

Aleksandra Papludis^{1*}, Slađana Alagić¹, Snežana Milić¹,
Dragana Medić¹, Ivana Zlatanović², Jelena Nikolić²,
Vesna Stankov Jovanović²

¹University of Belgrade, Technical Faculty in Bor, Bor, Serbia,

²University of Nis, Faculty of Sciences and Mathematics,
Department of Chemistry, Niš, Serbia

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The capacities of *Hedera helix* from the Bor region for PAH accumulation in the root and implications for phytostabilization

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are considered as the pollutants of highest priority, and their remediation is of a global concern. The purpose of this study was to investigate the phytoremediation potential of *Hedera helix* (Hh) determining the content of 16 priority PAHs in its soil and root samples collected from the rural and industrial zones of the Bor's municipality (Serbia). The content of $\Sigma 16$ PAHs in the soils was: 326.49 $\mu\text{g}/\text{kg}$ at the site Borsko jezero to maximal 1937.64 $\mu\text{g}/\text{kg}$ at the site Slatinsko naselje. The level of soil pollution (depending on the concentration of $\Sigma 16$ PAHs), was high at many tested sites and it was under the significant influence of anthropogenic activities. The concentration for $\Sigma 16$ PAHs in the samples of roots ranged from 480.71 $\mu\text{g}/\text{kg}$ at the site Krivelj to 1748.32 $\mu\text{g}/\text{kg}$ at the site Naselje Sunce. Interestingly, the extremely toxic benzo(a)pyrene, was not detected in the roots of Hh. Bio-concentration factors (BCFs) were applied to determine the capacity of Hh for PAH accumulation in the root, and consequently, for determination of its phytostabilization potential. In most cases, BCF values were higher at the locations from UI zone. The calculated BCFs were higher for LMW PAHs than for HMW PAHs. At the majority of the investigated locations, the tested plant species was especially successful in the root accumulation of the compounds such as acenaphthene, fluorene, anthracene, dibenzo(a,h)anthracene, and the sum of benzo(k)fluoranthene and benzo(b)fluoranthene. These findings showed that Hh can be successfully used in phytostabilization of many PAHs.

Keywords: Soil pollution, PAHs, *Hedera helix*, phytostabilization

1. INTRODUCTION

For more than 100 years, the Copper Mining and Smelting Complex in Bor has had a great negative impact on the environment of the city of Bor and its surrounding. Most importantly, all living organisms are endangered, primarily regarding the inorganic pollutants such as heavy metals [1].

In this study, the specific organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) were investigated in the same region using the local plant species - poison ivy (*Hedera helix*, Hh, the *Araliaceae* family); the main goal of this investigation was to establish the bioaccumulation

potential and possible utilization of Hh for soil PAH removal or stabilization. The samples of roots and spatial soils of Hh were sampled from the rural and urban-industrial places, from the spots positioned at different distances from the city heating plant and the copper smelter in the center of the town of Bor.

Polycyclic aromatic hydrocarbons belong to the group of persistent organic pollutants (POPs) [2] with over 100 compounds; 40 of them are the most commonly studied. The United States Environmental Protection Agency (USEPA) included 16 PAH compounds in its list of the pollutants of highest priority: naphthalene (Nap), anthracene (Ant), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flr), phenanthrene (Phe), benzo(a)anthracene (BaA), chrysene (CHR), fluoranthene (Flt), pyrene (Pyr), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DhA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(g,h,i)perylene (BgP) and indeno(1,2,3-c,d)pyrene (IcP). Seven of them, this agency

*Corresponding author: Aleksandra Papludis

E-mail: apapludis@tfbor.bg.ac.rs

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classified as possible carcinogens: BaA, CHR, BaP, DhA, BbF, BkF and IcP [1, 3-5].

PAHs can be also classified depending on the number of the rings present in the molecule as follows: light-molecular weight PAHs (LMW PAHs), having two or three aromatic rings), and high-molecular weight PAHs (HMW PAHs), having four or more aromatic rings) [6].

The structures of PAHs affect their low water solubility, low vapor pressure, and high melting and boiling points [6], which further significantly impacts their behavior in the environment and finally, their toxicity; the main effects of PAH toxicity are the carcinogenicity and mutagenicity [7]. Unfortunately, their concentrations in all environmental spheres are constantly rising because the sources of PAHs in the environment are also growing and they are associated with both - natural and anthropogenic sources [8].

