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SOURCE IDENTIFICATION AND ECOLOGICAL RISK OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS AND GROUNDWATER

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are formed from anthropogenic activities, i.e. industrial emissions, incomplete combustion of petroleum, coal and other fossil fuels and other industrial and domestic activities. Research areas of this study are four representative locations in the industrial complex, in the city of Banja Luka, Republic of Srpska, Bosnia and Herzegovina. The main objective of the paper is to determine the ecological risk and to assess probable sources of PAHs contamination in soil and groundwater. The results of this study reflect the effects of coal combustion (pyrogenic origin), petrogenic and biomass origin and may provide basic data for the remediation of PAHs in the location. The ecological risk in soil (at depths of 30, 100, 200, 300 and 400 cm) and groundwater is determined. The mean values of ecological risk in soil and groundwater decreased with soil depth. Values of $RQ_{(NCs)}$ for groundwater were found at high ecological risk, for Ant, Chr, DahA, Acy, Pyr, BaA, Phe, Flo, Nap, Ace and Fluo, with values 28.57, 20.59, 300.00, 242.86, 185.71, 1700.0, 76.67, 53.33, 15.83, 100.00 and 57.14, respectively. ∑16PAH indicated high ecological risk for most PAHs, which decreased with soil depth. The value of $RQ_{(NCs)}$ for ΣPAHs in groundwater indicates high ecological risk (ΣPAHs ≥ 800 and $RQ_{(MPCs)} \geq 1$). This is the first study on the ecological risk of PAHs in soil and groundwater in industrial soils in Banja Luka and provides baseline information for further studies and additional investigations of this industrial complex.

Keywords: soil, groundwaters, polycyclic aromatic hydrocarbons (PAHs), ecological risk, evaluation of sources

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) emitted from sources and formed by some specific activities. They result from anthropogenic activities and natural activities. [1-7]. Although there are more than 100 different types of PAHs [8] but most analyses and data reports typically focus on 16 individual PAHs on average.

PAHs in groundwater are non-degradable and remain present for long periods of time [9]. In soil and aquifer systems these components are sorbed into the organic and clay fraction restricting their bioavailability [10, 11]. They are present in the atmosphere, both in the gaseous state and associated with particles, and can potentially travel long distances reaching remote areas [12]. The main concern with PAHs is the danger they pose to human health, as some have toxic, mutagenic and/or carcinogenic effects [13]. The main route for PAHs intake in humans is inhalation, but dermal contact and ingestion are also to be taken into account [14]. Many health studies suggest link between lung cancer and exposure to PAHs [15], as well as infertility and damage in infants and adults [14]. PAHs also have a negative impact on the aquatic ecosystem and birds, causing tumor formation, reproductive and immunity problems. Due to persistence and the bioaccumulative effect, the concentrations of PAHs in fish and shellfish have values far higher than the environment in which they are found. On the other hand, plants absorb PAHs from the soil through the root system and from there they are distributed to other parts of the plant (trunk, leaves and fruits) [8].

This study examined the concentrations of 16 PAHs in soil and groundwater in a former Cellulose Factory (locality Incel) in the city of Banja Luka, Republic of Srpska, Bosnia and Herzegovina. Industrial complex Incel, as a large conglomerate, was built in 1954 and manufactured cellulose, viscose and paper products with separate electrolysis and power plant. The industrial complex was turned into a business zone and was opened to leasing, with about 60 small companies using the space, mostly as warehouses, employing around 1,500 workers. Near this industrial complex there is a city heating plant on biomass and diesel fuel oil. The most important and valuable aspect of this study is that soil samples have been taken from different layers, up to 4 m in depth. The main objectives of the study are to evaluate (a) the concentration of PAHs (b) probable sources of PAHs contamination in both soils and groundwater, and (c) the ecological risks of PAHs in the investigated industrial zone.

