other hand, the school R is located in area where the dominant emission of PAHs originates from coal combustion. However, around the school U/T, the dominant emissions of PAHs originated from traffic and coal combustion for individual heating.

One of the significant sources of atmospheric benzo[*a*]pyrene is residential wood burning. It can also be found in coal tar, in automobile exhaust fumes (especially from diesel engines) [13]. That is the reason why the highest concentration of BaP was observed at school U/T during heating season and at school R during non-heating season. Also, the heaviest PAHs, like dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[1,2,3-*cd*]pyrene, which are usually associated with vehicle emissions, were observed at school U/T during heating season and at school R during non-heating season.

The average outdoor temperature for non-heating period and indoor temperatures for both periods

did not vary substantially between site locations. For the non-heating period outdoor temperature was 12.9–20.7 °C. Indoor temperatures were 14.6–21.4 °C for the heating period and 19.6–25.2 °C for the non-heating period. Large variability existed in outdoor temperature for the heating period, –13.6–8.6 °C. Indoor relative humidity varied between 27.5–49.4% during heating period and 44.9–69.6% during non-heating period, and outdoor humidity between 56.6–80.1% during heating period and 57.8–72.8% during non-heating period (Tables 1 and 2).

I/O ratios of individual PAHs and  $\Sigma$ PAH at all sampling sites were less than 1 during heating season, which indicated that indoor PAHs originated mainly from the outdoors. Higher outdoor PAHs levels caused significantly higher PAHs emission from heating combustion sources during heating season. During non-heating season I/O ratios of  $\Sigma$ PAH were above 1. This is probably a consequence of the higher indoor concentrations of volatile PAHs (two- and three-rings) during non-heating season. This finding is in accordance with previous studies [4,30], suggesting that in some indoor environments the influence of indoor sources, such as: wood burning, heating or cooking sources and use fresheners and cleaning products [3], may be dominant. Table 3 shows median values of  $\Sigma$ PAH concentrations in G and PB phase. The highest median values of  $\Sigma$ PAH were associated with the G phase in both sampling periods, especially in heating season. The I/O ratios of  $\Sigma$ PAH for G phase were slightly above 1 for non-heating season at all sampling sites. Most of the I/O ratios for PB phase for both seasons and G phase during heating season were less than 1, which indicated that the indoor PAHs were mostly from outdoor sources.

Ring number distribution of PAHs in schools is shown in Figure 2. The highest presence of volatile (two- and three-ring) PAHs was observed at the school U/I during both seasons. Volatile PAHs, specifically naphthalene, were primarily dominated in industrial flue gases and could be tracer for industrial combustion [1]. At all sampling sites, naphthalene

Table 3. The median values of  $\Sigma$ PAH concentrations ( $\text{ng}/\text{m}^3$ ) in particle-bounded and gas phases at four sampling sites during heating and non-heating seasons ( $n = 5$ )

School site	$\Sigma$ PAH Particle-bound phase				$\Sigma$ PAH Gas phase			
	Heating		Non-heating		Heating		Non-heating	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
School U	20.79	36.22	1.25	2.07	89.65	165.48	35.66	24.93
School U/T	51.37	131.04	3.67	6.69	370.57	886.11	109.18	85.34
School U/I	11.98	22.43	2.72	2.07	76.48	202.03	38.07	26.16
School R	33.94	70.04	5.39	9.17	221.33	374.68	266.18	123.15