Polycyclic aromatic hydrocarbons arise in the environment from natural sources such as forest fires and volcanic eruptions, but emissions from anthropogenic activities predominate [4,6]. Many anthropogenic sources such as pyrolytic processes during the utilization of fossil fuels (coal, wood, gas, oil) and different organics (tobacco, grilled meat, waste materials) represent one of the main causes of PAH realizing into the air, together with traffic,

and residential heating; finally, the main reservoir for PAH accumulation are the upper layers of surface soil [1].

Phytoremediation is often used worldwide to remove or reduce organic pollutants from the soil, water, and sediments. Processes in this technology are naturally carried out by plants that can degrade pollutants and thus, they can reduce their presence in the environment [9]. Depending on the specific conditions, organic pollutants can be removed/reduced by one of the phytoremediation methods such as phytoextraction to the phytoaccumulation, phytodegradation, phytovolatilization, phytostabilization, rhizosphere biodegradation, etc. [9,10]. For complex, hydrophobic PAH molecules, the remediation technics, phytostabilization and rhizodegradation are shown to be the most prospective and they are based on the inter-relations between the present organics, plants, their rhizosphere microorganisms, and soil [1].

2. MATERIALS AND METHODS

2.1. The sampling area

The contents of PAH compounds were evaluated in the roots and spatial soils of Hh collected from different sites from rural (R) and urban-industrial (UI) zone.

