Chemometric evaluation of 16 priority PAHs in soil and roots of Syringa vulgaris and Ficus carica from the Bor region (Serbia): An insight into the natural plant potentials for soil biomonitoring and phytoremediation

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Abstract

In this work, soil biomonitoring, and phytoremediation potentials of *Syringa vulgaris,* and *Ficus carica* were evaluated regarding 16 priority polycyclic aromatic hydrocarbons (PAHs) using a modern chemometric approach and calculating the accumulation rates (i.e., bioconcentration factors, BCFs) for each individual PAH compound in plants roots from each location. Soil and root samples were collected from nine locations in the Bor region (Serbia) and PAHs were isolated using QuEChERS (Quick, Effective, Cheap, Easy, Rugged, Safe) method with some new modifications; their concentrations were detected by gas chromatography/mass spectrometry. The results were processed using Pearson's correlation analysis, hierarchical cluster analysis, and BCFs. Several central conclusions are: each plant species developed its own, a specific capability for individual PAH managing; only in the case of benzo(a)pyrene and chrysene, both plants developed a similar tactic, i.e. a total avoiding of assimilation (probably due to their high toxicity); both plants detained significant quantities of different PAHs in their roots, which further can recommend them for the restriction of PAH spreading in the soil, i.e., in PAH phytostabilization (particularly for fluorene, benzo(b)fluoranthene, and benzo(k)fluoranthene); in soil biomonitoring, both plantscannot be so helpful because their roots cannot reflect an actual situation in the soil; soil analysis gives a more safe insight into the current pollution level, as well as into the possible regional generators of PAH.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic, semi-volatile organic pollutants with the two or more benzene rings combined in different manners (Bishnoi et al., 2024; Jia et al., 2021; Zhu et al., 2023). According to the molecular structure and molecular weight, PAHs are divided into: light-molecular weight (LMW, with two or three aromatic rings) and high-molecular weight (HMW, with five or more benzene rings) PAHs (Papludis et al., 2022; Sumathi & Rameshpathy, 2023).

Polycyclic aromatic hydrocarbons can be formed during natural or anthropogenic processes where the latest were recognized as the main part of PAH sources (Zhu et al., 2023). Volcanic activities, wood fires, diagenesis, and some biogenic processes (resulting from microbial activities), can be counted as natural sources of PAHs, whereas anthropogenic sources include a range of industrial processes, traffic, incineration of various organic materials (tobacco, different organic waste materials, grilled meat), as well as all kinds of pyrolytic processes (Idowu et al., 2019).

The group of these dangerous micro-pollutants accounts more than hundred compounds but only 16 of them were the most examined in different environmental studies across the World as follows (Bishnoi et al., 2024; Alagić et al., 2015; Kaur et al., 2024): acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(g,h,i)perylene (BgP), benzo(k)fluoranthene (BkF), chrysene (CHR), dibenzo(a,h)anthracene (DhA), fluoranthene (Flt), fluorene (Flr), indeno(1,2,3-c,d)pyrene (IcP), naphthalene (Nap), phenanthrene (Phe) and pyrene (Pyr). Because of a great concern about their toxic effects and an easy transmission over the long distances (Jia et al., 2021; Kaur et al., 2024; Kicińska & Dmytrowski, 2023; Sumathi & Rameshpathy, 2023;), these compounds are included into the list of priority pollutants, created by the United States Environmental Protection Agency (USEPA). Seven of them: BaA, BaP, BbF, BkF, CHR, DhA and IcP, USEPA classified as probable carcinogens (Patel et al., 2020; Sakshi et al., 2019). Except that, USEPA also formed Risk-Based Screening Tables, referring to all important pollutants, together with 16 PAHs. Practically, these Generic Tables contain limit values (LVs) related to the so called, Regional Screening Levels (RSLs) for the concentrations in tap water, and residential, and industrial soil (USEPA, 2024). As for soil, RSLs refer to PAH concentrations that do not need any additional procedures regarding soil protection; but, when PAH concentrations are identical or surpass RSLs, further assessments (but not necessarily remediation) are needed. USEPA RSLs are defined on the basis of the target cancer risk (TR) of $1x10^{-6}$, and the two values of the target hazard quotients (THQ): 1.0, and 0.1 (USEPA, 2024). This agency paid a special attention to soil because it represents a non-renewable (or very slowly) renewable natural resource, which is as a main sink for the emitted PAHs (Cvetkovic et al., 2016). More precisely, lipophilic molecules of PAHs are naturally firmly attached to the soil particles, i.e. to soil organic matter (OM) such as: humins, humic acids, fulvic acids, etc., where they can persist for a very long period of time (Kicińska & Dmytrowski, 2023; Ukalska-Jaruga & Smreczak, 2020). Polycyclic aromatic hydrocarbons, which have low solubility in water and low vapor pressure but high organic carbon partitioning coefficient (Koc), are especially predisposed to the processes of sequestration into the soil micro pores that may lead to a PAH moving into deeper layers of soil, which is known as “ageing”; accordingly, PAHs are named - “recalcitrant” substances (Ukalska-Jaruga & Smreczak 2020). Very important - this relocation from the shallow, easy accessible layers of soil to the deeper and less reachable ones, causes, in final, a lower availability of PAHs to soil organisms, which is not desirable in the processes of their bioremediation as

environmentally friendly method for soil remedy. Namely, for PAH decomposition or their total elimination, bioremediation utilizes abilities of different soil organisms such as various microbes (having the biggest potential for PAH degradation) (Sumathi & Rameshpathy, 2023; Dai et al., 2022), and then a range of plant species (Alagić et al., 2015; Košnář et al., 2019; Xiao et al., 2015).

Namely, during the long time of evolution, in adaptive efforts to overcome the problems with the aggressive soil environments, some plant species successfully developed different and very specific mechanisms of resistance to PAHs, and they are known as tolerant species. Practically, except PAH destroying or immobilization in soil or on root surfaces (usually in cooperation with the associated soil microbes and using different root exudates such as organic acids, enzymes, etc.), plants may uptake and accumulate significant PAH quantities into the root cells (inside their specific organelles such as vacuoles). PAHs may be also translocated into the aerial parts through the transpiration pathway, depending on the nature of plant species and the features of the pollutant (molecular structure, lipo-solubility, and Henry's law constant) (Sakshi et al., 2019; Tarigholizadeh et al., 2024). The translocation of PAHs is mainly reserved for PAHs with the simplest structures, whereas robust structures of complex PAHs are less suitable for these processes. Further, in plant cells, PAHs may undergo the complicated processes of decomposition and transformation into the less poisonous metabolites (the processes of detoxification) which are very comparable with the processes in mammals (the so called: "green liver" concept) (Alagić et al., 2015; Gao et al., 2013).

Based on these facts, different phytoremediation methods, as a part of bioremediation approach are developed and today, they represent a relatively new and effective technology, especially for large contaminated soil surfaces. In contrast to other classical remediation methods (chemical or physical), this method has no negative and destroying effects (regarding the soil structure and quality), and very often, it is able to improve soil characteristics (Kaur et al., 2024). Phytoremediation consists of several different procedures for PAH removing or their partial degradation (Prabakaran et al., 2019; Włóka et al., 2019; Xiao et al., 2015).

For instance, phytoremediation method, known as phytostabilization, refers to the mentioned excretion of root exudates that may cause PAH destroying but also their immobilization, producing PAH reactive radicals in soil. These radicals can be precipitated, polymerized, or covalently attached to the soil OM, which practically stabilizes PAHs and restricts their spreading in soil matrix (Kaur et al., 2024). Most importantly, the excreted compounds can also regulate geochemical environment in the plant rhizosphere, in a manner that offers maximally optimal conditions for the expansion of colonies of useful soil microbiota that promote plant growth; in that case, plants support a practical cooperation with the associated soil microbes which may result in a considerable PAH decomposition in the rooting zone. The described synergistic effects between plants and rhizosphere microbes, helped in the creation of the most successful method for PAH phytoremediation namely, rhizosphere biodegradation (Alagić et al., 2015; Košnář et al., 2019).

Phytodegradation/phytotransformation is a method which is related to the effects of PAH biotransformation performed inside plant cells (the "green liver" concept), where plants are able only for partial modifications of PAHs, or for their accumulation inside cells. For instance, a classical phytoextraction/phytoaccumulation method refers to the extraction of soil PAHs by plant roots, and latter translocation/accumulation inside the above ground plant tissues (which further can be harvested and removed from the contaminated site) (Kaur et al., 2024; Sakshi et al., 2019). Some early studies reported that the accumulation of PAHs in the above ground parts cannot be recommended as one of useful phytoremediation methods; namely, it was found that the accumulation rates of PAHs in these parts, expressed through bioconcentration factors (BCFs, the ratio between the concentration of PAH compound in a plant part and its concentration in the soil), generally range from 0.001 to 0.4, and only sometimes to 2 (Alagić et al., 2015; Tao et al., 2006). However, some recent studies showed that, in the case of roots, BCFs for individual PAHs may reach enormously high values. For example, the examined roots of wild blackberry from the Bor region in eastern Serbia, showed extremely high potential for the extraction and accumulation of several HMW PAHs; namely, blackberry roots were able to extract the complete content of some PAHs from the corresponding soils which resulted in the impossibility to calculate their (enormously high) BCF values. Nevertheless, the utilization of roots in a classical phytoextraction/phytoaccumulation procedure is not so convenient due to the almost unfeasible conditions for their harvesting. At the same time, a significant accumulation of PAHs in plant roots may help in phytostabilization, i.e. in the restriction of PAH dispersion in soil (Alagić et al., 2016, 2017).

