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RESEARCH PAPER

Profile, Sources, Ecological and Health Risk Assessment of PAHs in Agricultural Soil in a Pljevlja Municipality

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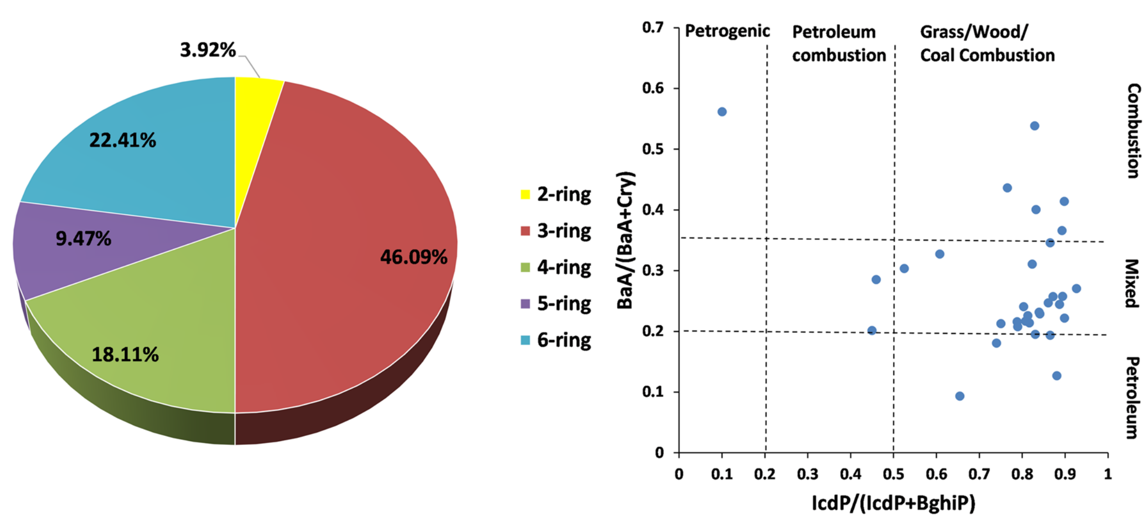
Abstract

The concentrations, profile, source of polycyclic aromatic hydrocarbons (PAHs) in agricultural soil samples ($n = 35$) in Pljevlja municipality (Montenegro), potential ecological and health risk were evaluated in this study. This area is an important industrial and agrarian region in the northern area of Montenegro and thus providing an insight regarding the content of PAHs in agricultural soil in this area is of great importance from the standpoint of the safety of agricultural products grown on this land and the health of inhabitants which may be exposed to the potentially contaminated agricultural soil. Mean concentrations of ΣPAHs and $\Sigma 7^{carc}$PAHs in soil were calculated to be 271.49 μg·kg^{-1} and 99.73 μg·kg^{-}, respectively. Based on the mean concentrations of ΣPAHs, soil was classified as uncontaminated according to Montenegrin legislation. PAHs diagnostic ratios and principal component analysis (PCA) indicated coal/wood combustion and traffic emissions as the main PAHs sources in soil. Ecological risk of the ΣPAHs based on the risk quotient (RQ) was characterised as low. Three-ring PAHs present the highest risk with a significant 77.35% ecological risk. The carcinogenic potential of PAHs based on the Benzo(a)pyrene potency equivalent (BaP_{eq}) was calculated to be 21.7 μg/kg^{-1} and carcinogenic PAHs were major contributors. Dibenz[a,h]anthracene (39.22%) and benzo[a]pyrene (25.16%) highly contributes to total BaP_{eq}. Health risk accessed through the total incremental lifetime cancer risk (ILCR) of exposure to PAHs from Pljevlja agricultural soil for children and adults was $1.16 \cdot 10^{-5}$ and $1.59 \cdot 10^{-5}$, respectively. It is characterised as a low health risk, and the main risk contributor were found to be dermal contact followed by ingestion while the inhalation route was insignificant.

Graphical abstract



Keywords Agricultural soil · PAHs · Source apportionment · Ecological risk · Health risk

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Introduction

Polycyclic (polynuclear) aromatic hydrocarbons (PAHs) or polyarenes are a large group of organic aromatic compounds composed of two or more condensed rings. This group of compounds includes about 10000 substances, with widely varying toxic features carcinogenicity, teratogenicity and mutagenicity (Zheng et al. 2018). The origin of PAHs in the environment can be classified into two groups: natural and anthropogenic source (Sun et al. 2021). The PAHs inputs into the environment such as oil seeps, volcanic activity, forest fires, and erosion of sediments are considered as natural sources of PAHs while PAHs inputs due to the different industrial activity, traffic exhaust, agricultural or urban runoffs and combustion of fossil fuels and biomass (coal and wood) are considered as anthropogenic sources (Lubecki and Kowalewska 2010; Rocha and Palma 2019). Moreover, PAHs can be classified according the temperature of their formation as biogenic or diagenetic (biological), pyrogenic and petrogenic (Yunker et al. 2002; Bakhtiari et al. 2009). The biogenic/diagenetic source of PAHs in the environment is a result of natural processes while the pyrogenic and petrogenic source of PAHs may be the result of natural or mainly anthropogenic activity (Rocha and Palma 2019).

Once, upon the PAHs reach the environment, they are widely spreading and pollute water, soil, dust and sediments. Once they reach the soil, the PAHs remain there because they are insoluble in water and thus cannot be further mobilized through the soil. As much as 90% of the PAHs that come from the atmosphere accumulate on the top soils (Gocht et al. 2007). High hydrophobicity and stable chemical structure of PAHs cause their poor solubility, so they are easily adsorbed primarily on organic components from the soil (Tang et al. 2005). After settling in the soil, PAHs can further accumulate in plants and thus reach the human body through the food chain and cause certain health problems. All the above facts are the reason why the soil system is considered as an indicator of the state of environmental pollution (Nam et al. 2003; Li et al. 2008).

Moreover, a human may be exposed to the toxic effects of PAHs through direct soil exposure via inhalation, ingestion, and direct dermal contact (Mallah et al. 2022). Short-term exposure to PAHs may cause eye or skin irritation, inflammation, confusion, but also cardiovascular, gastrointestinal, hematological, and musculoskeletal effects are of concern as well while hand, long-term exposure to PAHs may lead to more serious health problems like disorders of the immune system, cancer, hepatic and renal impairment (Sun et al. 2021). The most common disease resulting from prolonged exposure to PAHs is lung, skin, bladder and gastrointestinal cancers (Kim et al. 2013). Besides, PAHs have ability to bind endogenous receptors so they are endocrine disrupting compounds (Rajpara et al. 2017). Thus, the United States Envinronmental Protection Agency (USEPA) have been listed sixteen PAHs as priority pollutants (OFR 1982; Keith 2015). Moreover, according to International Agency for Research on Cancer, eight of PAHs are considered as possible carcinogenic agents for humans (IARC 2002).

Agricultural sector is one of the key sectors of the Montenegrin economy with a huge potential in terms of increasing value in primary production through processing. According to the Strategy for the development of agriculture and rural areas 2015–2020 in Montenegro (GOM 2014), some of the long-term goals for Montenegrin agriculture were to increase the amount of cultivated land and to EU standards for food safety. Pljevlja municipality is the largest municipality in the Norther region of Montenegro with great potential regarding the production of high-quality agricultural products. However, this potential has still not been realized. Montenegrin government undertakes different measures to encourage agricultural producers to improve and standardize the quality of their products and to thus become more competitive in both the domestic and foreign markets (GOM 2014). To achieve these goals preservation of soil quality is of great importance.