Experimental section

Study region

The study region is in the industrial complex Incel in major city Banja Luka (185,000 inhabitants). In the former industrial complex originally manufactured cellulose, viscose and paper products. Samples were taken at factory site. Figure 1 show location of sampling. Details are given in a companion paper [16]. The complex was structured as a large conglomerate, typical for socialist countries of the time, and was fully operational up until the Balkan Wars in 1992. Most industry collapsed during the war, and the recent economic recession in BiH resulted in lower production or complete shutdown. In turbulent times during and after the war, late 20^{th} century, majority of the equipment and machinery was destroyed, sold or vandalized. Incel complex was heavily damaged which resulted in the emission of toxic substances in the environment. Location is categorized as a hotspot

(waste from cellulose and viscose factory) [17, 18]. This location was highly contaminated with heavy metals (Cd, Pb, Ni, Cu, Hg) and organic pollutants (Polychlorinated Biphenyls (PCB), Total Petroleum Hydrocarbons (TPH) and PAH) [17, 18]. A study of atmosphere PAHs in urban and rural areas was done in the city of Banja Luka in 2008 [19, 20]. The results of this study show that the value of PAHs in the urban area was much higher than in the rural area.

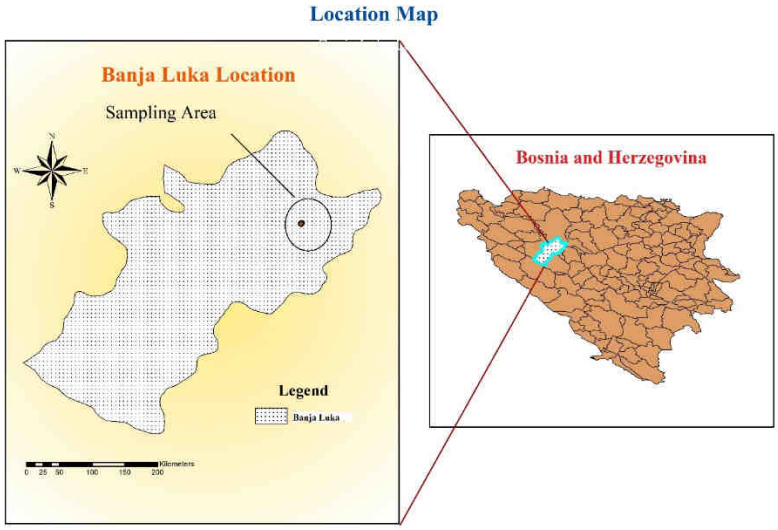


Fig. 1. Location of sampling

Sampling and analysis

A total of 16 soil and 4 groundwater samples were collected from four locations (S1-S4) in the industrial complex, from different layers of soil (at a depth of 30, 100, 200, 300, and 400 cm) and groundwater from each location.

Soil and groundwater samples were collected during August 2019. Chemical analyses were conducted for 16 types of PAHs by using gas chromatography. The detector used for PAH analysis is a mass detector coupled to gas chromatograph (GC-MS).

The analyses conducted in the soil were: acidity (pH) measured in deionized water, and organic matter (humus) content applying Tyurin's method. Analysed components of PAHs were: low molecular weight PAHs (LMWPAHs) with 2 and 3 aromatic rings such as naphthalene (Nap, 2-ring), acenaphthylene (Acy, 3-ring), acenaphthene (Ace, 3-ring), fluorine (Flo, 3-ring), phenanthrene (Phe, 3-ring) and anthracene (Ant, 3-ring) and high molecular weight PAHs (HMWPAHs) with 4-6 aromatic rings such as fluoranthene (Fluo, 4-ring) pyrene (Pyr, 4-ring) benzo[a]anthracene (BaA, 4-ring), chrysene (Chr, 4-ring), benzo[b]fluoranthene (BbF, 5-ring), benzo[k]fluoranthene (BkF, 5-ring), benzo[a]pyrene (BaP, 5-ring), indeno[1,2,3-cd]pyrene (IcdP, 6-ring), dibenzo[a,h]anthracene (DahA, 5-ring) and benzo[g,h,i]perylene (BghiP, 6-ring).

In the laboratory, soil samples were dried at room temperature, and impurities such as roots and stones were removed. The PAHs from soil samples were extracted using ultrasound-assisted extraction according to the US Environmental Protection Agency

(USEPA) 3550C method [54]. Soil samples (1 g) were mixed with Na_2SO_4 anhydride (2 g) and added solvent (acetone: dichloromethane, 1:1, v:v); the sample vessel was then transferred to an ultrasonic bath for 15 minutes extraction. Subsequently, the samples were decanted after centrifugation at 7000 r/min for 10 min. The extraction process was repeated three times. An alumina/silica gel column was used to clean up the extract. The PAHs were eluted with dichloromethane and n-hexane (2:3, v:v). The eluate was concentrated to 0.2 mL under a gentle nitrogen stream.