Many plants were investigated in terms of their application in some of PAH phytoremediation methods (Alagić et al., 2016, 2017; Bishnoi et al., 2024; Muratova et al., 2022; Prabakaran et al., 2019; Qiu et al., 2018; Sushkova et al., 2020; Tao et al., 2006; Włóka et al., 2019; Zhen et al., 2019) as well as in various biomonitoring procedures (Alagić et al., 2016, 2017; Ratola et al., 2010; Sari et al., 2020). In this work, the two plant species from the Bor region (Eastern Serbia), *Syringa vulgaris* L. (SV), and *Ficus carica* L. (FC)

cultivar crna Petrovača, were selected as testing plants for a chemometric examination of biomonitoring, and phytoremediation capacities (concerning 16 priority PAHs), together with the calculation of BCF for each compound at each investigated location. More precisely, given that the utilization of the aerial parts in classical phytoextraction, as one of the most attractive phytoremediation methods, cannot be an effective solution for structurally massive molecules such as PAHs, the main focus of this study was the extraction/bioaccumulation capacity of SV, and FC roots, as well as the possibility for their application in soil biomonitoring and phytostabilization as the two environmentally friendly methods for soil controlling, protection, and conservation. Both selected plants were not investigated earlier with this regard and the obtained results will represent an additional benefit of this work for all researches interested in the mentioned environmental issues. Another useful contribution of this work is introducing of some modifications in a relatively new method of PAH isolation, known as QuEChERS (Quick, Effective, Cheap, Easy, Rugged, Safe) method; at the first place, the modifications were applied in terms of obtaining a maximal precision of the complete chemical analysis. In terms of identification of eventually increased PAH concentrations in soils of the investigated Bor's region, the results obtained for the sampled soils of both plants are compared with the published results for the related soils of wild blackberry from the same region (Alagić et al., 2016, 2017). Finally, soil results are compared with the related USEPA RSLs, with the aim to discover possible toxic, i.e., risk concentrations for local human population (USEPA, 2024).

Materials and methods

The sampling area

Bor is a town in Eastern Serbia, surrounded by mountains rich in diverse vegetation. Its geographic coordinates are: 44º25′N, and 22º06′E. Dominant winds in the region are north-west (NW), west–northwest (WNW), and west (W). The main parts of the regional economy are copper mining and processing. The possible major sources of PAHs in this region are the copper smelter plant and the neighboring city heating plant placed in an industrial complex at the north-eastern periphery of the city of Bor. In this study, the investigated locations are selected at the positions differently distant from the industrial complex, practically from the new “flash” smelter and the heating plant because both plants spread their waste gases jointly. Over the years, including the year of sampling for this study, the heating plant employed different kind of coal. In rural settlements, the domestic heating is present, mainly based on wood, coal, and sometimes - fuel combustion. Also, in rural fields, the controlled stubble burning is not so unusual. Finally, during the long, hot summers, an inappropriate deposition of various waste materials at the city landfill represents a considerable source of the spontaneous, massive ignitions, fuming a significant part of the investigated territory.

The contents of 16 PAHs were determined in soils and roots of SV and FC that were grown in both zones of interest: rural (RZ), and urban/industrial (UIZ), at the positions differently distant from the industrial/metallurgical complex (Fig. 1).

Urban/industrial zone enclosed several parts of the town of Bor, and they are listed here with their assigned labels and distances from the complex: 1) Flotacijsko jalovište (FJ, a flotation tailings pond, out of use) – 0.7 km; 2) Bolničko naselje (BN, a central part in Bor, near the city hospital) – 1.3 km; 3) Slatinsko naselje (SN) – (very close to this place, in the local pathway to Oštrelj from RZ, the city landfill is placed) – 3.2 km, and 4) Naselje Sunce (NS, a residential part at the periphery of Bor) – 3.6 km. Rural zone included 4 rural sites, and a touristic site: 5) Oštrelj (O) – 4.5 km; 6) Slatina (S) – 6.5 km; 7) Borsko jezero (BJ, Bor Lake, a touristic site) – 7 km; 8) Krivelj (K) – 8 km, and 9) Gornjane (G) – 19 km.

Sample collection, and pretreatment

The sampling of roots and the corresponding soils of the selected plant species was conducted in individual backyards in UIZ, and RZ, where they were planted, except in the case of FJ, where the plants of both investigated species were found as spontaneously growing.

Roots and soil samples from the corresponding rooting zones of SV and FC were collected from the chosen sites during September 2020. The samples of plant and soil material (about 1 kg each) for both investigated plant species were collected from the rooting zone (depth: 0–30 cm) using means of stainless steel. At each location, the samples of soils and roots of SV and FC were taken from 3 (site FJ) to 5 individual plants; maximum distance between plants of both investigated species was 50 m. These first, separated samples were later jointed to obtain a representative sample of roots or soils of each investigated plant, for each selected location. Collected samples were placed into the bags made of aluminum foil and delivered to the laboratory for further preparation.

At the first place, root samples were divided into the fine roots (which were discarded) and coarse roots, which were subjected to a careful cleaning. Where soil particles were removed from the coarse roots, they additionaly were gentle cleaned by fine sandpaper; finally, they were washed with tap and distilled water. All soil and root samples were air-dried to a constant weight in an isolated room, kept safe from any unwanted contamination. After drying, plant samples were homogenized in a vibratory disc mill, while soil samples were riddled through stainless steel sieve (2-mm). Before the subsequent steps such as: extraction, cleaning up, and gas-chromatography/mass-spectrometry (GC/MS) analysis, the prepared samples were placed in sealed/closed bags, and kept at 4ºC.

Extraction of PAHs from soil and plants samples and chemical analyses

Used reagents and measured soil parameters

The list of used reagents is given in Online Resource, in the List 1OR, as well as measured soil parameters (pH, OM, and electrical conductivity, EC), which are given in Table 1OR.

pH values and (μS/cm) of soil samples (in solid to distilled water ratio – 1:2.5 w/v) were measured consecutively using a CyberScan pH 510 Eutech (NL) pH meter and 4510 Jenway (UK) conductometer. The content of soil OM (%) was determined by loss-on-ignition method at 550°C (Jolivet et al., 1998).

Extraction and instrumental analysis of PAHs with QA/QC

The extraction of PAHs from the collected soil and root samples was conducted using QuEChERS technique, as a relatively new and very precise method in PAH analysis, which was confirmed in many environmental studies (Cvetkovic et al., 2016; Sadowska-Rociek et al., 2013), including the study on wild blackberry from Bor's municipality (Alagić et al., 2016, 2017). In the present study, some modifications of the latest version given in Alagić et al. (2016, 2017), are related to different quantities of used reagents, and most importantly, instead of primary–secondary amine (as a sorbent in the second, purification step), diatomaceous earth was used, as a low cost sorbent, with wide surface area, which positively affects the precision as well as the costs of the analysis; this represents the first time of its utilization in refining of plant material during PAHs analysis. Practically, in this work, each sample of soil and plant material (10 g of each), was weighed into a 50 mL QuEChERS tube and 300 μL of surrogate standard was added. After that, 30 mL of water/acetonitrile mixture (1:2, v/v) was added, too. The tubes with samples were shaken for 1 min and then extracted in an ultrasonic bath for 30 min. Then, 2 g of NaCl and 8 g of $MgSO_4$ were also added into each tube and the obtained mixtures were shaken about 1 min and centrifuged at 4000 rpm for 10 min. In the next, cleaning step, for soil samples, an aliquot of the supernatant (1.5 mL) was transferred into 2 mL tubes containing 50 mg diatomaceous earth and 150 mg $MgSO_4$; for plant samples, this step was performed using 100 mg diatomaceous earth and 500 mg $MgSO_4$. After 5 min shaking, the tubes were centrifuged at 8000 rpm for 10 min. The supernatants of 1 mL volume were transferred to vials.

Soil and plant samples from an unpolluted area were spiked using PAH standard solution mixture, in order to perform method validation. Spiked samples were prepared in the same way described in the previous paragraph. Method validation parameters are presented in Table 1.