The soil quality in Pljevlja municipality is greatly influenced by different industrial activities, especially the combustion process, given that one of the largest Montenegrin producers of electricity, a coal-fired power station, is located in this town and traditional material for residential burning is firewood. Available data indicates a considerable consumption of coal and firewood in Pljevlja municipality. The annual consumption of coal in the thermal power plant is about 1.6 million tons (Statistical Office of Montenegro 2014). Wood is mainly used for heating households, facilities of public importance (kindergartens and schools), facilities of a commercial nature (bakeries, roasters and restaurants). The total area of buildings in Pljevlje in 2018 that are heated using wood amounted to 360,000 m^2 and an average of 0.14 m^3 of wood was used for heating one square meter (Statistical Office of Montenegro 2014). So, taking into account the above data, it was necessary to carry out a comprehensive analysis of potential soil pollution by different inorganic and organic pollutants in the municipality of Pljevlja. Besides, the risks of potentially polluted soil to human health had to be considered according to the recommended guidance for human health risk assessment of pollutants in soil (de Lima Brum et al. 2022). Previous investigations indicated agricultural soil pollution by heavy metals in this municipality as a result of different industrial activities (Đurovic et al. 2022). To complete data on soil pollution in this area, taking into account the mentioned consumption of coal and wood, it was necessary to conduct an analysis of soil pollution by PAHs, since coal and wood combustion is recognized as a major anthropogenic source of PAHs emission into the environment (Liu et al. 2008; Han et al. 2020). Incomplete combustion of coal and wood leads to the PAHs emission into the air (Liu et al. 2008) and wet and dry atmospheric deposition further leads to the PAHs entering the environmental terrestrial (Klimkowicz-Pawlas et al. 2017) whereby soil is considered the main PAH reservoir. (Zhang et al. 2007). Contaminated soil represents a potential risk for PAH accumulation in plants. Since the food chain is one of the main routes for PAHs to enter human bodies, monitoring the content of PAHs in agricultural land used for crop production is of great importance.

Thus, this paper aimed to analyse the presence and characteristics of PAHs in agricultural soil in Pljevlja municipality (Montenegro) and to assess the ecological and human health risk of the PAHs presence in the soil. To the best of our knowledge, this is the first study of soil pollution by PAHs in Pljevlja municipality so this research is of great importance since in many countries, PAHs are considered as a precise and authoritative indicator of the status and monitoring of the environment.

Study Area and Soil Sampling

Pljevlja municipality is the greatest municipality in the Northern region of Montenegro located at the bottom of the valley closed by the sides of the mountains from 1500 to 2238 m above sea level days (Doderović et al. 2021). The main climate characteristic of this area are: average annual temperature of 8.5 °C, average annual rainfall of 802 mm, average annual number of days with snow cover is about 65 days (Doderović et al. 2021). The most important agricultural and arable land are located on the territory of this municipality (Jovanović and Despotović 2010). Agricultural production of cereals, vegetables and fodder in this region is one of the key development resources of Montenegro (GOM 2014). In Pljevlja municipality, the production of potatoes is at the level of about ¼ of the total Montenegrin production. This region also yielding apple, pear and plum trees at the level of about 1/5 of the total return on the level of Montenegro (Jovanović and Despotović 2010). On the other hand, Pljevlja municipality is one of the major industrialized area in Montenegro. Coal-fired power station which provides around 40% of electric power in Montenegro is located in this area, mine of coal and mine of lead and zinc are also located in this area. Since this region is located in the border area of Montenegro with Serbia and Bosnia and Herzegovina, heavy traffic is another problem that, along with industrialization, can negatively affect human health. Thus, besides the agricultural activities and related agricultural runoffs, Pljevlja municipality takes over discharges from coal-fired power station and vehicular emissions which present a possible issue in soil pollution with PAHs. Moreover, individual fireplaces in households where citizens burn wood and coal also present a big environmental problem.

A topsoil samples ($n = 35$) were collected from a maximum of 20 cm of depth from agricultural fields in the vicinity of coal-fired power station (43°20′09.1"N, 19°19′34.6" E) during the period of August to November 2019 (Fig. 1) Sampling points were selected in a way that reflects the impact of anthropogenic activities, coal combustion in coal-fired power plant, wood combustion for heating residential buildings as well as the impact of traffic exhaust.

Materials and Methods

Sample Extraction

The concentrations of fifteen PAHs were determined in collected topsoil samples: naphthalene (Np), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Cry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) and indeno[1,2,3-cd]pyrene (IcdP). According to the modified standard method EPA 3550C (USEPA 2007), soil samples (2 g dry weight (dw)) were extracted by adding 15 mL hexane/acetone (4:1) and 3 min sonication (Bandelin Sonorex RK 52 H). This procedure has been repeated three times and extracts were collected and centrifuged at 4,000 rpm for 5 min. The final extracts were evaporated in a gentle stream of nitrogen at 35–40 °C, diluted to 5 ml total volume in acetonitrile, cleaned using a 0.45 µm, R 25 mm, filter (Branchia SFNY-245–100, Nonsterile Nylon) and analysed with HPLC/UHPLC (Shimadzu LC-20AB).

Determination of PAH Content

PAHs quantification was performed using a SHIMADZU LC-20AB liquid chromatograph, equipped LC-20AT binary pump, a DGU-20A online degasser, a SIL-20A autosampler, a CTO-20A column oven, an RF-10-AXL fluorescence detector and a CBM-20A lite system controller. The separation was performed on a Supelco PAHs column (250 × 4.6 mm, 5 µm) maintained at 31 °C at a flow rate of 0.85 ml/min. Total run time was 55 min. Quantification of the PAHs was obtained by applying the mobile phase gradient elution program shown in Table 1 and the wavelength switching program for fluorescence detector (FD) shown in Table 2.