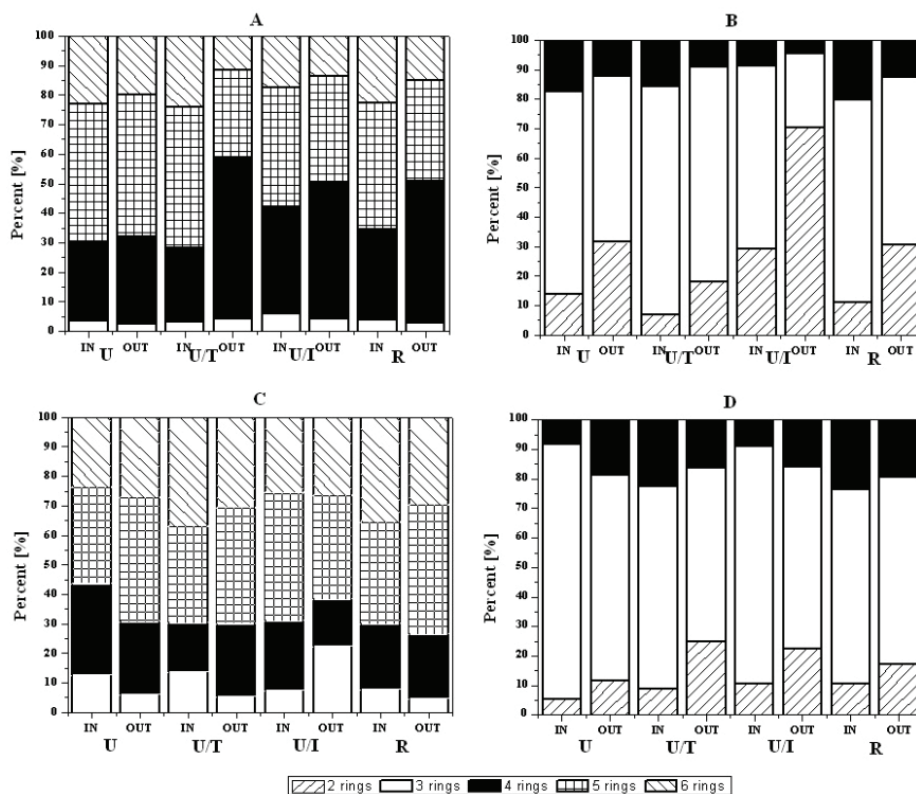


Figure 2. Ring number distribution of PAHs in schools (U-urban; U/T-urban/traffic; U/I-urban/industrial; R-rural; IN-indoor; OUT-outdoor): A) PAHs in particle-bound phase during heating season; B) PAHs in gas phase during heating season; C) PAHs in particle-bound phase during non-heating season; D) PAHs in gas phase during non-heating season.

was dominant in outdoor air, while three-ring PAHs were dominant in indoor environment. This indicates indoor sources of three-ring PAHs, *e.g.*, evaporation from building materials, and outdoor origin of naphthalene [31]. The four-ring PAHs (fluoranthene, pyrene, benz[*a*]anthracene and chrysene) were present in both phases. The highest presence of these PAHs was observed at school U/T and school R during heating season, and they are probably associated with the coal combustion [20]. Indoor concentrations of four-ring PAHs in both phases were lower than outdoor, which proved that outdoor sources of these PAHs were prevailing. The heaviest (five- and six-ring) PAHs, which are usually associated with vehicle emissions, were observed at all sampling sites with higher presence in indoor environment during heating season. They were dominant in PB phase, while in G phase they were not detected in general. The reason for this is the lower volatility of these PAH and their adsorption to particles. The outdoor concentrations of heaviest PAHs during non-heating season were higher than indoor concentrations.

The diagnostic ratios of PAHs may be used to identify the origin of PAHs in ambient air. Tobiszewski and Namiesnik suggested that the total concentra-

tions of atmospheric PAHs (G+PB) should be used to calculate diagnostic ratios, because there are differences when G and PB phase are considered separately [33]. In this study, diagnostic ratios were calculated between outdoor G and PB phases PAHs during both seasons as shown in Table 4. The ratios of combustion PAHs to the total PAHs ( $CPAH/\Sigma PAH$ ) were higher in PB phase than those in G phase during both seasons at all sites. These values were close to 1 for PB phases, which indicated that coal combustion was potential source of PB-PAHs [33,34]. Only at school U/I value of this ratio in PB phase during non-heating season was 0.75, which suggested that diesel engines were dominant PAHs source. The  $Flu/(Flu+Pyr)$  ratios were determined to be  $< 0.5$  at all sampling sites in PB phase, which were similar to the values for petrol emissions, except in school U/I in non-heating season where the value was 0.57 and indicated diesel emissions [1,33]. The  $Flu/(Flu+Pyr)$  ratios for G phase were  $> 0.5$  at all sites. The  $Ant/(Ant+Phe)$  ratio higher than 0.1 was associated with combustion processes [1]. The values of this ratio were higher for PB phase and higher in heating than those in non-heating period. The lowest values of  $Ant/(Ant+Phe)$  ratio were recorded in the