Table 1
Retention times, corresponding ions, and method validation parameters for analyzed PAHs

Compound	Rt (min)	Quantifier ion	LOD (µg/kg)	LOQ (µg/kg)	Calibration curve equation	Correlation coefficient	$Recovery_s$ (%)	$Recovery_p$ (%)	RSD_s (%)	RSD_p (%)
Nap	11.792	128.0	0.78	2.60	y = 0.0343x	0.99	113	102	10.8	5.6
Acy	17.721	152.0	0.29	0.96	y = 0.0056x	0.99	100	99	6.37	4.17
Ace	18.460	153.0	0.19	0.65	y = 0.0627x	0.99	94	110	2.74	5.37
Flr	20.380	166.0	0.48	1.60	y = 0.004x	0.99	95	88	7.38	6.74
Phe	24.000	178.0	1.50	5.00	y = 0.298x	0.99	96	95	9.11	7.44
Ant	24.177	178.0	0.39	1.30	y = 0.109x	0.98	100	111	4.79	9.54
Flt	28.575	202.0	0.51	1.70	y = 0.069x	0.98	96	93	6.34	7.45
Pyr	29.383	202.0	0.60	2.00	y = 0.104x	0.99	96	89	4.76	6.54
CHR	34.072	228.0	1.02	3.40	y = 0.053x	0.98	116	106	4.97	5.42
BaA	34.238	228.0	0.50	1.67	y = 0.029x	0.99	112	95	7.98	8.42
BbF + BkF	38.103	253.0	0.05	0.18	y = 1.495x	0.99	91	98	3.87	2.97
BaP	39.039	253.0	0.60	2.00	y = 0.0225x	0.99	92	98	6.54	5.56
IcP	42.760	277.0	0.63	2.10	y = 0.076x	0.99	99	84	4.79	5.45
DhA	42.878	279.0	1.17	3.90	y = 0.0037x	0.99	90	107	7.86	5.87
BgP	43.637	276.0	0.90	2.00	y = 0.626x	0.99	96	100	8.93	6.87

Rt - retention time; LOD – limit of detection; LOQ – limit of quantification; $Recovery_s$ – recovery values for soil samples; $Recovery_p$ - recovery values for plant samples; RSD_s – relative standard deviation for soil samples; RSD_p – relative standard deviation for plant samples

Table 1 Retention times, corresponding ions, and method validation parameters for analyzed PAHs

The calibration curves of 16 analyzed components were constructed by using a series of standard PAH solution in the concentration range of 0.017–16.667 µg m/L. Solution of the internal standards containing perylene d_{12} and acenaphthene d_{10} was added to every vial prior GC-MS analysis, to calculate each PAH concentration by comparison of the peak areas of internal standard and each PAH compound. Surrogate standard solution (2-fluorobiphenyl, p-terphenyl-d_{14}, and 2,4,6-tribromophenol) was also added to each sample, before extraction, to monitor the efficiency of the extraction process. In method optimization experiments, soil samples were obtained from unpolluted area and have been used for blank and spiked sample preparation. Before spiking, the absence of PAHs in question was verified by analysis of the soil sample applying the standard procedure (EAHO, 2003). GC-MS analysis of blank showed the absence of the potential interferences. LOD was calculated to be 3 times higher than the level of noise, while LOQ was equal to 10 times the noise level. Accuracy was evaluated at 3 different spiking levels, for both soil and plant samples and expressed as recovery values (Table 1).

After the addition of 200 µL of internal standards (perylene d_{12}, and acenaphthene d_{10}, each in concentrations of 80 µg/mL) in all vials, GC/MS analysis was performed. All samples of soil and root for both plant species were prepared in triplicate and the obtained results were expressed in µg/kg dry weight (DW).

Prepared extracts were analyzed on a 7890/7000B GC-MS-MS triple quadrupole device (Agilent Technologies, USA, equipped with a Combi PAL auto sampler and a HP-5MS capillary column (5% Phenyl Methyl Siloxane, dimensions: 30 m x 250 µm, film thickness

0.25 µm). First, the recording was performed in SCAN mode, with the aim of determining the retention times and characteristic ions that were used for the analysis of the related compounds.

After determining the retention times of elution of the analyzed compounds and the identification of ions that can be used for the compounds quantification, the recording was continued in SIM mode. The temperature regime was as follows: isothermal at 75ºC for the first 3 min, then a linear increase up to 300ºC (gradient 6°C/min), and finally, isothermal at 300ºC for the last 10 min. The total analysis time was 50.5 min. The injected volume was 2.5 µL, in splitless mode. A carrier gas was helium with a flow rate of 1.0 mL/min. The ionization potential was – 70 eV. Quantitative and qualitative analyses were performed based on the corresponding quantifier ions and the retention times given in Table 1 using the program MassHunter QQQ Quantitative Analysis software (Agilent Technologies, USA). It should be mentioned here that the results for BkF, and BbF are given as a sum: BkF + BbF, because the separation achieved during GC/MS analysis was not adequate under the applied instrumental conditions.

Data processing

In order of studying the existing relations between the investigated variables such as the detected contents of 16 PAHs in SV, and FC roots and soils (including also measured soil parameters: pH, EC, and OM), the statistical method of Pearson's correlation analysis was performed. The same method was applied to PAH contents and the distances of the selected locations from the industrial/metallurgical complex, in terms of identification of this complex as a possible main source of pollution. Hierarchical cluster analysis (HCA) was conducted for biomonitoring purposes, i.e. to illustrate the classification of the investigated polluted locations according to their similarities (Miller & Miller, 2005). For all statistical methods, IBM SPSS Statistics 20 software (USA) was used.

The accumulation rates of PAHs in the roots of SV and FC were calculated using the bio-concentration factor, BCF. In this, paper, BCF signifies a ratio of the concentration of a compound in the root to its concentration in the soil: BCF = C_{root}/C_{soil} (Tao et al., 2006). A good accumulation of PAH compound in the roots of the investigated plants is confirmed by BCF higher than 1, which practically implies their good potential for the application in the phytoremediation method - phytostabilization (Alagić et al., 2016).

Results and discussion

Measured concentrations of individual PAH compounds in soil and plant samples of SV, and FC from the selected sites are shown in Tables 2, and 3, respectively. It is obvious that PAHs such as BgP and IcP were not detected in both kinds of the investigated samples, and plus, BaP and CHR were not detected in all root samples. The most of measured soil PAHs were present at almost all locations. Generally speaking, the most abundant soil compounds were Nap, Phe, and Flt for both investigated plants. In the case of plant roots, only Nap, Ace, and Flr were present at all locations. At the same time, these compounds were the most abundant in the plants' roots, (partly including Phe). The compounds such as Ant, Flt, and Pyr in the root of FC were detected only at the site FJ, which is the closest to the industrial/metallurgical complex containing the city heating plant. The highest concentration in soil samples was found for Flt: 1504 µg/kg in SV at the site BN, while in the plant roots, it was for Flr – 5592 µg/kg in SV at the site K, and also – 4990 µg/kg at the site G.

Table 2
The concentrations of PAHs (μg/kg, DW) in the soil samples of SV, and FC

Location/ Plant		LMW PAHs						
		Nap	Acy	Ace	Flr	Ant	Phe	
FJ	SV	106 ± 14	12 ± 1	3.6 ± 0.6	11.9 ± 0.3	3.4 ± 0.7	49 ± 4	
	FC	149 ± 3	17.8 ± 0.5	4.3 ± 0.5	12.0 ± 0.1	2.3 ± 0.3	69 ± 4	
BN	SV	178 ± 4	52 ± 4	38 ± 5	36 ± 3	166 ± 6	395 ± 13	
	FC	68 ± 1	16.8 ± 0.8	5.8 ± 0.3	10.0 ± 0.8	14 ± 1	65 ± 8	
SN	SV	165 ± 3	31.0 ± 0.2	15.8 ± 0.7	24 ± 3	9.2 ± 0.6	154 ± 13	
	FC	158 ± 13	35 ± 3	16.4 ± 0.7	28 ± 2	8.0 ± 0.6	119 ± 15	
NS	SV	64 ± 2	32 ± 1	4.6 ± 0.1	10.1 ± 0.1	17 ± 2	96 ± 2	
	FC	165 ± 10	36 ± 2	10.2 ± 0.6	20 ± 2	11.5 ± 0.4	116 ± 8	
O	SV	187 ± 26	29 ± 4	16.1 ± 0.8	33 ± 1	4.7 ± 0.3	109 ± 17	
	FC	85 ± 6	14.6 ± 0.9	9.0 ± 0.2	26 ± 3	nd	102 ± 9	
S	SV	147 ± 8	18.4 ± 0.4	8.2 ± 0.6	33 ± 1	nd	189 ± 11	
	FC	111 ± 11	46 ± 1	24.3 ± 0.4	37 ± 2	53 ± 4	160 ± 4	
BJ	SV	106 ± 5	21 ± 1	37 ± 2	27 ± 3	nd	255 ± 18	
	FC	190 ± 17	35 ± 5	13 ± 1	20 ± 3	nd	86 ± 8	
K	SV	66 ± 5	6.2 ± 0.7	13.6 ± 0.4	11 ± 2	nd	221 ± 13	
	FC	86 ± 4	9 ± 1	7.5 ± 0.3	14 ± 2	nd	71 ± 3	
G	SV	108 ± 7	15 ± 1	9.4 ± 0.1	19.3 ± 0.9	nd	73 ± 5	
	FC	143 ± 8	22 ± 2	8.7 ± 0.3	15.5 ± 0.9	5.6 ± 0.9	96 ± 2	
USEPA RSL[a] (mg/kg)								
Residential		2.0[b,c]	ne[b,c]	3600[b]/ 360[c]	2400[b]/ 240[c]	18000[b]/ 1800[c]	ne[b,c]	
Industrial		8.6[b,c]	ne[b,c]	45000[b]/ 4500[c]	30000[b]/ 3000[c]	230000[b]/ 23000[c]	ne[b,c]	
Location/ Plant		HMW PAHs						
		Flt	Pyr	BaA	CHR	BaP	BbF + BkF	DhA