The process of extraction and obtained PAHs concentrations were further processed based on the principles described in standard methods with disintegration techniques and analysed in accordance with national legislation [21, 22] and accredited standard method EPA 8270D/3550C:2007 for soil and EPA 8270D/EPA 3510 for water [23]. Accredited quantification limit for PAHs in soil is 0.02 mg/kg and for water 0.03 µg/L for individuals PAHs. More details of the sampling and analytical methods are given in the companion paper [16].

Identification of emission sources

The research of emission sources was applied factor analysis (FA), whose results determine the effective variable factors. The aim FA is to create fewer factors by combining two or more variables. These fields may easily hypothesize too many variables, so factor analysis helps to find essentials of a theory. Principal component analysis (PCA) was used. The primary output for PCA shows the correlation between each variable of a principal component and the variable factors (RC1, RC2 and RC3) [17].

Ecological risk of PAHs in soils and groundwater

Risk quotient (RQ ($RQ_{(NCs)}$ and $RQ_{(MPCs)}$)) was used to assess the ecological risk of PAHs. The maximum permissible concentrations (MPCs) (concentrations of PAHs above which the risk of adverse effects is considered unacceptable) and negligible concentrations (NCs) (MPC/100) of PAHs in soils and groundwater were used, according to the research of Kalf et al. [24], Wang et al. [3] and Lan et al. [25].

$RQ_{(NCs)}$ and $RQ_{(MPCs)}$ were defined as follows [3, 24]:

$$RQ_{(NCs)} = C_{PAHs} / C_{QV(NCs)} \quad (1)$$

$$RQ_{(MPCs)} = C_{PAHs} / C_{QV(MPCs)} \quad (2)$$

where C_{PAHs} was the PAHs measured concentration in the soil and groundwater and values C_{QV} ($C_{(NCs)}$ and $C_{(MPCs)}$)) were the corresponding quality values of PAHs in the soil and groundwater. Table 1 shows the ecological risk classification of individual PAHs and ΣPAHs, according to the research of Lan et al. [25].

Table 1

Risk classification of individual PAHs and ∑16PAHs [25, 3]

Individual PAHs			**ΣPAHs**		
$RQ_{(NCs)}$	**$RQ_{(MPCs)}$**	**Risk rank**	**Risk rank**	**$RQ_{(NCs)}$**	**$RQ_{(MPCs)}$**
0		Risk-free	Risk-free	0	
			Low risk	≥ 1, < 800	0
≥1	<1	Moderate risk	Moderate risk 1	≥ 800	0
			Moderate risk 2	< 800	≥ 1
	≥1	High-risk	High-risk	≥ 800	≥ 1

Results and discussion

Source identification of PAHs in soils (PAHs molecular ratios)

The PAHs sources can be summarized into groups by origin: pyrogenic, petrogenic, and phytogenic [4]. Diagnostic PAHs molecular ratio methods were used for the identification of PAHs sources of the contamination: Fluo/(Fluo+Pyr), low molecular weight (LMW) (2-3 rings)/high molecular weight (HMW) (≥ 4 rings), IcdP/(IcdP+BghiP), BaA/(BaA+Chr), ΣCOMB/TPAH (Σ combustion/total PAH) and PAH4/PAH(5+6) [3-5, 26-28], by comparing the concentrations of individual PAHs (Fluo, Pyr, BaA, Chr, IcdP, BghiP, Ant, Phe, BaP, etc.) and qualitatively distinguishing pyrolytic and petrogenic sources [28]. Molecular ratios can help to elucidate the origin of PAH in the environment [29].

In the study, four specific diagnostic molecular ratios of PAHs were used for the identification of sources of PAHs pollution: LMW/HMW, Fluo/(Fluo+Pyr), IcdP/(IcdP+BghiP) and BaA/(BaA+Chr) (Fig. 2).

The LMW/HMW ratios between low and high molecular weight PAHs were interpreted by source apportionment [30]. Soils and groundwater have a higher mean value compared to those from urban areas, with a mean value of 0.70 (from 0 to 2.28). Values of ≥ 1 indicate petrogenic source and of ≤ 1 pyrogenic combustion [29, 31]. These values indicate that the most likely sources of PAHs in researched location may be related to emissions from pyrogenic (combustion) origin and partially petrogenic source.