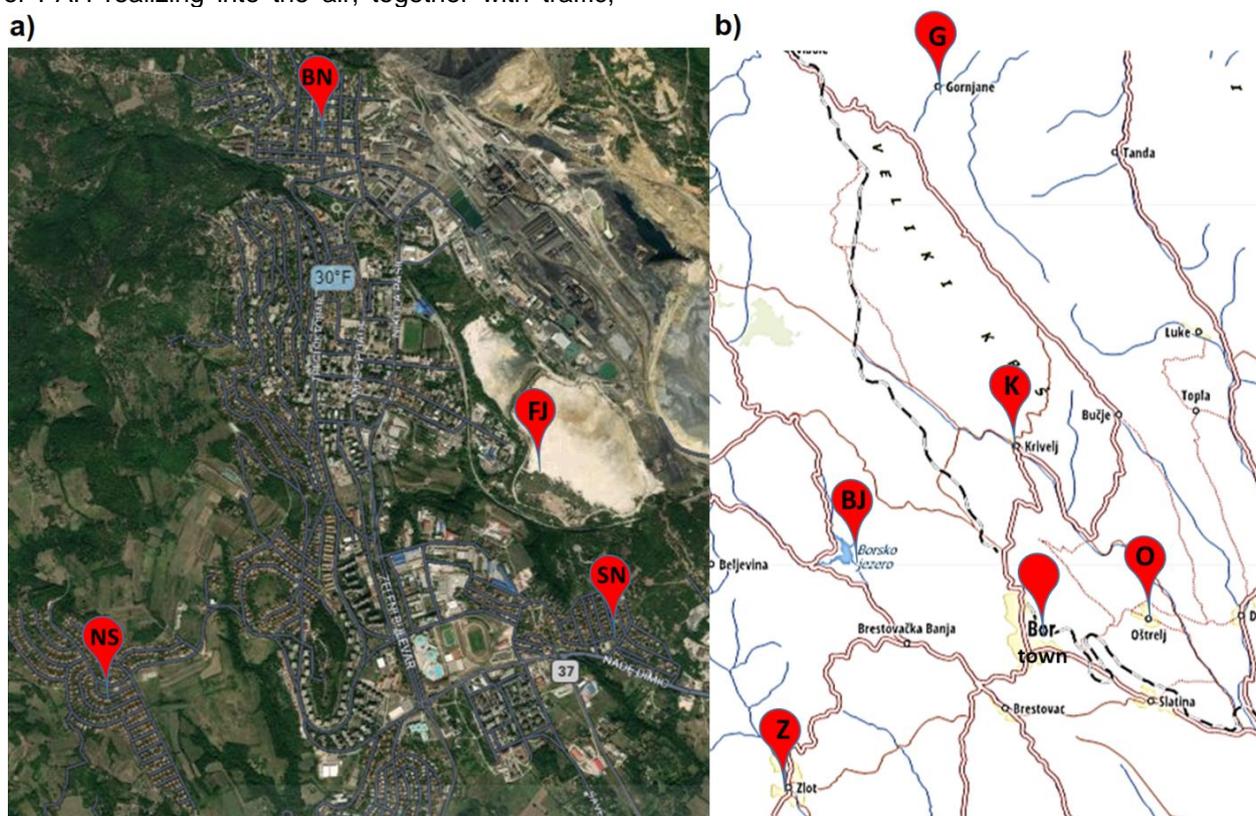


Figure 1. Map of sampling area a) urban-industrial and b) rural zone

Slika 1. Mapa ispitivanog područja a) urbano-industrijska i b) ruralna zona

The R zone includes five sites: Oštrej (O), Borsko jezero (BJ) Krivelj (K), Zlot (Z) and Gornjane (G), while UI zone includes four sites which are localized very close to the industrial sector: Flotacijsko jalovište (FJ), Bolničko naselje (BN), Slatinsko naselje (SN) and Naselje Sunce (NS). The distances of these locations from the heating plant and the copper smelter are as follows: 0.7 km for the site FJ – a deserted flotation tailings pond, 1.3 km for the site BN, which is positioned near the Technical faculty in Bor and the local hospital, then for the two suburb sites - 3.2 km site SN and 3.6 km site NS. The sites from rural zone are located away from Bor town as follows: 4.5 km for the site O, 7 km for the site BJ, 8 km for the site K, 13 km for the site Z and 19 km for the site G.

2.2. Sample collection, preparation and analysis

The samples of roots and spatial soils of Hh were taken from the selected sites in September 2020. The samples of roots and soils of Hh were collected from 3 plants at each site. For each site, these sub-samples were pooled to obtain a representative sample. The roots were carefully cleaned from soil particles, followed by gentle cleaning by fine sandpaper. Soil samples were taken from the rooting zone by means made of stainless steel. Collected material was placed into paper bags and sent to the laboratory. After described dry cleaning, the samples of roots were washed with tap water and then with distilled water. All collected samples were air-dried in the dark room secured from any contamination. Dried plant samples were milled in a laboratory mill, whereas soil samples were riddled over stainless steel sieve (2 mm). The prepared samples were kept in sealed bags and retained at 4°C in the fridge prior the chemical analysis.

Before that, QuEChERS (Quick, Effective, Cheap, Easy, Rugged, Safe) method was carried out for PAH extraction from the root and soil samples (10 g of each), using the solvent - acetonitrile/water (2:1 v/v, in 30 minutes duration). In the second, cleansing step, 150 mg MgSO₄ and 50 mg of diatomaceous earth were used for soil samples, whereas 500 mg MgSO₄ and 100 mg of diatomaceous earth were used for plant samples. Finally, gas chromatographic-mass spectrometric (GC/MS) analysis was conducted preparing all samples in triplicate. The results are given in µg/kg DW (dry weight).

The accumulation rates of the investigated PAHs in Hh roots were calculated using bio-concentration factors (BCFs) [3]. The bio-concentration factor represents a ratio of the compound concentration in the root to its

concentration in the corresponding soil ($BCF = C_{\text{root}}/C_{\text{soil}}$). The values of $BCF > 1$ indicate a good extraction and accumulation of a particular compound in roots, whereas $BCFs < 1$ point to the exclusion of the compound from the uptake [1,3].

3. RESULTS AND DISCUSSION

The results for measured PAH concentrations are given in Tables 1 and 2. For a better clarity, the results in the Tables 1 and 2, are corresponding to LMW and HMW PAHs, respectively. The values for BkF and BbF are given as a sum: BkF+BbF, because of their identical molecular weights, and consequently – a difficult separation of individual compounds during GC/MS.

High molecular weight PAHs such as IcP and BgP were not detected in all soil samples, while BaP, IcP and BgP were not detected in roots samples.

The concentrations of PAHs in Hh spatial soils ranged as follows: for Nap from 84.27 µg/kg at the site BJ to 192.26 µg/kg at the site FJ; for Acy from 10.52 µg/kg at the site G to 169.94 µg/kg at the site K; for Ace from 4.98 µg/kg at the site FJ to 22.53 µg/kg at the site SN; for Flr from 11.94 µg/kg at the site BN to 37.94 µg/kg at the site SN; Ant was not detected at five sites (FJ, BJ, K, Z, and G) and the lowest detected concentration was 7.59 µg/kg at the site NS, while the highest concentration was 54.98 µg/kg at the site SN; the concentrations for Phe were from 73.95 µg/kg at the site BJ to 205.96 µg/kg at the site O; for Flt from 32.85 µg/kg at the site BJ to 584.88 µg/kg at the site SN; for Pyr from 17.56 µg/kg at the site BJ to 323.96 µg/kg at the site O; for BaA from 41.28 µg/kg at the site G to 324.83 µg/kg at the site SN; for CHR from 5.29 µg/kg at the site Z to 55.66 µg/kg at the site SN (it was not detected at site G); for BaP from 6.21 µg/kg at the site BN to 10.60 µg/kg at the site G; the sum of BkF+BbF was not detected at five sites (FJ, BN, NS, BJ, and Z), the lowest detected concentration was 8.34 µg/kg at the site SN, while the highest concentration was 9.48 µg/kg at the site G; DhA was not detected at seven of nine sites (FJ, BN, NS, O, BJ, Z, and G), the lowest detected concentration was 72.75 µg/kg at the site SN, and the highest concentration was 106.93 µg/kg at the site K.