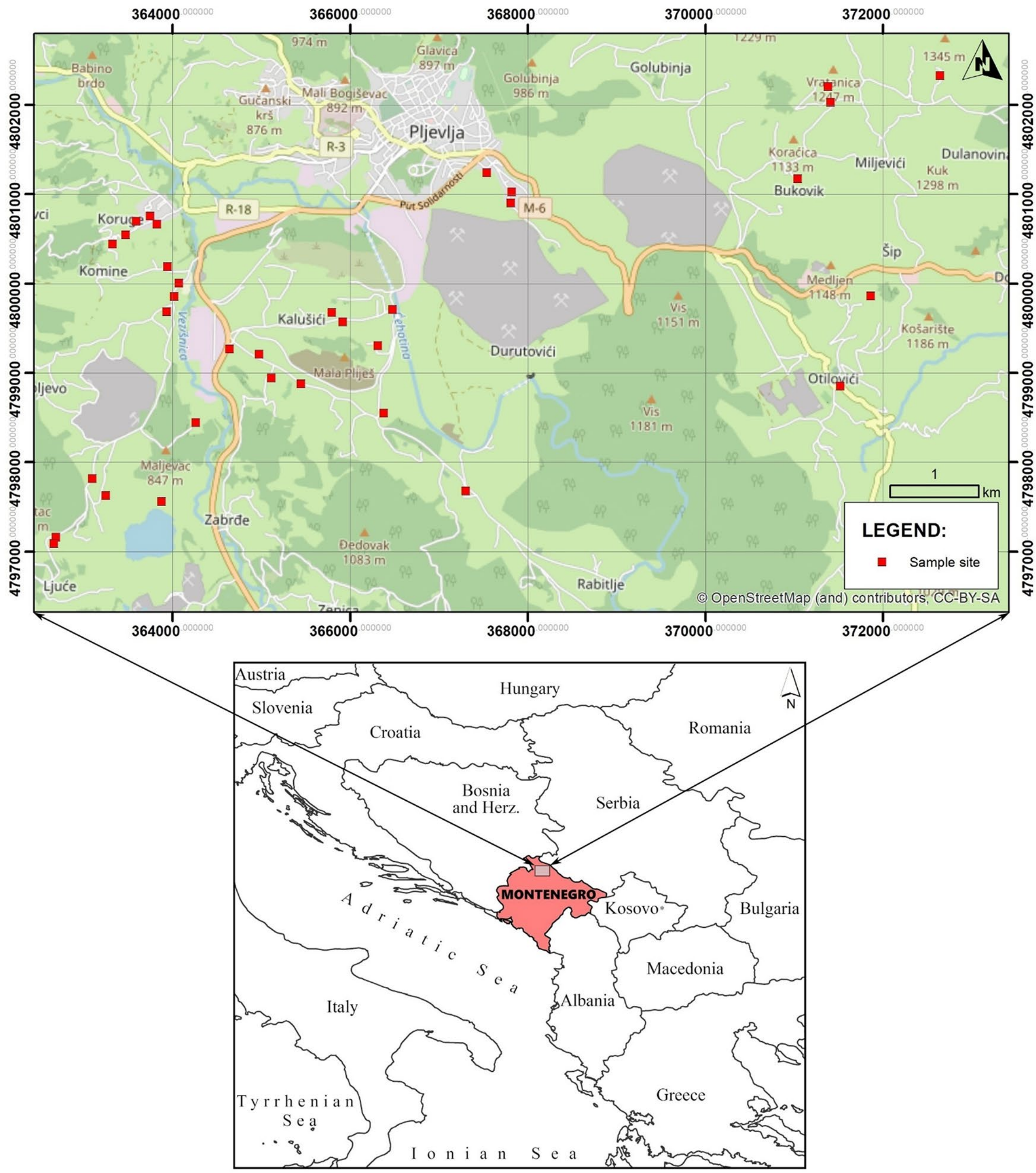

Fig.1 Sampling sites in Pljevlja municipality

Table 1 Mobile phase gradient for PAHs analysis

Time (min)	Acetonitrile (%)	Water (%)
0	40	60
36	95	5
53	95	5
54	40	60

Table 2 Wavelength switching program for FD

Detected compound	Time, (min)	λ_{ex}, nm	λ_{em}, nm
Np, Ace,	0	270	323
Fl	19	252	370
Phe	23	260	350
Ant, Flu, Pyr BaA, Cry	25	260	420
BbF, BkF, BaP	36	260	440
BghiP	43	260	420
DahA	48	260	500
IcdP	52	270	323

Quality Control

External standard calibration method (seven-point calibration; 0.5, 10, 50, 100, 200, 400 and 600 µg/L) was used for quantitation as well as correlation coefficients (R^2) for the calibration curves that were all greater than 0.9998. Precision and accuracy were checked for analytical methods. Limits of detection (LODs) were calculated based on the ratio of three times of the standard deviation of the response of six replicate measurements and the slope of the calibration graph. LODs of all 16 PAHs were in a range of 0.5–2.0 µg/kg dw. Recoveries of certified reference materials were for Ace: 96 ± 3%, Phe:99 ± 3%, Ant99 ± 5%, Flu:101 ± 3%, Pyr:98 ± 6%, BaA:98 ± 3%, Cry:97 ± 4%, BbF:102 ± 3%, BkF:92 ± 4%, BaP:93 ± 5%, BghiP:96 ± 2%, IcdP:97 ± 5%.

With each series of samples blanks which contained no detectable PAHs and a standard of 100 µg/kg were run. Recovery for 100 µg/kg in each batch of samples ranged 98–101%. The variation coefficients of PAHs concentration in duplicates were less than 13%.

Ecological Risk Assessment

Ecological risk posed by the presence of individual PAHs in agricultural soil was evaluated on the basis risk quotients (RQ_{NCs}) and (RQ_{NCs}) (Eq. 1 and 2). To assess the ecosystem risk of ΣPAHs, the ecosystem risk posed by the combination of all investigated PAHs was characterized based on the Eq. 3 and 4., (Cao et al. 2010; Dudhagara et al. 2016)

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV_{(NCs)}}} RQ_{NCs} = \frac{C_{PAHs}}{C_{QV_{(NCs)}}} \tag{1}$$

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV_{(MPCs)}}} RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV_{(MPCs)}}} \tag{2}$$

$$RQ_{\sum PAHs(NCs)} = \sum_{i=1}^{n} RQ_{NCs} RQ_{\sum PAHs(NCs)} = \sum_{i=1}^{n} RQ_{NCs} \tag{3}$$

$$RQ_{\sum PAHs(MPCs)} = \sum_{i=1}^{n} RQ_{MPCs} RQ_{\sum PAHs(MPCs)} = \sum_{i=1}^{n} RQ_{MPCs} \tag{4}$$

where C_{PAHs} is the concentration of certain PAHs in the soil and C_{QV} is the corresponding quality values of PAHs in the soil (Kalf et al. 1997; Cao et al. 2010). $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ are the quality values of the negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) in the soil. The values of $RQ_{\Sigma PAHs(NCs)}$ and $RQ_{\Sigma PAHs(MPCs)}$ were calculated by summating the $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ of individual PAHs which were not less than 1. Ecological risk classification of individual PAHs and ΣPAHs is given in Table 3.

Table 3 Ecological risk classification of individual PAHs and ΣPAHs

Individual PAH		Ecological risk
RQ_{NCs}	RQ_{MPCs}	
0	–	Risk free
≥ 1	< 1	Moderate risk
–	≥ 1	High risk
ΣPAHs		Ecological risk
$RQ_{\Sigma PAHs(NCs)}$	$RQ_{\Sigma PAHs(MPCs)}$	
0	–	Risk free
≥ 1, < 800	0	Low risk
≥ 800	0	Moderate risk$_1$
< 800	≥ 1	Moderate risk$_2$
≥ 800	≥ 1	High risk

Health Risk Assessment

Assessment of human health risk considers the probability of adverse health effects in humans who may be exposed to toxicants in polluted media (water, air, soil, food). The carcinogenic potency of PAHs detected in soil samples was assessed through Benzo(a)pyrene potency equivalent (BaP_{eq}) calculated using Eq. 5. The carcinogenic potency of total PAHs, (TEQ) is obtained as a sum of Benzo(a)pyrene potency equivalent (BaP_{eq}), (Eq. 6).

$$BaPeq_i = C_{PAH_i} \cdot TEF_{PAH_i} BaPeq_i = C_{PAH_i} \cdot TEF_{PAH_i} \tag{5}$$

$$TEQ = \sum BaPeq_i = \sum C_{PAH_i} \cdot TEF_{PAHi} TEQ = \sum BaPeq_i = \sum C_{PAH_i} \cdot TEF_{PAHi} \tag{6}$$