Fluo/(Fluo + Pyr) ratios with mean 0.01 ranged from 0 to 0.08. Yunker et al. [26] reported that the most likely sources of PAHs with value of < 0.20 are from petroleum/petrogenic source. Values Fluo/(Fluo + Pyr) of 0.4-0.5 indicate fossil fuel combustion and of > 0.5 biomass and coal combustion [26, 29, 32].

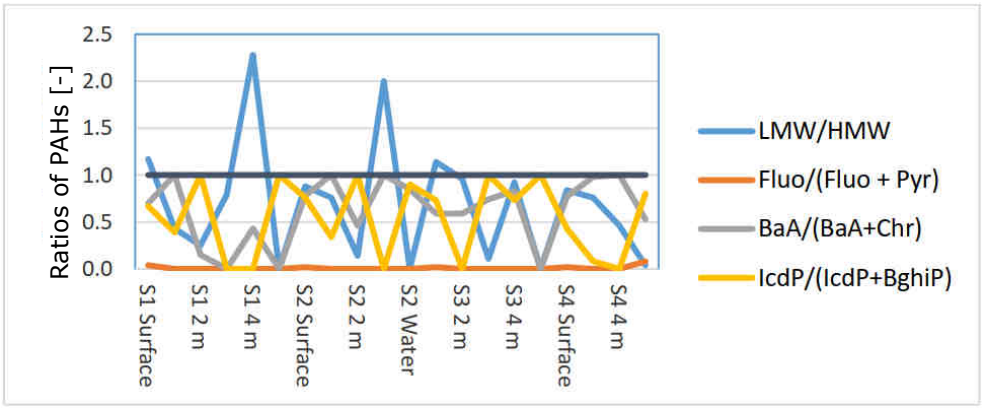


Fig. 2. Specific diagnostic molecular ratios of PAHs

BaA/(BaA+Chr) values range from 0 to 1 (mean value of 0.62) and these values indicate ratio traffic emission and partially petrogenic source in three localities. Yunker et al. [26] explained that value (> 0.35) indicate traffic emission, Tobiszewski and Namiesnik [33] values 0.2-0.35 indicate coal combustion and Davis et al. [34] BaA/(BaA+Chr) values

< 0.20 indicate petrogenic source. Values below 0.4 are characteristic of a petroleum source suggesting a combustion influence [30] (Fig. 3).

Ratios of IcdP/(IcdP+BghiP) had mean value 0.54 (from 0 to 1) indicating that it is a source of pollution of PAHs coal and biomass combustion and partially fuel combustion in two localities (pyrogenic source). Tobiszewski and Namiesnik [33] reported that the coal and biomass combustion is > 0.50 and fuel combustion ranges from 0.20 to 0.50.

The contribution of the LMW was of 69.41 %, while HMW was 30.59 %, which suggested petrogenic sources [35].

PAHs in soils may enter bodies of water, which poses a potential environmental risk [3]. The ecological risk of PAHs was assessed by a risk quotient method based on toxic equivalency factors [24]. A risk quotient (RQ) was used to assess the ecological risk of PAHs [22] and shown in Table 2 according to risk quotient ($RQ_{(NCs)}$ and $RQ_{(MPCs)}$ in research Kalf et al. [24], Wang et al. [3] and Lan et al. [25].

Table 2

Descriptive statistics of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ of PAHs [mg/kg] in soils and groundwater