SV - *Syringa vulgaris*; FC - *Ficus carica* cv. crna Petrovača

nd – not detected; ne – criterion not established

a - USEPA regional screening levels (RSL) from generic tables defining maximally allowed concentrations of PAHs in residential and industrial soil (USEPA, 2024)

b - USEPA Summary Table based on criteria TR = $1x10^{-6}$ and THQ = 1.0 (USEPA, 2024)

c - USEPA Summary Table based on criteria TR = $1x10^{-6}$ and THQ = 0.1 (USEPA, 2024)

Location/ Plant		LMW PAHs						
		Nap	Acy	Ace	Flr	Ant	Phe	
FJ	SV	67 ± 4	35.5 ± 0.3	83 ± 9	17 ± 2	8 ± 2	12 ± 1	30 ± 2
	FC	99 ± 4	52 ± 4	71 ± 5	14.6 ± 0.8	7.7 ± 0.9	10.0 ± 0.1	24.7 ± 0.7
BN	SV	1504 ± 70	831 ± 39	560 ± 41	270 ± 25	6.5 ± 0.5	5.0 ± 0.6	70 ± 7
	FC	199 ± 10	119 ± 13	107 ± 5	39 ± 4	5.8 ± 0.6	nd	nd
SN	SV	232 ± 6	131 ± 2	165 ± 20	28 ± 5	9.4 ± 0.3	11.1 ± 0.3	nd
	FC	147 ± 13	81 ± 4	61 ± 6	18 ± 1	9.5 ± 0.3	7.4 ± 0.5	nd
NS	SV	256 ± 3	194 ± 3	108 ± 6	34 ± 2	7.0 ± 0.8	nd	nd
	FC	307 ± 37	260 ± 20	248 ± 13	75 ± 3	9.7 ± 0.1	50 ± 4	**128 ± 6**
O	SV	68 ± 8	30 ± 2	59 ± 7	nd	9.3 ± 0.2	10.1 ± 0.3	nd
	FC	58 ± 5	23 ± 3	63 ± 5	6.3 ± 0.5	9.8 ± 0.4	13 ± 2	nd
S	SV	271 ± 12	132 ± 9	99 ± 9	42 ± 4	9.3 ± 0.7	8.2 ± 0.3	69 ± 5
	FC	401 ± 15	230 ± 6	309 ± 33	44 ± 3	9.4 ± 0.8	nd	109 ± 6
BJ	SV	38.5 ± 0.6	25 ± 3	42 ± 5	10.0 ± 0.5	10.7 ± 0.5	nd	nd
	FC	102 ± 14	65 ± 7	155 ± 8	14 ± 1	8.7 ± 0.6	8.7 ± 0.4	nd
K	SV	21 ± 2	12.8 ± 0.4	nd	nd	8.2 ± 0.7	nd	nd
	FC	19.5 ± 0.6	11.0 ± 0.6	nd	nd	9.3 ± 0.3	nd	nd
G	SV	24 ± 3	13.2 ± 0.4	38 ± 5	nd	9.0 ± 0.6	nd	nd
	FC	177 ± 1	117 ± 2	68 ± 17	28.6 ± 0.4	9.5 ± 0.6	nd	nd
USEPA RSL[a] (mg/kg)								
Residential		2400[b]/ 240[c]	1800[b]/ 180[c]	1.1[b,c]	110[b,c]	0.11[b,c]	BbF 1.1[b,c]	BkF 11[b,c]	0.11[b,c]
Industrial		30000[b]/ 3000[c]	23000[b]/ 2300[c]	21.0[b,c]	2100[b,c]	2.1[b,c]	21[b,c]	210[b,c]	2.1[b,c]

SV - *Syringa vulgaris*; FC - *Ficus carica* cv. crna Petrovača

nd – not detected; ne – criterion not established

a - USEPA regional screening levels (RSL) from generic tables defining maximally allowed concentrations of PAHs in residential and industrial soil (USEPA, 2024)

b - USEPA Summary Table based on criteria TR = $1x10^{-6}$ and THQ = 1.0 (USEPA, 2024)

c - USEPA Summary Table based on criteria TR = $1x10^{-6}$ and THQ = 0.1 (USEPA, 2024)

Table 3
The concentrations of PAHs (μg/kg, DW) in the root samples of SV, and FC

Location/		LMW PAHs						
Plant		Nap	Acy	Ace	Flr	Ant	Phe	
FJ	SV	32 ± 2	35 ± 6	60 ± 7	68 ± 8	21 ± 2	301 ± 34	
	FC	31 ± 1	25.7 ± 0.7	38 ± 3	143 ± 9	14 ± 1	269 ± 16	
BN	SV	23.4 ± 0.9	3.9 ± 0.1	94 ± 8	127 ± 6	nd	335 ± 12	
	FC	129 ± 3	185 ± 9	10.4 ± 0.4	51 ± 3	nd	138.4 ± 0.7	
SN	SV	25 ± 3	4.39 ± 0.05	10 ± 1	403 ± 24	19.68 ± 0.05	157 ± 8	
	FC	59 ± 2	30 ± 2	15.4 ± 0.1	131 ± 5	nd	133 ± 1	
NS	SV	27 ± 2	nd	10 ± 1	222 ± 4	nd	426 ± 19	
	FC	99 ± 5	nd	16 ± 2	85 ± 5	nd	145 ± 5	
O	SV	24 ± 3	183 ± 17	65 ± 1	331 ± 54	nd	52 ± 2	
	FC	29.6 ± 0.7	2.91 ± 0.05	21.2 ± 0.8	81.4 ± 0.8	nd	108.2 ± 0.4	
S	SV	52 ± 5	nd	29 ± 1	279 ± 40	nd	nd	
	FC	114 ± 7	nd	15 ± 2	300 ± 28	nd	101 ± 3	
BJ	SV	20 ± 3	nd	15.0 ± 0.7	627 ± 33	nd	16 ± 2	
	FC	89 ± 4	3.1 ± 0.2	5.2 ± 0.6	64 ± 5	nd	nd	
K	SV	18 ± 2	nd	111 ± 8	5592 ± 90	nd	nd	
	FC	82 ± 8	nd	9.4 ± 0.8	98 ± 8	nd	141 ± 4	
G	SV	15.0 ± 0.9	nd	55 ± 3	4990 ± 156	nd	79 ± 9	
	FC	79 ± 4	2.3 ± 0.3	7.7 ± 0.8	189.7 ± 0.5	nd	149 ± 8	
Location/		**HMW PAHs**						
Plant		**Flt**	**Pyr**	**BaA**	**CHR**	**BaP**	**BbF + BkF**	**DhA**
FJ	SV	36 ± 5	14 ± 1	nd	nd	nd	2.8 ± 0.5	nd
	FC	124 ± 4	12.5 ± 0.6	77 ± 3	nd	nd	4.5 ± 0.3	90 ± 2
BN	SV	14.2 ± 0.1	5.6 ± 0.4	nd	nd	nd	7.4 ± 0.4	58 ± 5
	FC	nd	nd	192 ± 4	nd	nd	20 ± 1	146 ± 33
SN	SV	385 ± 52	78 ± 13	50 ± 2	nd	nd	nd	nd
	FC	nd	nd	8 ± 1	nd	nd	nd	97 ± 6
NS	SV	36 ± 4	7.2 ± 0.2	nd	nd	nd	8.3 ± 0.2	901 ± 16
	FC	nd	nd	816 ± 52	nd	nd	nd	nd
O	SV	2.5 ± 0.3	2.6 ± 0.1	nd	nd	nd	4.7 ± 0.5	285 ± 26
	FC	nd	nd	nd	nd	nd	nd	172.8 ± 0.3
S	SV	7.1 ± 0.7	6.4 ± 0.8	nd	nd	nd	nd	220 ± 2

SV - *Syringa vulgaris*; FC - *Ficus carica* cv. crna Petrovača

nd – not detected

	FC	nd	nd	148 ± 27	nd	nd	9.7 ± 0.5	129 ± 3
BJ	**SV**	231 ± 4	39.5 ± 0.5	nd	nd	nd	8.3 ± 0.3	329 ± 42
	FC	nd	nd	47 ± 6	nd	nd	7.4 ± 0.4	29 ± 4
K	**SV**	20 ± 3	6.7 ± 0.5	nd	nd	nd	3.7 ± 0.2	191 ± 5
	FC	nd	nd	nd	nd	nd	nd	48.7 ± 0.9
G	**SV**	17 ± 4	4.3 ± 0.2	nd	nd	nd	2.6 ± 0.3	278 ± 27
	FC	nd	nd	nd	nd	nd	7.3 ± 0.4	55 ± 6
SV - *Syringa vulgaris*; FC - *Ficus carica* cv. crna Petrovača								
nd – not detected								

The concentrations of the investigated PAHs in the corresponding soils of SV, and FC from the chosen sites (Table 2) ranged from nd for Ant (in SV, sites S, BJ, K and G, and in FC, sites O, BJ and K), BaA (in SV and FC, site K), CHR (in SV and FC, site K, and also in SV, sites O and G), BbF + BkF (in SV, sites NS, BJ, K and G, and in FC, sites BN, S, K and G), and DhA (in SV, and FC, sites SN, O, BJ, K and G, and also in FC, site BN) to 1503.69 µg/kg (in SV, site BN) for Flt.