The concentrations of PAHs in roots of Hh ranged as follows: for Nap from 18.51 µg/kg at the site BJ to 140.11 µg/kg at the site BN; Acy was not detected at five sites (FJ, NS, K, Z, and G), the lowest detected concentration was 3.37 µg/kg at the site O, while the highest concentration was 30.26 µg/kg at the site BN; for Ace from 7.26 µg/kg at the site BJ to 62.29 µg/kg at the site BN; for Flr

from 98.41 µg/kg at the site O to 442.52 µg/kg at the site NS; Ant was not detected at five sites (SN, NS, BJ, K, and Z), the lowest detected concentration was 3.15 µg/kg at the site O, while the highest concentration was 19.06 µg/kg at the site BN; the concentrations for Phe were from 52.79 µg/kg at the site BJ to 237.42 µg/kg at the site FJ (it was not detected at the two sites: SN and G); for Flt from 16.37 µg/kg at the site G to 585.04 µg/kg at the site BN (it was not detected at the two sites: SN, and Z); for Pyr from 9.18 µg/kg at the site K to 142.77 µg/kg at the site NS; for BaA from 19.41 µg/kg at the site BJ to 628.53 µg/kg at the site NS (it was not detected at the three sites: BN, K, and G); for CHR from n.d. (at the sites BN, SN, NS, O, BJ, K, Z, and G) to 18.87 µg/kg at site FJ;

BkF+BbF were not detected at the two sites: O and BJ, the lowest detected concentration was 3.92 µg/kg at the location K, while the highest concentration was 7.33 µg/kg at site BN; the concentrations for DhA were from 78.19 µg/kg at site O to 207.11 µg/kg at site SN (it was not detected at the site Z).

In the soils samples, the most abundant PAH compound was Flt (584.88 µg/kg) at the site SN, while in the roots samples, the most abundant was BaA (628.53 µg/kg) at the site NS. It is very interesting that BaP was not detected in the tested roots of Hh, which suggests that this (toxic) plant successfully avoided the assimilation of this extremely toxic compound.

Table 1. Concentrations of LMW PAHs (µg/kg DW) in root and soil samples of *Hedera helix*

Tabela 1. Koncentracije niskomolekularnih (NM) PAU (µg/kg, suve mase) u korenu i zemljištu *Hedera helix*

Location	Nap	Acy	Ace	Flr	Ant	Phe
FJ						
Soil	192.26±15.63	22.86±0.12	4.98±0.49	12.17±0.26	nd	88.66±6.64
Root	29.77±2.92	nd	15.91±0.94	218.79±11.55	7.86±0.14	237.42±5.44
BN						
Soil	90.98±4.11	26.69±2.57	9.28±0.42	11.94±0.68	35.53±1.89	89.74±3.57
Root	140.11±16.15	30.26±2.00	62.29±7.52	405.25±29.37	19.06±1.73	53.08±2.55
SN						
Soil	188.27±6.61	84.84±4.85	22.53±1.26	37.94±2.96	54.98±8.92	188.17±14.11
Root	40.54±0.70	3.55±0.01	20.68±2.10	349.25±13.91	nd	nd
NS						
Soil	119.56±18.41	22.55±1.17	9.75±0.30	18.43±1.32	7.59±0.38	89.53±5.09
Root	33.24±5.34	nd	15.24±0.98	442.52±4.06	nd	69.08±7.06
O						
Soil	149.04±10.85	54.84±4.73	12.62±0.95	27.51±3.33	20.31±0.83	205.96±24.65
Root	23.51±1.04	3.37±0.59	16.07±1.10	98.41±8.59	3.15±0.49	146.09±9.42
BJ						
Soil	84.27±3.39	11.92±1.89	9.48±0.04	18.53±0.58	nd	73.95±7.38
Root	18.51±1.47	19.08±0.40	7.26±0.21	115.13±2.60	nd	52.79±8.11
K						
Soil	92.42±7.86	169.94±18.51	13.99±0.06	27.09±2.34	nd	91.18±2.28
Root	24.46±0.32	nd	22.66±0.61	205.79±4.37	nd	76.67±6.64
Z						
Soil	148.77±11.46	16.46±1.47	9.99±0.51	18.21±1.05	nd	81.56±9.00
Root	28.76±0.62	nd	52.03±3.29	437.86±16.85	nd	68.23±2.28
G						
Soil	88.34±1.17	10.52±1.04	7.68±0.47	16.49±0.84	nd	84.29±7.84
Root	26.67±5.66	nd	28.62±2.59	388.85±31.71	7.80±0.05	nd

nd – not detectable

Table 2. Concentrations of HMW PAHs ($\mu\text{g}/\text{kg}$ DW) in root and soil samples of *Hedera helix*Tabela 2. Koncentracije visokomolekularnih (VM) PAU ($\mu\text{g}/\text{kg}$, suve mase) u korenu i zemljištu *Hedera helix*