TEF_{PAH} is equivalency factor of PAHs (Table 5). Human health risk associated with the PAHs present in agricultural soil was assessed using incremental lifetime cancer risk (ILCR). Ingestion, inhalation and dermal contact are the three main pathways of humans exposing to PAHs through soil, and each pathway of exposure for two age groups (children and adults) was calculated according to Eq. 7, 8, 9.:

$$ILCR_{ing} = \frac{CS_{soil} \cdot \left(CSF_{ing} \cdot \sqrt[3]{(BW/70)}\right) \cdot IR_{ing} \cdot EF \cdot ED}{BW \cdot AT} \cdot 10^{-6} ILCR_{ing} = \frac{CS_{soil} \cdot \left(CSF_{ing} \cdot \sqrt[3]{(BW/70)}\right) \cdot IR_{ing} \cdot EF \cdot ED}{BW \cdot AT} \cdot 10^{-6} \tag{7}$$

$$ILCR_{inh} = \frac{CS_{soil} \cdot \left(CSF_{inh} \cdot \sqrt[3]{(BW/70)}\right) \cdot IR_{inh} \cdot EF \cdot ED}{BW \cdot AT \cdot PEF} ILCR_{inh} = \frac{CS_{soil} \cdot \left(CSF_{inh} \cdot \sqrt[3]{(BW/70)}\right) \cdot IR_{inh} \cdot EF \cdot ED}{BW \cdot AT \cdot PEF} \tag{8}$$

$$ILCR_{der} = \frac{CS_{soil} \cdot \left(CSF_{der} \cdot \sqrt[3]{(BW/70)}\right) \cdot SA \cdot SAF \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \cdot 10^{-6} ILCR_{der} = \frac{CS_{soil} \cdot \left(CSF_{der} \cdot \sqrt[3]{(BW/70)}\right) \cdot SA \cdot SAF \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \cdot 10^{-6} \tag{9}$$

$$TILCR = ILCR_{ing} + ILCR_{inh} + ILCR_{der} TILCR = ILCR_{ing} + ILCR_{inh} + ILCR_{der} \tag{10}$$

where CS_{soil} is the toxic equivalent concentration of PAHs in the soil (ng·g^{-1}); *CSF* is a carcinogenic slope factor based on the cancer-causing ability of BaP (7.3, 3.85 and 25 (mg·kg^{-1} day^{-1})$^{-1}$ for ingestion, inhalation and dermal contact, respectively) (Yu et al. 2014). Factors used in the risk assessment equations are given in Table 4. The total lifetime cancer risk (TILCR) was evaluated as the sum of ILCR values of each exposure pathways (Eq. 10). Mainly, the tolerable cancer risk is considered in the range $1 \cdot 10^{-6}$–$1 \cdot 10^{-4}$ while the cancer risk is considered harmful when TCR is higher than $1 \cdot 10^{-4}$ (USEPA, 2015). However, New York State Department of Health proposed more precise qualitative descriptions of lifetime cancer risk as very low when the estimated value is $\leq 10^{-6}$, low from $> 10^{-6}$ to $< 10^{-4}$, moderate from $\geq 10^{-4}$ to $< 10^{-3}$, high from $\geq 10^{-3}$ to $< 10^{-1}$ and very high when the value is $\geq 10^{-1}$ (NYS DOH 2012).

Source Identification

Diagnostic ratios and Principal component analysis (PCA) were used to identify the source of PAHs in agricultural soil in Pjevlja municipality. Diagnostic ratios are often used to determine pyrogenic and petrogenic sources of PAHs by comparing the content of individual PAHs (Yunker et al. 2002). These ratios involve the ratios between PAHs isomer to minimise differences in properties (volatility, solubility and adsorption) (Stogiannidis and Laane 2015). Three diagnostic ratios were used in this study (IcdP/(IcdP + BghiP), BaA/(BaA + Cry), and Bap/BghiP. The (IcdP/(IcdP + BghiP) abd BaA/(BaA + Cry) ratios provide insight into petrogenic and combustion (pyrogenic) sources but also includes a range for mixed sourcing while BaP/BghiP ratio is an indicator for traffic and non-traffic sources (Chunhui et al. 2017).

PCA method incorporates all PAHs analytes and samples and by evaluation of the factor loadings, provide a qualitative comparison of their composition and an estimation of the chemical sources by the analysis of each factor (Rocha and Palma 2019). PCA was performed with varimax rotation and principal components (factors) having eigenvalues > 1 was used to extract the possible source.

Statistical Analysis

Data processing and statistical analysis were performed using Microsoft Excel 2003 (Microsoft, Redmond, WA, USA). SPSS v.20.0 for Windows (SPSS, Inc., USA) was used to perform Pearson's correlation analysis.

Table 4 Factors used in the risk assessment equations

Factor	Value		References
	Children	Adults	
Ingestion rate of the soil, IR_{ing} (mg·day^{-1})	200	100	USEPA, (2002)
Inhalation rate of the soil IR_{inh} (m^3·day^{-1})	7.6	20	USEPA (2002)
Exposure frequency, *EF* (days·year^{-1})	350	350	USEPA (2009)
Exposure duration, *ED* (years)	6	24	USEPA (2002); Hu et al. (2014)
Body weight, *BW* (kg)	24.5	59.4	Hu et al. (2014)
Averaging time, *AT* (days)	25,550	25,550	USEPA (1989)
Particle emission factor, *PEF* (m^3·kg^{-1})	$1.36 \cdot 10^9$	$1.36 \cdot 10^9$	USEPA (2002)
Surface area, *SA* (cm^2)	2800	5700	USEPA (2002)
Skin adherence factor, *SAF* (mg·cm^{-2} day^{-1})	0.2	0.07	USEPA (2002)
Dermal absorption factor, *ABS*	0.13	0.13	USEPA (2002)

Table 5 Descriptive statistic of PAHs concentration (μg·kg^{-1}) and toxic equivalent concentrations of PAHs (μgBaP$_{eq}$·kg^{-1}) in agricultural soils in Pljevlja municipality, Montenegro

PAHs concentration, (μg/kg^{-1})					TEF	BaPeq (μg/kg^{-1})			
	Mean	Min	Max	SD		Mean	Min	Max	SD
Np	12.19	1.28	33.79	9.38	0.001	0.00	0.00	0.03	0.01
Ace	75.25	14.71	224.78	46.73	0.001	0.08	0.01	0.22	0.05
Fl	54.39	9.64	211.32	43.11	0.001	0.03	0.00	0.21	0.04
Phe	11.81	0.61	29.54	9.02	0.001	0.01	0.00	0.03	0.01
Ant	1.96	0.23	30.77	5.78	0.001	0.00	0.00	0.03	0.01
Flu	19.30	1.43	118.64	27.03	0.01	0.19	0.00	1.19	0.27
Pyr	13.68	2.01	92.85	20.47	0.001	0.01	0.00	.0.09	0.02
BaA	6.37	0.66	34.49	8.47	0.1	0.64	0.07	3.45	0.85
Cry	17.00	0.67	86.39	21.10	0.01	0.17	0.01	0.86	0.21
BbF	11.46	0.96	66.39	16.47	0.1	1.15	0.10	6.64	1.65
BkF	3.57	0.38	27.73	5.47	0.1	0.36	0.04	2.77	0.55
BaP	5.64	0.59	34.97	8.34	1	5.64	0.59	34.97	8.34
DahA	8.80	0.38	74.51	13.99	1	8.55	0.00	74.51	13.86
BghiP	18.39	1.18	168.03	38.80	0.01	0.18	0.01	1.68	0.39
IcdP	51.33	2.03	627.45	117.11	0.1	4.69	0.00	62.75	11.28
ΣPAHs	271.49	60.83	1457.44	273.49		21.70	2.57	187.37	36.12
Σ7carcPAHs	99.53	4.37	929.95	175.46		21.20	1.14	184.89	35.70