Interestingly, all detected soil concentrations were below the related USEPA RSLs (Table 2) (USEPA, 2024), except in the case of DhA in FC (128 µg/kg, given in bold in the same Table 2) at the suburb site NS, considering both criteria: 1) TR = $1x10^{-6}$, and THQ = 1.0, and 2) TR = $1x10^{-6}$, and THQ = 0.1 for residential soil. These findings suggest that only DhA (a probable carcinogen) in FC soil at UI site NS may represent some risk for human health. However, at the same time, the comparison of the detected soil concentrations with the matching concentrations in wild blackberry soils from several identical locations in the region of Bor, from an earlier period (Alagić et al., 2016, 2017), showed that in most cases, there was a rising in individual PAH contents, except in the case of BaP, where the soil content was noticeably decreasing (Table 2). This increasing in PAH soil concentrations suggests that environmental concerns and protective measures should be also raised considering the complete local ecosystem. For instance, the filters in the stacks of the city heating plant should be modernized in terms of reducing the emissions of cancerognic and all other PAHs. Also, the type of vehicles should be in favor of novel solutions, such as the electric cars, etc.

In final, it can be said that, in most cases, the concentrations of individual LMW PAHs were higher in SV soils, whereas the concentrations of individual HMW PAHs were higher in FC soils (Table 2). There was not any possibility for definition of some similar rules for the analyzed root samples (Table 3).

The concentrations of individual PAHs in roots of both investigated plants from different sites ranged as follows (Table 3): from nd for Acy (in SV and FC, sites NS, S and K, as well as in SV, sites BJ and G), Ant (in SV, and FC, sites BN, NS, O, S, BJ, K, and G, as well as in FC, site SN), Phe (in SV, sites S and K, and in FC, site BJ), Flt (in FC, sites BN, SN, NS, O, S, BJ, K and G), Pyr (in FC at the sites BN, SN, NS, O, S, BJ, K and G), BaA (in SV and FC at the sites O, K and G, as well as in SV at the sites FJ, BN, NS, S and BJ), BbF + BkF (in both plants, sites K and G, as well as in SV, sites SN and S, and in FC, sites SN, NS, O and K), and DhA (in SV, sites FJ and SN, and in FC, site NS) to 5592.09 µg/kg (in SV, site K) for Flr.

Comparing these concentrations with the matching concentrations in blackberry roots from the same selected locations (Alagić et al., 2016, 2017), it was noticeable that the contents of LMW PAHs in SV, and FC roots were generally higher than in blackberry roots, except in the case of Ant. For HMW PAHs, it was not possible to describe any rule, except in the case of CHR which was not detected in blackberry roots, too. It is worth to mention that BaP was significantly absorbed by blackberry roots, much higher than SV, and FC roots. Finally, the detected concentrations clearly showed that, in the Bor region, UIZ had no so many cases of locations with the elevated values in comparison with the related PAH contents in RZ, which was a first sign of different generators of PAHs in the investigated region.

In terms of a better understanding of relations of the detected PAH concentrations (Tables 2 and 3), and distance of the selected locations from the industrial/metallurgical complex (as a possible main source of pollution), the Pearson's correlation study was applied.

It was shown that all detected SV soil concentrations were in negative correlations with the distance, except for BaP; namely, BaP concentrations were in a (weak) positive correlation, with the calculated Pearson's coefficient of p = 0.280 (Table 2OR). SV root concentrations had mostly negative correlation coefficients with distance but in several cases, positive: Ace, p = 0.040, Flr, p = 0.762*, and DhA, p = 0.135 (the coefficient for Flr was at the statistically significant level, which is labeled with the asterisk in the superscript) (Table 2OR). In general, positive correlation means that with distance increasing, the concentrations also increase, whereas negative correlation denotes the concentrations' decreasing. Numerous negative correlation coefficients, calculated for SV, further indicated that the metallurgical plant and the city heating plant, represent the emitters of most investigated PAHs (because, in most cases, the detected concentrations decreased with distance increasing). However, given that the calculated correlation coefficients were mostly at the low-to-medium levels (without correlations at the statistically significant levels), it can be concluded that the impact of the mentioned point sources was not of key importance; this further confirmed the presence of some other sources of PAHs that may include various point, and diffusion sources in the investigated area. These sources may include: traffic based on fuel combustion (in constant developing, in all zones), the domestic heating in all zones (coal, wood, and sometimes - fuel), the controlled fires in agricultural fields (every year, during autumn) in RZ, some rare accidental fires in forests across RZ, and also, the spontaneous ignitions at the city landfill for various waste disposal (in UIZ).

In the case of FC (Table 3OR), the computed correlation coefficients, although with different values in comparison with SV, also directed to a very similar final conclusion. Additionally, in this case, the number of positive correlations (considering both – plant and soil correlations) was slightly higher than in the case of SV (Table 2OR).

The results of the Pearson's correlation study (Tables 2OR and 3OR) also helped in a better understanding of root accumulation levels in both plants. Namely, the accumulation rates of the investigated PAHs in each plant, expressed through the calculated BCFs, showed different accumulation capacities of the investigated plants regarding the individual PAH compounds. The calculated values for PAH BCFs in SV, and FC from all selected sites are given in Table 4.

Table 4
Bioconcentration factors (BCFs) of LMW and HMW PAHs of SV, and FC

Location/ Plant		LMW PAHs						
		Nap	Acy	Ace	Flr	Ant	Phe	
FJ	SV	0.30	2.77	16.88	5.71	6.10	6.12	
	FC	0.21	1.44	8.91	11.92	6.30	3.90	
BN	SV	0.13	0.08	2.45	3.48	nc	0.85	
	FC	1.90	11.02	1.81	5.12	nc	2.14	
SN	SV	0.15	0.14	0.66	16.60	2.14	1.01	
	FC	0.37	0.88	0.94	4.74	nc	1.12	
NS	SV	0.42	nc	2.09	21.94	nc	4.42	
	FC	0.60	nc	1.55	4.18	nc	1.24	
O	SV	0.13	6.26	4.05	10.07	nc	0.48	
	FC	0.35	0.20	2.34	3.20	nc	1.06	
S	SV	0.35	nc	3.54	8.52	nc	nc	
	FC	1.03	nc	0.62	8.01	nc	0.63	
BJ	SV	0.19	nc	0.41	23.14	nc	0.06	
	FC	0.47	0.09	0.40	3.23	nc	nc	
K	SV	0.27	nc	8.15	499.55	nc	nc	
	FC	0.47	0.09	0.40	3.23	nc	nc	
G	SV	0.14	nc	5.85	258.51	nc	1.08	
	FC	0.55	0.10	0.89	12.27	nc	1.55	
Location/ Plant		**HMW PAHs**						
		Flt	**Pyr**	**BaA**	**CHR**	**BaP**	**BbF + BkF**	**DhA**
FJ	SV	0.54	0.39	nc	nc	nc	0.24	nc
	FC	1.26	0.24	1.09	nc	nc	0.45	3.63
BN	SV	0.01	0.01	nc	nc	nc	1.47	0.84
	FC	nc	nc	1.79	nc	nc	nc	nc
SN	SV	1.65	0.59	0.31	nc	nc	nc	nc
	FC	nc	nc	0.13	nc	nc	nc	nc
NS	SV	0.14	0.04	nc	nc	nc	nc	nc
	FC	nc	nc	3.29	nc	nc	nc	nc
O	SV	0.04	0.09	nc	nc	nc	0.46	nc
	FC	nc	nc	nc	nc	nc	nc	nc
S	SV	0.03	0.05	nc	nc	nc	nc	3.19

SV - *Syringa vulgaris*; FC - *Ficus carica* cv. crna Petrovača

nc-not calculable

	FC	nc	nc	0.48	nc	nc	nc	1.18
BJ	SV	5.98	1.59	nc	nc	nc	nc	nc
	FC	nc	nc	0.30	nc	nc	0.85	nc
K	SV	0.95	0.52	nc	nc	nc	nc	nc
	FC	nc	nc	nc	nc	nc	nc	nc
G	SV	0.71	0.32	nc	nc	nc	nc	nc
	FC	nc	nc	nc	nc	nc	nc	nc
SV - *Syringa vulgaris*; FC - *Ficus carica* cv. crna Petrovača								
nc-not calculable								

Very high BCF values were observed for the compound from the group of LMW PAHs, namely Flr, in the roots of SV at the sites K (499.55), and G (281.51). BCF values for this compound were greater than 1 for both plants at all tested locations and ranged from 3.20-499.55. On the basis of these facts, it can be supposed that both plants can be successfully used in Flr phytoextraction by roots. As explained, in this case, when the roots may accumulate significant quantities of the pollutant, the most recommended phytoremediation method is phytostabilization because dispersal of the pollutant is restricted being stored in plant roots. The values of BCF > 1 were also noticed for Ace at several locations: FJ, BN, NS, and O for both plants, and additionally - for SV at the sites S, K, and G (Table 4).