Location	Flt	Pyr	BaA	CHR	BaP	BkF+BbF	DhA
FJ							
Soil	130.60 \pm 7.53	68.06 \pm 6.83	58.62 \pm 3.53	12.57 \pm 2.15	6.64 \pm 0.36	nd	nd
Root	212.28 \pm 10.00	11.01 \pm 0.88	87.11 \pm 4.35	18.87 \pm 1.31	nd	6.10 \pm 0.17	105.88 \pm 7.62
BN							
Soil	310.47 \pm 31.32	169.00 \pm 14.76	129.31 \pm 7.12	47.20 \pm 1.91	6.21 \pm 0.42	nd	nd
Root	585.04 \pm 78.37	10.97 \pm 0.84	nd	nd	nd	7.33 \pm 0.11	110.50 \pm 5.89
SN							
Soil	584.88 \pm 29.66	303.98 \pm 7.61	324.83 \pm 32.10	55.66 \pm 3.34	10.47 \pm 0.86	8.34 \pm 0.24	72.75 \pm 4.86
Root	nd	16.52 \pm 0.34	62.52 \pm 1.65	nd	nd	6.14 \pm 0.26	207.11 \pm 14.19
NS							
Soil	102.88 \pm 7.70	69.37 \pm 3.50	211.35 \pm 9.47	16.40 \pm 2.11	9.17 \pm 0.83	nd	nd
Root	272.60 \pm 24.79	142.77 \pm 4.78	628.53 \pm 40.43	nd	nd	6.85 \pm 0.52	137.49 \pm 13.52
O							
Soil	541.51 \pm 48.32	323.96 \pm 19.58	145.86 \pm 13.35	53.64 \pm 4.10	8.72 \pm 0.40	9.02 \pm 0.24	nd
Root	129.51 \pm 6.35	71.39 \pm 7.01	29.80 \pm 5.21	nd	nd	nd	78.19 \pm 4.48
BJ							
Soil	32.58 \pm 0.43	17.56 \pm 0.60	60.73 \pm 5.07	8.65 \pm 0.88	8.82 \pm 0.29	nd	nd
Root	199.91 \pm 11.83	79.21 \pm 5.42	19.41 \pm 3.96	nd	nd	nd	97.87 \pm 6.72
K							
Soil	118.58 \pm 7.71	77.29 \pm 9.02	83.13 \pm 21.85	49.42 \pm 5.66	6.94 \pm 0.68	8.58 \pm 0.19	106.93 \pm 5.50
Root	47.04 \pm 2.55	9.18 \pm 0.96	nd	nd	nd	3.92 \pm 0.22	90.99 \pm 8.31
Z							
Soil	43.23 \pm 6.20	28.75 \pm 2.91	169.97 \pm 6.26	5.29 \pm 0.16	10.58 \pm 1.39	nd	nd
Root	nd	85.18 \pm 9.42	27.98 \pm 2.63	nd	nd	5.47 \pm 0.38	nd
G							
Soil	39.29 \pm 1.20	23.81 \pm 1.02	41.28 \pm 1.12	nd	10.60 \pm 0.47	9.48 \pm 0.73	nd
Root	16.37 \pm 0.19	47.50 \pm 5.24	nd	nd	nd	5.81 \pm 0.41	168.93 \pm 19.76

nd – not detectable

The concentrations of Σ LMW and Σ HMW PAHs ($\mu\text{g}/\text{kg}$) in soil and roots of Hh from sampling sites are given in Table 3.