SD standard deviation, Σ7^{carc}PAHs (Cry,BaA, BkF,BbF, BaP,IcdP,DahA)

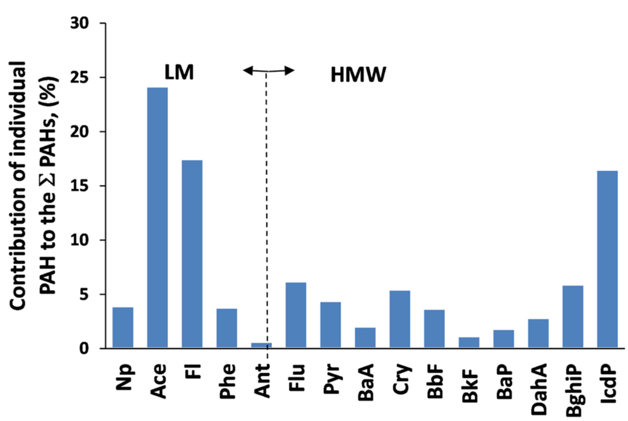

Fig.2 Contribution of individual PAHs to ΣPAHs

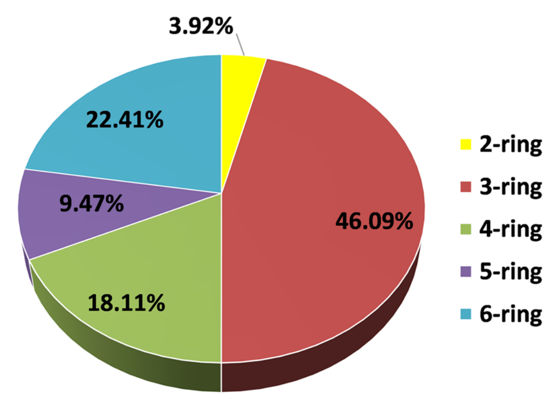

Fig.3 Contributions different ring numbers PAHs to ΣPAHs

Results and Discussion

Concentration of PAHs in Agricultural Soil

The 16 PAHs has identified by US EPA as a priority pollutant. Fifteen PAHs were detected in collected topsoil samples: naphthalene (Np), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Cry), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a] pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[ghi] perylene (BghiP) and indeno[1,2,3-cd]pyrene (IcdP). Their mean concentrations along with ΣPAHs and Σ7$_{carc}$PAHs are given in Table 5. The ΣPAHs concentration ranged from 60.83 μg·kg^{-1} to 1457.44 μg·kg^{-1} with a mean value of 271.49 μg·kg^{-1}. PAHs concentrations in soli follow descending order: Ace (75.25 μg·kg^{-1}) > Fl (54.39 μg·kg^{-1}) > IcdP (51.33 μg·kg^{-1}) > Flu (19.30 μg·kg^{-1}) > BghiP (18.39 μg·kg^{-1}) > Cry (17.00 μg·kg^{-1}) > Pyr (13.68 μg·kg^{-1}) > Np (12.19 μg·kg^{-1}) > Phe (11.81 μg·kg^{-1}) > BbF (11.46 μg·kg^{-1}) > DahA (8.80 μg·kg^{-1}) > BaA (6.37 μg·kg^{-1}) > BaP (5.64 μg·kg^{-1}) > BkF (3.57 μg·kg^{-1}) > Ant (1.96 μg·kg^{-1}).

The major PAHs detected in agricultural soil samples were Ace, Fl and IcdP with contributions to ΣPAHs of 24.18%, 17.48% and 16.50%, respectively, (Fig. 2). All other individual PAHs contribute mutually with 41.84%

to ΣPAHs following the order: Flu (6.20%) > BghiP (5.91%) > Cry (5.46%) > Pyr (4.40%) > Np (3.92%) > Phe (3.80%) > BbF (3.68%) > DahA (2.83%) > BaA (2.05%) > BaP (1.81%) > BkF (1.15%) > Ant(0.63%). The sum of carcinogenic PAHs ($\Sigma 7^{carc}$PAHs) varies between 4.27 and 929.95 $\mu g \cdot kg^{-1}$ with a main value of 99.53 $\mu g \cdot kg^{-1}$ contributing 33.48% of Σ PAHs following the order of IcdP > Cry > BbF > DahA > BaA > BaP > BkF.

Contributions of PAHs based on the number of aromatic rings are given in Fig. 3. It is evident the 3-rings PAHs (Ace, Fl, Phe and Ant) dominated the ΣPAHs with 46.09% followed by 6-ring PAHs (BghiP and IcdP) with 22.41%, 4-ring PAHs (Fly, Pyr, BaA, Cry) with 18.11%, 5-ring PAHs (BbF, BkF, BaP and DahA) with a 9.47% and 2-ring PAHs (Np) with 3.92%. Mean concentration of ΣHMW PAHs (4-, 5- and 6-ring PAHs) and ΣLMW PAHS (2- and 3-ring PAHs) in agricultural soil samples were the same: 155.55 $\mu g \cdot kg^{-1}$ and 155. 61 $\mu g \cdot kg^{-1}$, respectively.

The PAHs level in agricultural soils in the world varied significantly because variation in a soil property, pollution source, meteorological conditions etc. Results obtained in this study were compared to Montenegrin and international guidelines for a permeable concentration of toxic components in soil. Moreover, our results were compared with the reported literature data (Table 6).

The target values of the acceptable PAH concentrations ($\mu g \cdot kg^{-1}$) for agricultural use soils according to the Dutch legislation (VROM 1994) are 15 for Np, 50 for Phe and Ant, 15 for Flu, 20 for BaA, BghiP and Cry, 25 for BkF, BaP and IcdP. Only the concentration of IcdP in soil from Pljevlja municipality exceeds the Dutch target value while concentrations of all other PAHs were below the corresponding target values.

Table 6 Comparison of PAHs concentrations in agricultural soils worldwide

Location	ΣPAHs	References
Serbia	1190	Škrbić et al. (2021)
China (Shanxi)	2780.42	Liu et al. (2016)
China (Ningde)	489	Zheng et al. (2019)
China (Huanghuai)	130	Yang et al. (2012)
Lebanon	158.8	Soukarieh et al. (2018)
Polish	1253	Klimkowicz-Pawlas et al. (2017)
Kenya	3353.04	Mungai et al. (2019)
Turkey	398.06	Hanedar et al. (2019)
China (Shanghai)	665.8	Jiang et al. (2011)
China (Liaoning)	448	Cao et al. (2013)
China (Zeguo)	1118.2	Tang et al. (2010)
China (Jilin)	439.09	Chen et al. (2018)
China	7463	Zou et al. (2021)
China (Shaanxi)	792	Tian et al. (2018)
China (Bejing)	189.3	Liu et al. (2018)
China (Xuzhou)	1089.69	Ma et al. (2016)

Contamination level of agricultural soil was evaluated by comparing the ΣPAHs with Montenegrin and international standards. According to the Montenegrin standard (OGRM 1997) agricultural soil in the municipality Pljevlja was classified as unpolluted since the mean value of ΣPAHs (271.49 $\mu g \cdot kg^{-1}$) detected in soil samples was found to be below the maximum allowed concentration of 600 ($\mu g \cdot kg^{-1}$). The value of ΣPAHs obtained in this study was also lower than the target value (1000 $\mu g \cdot kg^{-1}$) and intervention values (4000 $\mu g \cdot kg^{-1}$) set by the Dutch government (VROM 2000).