Table 4. Diagnostic ratios of PAHs (mean  $\pm$  standard deviation) in outdoor PB and G phases at four sampling sites during heating and non-heating seasons

School	Phase	CPAH/ $\Sigma$ PAH		Flu/(Flu+Pyr)		Ant/(Ant+Phe)		Fla/(Fla+Pyr)		BaA/(BaA+Chy)		BaP/BgP		Ind/(Ind+BgP)	
		H	HN	H	HN	H	HN	H	HN	H	HN	H	HN	H	HN
U	PB	0.95	0.9	0.06	0.2	0.22	0.1	0.48	0.5	0.39	0.33	1.19	0.72	0.44	0.42
	G	0.13	0.18	0.65	0.71	0.08	0.09	0.57	0.55	0.33	0.44	-	-	-	-
	T	0.28	0.24	0.6	0.7	0.08	0.04	0.55	0.54	0.39	0.39	-	-	-	-
U/T	PB	0.94	0.9	0.12	0.24	0.37	0.14	0.48	0.42	0.46	0.36	1.51	0.52	0.48	0.39
	G	0.09	0.15	0.72	0.64	0.17	0.07	0.56	0.52	/	0.4	-	-	-	-
	T	0.2	0.21	0.64	0.63	0.17	0.07	0.54	0.52	0.46	0.38	-	-	-	-
U/I	PB	0.94	0.75	0.07	0.57	0.26	0.08	0.47	0.6	0.34	0.43	1.08	0.56	0.41	0.49
	G	0.05	0.16	0.72	0.7	0.09	0.09	0.6	0.6	/	0.41	-	-	-	-
	TI	0.13	0.21	0.63	0.7	0.1	0.09	0.56	0.6	0.34	0.44	-	-	-	-
R	PB	0.95	0.92	0.18	0.12	0.21	0.15	0.45	0.39	0.42	0.38	1.15	0.61	0.45	0.4
	G	0.15	0.19	0.64	0.53	0.15	0.11	0.54	0.52	0.39	0.48	-	-	-	-
	T	0.27	0.25	0.58	0.52	0.15	0.11	0.52	0.51	0.41	0.44	-	-	-	-
Values range and sources	0.73 Gasoline engine		<0.5 Petrol emissions		<0.1 Pertogenic >0.1 Pyrogenic		<0.4 Petrogenic 0.4-0.5 Fossil fuel combustion		>0.35 Coal combustion		>0.6 Grass, coal, wood combustion		<0.4 Vehicle emission		
	0.78 Diesel engine		>0.5 Diesel emissions				>0.5 Grass, wood, coal combustion		0.2-0.35 Vehicular emission		<0.6 Fuel combustion		>0.5 Coal combustion		
	0.87 Coal combustion								0.43 Wood combustion		0.35-0.47 Mixed sources				
	~1 Combustion														

school U and school U/I and could be explained by the fact that the schools are located in the vicinity of residential buildings which are heated by district heating system. Similar values were obtained for G and PB phases for Fla/(Fla+Pyr) ratio. The values for total (PB + G) Fla/(Fla+Pyr) ratio were higher at school U/I especially during non-heating season and suggested the emission from grass, wood and coal combustion [33]. The values of BaA/(BaA+Chy) ratio indicated traffic emissions PB-PAHs during non-heating season at school U and school U/T [26], and mixture source of traffic emissions and coal/wood combustion during heating season at all sites [2]. The lowest recorded value of this ratio was in the school U/I during heating season. The BaP/BgP and Ind/(Ind+BgP) ratios were taken only for PB phase because in the G phase five- and six-ring PAHs were not detected. The values of BaP/BgP ratio indicated emissions mainly from coal combustion during heating season and fuel combustion during non-heating season at all sites [35]. Without site difference, the values of Ind/(Ind+BgP) ratio indicated mixed sources of PAHs at all sites and traffic emissions at school U/T in non-heating season [35].