Table 3. The concentrations of Σ LMW and Σ HMW PAHs ($\mu\text{g}/\text{kg}$) in soil and roots of *Hedera helix* from sampling sitesTabela 3. Koncentracije Σ LMW i Σ VM PAU ($\mu\text{g}/\text{kg}$) u zemljištu i korenju *Hedera helix* sa ispitivanih lokacija

Sampling site/ Σ PAHs	Σ LMW soil	Σ HMW soil	Σ LMW root	Σ HMW root
FJ	320.93	276.51	509.77	441.25
BN	264.16	662.18	710.05	713.84
SN	576.74	1360.90	414.02	292.29
NS	267.40	409.17	560.08	1188.24
O	470.28	1082.70	290.59	308.89
BJ	198.15	128.34	212.78	396.40
K	394.62	450.86	329.58	151.12
Z	274.98	257.81	586.87	118.64
G	207.32	124.45	451.93	238.61

Sum of the detected LMW PAH concentrations in soil from different locations decreased as follows: 576.74 µg/kg (SN) > 470.28 µg/kg (O) > 394.62 µg/kg (K) > 320.93 µg/kg (FJ) > 274.98 µg/kg (Z) > 267.40 µg/kg (NS) > 264.16 µg/kg (BN) > 207.32 µg/kg (G) > 198.15 µg/kg (BJ), while the sum of the detected soil HMW PAH concentrations decreased as follows: 1360.90 µg/kg (SN) > 1082.70 µg/kg (O) > 662.18 µg/kg (BN) > 450.86 µg/kg (K) > 409.17 µg/kg (NS) > 276.51 µg/kg (FJ) > 257.81 µg/kg (Z) > 128.34 µg/kg (BJ) > 124.45 µg/kg (G).

Sum of the detected LMW PAH concentrations in the investigated roots decreased as follows: 710.05 µg/kg (BN) > 586.87 µg/kg (Z) > 560.08 µg/kg (NS) > 509.77 µg/kg (FJ) > 451.93 µg/kg (G) > 414.02 µg/kg (SN) > 329.58 µg/kg (K) > 290.59 µg/kg (O) > 212.78 µg/kg (BJ). The most abundant LMW PAHs in root samples from all investigated

sites was Flr. The sum of the detected root HMW PAH concentrations decreased as follows: 1188.24 µg/kg (NS) > 713.84 µg/kg (BN) > 441.25 µg/kg (FJ) > 396.40 µg/kg (BJ) > 308.89 µg/kg (O) > 292.29 µg/kg (SN) > 238.61 µg/kg (G) > 151.12 µg/kg (K) > 118.64 µg/kg (Z).

Generally, it can be said that the tested plant species showed to be very successful in the accumulation of most of the specified 16 PAHs in the roots at the investigated sites.

The total concentrations of 16 priority PAHs in the soils of the study area ranged from 326.49–1937.64 µg/kg, DW. The values for Σ16 PAHs for soils from different locations decreased in the order as follows: 1937.64 µg/kg (SN), 1552.98 µg/kg (O), 926.34 µg/kg (BN), 845.48 (K), 676.56 (NS), 597.44 (FJ), 532.79 (Z), 331.77 (G), 326.49 (BJ) (Table 4).

Table 4. The concentrations of Σ16, Σ10 and Σ7 carcinogenic PAHs (µg/kg) in the soils at the investigated sampling sites

Tabela 4. Koncentracije za Σ16, Σ10 i Σ7 kancerogenih PAU (µg/kg) u zemljištu sa ispitivanih lokacija

Site/ΣPAHs	Σ16 PAHs ^a	Σ10 PAHs ^b	Σ7 PAHs ^c
FJ	597.44	489.37	77.84
BN	926.34	709.43	182.72
SN	1937.64	1415.61	472.05
NS	676.56	556.47	236.92
O	1552.98	1134.06	217.23
BJ	326.49	269.00	78.20
K	845.48	450.24	254.99
Z	532.79	459.39	185.84
G	331.77	273.28	61.35

a – 16 USEPA PAHs

b – 10 PAHs defined by Serbian legislation (Nap, Ant, Phe, BkF, BaA, BaP, CHR, Flt, BgP, and IcP)

c – 7 USEPA carcinogenic PAHs

A classification based on the level of soil pollution, considering the concentrations of Σ16 PAHs, can be organized into four categories: non-contaminated soil (<200 µg/kg), weakly contaminated (200–600 µg/kg), contaminated (600–1000 µg/kg) and heavily contaminated (>1000 µg/kg) [4,6,11-18]. According to the given classification, 2 out of 9 sites can be classified as heavily contaminated (SN-1937.64 µg/kg and O-1552.98 µg/kg), the three sites as contaminated (BN, NS, and K), the four sites as weakly contaminated (FJ, BJ, Z, and G); none of the soil samples belonged to the class of unpolluted soil (Table 4). This indicated that the soils collected from sampling sites were under the significant influence of anthropogenic activities.

Based on the values in the Table 4, it can be noticed that the concentrations in soils samples for Σ16, Σ10 and Σ7 PAHs were the highest at same site SN, and the concentrations for Σ16 and Σ10 PAHs were high at site O.