However, a comparison of PAHs content in Pljevlja soils with other international limits is of concern. Based on the Canadian classification (limits of 100 ($\mu g \cdot kg^{-1}$) in total PAHs in soil samples) (CCME 2010), Pljevlja soils could be considered contaminated. Based on the classification of Maliszewska-Kordybach (Maliszewska-Kordybach et al. 2008), agricultural soil in Pljevlja municipality are considered as weakly contaminated since the mean value of ΣPAHs falls in the range of 200–600 ($\mu g \cdot kg^{-1}$).

Moreover, PAHs content in agricultural soil obtained in this study was compared with PAHs concentrations in agricultural soils worldwide (Table 6). Content of ΣPAHs in Pljevlja soil was lower than the ΣPAHs in the soils in the vicinity of coal-fired power stations reported by Zou (7463 $\mu g \cdot kg^{-1}$) (Zou et al. 2021), Tian (792 $\mu g \cdot kg^{-1}$) (Tian et al. 2018) and Ma (1089.69 $\mu g \cdot kg^{-1}$)(Ma et al. 2016) but higher in comparison to the value reported by Liu (189.3 $\mu g \cdot kg^{-1}$) (Liu et al. 2018). The mean concentration of ΣPAHs obtained in this study was higher than Lebanese agricultural soil (158.8 $\mu g \cdot kg^{-1}$) (Soukarieh et al. 2018) and Chinese (Huanghuai) soil (130 $\mu g \cdot kg^{-1}$) (Yang et al. 2012) but lower than those in Serbian agricultural soil (1190 $\mu g \cdot kg^{-1}$) (Škrbić et al. 2021), agricultural soil in Polish, Czerwionka region (1253 $\mu g \cdot kg^{-1}$) (Klimkowicz-Pawlas et al. 2017), Turkish agricultural soil (398 $\mu g \cdot kg^{-1}$) (Hanedar et al. 2019) and agricultural soil in Kenya (3353.04 $\mu g \cdot kg^{-1}$) (Mungai et al. 2019). Content of ΣPAHs in Pljevlja soil were also lower than those reported for Chinese agricultural soils in provinces: Shanxi (2780.42 $\mu g \cdot kg^{-1}$) (Liu et al. 2016), Ningde (489 $\mu g \cdot kg^{-1}$) (Zheng et al. 2019), Liaoning (448 $\mu g \cdot kg^{-1}$) (Cao et al. 2013), Shanghai (665.8 $\mu g \cdot kg^{-1}$) (Jiang et al. 2011), Zeguo (1118.2 $\mu g \cdot kg^{-1}$) (Tang et al. 2010) and Jilin (439.09 $\mu g \cdot kg^{-1}$) (Chen et al. 2018).

Source of PAHs

The PAHs source was identified using PAHs diagnostic ratios and principal component analysis (PCA). In this study, the next PAH ratios IcdP/(IcdP + BghiP), BaA/(BaA + Cry), Bap/BghiP (Pandey et al. 1999; Yunker et al. 2002) were

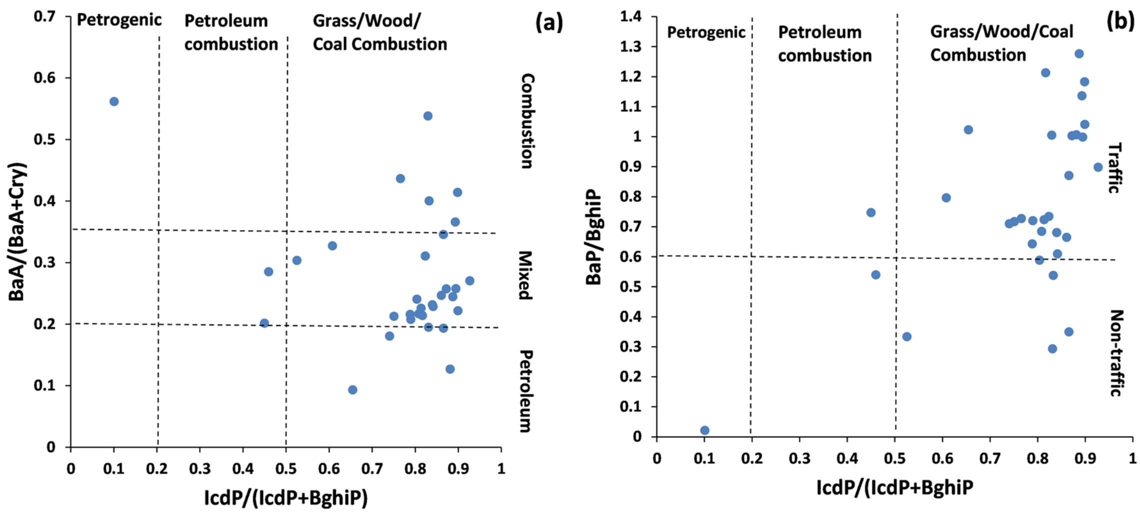

Fig.4 Diagnostic ratio charts: (a)- (IcdP/(IcdP + BghiP)/(BaA/(BaA + Cry) and (b)- (IcdP/(IcdP + BghiP)/BaA/(BghiP)

used to identify the source of PAHs in agricultural soil in Plevlja municipality.

The three values of IcdP/(IcdP + BghiP) ratio were used to identify the source of PAHs. Ratio values < 0.2 indicate a petrogenic source, values between 0.2 and 0.5 indicate petroleum combustion as a PAHs source while ratio values > 0.5 indicate that PAHs in soil originate from the grass, wood and coal combustion (Yunker et al. 2002). The values of BaA/(BaA + Cry) below 0.2 imply petrogenic source while values above 0.35 suggest a combustion source. The values between 0.2 and 0.35 indicate the mixed (petrogenic/combustion) source of PAHs (Yunker et al. 2002). In addition, values of BaP/BghiP ratio below 0.6 suggest non-traffic source while values above 0.6 imply traffic source of PAHs (Pandey et al. 1999). The results obtained in this study indicate a combined influence of traffic and grass/wood/coal combustion. The results presented in Fig. 4a showed that 68.7% of soil samples had a IcdP/(IcdP + BghiP) values above 0.5 and values of BaA/(BaA + Cry) between 0.2 and 0.35 suggesting a mixed source of PAHs in soil samples (combustion/petroleum). Moreover, results presented in Fig. 4b indicated that 80% of soil samples had an IcdP/(IcdP + BghiP) ratio values above 0.5 and BaA/(BghiP) values above 0.6 suggesting combined traffic and grass/wood/coal combustion sources of PAHs in soils.