It should be explained here that enormously high BCF values were also present in the cases where the soil concentrations were at the level: nd, whereas the corresponding root concentrations had some (more or less) high detected values. This means that the extraction/accumulation of some PAH compounds such as: 1) BbF + BkF (sites G, K, BJ and NS) in SV, and 2) BbF + BkF (sites G, S and BN), as well as DhA (sites G, K, BJ, O and SN) in FC was at the extremely high level, and practically, all the corresponding soil concentrations were extracted by root. Here, the related BCFs were not possible for calculation. In these cases, the extraction/accumulation by root may be also suggested for the application in PAH phytostabilization. It was also impossible to calculate the accumulation rates in the cases where the root concentrations were at the level: nd (a sign of the absence of PAH uptake/accumulation, especially in the case of BaP and CHR) (Table 4).

Comparing the values of the calculated BCFs for each compound of each plant species at each location, it was noticed that generally, SV was more successful in Ace, and Flr uptake and accumulation, whereas FC was more successful in Nap, and DhA uptake/accumulation. For Acy, Ant, Phe, Flt, Pyr, BaA, and BbF + BkF, there were not any rules that could be used for a safe recognition of a more successful plant. Also, these findings may represent one of the first signals that each plant species has a specific ability for individual PAH uptake/accumulation in the root.

As it was mentioned, it was also supposed that there were some factors (basically soil's) that could affect these, very dissimilar BCF values, i.e., the level of individual PAH uptake and accumulation in SV, and FC roots. In that sense, the influence of soil pH, EC, OM and soil PAH concentrations on individual PAH uptake/accumulation in the roots was investigated using the Pearson's correlation study (Tables 2OR and 3OR).

In the case of SV, the results of the Pearson's correlation analysis (Table 2OR) showed that soil parameters such as pH, EC, and OM were in some low and sometimes medium correlations with the root concentrations, having positive and negative character, too. In addition, there was a total lack of domination of some of them, i.e., some of individual PAH compounds had positive, whereas the others had negative correlation coefficients with the soil pH, EC, or OM. The only correlation with the statistically significant value was noticed in the case of correlation between soil OM and root Flr concentration, OMsoil-Flrroot: p = −0.788*, with the meaning that the locations with the high soil OM, had very low concentrations of root Flr (Table 2OR). All other correlations, suggest that there was different kind of influence of the mentioned soil parameters but not at some strong or controlling level. In the case of FC (Table 3OR), the situation was similar - numerous positive and negative correlations were present, with the only one statistically significant coefficient for the relation: ECsoil-Flrroot: p = 0.694*; this means that the locations with the high soil EC, also had very high root Flr concentrations.

When the relations between soil and root PAH concentrations in both plants were investigated using the Pearson's correlation analysis (Tables 2OR and 3OR), it was evident that all kind of correlation coefficients were present: low, medium, and high, having positive or negative character and a number of them was even at the statistically significant level (excluding the cases of pairs of the corresponding root and soil PAHs).

For example, the correlations between individual PAHs in roots and the related, i.e. corresponding soil concentrations were as follows (Tables 2OR and 3OR): 1) for Nap in SV: p = 0.215, and in FC: p = −0.157; 2) for Acy in SV: p = 0.104, and in FC: p = −0.270; 3) for Ace in SV: p = 0.152, and in FC: p = −0.267; 4) for Flr in SV: p = −0.419, and in FC: p = 0.608; 5) for Ant in SV: p = −0.168, and in FC: p = −0.183; 6) for Phe in SV: p = −0.043, and in FC: p = −0.279; 7) for Flt in SV: p = −0.143, and in FC: p = −0.213; 8) for Pyr in SV: p = −0.130, and in FC: p = −0.235; 9) for BaA in SV: p = −0.082, and in FC: p = 0.609; 10) for BbF + BkF in SV: p = −0.560, and in FC: p = −0.442, and 11) for DhA in SV: p = −0.346, and in FC: p = −0.258.

Clearly, most of these correlations were at the very low level and with negative character (except in the cases of BbF + BkF in SV, and Flr, and BaA in FC), which symbolizes the decreasing in PAH uptake with the soil concentrations increasing (although in a very low extent). At the first sight, this is a little unusual, because generally, most root/plant concentrations have positive correlations with the corresponding concentrations in the soil. However, this situation may be also a new indication that, in general, each plant species had a specific mechanism for the uptake/accumulation of individual PAHs (as well known toxic compounds), including probably, a different lipid content in the root membrane and maybe an excretion of different kinds of root exudates. In that sense, it seems that, for some PAHs, both tested plant species developed a strategy of the avoiding of the compound assimilation, which is the most obvious in the cases of CHR and BaP, where the detected soil concentrations were probably toxic for both plants. It can be said that some of the detected soil quantities of PAHs were toxic for SV, and FC, and especially CHR, and BaP that were not present in all tested plant roots. Unlike this situation, Alagić et al. (2016) showed that blackberry roots from the same locations were very tolerant to BaP, because, they were able to accumulate its significant quantities in the roots, often at the BCF level a little higher than 1. Finally, in the present work, there were no correlations with the statistically significant coefficients between the corresponding root-soil concentrations for SV and FC (Tables 2OR and 3OR).

On the other hand, some statistically significant coefficients were found in the cases of relations between several individual root PAHs and various PAHs in soils:

1) for SV: Antroot-BbF + BkFsoil, p = 0.678*; Pheroot–BaPsoil, p = −0.740* (Table 2OR), and 2) for FC: Acyroot–BaPsoil, p = −0.899**; Flrroot–Antsoil, p = 0.772*; BaAroot–Pyrsoil, p = 0.766*; BaAroot–CHRsoil, p = 0.884**; BaAroot–BbF + BkFsoil, p = 0.879**; BaAroot–DhAsoil, p = 0.787*; BbF + BkFroot-BaPsoil, p = −0.795*; DhAroot–Napsoil, p = −0.686* (Table 3OR).

This situation may be a sign that (in the case of both plants), the locations with high soil concentrations of some PAHs also had very high concentrations of some other individual root PAHs; practically, it seems that some soil PAHs enhanced the uptake of some other PAHs, whereas in other cases, present soil PAHs made the uptake of other individual PAHs more difficult (which is denoted with negative coefficients). This further may represent an indication of some strong competitive but also some synergistic effects during the uptake of several PAHs at different investigated locations. All other root-soil correlations (both: positive or negative) were mostly at the very low levels, and only sometimes at the medium levels, which means that they cannot be counted as influencing parameters.

The reflection of these specifics can be also seen in the statistically significant correlations between the concentrations of individual root PAHs, such as:

1) for SV: Fltroot–Pyrroot, p = 0.992**, Fltroot–BaAroot, p = 0.847**, Pyrroot-BaAroot, p = 0.893** (Table 2OR), and 2) for FC: Acyroot-BbF + BkFroot, p = 0.782*, Aceroot–Antroot, p = 0.868**, Aceroot-Pheroot, p = 0.757*, Aceroot-Fltroot, p = 0.868**, Aceroot-Pyrroot, p = 0.868**, Antroot-Pheroot, p = 0.745*, Antroot-Flrroot, p = 1.000**, Antroot-Pyrroot, p = 1.000**, Pheroot-Fltroot, p = 1.000**, Pheroot-Pyrroot, p = 0.745*, and Fltroot-Pyrroot, p = 1.000** (Table 3OR).

Obviously, these different individual PAHs in plant roots were in very strong positive correlations with a meaning that the investigated locations had an important number of pairs of root PAHs with positive correlated concentrations (indicating synergistic effects). Similarly to the case with the root-soil correlations, all the rest of root-root correlations (positive or negative) were at the very low levels, and very rarely, at the medium levels.