It can be supposed that the anthropogenic sources of pollution such as heating plant, copper smelter and traffic are the main sources of pollution at the sites from urban-industrial zone while in the rural area, individual fireplaces contributed additionally. For example, soils from the sites in rural zone: G, Z, and BJ, contained a high level of PAHs although they are far away from the heating plant and the copper smelter.

The sum of 10 PAHs (Nap, Ant, Phe, BkF, BaA, BaP, CHR, Flt, BgP, and IcP) in the soils collected at the two sites: SN (1415.61 µg/kg), and O (1134.06 µg/kg) (Table 4), exceeded the maximum allowed concentration (MAC) of 1000 µg/kg, which is defined by Serbian and Netherlands regulations (Table 5). The sum of concentrations for 7 EPA carcinogenic PAHs (BaA, CHR, BaP, BbF, BkF, IcP, and DhA) was higher than the defined concentration of 300 µg/kg (by Swedish regulation) only at the site SN (472.05 µg/kg) (Table 5).

Table 5. Maximum allowed concentrations ($\mu\text{g}/\text{kg}$) of PAHs in the soil according to the legislations of Serbia and several European countries

Tabela 5. Maksimalno dozvoljene koncentracije ($\mu\text{g}/\text{kg}$) PAU u zemljištu po zakonodavstvu Srbije i različitih zemalja Evrope

Regulation	$\Sigma 16$ PAHs	$\Sigma 10$ PAHs	$\Sigma 7$ PAHs
MAC, Serbian	/	1000 ^[23]	/
MAC, Dutch	50 ^[15]	<1000 ^[22,23]	/
MAC, Sweden	20 ^[22]	/	300 ^[15,20]
MAC, Switzerland	200 ^[21]	/	/
MAC, Poland	<1000 ^[13,19]	/	/

/ - no data

As mentioned, the accumulation rates of the investigated individual PAH compounds in Hh roots were calculated using BCFs [3]. BCF values for LMW PAHs are given in Table 6, while BCF values for HMW PAHs are shown in Table 7.

Table 6. BCFs for LMW PAHs

Tabela 6. BCF za NM PAU

Location	Nap	Acy	Ace	Flr	Ant	Phe
FJ	0.2	nc	3.2	18.0	nc	2.7
BN	1.5	1.1	6.7	33.9	0.5	0.6
SN	0.2	0.04	0.9	9.2	nc	nc
NS	0.3	nc	1.6	24.0	nc	0.8
O	0.2	0.1	1.3	3.6	0.2	0.7
BJ	0.2	1.6	0.8	6.2	nc	0.7
K	0.3	nc	1.6	7.6	nc	0.8
Z	0.2	nc	5.2	24.0	nc	0.8
G	0.3	nc	3.7	23.6	nc	nc

Table 7. BCFs for HMW PAHs

Tabela 7. BCF za VM PAU

Location	Flt	Pyr	BaA	CHR	BaP	BkF+BbF	DhA
FJ	1.6	0.2	1.5	1.5	nc	nc	nc
BN	1.9	0.1	nc	nc	nc	nc	nc
SN	nc	0.1	0.2	nc	nc	0.7	2.8
NS	2.6	2.1	3.0	nc	nc	nc	nc
O	0.2	0.2	0.2	nc	nc	nc	nc
BJ	6.1	4.5	0.3	nc	nc	nc	nc
K	0.4	0.1	nc	nc	nc	0.5	0.9
Z	nc	3.0	0.2	nc	nc	nc	nc
G	0.4	2.0	nc	nc	nc	0.6	nc

nc – not calculable

The highest accumulation rate for LMW and HMW PAHs (considering all 16 PAHs) was found in the case of Flr in Hh roots from the site BN. The calculated BCF for this site reached a huge value of 33.9. Also, all other BCF values for this compound were much higher than 1 which signalized that the investigated plant showed a significant ability to accumulate this compound and its applicability in Flr phytoextraction and further phytoaccumulation in the root i.e., the phytostabilization of the mentioned compound can be recommended.

Also, the high values of BCFs were noticed in the case of LMW PAH, such as Ace, where they ranged from 1.3 to 6.7, which points to good abilities of Hh for Ace phytostabilization too.

It is interesting that the roots of Hh extracted Ant maximally at the sites FJ and G (n.d., Table 1), which means that the values of BCFs at these sites were enormously high but not possible for calculation, of course.