Further, PAHs source was identified based on the PCA analysis and two principal components were extracted with the eigenvalues > 1 accounting for 73.62% of the total variances (Table 7 and Fig. 5). PC1 explained 62.57% of the total variance and was characterized by the high loading of HMW PAHs (4-,5- and 6-rings PAHs: Pyr, BkF, BbF, Flu, BaP, BaA, DahA, IcdP and Cry) and lower loading of LMW PAHs (3-ring PAHs: Ant, Phe and Ace). Pyr, Flu, BaP, BaA and Cry are typical markers for coal combustion (Larsen and Baker 2003)(Tian et al. 2018) while Pyr, Flu, Ant and Phe suggest the presence of combustion products from low-temperature pyrogenic processes mainly produced from wood combustion (Jenkins et al. 1996; Jiang et al. 2014). Bbf, BkF, DahA and IcdP indicates traffic emission source (Duval and Friedlander 1981; Bao et al. 2018; Tian et al. 2018). Thus, PC1 represents a combination of pyrogenic

Table 7 Principal component analysis for PAHs in agricultural soils from Pljevlja municipality

	Component	
	PC1	PC2
Eigenvalues	9.39	1.66
Variance (%)	62.57	11.04
Cumulative (%)	62.57	73.62
BkF	,992	
Pyr	,983	
BbF	,965	
Flu	,955	
BaP	,951	
DahA	,947	
BaA	,935	
IcdP	,928	
Cry	,812	
Ant	,802	
Phe	,623	
Ace	,457	,428
Fl		,797
BghiP		,643
Np		,642

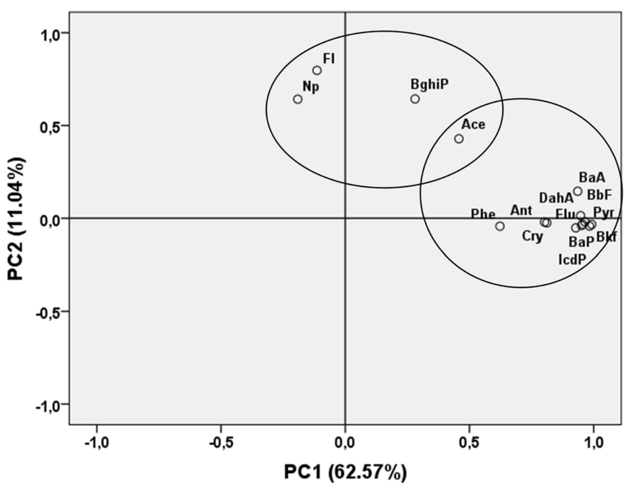

Fig.5 Principal component analysis in analysed agricultural soils

(coal and wood combustion) and traffic emission sources. PC2 explained 11.04% of the total variance and was loaded by Ace, Fl, Np and BghiP. Ace, Fl and Np which are a typical marker for wood combustion (Jiang et al. 2014) while BghiP is typical for traffic emission source (Larsen and Baker 2003). Thus PC2 represents a combination of wood combustion and traffic emission sources. Similar load on PC1 and PC2 was observed for Ace which suggests that a similar contribution could be reflected in both components.

Overall, these results indicate that PAHs detected in agricultural soils derive from pyrogenic sources (coal and wood combustion) and traffic emission sources. This is in agreement with fact that coal-fired plant operating in Pljevlja municipality and wood is still in a use for individual house heating. Moreover, emissions from traffic source are also present since traffic around coal-fired power station is also a contributor to PAHs pollution.

Ecological Risk Assessment

Mean values of $RQ_{(MPCs)}$ and $RQ_{(NCs)}$ were used to assess the potential ecosystem risk of PAHs in agricultural soil in Pljevlja municipality (Table 8). Mean values of $RQ_{(MPC)}$ of each individual PAH are less than for all individual PAHs. The values of $RQ_{(NC)}$ for Np, Ace, Fl, Phe, Ant, Pyr, BaA, BbF, BaP and DahA were higher than one indicating that these PAHs showed moderate level of ecological risk and some control and prevention measures must be taken. On the other hand, mean values of $RQ_{(NC)}$ for Flu, Cry, BghiP and IcdP were below one suggesting no ecological risk. Toxicological assessment of PAHs in the agricultural soils of Kenya also indicated a moderate level of ecological risk with respect to the presence of 3-ring (Np, Ace, Fl, Phe and Ant) and 4-ring (Pyr and BaA) PAHs in soil due to the combustion process and traffic exhaust, while 5-ring and 6-ring PAHs showed low ecological risk (Mungai et al. 2019). The value of $RQ_{\Sigma PAHs(NCs)}$) obtained in this study was 144.79 suggesting that the soil contamination by PAHs is accompanied by a low ecological risk which is quite satisfactory compared to soil pollution in other regions where the combustion process was found as the main source of PAHs in soil. The value of $RQ_{\Sigma PAHs(NCs)}$ for agricultural soil in Kenya was reported to be higher than 800, suggesting high ecological risk (Mungai et al. 2019). Similar results were reported for Nigerian agricultural soils were also high ecological risk was found with respect to the presence of PAHS in soli (Anifowose et al. 2020). On the other hand, a low ecological risk was reported for agricultural soil in Wuhan (China) (Gereslassie et al. 2018).

The proportion of RQ(NCs) of PAHs in agricultural soil is given in Fig. 6. It is evident that 3-ring PAHs mainly contributed to the ecological risk with 77.35% followed by 4-ring, 5-ring and 2-ring PAHs accounting for 9.63%, 7.00% and 6.01%, respectively.

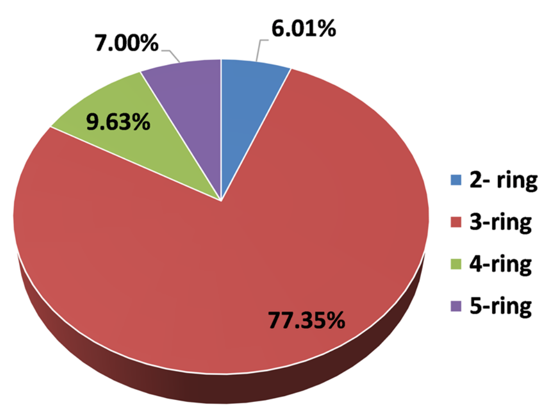

Fig.6 Contributions different ring numbers PAHs ecological risk

Table 8 Mean values of $RQ_{(MPCs)}$ and $RQ_{(NCs)}$ of individual PAHs in agricultural soil ($\mu g \cdot kg^{-1}$)

	Np	Ace	Fl	Phe	Ant	Flu	Pyr	BaA	Cry	BbF	BkF	BaP	DahA	BghiP	IcdP	RQ_{SPAHs}
MPCs	140	120	120	510	120	2600	120	250	10,700	250	2400	260	260	7500	5900	
NCs	1.4	1.2	1.2	5.1	1.2	26	1.2	2.5	107	2.5	24	2.6	2.6	75	59	
$RQ_{(MPCs)}$	0.09	0.6	0.45	0.02	0.02	0.01	0.11	0.03	0	0.05	0	0.02	0.03	0	0.01	0
$RQ_{(NCs)}$	8.71	62.71	45.33	2.32	1.64	0.74	11.4	2.55	0.16	4.59	0.15	2.17	3.38	0.25	0.87	144.79

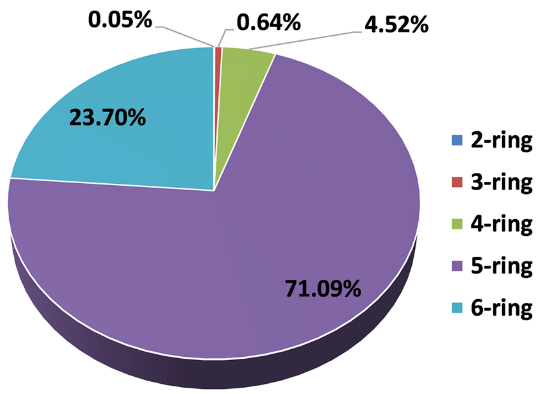

Fig. 7 Contribution for the different number of aromatic rings PAHs to total BaPeq