Taking into account the diagnostic ratios at school U/I, a clear differences in the origin of PAHs were recognized in comparison with the other schools. This points out that the dominant contribution source were diesel engines. This is related to the use of oil

as fuel in the manufacturing and processing of copper [36]. The same ratio could be a result of the atmospheric reactions and should be used with the caution because it is often difficult to determine a difference between some potential sources. As shown above, the values of diagnostic ratio are different for G and PB phase and should be used together into account, as suggested by Tobiszewski and Namiesnik [33].

## CONCLUSION

The PAHs levels, seasonal variations and distributions between G and PB phase were investigated in 4 schools in Serbia during heating and non-heating seasons. Significant seasonal variations of gas and particle-bound phase were observed with higher levels during heating season. The median values of  $\Sigma$ PAH concentrations in gas phase were much higher than concentrations in particle-bound phase at all sampling sites. The most abundant PAHs at all sampling sites were naphthalene and phenanthrene during both seasons.

Based on the ring number distribution and diagnostic ratios, two main sources of PAHs were found at all sites - traffic emission and coal combustion. Traffic emissions were the major source in non-heating season, while coal combustion was the major source in heating season. Significant differences between dia-

gnostic ratios for G and PB phase were shown. Only the diagnostic ratios at school U/I showed significant deviation compared to other schools, and suggested diesel emissions as the main source of PAHs that have been related to the use of oil during the manufacturing and processing of copper. More dangerous PM fractions and qualitative methods, such as PCA and factor analysis approaches, are planned in further investigation in the aim of providing quantitative source apportionments results.

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NAUČNI RAD

## NIVO POLICIKLIČNIH AROMATIČNIH UGLJOVODONIKA U GASNOJ I ČESTIČNOJ FAZI U ŠKOLAMA NA RAZLIČITIM LOKACIJAMA U SRBIJI

*U ovom radu su istraživane sezonske promene PAH i njihova raspodela, u gasnoj fazi i respirabilnim česticama u vazduhu unutrašnjeg prostora i spoljašnje sredine u 4 škole u Srbiji koje se nalaze na različitim lokacijama. Kampanja uzorkovanja je sprovedena tokom jedne radne nedelje u toku grejnog i negrejnog perioda (od decembra 2011. do juna 2012.) u svakoj školi. Uočene su sezonske promene nivoa PAH u gasnoj fazi i česticama, sa višim koncentracijama tokom grejnog perioda. Izmerena je veća vrednost zbira ukupnih PAH tokom oba perioda u gasnoj fazi nego PAH u česticama. Ukupna koncentracija PAH tokom grejnog perioda u unutrašnjem prostoru se kretala u opsegu od 88,45 do 447,72 ng/m<sup>3</sup>, a u spoljašnjoj sredini od 201,69 do 1017,15 ng/m<sup>3</sup>. Tokom negrejnog perioda, ukupna koncentracija PAH-ova je bila 36,91-271,57 ng/m<sup>3</sup> u unutrašnjem prostoru, dok je u spoljašnjoj sredini bila 27,00-132,32 ng/m<sup>3</sup>. Većina I/O odnosa je bila manja od 1, što ukazuje da PAH u unutrašnjem prostoru uglavnom potiču iz spoljašnjeg vazduha. Na osnovu dijagnostičkih odnosa zaključeno je da su saobraćaj i sagorevanje uglja glavni izvori PAH. Jedino dijagnostički odnosi za školu koja se nalazi u blizini industrijske zone pokazuju značajno odstupanje u poređenju sa drugim školama.*

*Ključne reči: PAH, škole, sezonske promene, I/O odnosi, dijagnostički odnosi.*