The general situation with HMW PAHs was as follows: most BCF values were less than 1, while,

BCFs > 1 were calculated for Flt at the following sites: FJ (1.6), BN (1.9), NS (2.6) and BJ (6.1); for Pyr at the sites: NS (2.1), BJ (4.5), Z (3.0) and G (2.0); for BaA at the sites: FJ (1.5) and NS (3.0); for CHR at the sites: FJ (1.5); for BaP, the values were not calculable, due to its absence in the investigated roots; for DhA only at the SN location, the value of BCF was 2.8.

In most cases, BCF values were higher at the locations from UI zone. Also, the calculated BCFs were higher for LMW PAHs than HMW PAHs.

Similarly, to Ant, in most cases, HMW PAHs such as BkF+BbF and DhA were not detected in the soil at the tested sites and again, BCF values were not calculable - Hh practically extracted all quantities of these compounds from the soil which suggested that it can be successfully used in their phytostabilization.

4. CONCLUSION

This investigation showed that HMW PAHs such as IcP and BgP were not detected in all soil samples, while BaP, IcP and BgP were not detected in roots samples. The concentrations for $\Sigma 16$ PAHs for all investigated locations in the samples of roots ranged from 480.71 $\mu\text{g}/\text{kg}$ at site K to 1748.32 $\mu\text{g}/\text{kg}$ at site NS, while in the samples of soils, they ranged from 326.49 $\mu\text{g}/\text{kg}$ at site BJ to 1937.64 $\mu\text{g}/\text{kg}$ at site SN. The most abundant PAH compound in the soil samples was Flt (584.88 $\mu\text{g}/\text{kg}$) at the site SN, while in the root samples, it was BaA (628.53 $\mu\text{g}/\text{kg}$) at the site NS. The soil contamination was at a significant level at many sites. The highest calculated BCF values were found in the case of LMW PAHs such as Flr (33.9) and Ace (6.7) at the same sampling site - BN. The BCF values indicated that the investigated plant has a significant ability to accumulate these two compounds and may be very applicable in their phytoextraction and phytoaccumulation in the root i.e., in their phytostabilization. In the case of Ant, BkF+BbF and DhA, BCF values were not calculable, because, in most cases, *Hedera helix* practically extracted all quantities of these compounds from the soil, which suggests that it can be also used for their phytostabilization. Interestingly, BaP was not detected in all the tested roots of Hh, which means that this plant successfully avoided assimilating this extremely toxic compound. However, generally, it can be considered that the tested plant species showed to be very efficient in the extraction and accumulation of many PAH compounds in its roots and consequently in PAH phytostabilization.

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IZVOD

Kapaciteti hедера helix iz borskog regiona za akumulaciju pau u korenu i implikacije za fitostabilizaciju

Policiklični aromatični ugljovodonici (PAU) smatraju se zagađujućim materijama najvišeg prioriteta, a remedijacija PAU iz životne sredine predstavlja problem na globalnom nivou. Cilj ovog istraživanja bio je da se ispita fitoremedijacioni potencijal Hedera helix i da se utvrdi sadržaj 16 prioriternih PAU u uzorcima zemljišta i korena koji su prikupljeni iz ruralnih i industrijskih zona opštine Bor (Srbija). Sadržaj Σ16 PAH u zemljištu je bio od 326,49 µg/kg na lokalitetu Borsko jezero do 1937,64 µg/kg na lokalitetu Slatinsko naselje. Stepenn zagađenosti zemljišta (u zavisnosti od koncentracije Σ16 PAU) bio je visok na većem broju ispitivanih lokacija i pod značajnim uticajem antropogenih aktivnosti. Koncentracije Σ16 PAU u uzorcima korena kretala su se od 480,71 µg/kg na lokaciji Krivelj do 1748,32 µg/kg na lokaciji Naselje Sunce. Zanimljivo je da ekstremno toksičan benzo(a)piren nije detektovan u korenu ispitivane biljke ni na jednoj ispitivanoj lokaciji. Bio-koncentracioni faktori (BCF) bili su primenjeni za određivanje kapaciteta Hedera helix za akumulaciju PAU u korenu, a samim tim i za određivanje njenog fitostabilizacionog potencijala. U većini slučajeva, BCF vrednosti su bile veće na lokacijama UI zone. Takođe, izračunati BCF su bili veći za nisko molekularne u poređenju sa visoko molekularnim PAU. Na većem broju lokacija ispitivana biljna vrsta pokazala se veoma uspešno u akumulaciji jedinjenja u korenu, kao što su acenaften, fluoren, antracen, dibenzo(a,h)antracen i zbirna benzo(k)fluorantena i benzo(b)fluorantena. Dobijeni rezultati su pokazali da se Hh može uspešno koristiti u fitostabilizaciji mnogih PAU jedinjenja.

KLjučne reči: Zagađenje zemljišta, PAU, Hedera helix, fitostabilizacija

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