Health Risk Assessment

The carcinogenic potential of PAHs was evaluated using the total BaPeq. The total BaPeq values of ΣPAHs (which present carcinogenic potency of total PAHs (TEQ)) detected in soil samples investigated in this study were in the range of 2.57 μg/kg^{-1} to 187.37 μg/kg^{-1} with the main value of 21.7 μg/kg^{-1} (Table 5). The Σ7carcPAHs contribute 97.67% to total BaPeq in soil samples and falls in the range of 1.14 μg/kg^{-1} to 184.89 μg/kg^{-1}. The contribution of PAHs to the total BaPeq decreased as follows: DahA (39.22%) > BaP (25.16%) > BbF (5.11%) > BaA (2.84%) > BkF (1.59%) > Flu (0.86%) > BghiP (0.82%) > Cry (0.76%) > sum of Np, Ace, Fl, Phe, Ant, Pyr (0.75%). Contribution for the different number of aromatic rings PAHs to total BaPeq decreased in order: 5-ring (71.09%) > 6-ring (23.70%) > 4-ring (4.52%) > 3-ring (0.64%) > 2-ring (0.05%), (Fig. 7).

The results obtained were compared with the results of other studies of soil pollution by PAHs due to the combustion process. The total BaPeq values of ΣPAHs for Serbian (Vojvodina) (Škrbić et al. 2021) and Indian (Delhi) (Agarwal et al. 2009) agricultural soils were reported to be 156 μg/kg^{-1} and 154.12 μg/kg^{-1}, respectively, which is 7 times higher than that obtained in our study. Reported total BaPeq values for Shanxi province in China (44.6 μg/kg-$^{1)}$ (Duan et al. 2015) is two times higher in comparison to values obtained for Pljevlja municipality. The BaPeq value of ΣPAHs of 211.9 μg/kg^{-1} in the soil in Shandong (China) (Cheng et al. 2019) indicated almost 10 times higher soil pollution in comparison to soil from Pljevlja municipality. Four times higher total BaPeq value (97.16 μg/kg^{-1}) is reported for agricultural soil in Shanghai, China (Jiang et al. 2011) in comparison to that in our study area. All mentioned studies indicated that the dominant contribution to total BaPeq values of ΣPAHs came from carcinogenic as was found in our study.

The value of total BaPeq for agricultural soil in Pljevlja municipality is much lower than 600 μg/kg^{-1} which is set as a safe value for total BaPeq according to the Canadian soil quality guideline for the protection of environmental and human health (Soukarieh et al. 2018; Škrbić et al. 2021). This indicates that the concentration of PAHs determined in agricultural soil in Pljevlja municipality can not cause significant potential carcinogenic risk.

The results of the health risk assessment are given in Table 9. Cancer risk via inhalation was negligible since values of $ICLR_{inh}$ were very low, 10^{-11} and 10^{-10} for children and adults, respectively. The values of $ICLR_{ing}$ for both populations were the same order of magnitude (10^{-6}) while $ICLR_{der}$ value for adults (10^{-5}) was higher than for children (10^{-6}). Dermal contact was the most dominant exposure pathway for both populations (55.49% for children and 63.98% for adults), followed by ingestion (44.51% for children and 36.02% for adults) and insignificant inhalation routes. Total cancer risk for children ($1.16\cdot10^{-5}$) and adults ($1.59\cdot10^{-5}$) was estimated to be low. Dermal contact and ingestion as dominant exposure pathways of humans exposing to PAHs through soil, were also reported in other agricultural soil (Tong et al. 2018; Zheng et al. 2019).

Limitation and Recommendation

Although the study provided insight into the state of agricultural soil quality with respect to PAHs content, some limitations and recommendation for future work are necessary to be commented. Since one of a dominant characteristics of PAHs is seasonal variation, the main limitation of this study is the fact that soil sampling was conducted during the autumn season. So, future work should be the analysis of the presence and characteristics of PAHs in agricultural soil with respect to seasonal variation. Moreover, this study is limited to the vicinity of coal-fired power station but the influence of other possible source of pollution like mines of

Table 9 Cancer risk due to children and adults exposure PAHs via agricultural soils in Pljevlja municipality

	Children				Adults			
	$ICLR_{ing}$	$ICLR_{inh}$	$ICLR_{der}$	Cancer risk	$ICLR_{ing}$	$ICLR_{inh}$	$ICLR_{der}$	Cancer risk
Mean	5.16E-06	7.61E-11	6.44E-06	1.16E-05	5.72E-06	4.44E-10	1.02E-05	1.59E-05
Min	6.78E-09	9.98E-14	8.45E-09	1.52E-08	7.51E-09	5.82E-13	1.33E-08	2.08E-08
Max	3.04E-05	4.48E-10	3.79E-05	6.82E-05	3.37E-05	2.61E-09	5.98E-05	9.35E-05

coal should also be analysed. Finally, the content of PAHs in plant crops grown on agricultural soil in Pljevlja municipality will be the focus of future research.

Conclusions

Pljevlja municipality is an important area in northern Montenegro with a great potential for agricultural and industrial development. Since the development of agriculture and industry in this area on the one hand and the protection of the environment and human health, on the other hand, are extremely important for the accession of Montenegro to the European Union, it was necessary to evaluate the state in one of environment segment (soil pollution) and risk for human health. This study was carried out to provide the first insight into content, profile and sources of PAHs in agricultural soil in Pljevlja municipality. Potential ecological and health risk for children and adults in this municipality was evaluated as well. The results obtained from the analysis of PAHs content in 35 top soil samples have shown the mean concentrations of ΣPAHs and $\Sigma7^{carc}$PAHs concentration of 271.49 $\mu g \cdot kg^{-1}$ and 99.53 $\mu g \cdot kg^{-1}$, respectively. The most dominant PAHs present in soil were Ace, Fl and IcdP and 3-rings PAHs dominated the ΣPAHs followed by 6-,4-, 5- and 2-ring PAHs. As for contamination level, agricultural soils in Pljevlja municipality are classified as uncontaminated by PAHs according to the Montenegrin environmental legislation but contamination is of concern with respect to international legislations. Evaluation of PAHs source indicated that coal/wood combustion and traffic emissions could be primary sources in agricultural soils from the Pljevlja municipality. Ecological risk assessment indicated low level of risk, and LMW PAHs present much more risk than HMW PAHs. Carcinogenic potency assessed through BApeq was 21.7 $\mu g/kg^{-1}$, and $\Sigma7^{carc}$PAHs highly contributed (97.67%) to BaP-equivalent concentration. Health risk for both age groups was within acceptable limits, it is characterized as low and dermal contact was found to be the highest contributor to the cancer risk.

This study is important from the standpoint of understanding the characteristic and source of PAHs in agricultural soil in Pljevlja municipality and the necessity for continual monitoring of their content in agricultural soil to prevent environmental and health problems. Based on the risk assessment analysis, this area is not a priority for remediation but the government regulators should take efforts to manage these anthropogenic sources to prevent PAHs emission into environment and prevent potential soil pollution effect on human health.

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Author contributions MB: Investigation, Conceptualization, Methodology, Formal analysis, Validation, Data curation, Writing- review. DĐ: Project administration, Supervision, Writing-review & editing, Resources. IN: Methodology, Writing- original draft & editing. LjI: Methodology, Formal analysis, Validation, Data curation. BB: Conceptualization, Methodology, Writing- review.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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