Finally, the statistically significant correlations were also found between different soil PAHs:

1) for SV: Napsoil-Flrsoil, p = 0.870**, Napsoil-BbF + BkFsoil, p = 0.668*, Acysoil–Antsoil, p = 0.809**, Acysoil–Fltsoil, p = 0.827**, Acysoil–Pyrsoil, p = 0.842**, Acysoil–BaAsoil, p = 0.859**, Acysoil–CHRsoil, p = 0.798*, Acesoil–Phesoil, p = 0.850**, Acesoil–Phesoil, p = 0.850**, Antsoil-Phesoil, p = 0.744*, Antsoil-Fltsoil, p = 0.984**, Antsoil-Pyrsoil, p = 0.983**, Antsoil-BaAsoil, p = 0.973**, Antsoil-CHRsoil, p = 0.987**, Antsoil-BaPsoil, p = −0.677 *, Phesoil–Fltsoil, p = 0.750*, Phesoil–Pyrsoil, p = 0.734*, Phesoil–BaAsoil, p = 0.697*, Phesoil–CHRsoil, p = 0.762*, Phesoil–BaAsoil, p = 0.697*, Fltsoil-Pyrsoil, p = 0.997**, Fltsoil-BaAsoil, p = 0.987**, Fltsoil-CHRsoil, p = 0.997**, Fltsoil-DhAsoil, p = 0.694*, Pyrsoil-BaAsoil, p = 0.984**, Pyrsoil-CHRsoil, p = 0.993**, Pyrsoil-BaPsoil, p = −0.697*, CHRsoil-DhAsoil, p = 0.709*, BaAsoil-CHRsoil, p = 0.983** (Table 2OR), and 2) for FC: Acysoil-Acesoil, p = 0.842**, Acysoil-Flrsoil, p = 0.728*, Acysoil-Phesoil, p = 0.811**, Acysoil-Fltsoil, p = 0.768*, Acysoil-Pyrsoil, p = 0.727**, Acysoil-BaAsoil, p = 0.831**, Acesoil-Flrsoil, p = 0.921**, Acesoil-Antsoil, p = 0.768*, Acesoil-Phesoil, p = 0.900**, Flrsoil-Antsoil, p = 0.671*, Flrsoil-Phesoil, p = 0.941**, Antsoil-Phesoil, p = 0.759*, Antsoil-Fltsoil, p = 0.867**, Antsoil-Pyrsoil, p = 0.706*, Antsoil-BaAsoil, p = 0.788**, Phesoil-Fltsoil, p = 0.737*, Phesoil-BaAsoil, p = 0.713*, Fltsoil-Pyrsoil, p = 0.957**, Fltsoil-BaAsoil, p = 0.900**, Fltsoil-CHRsoil, p = 0.849**, Fltsoil-DhAsoil, p = 0.829**, Pyrsoil-BaAsoil, p = 0.882**, Pyrsoil-DhAsoil, p = 0.953**, BaAsoil-CHRsoil, p = 0.771**, BaAsoil-DhAsoil, p = 0.868**, and CHRsoil-DhAsoil, p = 0.815** (Table 3OR).

The rest of correlations for soil-soil PAH concentrations were at the low or medium level, practically, with insignificant effects.

As it can be seen from the all presented Pearson's correlations, the maximum number of the statistically significant correlations was found in the latest example, i.e., in the cases of different pairs of soil PAHs (for each plant). Many authors provided evidence that the identified pairs of pollutants with positive correlations may represent a verification of their common origin (Fu et al., 2014). As clarified before, albeit prevailingly of anthropogenic origin, some minor quantities of PAHs in soils may also originate from natural processes (occurring in soils and in the atmosphere, too) (Idowu et al., 2019; Vane et al., 2014). It can be supposed that the sampled soils from the city of Bor and its surroundings also contained both kinds of PAHs – naturally and anthropogenically formed from pirogenic, petrogenic, diagenetic, and biogenic sources. Also, due to their recalcitrant nature, PAHs may form an important recalcitrant pool in soil, reflecting in that way a situation mainly resulting from a long-term soil exposure (Lourenço et al., 2023; Ukalska-Jaruga & Smreczak 2020). The greatest amounts of significant positive correlation coefficients (≈1) between the pairs of different soil compounds (for each plant) pointed that their origin was the most similar (probably anthropogenic), whereas negative correlation coefficients between BaP and some other soil PAHs pointed that this particular compound had the most dissimilar, i.e. natural (most probable diagenetic, or biogenic) origin, and especially in SV soil, where BaP was in negative correlations with all PAHs (and in particular with Ant, and Pyr, Table 2OR).

All described specifics in the investigated matrices, namely, soils and roots, pointed to very complicated processes during PAH extraction/accumulation and supported some similar details found also in the case of wild blackberry from the Bor region (Alagić et al., 2016, 2017). First similarity - the roots of both investigated plants are not capable to reflect an actual situation in the soil totally precisely, so that, they cannot be used in classical biomonitoring procedures as a safe tool for the detection of soil pollution; second similarity - the level of the current soil pollution can be better estimated analyzing the sampled soils, which also may provide some useful directions regarding the origin and possible sources of individual PAHs, and finally - the two investigated plant species showed different abilities for individual PAHs managing, because each plant showed a special capability, sensitivity, and tolerance regarding the most of the investigated compounds like in the case of wild blackberry; only for BaP, and CHR both plants developed a similar avoiding strategy, excluding totally these compounds from the uptake (probable due to their high toxicity), which is the most important dissimilarity with wild blackberry.

The described specifics of the two investigated plants are evidently illustrated through different classifications of the polluted locations in the related hierarchical dendrograms for plants' soil and roots (Fig. 2). They were computed based on soil as well as on root PAH concentrations of SV (Fig. 2a), and 2b), respectively), and FC (Fig. 2c), and 2d), respectively). During the performed HCA, these concentrations were treated as variables, the chosen locations were treated as cases, while the applied method was Ward's linkage with the squared Euclidean distance as a measure interval.

Big differences between SV hierarchical dendrograms based on soil (Fig. 2a)), and root concentrations (Fig. 2b)), are obvious. Although they both have the two main clusters, the arrangements of locations are totally different. The dendrogram based on soil

concentrations (Fig. 2a)), separated UI location BN (as the most polluted) into an isolated (the first) main cluster, whereas the first main cluster, based on root concentrations (Fig. 2b)), consisted of the two R locations: K-G. The second main cluster in the dendrogram based on soil concentrations (Fig. 2a)) was constituted of the two main subclusters containing numerous other subclusters in the grouping as follows: NS-S-SN/O-G-FJ-K-BJ, whereas the second main cluster in the dendrogram based on root concentrations (Fig. 2b)) was even simpler: NS-BJ-N-S-O-BN-FJ.

The groupings of locations in the analogous hierarchical dendrograms for FC (Fig. 2c), and 2d)), were a little more complicated but again, the differences between the dendrograms based on soil (Fig. 2c)), and root concentrations (Fig. 2d)) were very clear.

It can be supposed that the present dissimilarities between the investigated plant species may be ascribed to their different managing actions and sensitivity regarding the individual PAHs. Namely, it is possible that the roots of SV, and FC have different phospho-lipid components in their cell membranes, or can excrete different kinds of exudates, which may help in: 1) immobilization or 2) liberation from soil (existing there in different forms) and later – extraction and capturing of soil PAHs. These potentials may be suitably applied in PAH phytostabilization. Finally, the roles of the specific microorganisms from the plant rizospheres, as well as from the complete rooting zone cannot be absolutely excluded from the complicated processes of PAH behavior in soil, which will be deeper examined in some of future studies.

Conclusions

On the basis of results of this study, and regardless to all mentioned, complicated processes during PAH managing by plants, it can be concluded that the designed approach, i.e., the applied methods in this work, provided the formulation of very useful and precise conclusions regarding the possibilities of the utilization of both tested plants in soil biomonitoring and remediation. The interpretation of the results obtained from the performed chemical analysis, including the modifications in QuEChERS method, led to several basic conclusions:

- In soil samples, PAH concentrations ranged from nd (in several cases) to 1503.69 μg/kg for Flt in SV, site BN, while in root samples, they ranged from nd (also in several cases) to 5592.09 μg/kg for Flr in SV, site K;

- BgP and IcP were not detected in all investigated samples, and also, BaP and CHR were not detected in root samples; this may point that BaP, and CHR are toxic compounds for both plant species;

- Only the concentration of DhA in FC soil (128.16 μg/kg) at the site NS surpassed the related USEPA RSL value for both criteria considered, which indicated that only in this case, the potential risk to human health may exist;

- However, the comparison of the detected soil concentrations with the related ones from an earlier period, showed that generally, there was an increasing in individual PAH concentrations (except in the case of BaP, whose concentrations decreased over time); this signalizes that environmental concerns and protection should be also raised in the investigated ecosystem;

- There were not any rules regarding the presence of individual PAH in UIZ and RZ.

More informative data on practical, natural remediation and monitoring potentials of the investigated plant species were obtained from the results of the calculated BCF values, as well as from the applied statistical methods such as the Pearson¢s correlation study and HCA:

- Comparing BCFs for each PAH compound in each plant species at each location, it was clear that in general, the roots of SV were more successful in Ace, and Flr uptake and accumulation, whereas roots of FC were more successful in Nap, and DhA uptake/accumulation; given that at all locations, both plants had BCFs>1 for Flr, it can be concluded that they can be successfully used in Flr extraction by root and applied in its phytostabilization; BCFs>1 were also observed for Ace at most locations, for both plants; enormously high BCF values were in the cases when roots extracted practically all quantities of the corresponding soil PAH compound (DhA at the majority of locations in FC and BbF+BkF in both plants but at different number of locations); although these findings suggest that each plant species has its own, a specific ability for each individual PAH extraction/accumulation in the investigated plant organ, it is clear that both plants detained significant quantities of different PAH compounds in their roots, which further can recommend them both for limitation of PAH spreading in soil, i.e., in phytostabilization; only in the case of BaP, and CHR,

both plants developed a similar strategy, practically, the avoiding of their uptake which supports the assumption of their high toxicity for SV and FC;

- As for soil parameters, Pearsonçs correlation study pointed that only one PAH compound, namely, Flr, was under the influence of soil OM in the case of SV (a significant negative correlation), and soil EC, in the case of FC (a significant positive correlation); namely, only these two parameters can be counted as the controlling factors in PAH uptake; in addition, the correlations between the corresponding soil and root concentrations were not at the statistically significant levels, which is all in support of previous assumptions that the key role in PAH assimilation/accumulation has the plant species and itsç tolerance to these dangerous micro-pollutants;

- The correlations between the detected soil concentrations, and distance from the industrial/metallurgical complex showed that the mentioned complex with the city heating plant, represents only one of possible but not so significant source of PAHs; the other sources may include: traffic, domestic heating, controlled fires in agricultural fields, accidental fires in the surrounding forests, and also, the spontaneous ignitions at the city landfill;

- The Pearsonçs correlation analysis also showed that in many cases, individual root PAHs, as well as various root PAHs and different PAHs in soils, were in statistically significant correlations (positive and negative, too), which pointed to competitive but also some synergistic actions between the presented PAH pairs; in final, a number of statistically significant positive correlations between different soil PAHs pointed on their common, most probable anthropogenic origin;

- The dendrograms based separately on soil and root contents, for each individual plant, showed that plant roots cannot illustrate an authentic situation in the corresponding soils; it pointed on problematic utilization of SV, and FC roots in classical biomonitoring procedures; only the data, obtained from the analysis of their corresponding soils provided more informative and more safe insight into the level of the existing soil pollution, as well as into the possible PAH sources.

Based on the closing results of this study, it can be said that, in general, a modern approach in environmental protection and management cannot be organized without the careful planning and application of environmentally friendly technologies in combination with the highly accurate chemical analytical methods and a safe and sound statistical processing of the obtained results.

Declarations

“All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors”.

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Figures

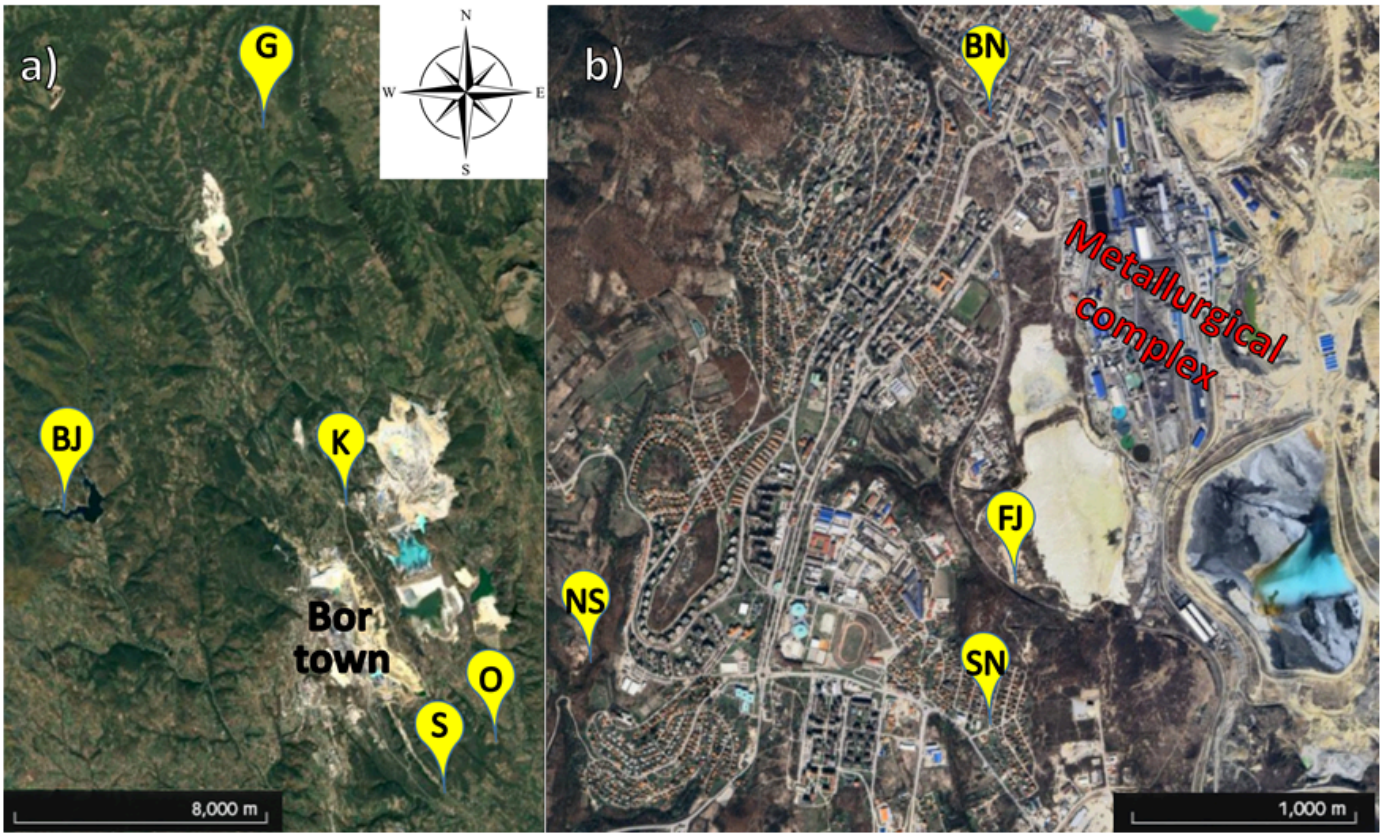

Figure 1

Map of the investigated locations in the Bor region in rural zone, a), and urban/industrial zone, b)

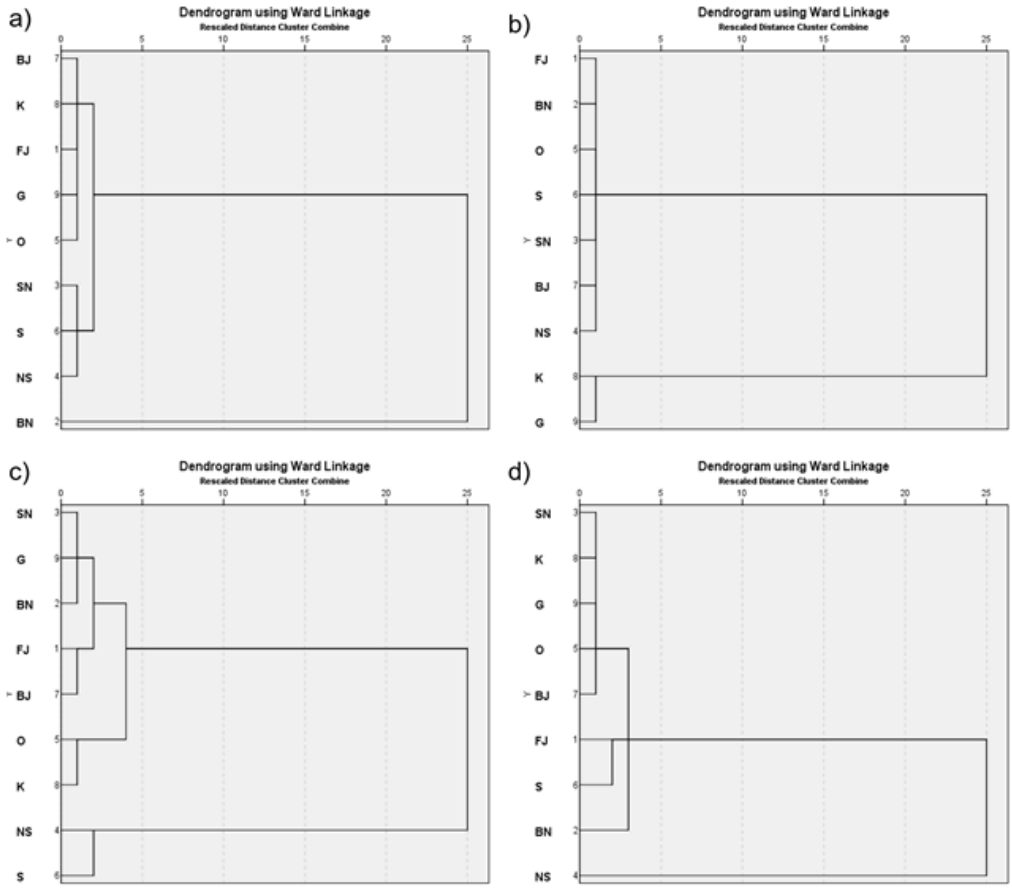

Figure 2

Classifications of the polluted locations based on soil 2a) and root 2b) PAH concentrations in SV, and soil 2c) and root 2d) PAH concentrations in FC

Supplementary Files

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