	NCS	MCS	NCS	MCS	30 cm		100 cm		200 cm		300 cm		400 cm		Groundwater	
PAHs	**Soil**		**Water**		**RQ**											
					NCs	**PCs**	**NCs**	**PCs**	**NCs**	**PCs**	**NCs**	**PCs**	**NCs**	**PCs**	**NCs**	**PCs**
BbF	0.0025	0.25	0.0001	0.01	56.00	0.56	16.00	0.16	8.00	0.08	8.00	0.08	4.00	0.04	0.00	0.00
BkF	0.024	2.4	0.0004	0.04	10.00	0.10	0.42	0.00	0.42	0.00	0.42	0.00	0.42	0.00	0.00	0.00
BaP	0.0026	0.26	0.0005	0.05	34.62	0.00	23.08	0.23	11.54	0.12	7.69	0.08	11.54	0.12	0.00	0.00
BghiP	0.075	7.5	0.0003	0.03	2.00	0.02	0.13	0.00	0.13	0.00	0.00	0.00	0.40	0.00	0.00	0.67
IcdP	0.059	5.9	0.0004	0.04	0.34	0.00	0.17	0.00	0.17	0.00	0.17	0.00	0.68	0.01	0.00	0.00
Ant	0.0012	0.12	0.0007	0.07	166.67	1.67	16.67	0.17	16.67	0.17	8.33	0.08	25.00	0.25	28.57	0.29
Chr	0.107	10.7	0.0034	0.34	0.56	0.01	0.28	0.00	0.19	0.00	0.19	0.00	0.28	0.00	20.59	0.21
DahA	0.0026	0.26	0.0005	0.05	146.15	1.46	0.00	0.00	0.00	0.00	0.00	0.00	3.85	0.04	300.00	3.00
Acy	0.0012	0.12	0.0007	0.07	91.67	0.92	8.33	0.08	33.33	0.33	0.00	0.00	0.00	0.00	242.86	2.43
Pyr	0.0012	0.12	0.0007	0.07	25.00	0.25	0.00	0.00	16.67	0.17	0.00	0.00	8.33	0.08	185.71	1.86
BaA	0.0025	0.25	0.0001	0.01	24.00	0.24	12.00	0.12	8.00	0.08	12.00	0.12	0.00	0.00	1700.0	17.00
Phe	0.0051	0.51	0.003	0.3	7.84	0.08	9.80	0.10	9.80	0.10	5.88	0.06	5.88	0.06	76.67	0.77
Flo	0.026	2.6	0.003	0.3	4.23	0.04	1.54	0.02	0.77	0.01	0.77	0.01	0.38	0.00	53.33	0.53
Nap	0.0014	0.14	0.012	1.2	21.43	0.21	21.43	0.21	7.14	0.07	0.00	0.00	7.14	0.07	15.83	0.16
Ace	0.0012	0.12	0.0007	0.07	16.67	0.17	8.33	0.08	8.33	0.08	0.00	0.00	0.00	0.00	100.00	1.00
Fluo	0.0012	0.12	0.0007	0.07	16.67	0.17	41.67	0.42	8.33	0.08	16.67	0.17	0.00	0.00	57.14	0.57
∑ 16 PAHs					623.84	5.89	159.85	1.60	129.49	1.29	60.12	0.60	67.90	0.68	2780.7	28.47

The result of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ in soil and groundwater are shown in Table 2. The mean values of $RQ_{(NCs)}$ of BbF in the surface layer of soil are higher than 1.0 for ∑16PAHs, except for IcdP and Chr and results indicated high ecological risk in location. Results for IcdP (0.34) and Chr (0.56) indicate moderate ecological risks. High ecological risks are at a depth of 100 cm for BbF (16.00), BaP (23.08), Ant (16.67), Acy (8.33), BaA (12.00), Phe (9.80), Flo (1.54), Nap (21.43), Ace (8.33) and Fluo (41.67), at a depth of 200 cm BbF (8.00), BaP (11.54), Ant (16.67), Acy (33.33), Pyr (16.67), BaA (8.00), Phe (9.80), Nap (7.14), Ace (8.33) and Fluo (8.33). At a depth of 300 cm, high ecological risk was recorded for BbF, BaP, Ant, BaA, Phe and Fluo, with values 8.00, 7.69, 8.33, 12.00, 5.88 and 16.67, respectively. At a depth of 400 cm high ecological risk are for BbF, BaP, Ant, DahA, Pyr, Phe, and Nap, with values 4.00, 11.54, 25.00, 8.33, 5.88 and 7.14, respectively.

The mean values of ecological risk in soil and groundwater decreased with soil depth. Values of groundwater are a high ecological risk, for Ant, Chr, DahA, Acy, Pyr, BaA, Phe, Flo, Nap, Ace and Fluo, with values 28.57, 20.59, 300.00, 242.86, 185.71, 1700.0, 76.67, 53.33, 15.83, 100.00 and 57.14, respectively.

Low molecular PAHs (2-, 3-ring) are potentially mutagenic and carcinogenic [3]. Only BaP (5-ring) is proven carcinogen within PAH. In Table 2 that groundwater risk is associated with low and molecular PAHs and indicates high ecological risk. 2-, 3-ring PAHs mainly contributed to the ecological risk in groundwater, except for DahA (5-ring PAHs), while 4, 5, 6-ring PAHs indicated the high ecological risks in soils. The $RQ_{(NCs)}$ of HMW PAHs in soils was higher than that in groundwater.

The value of $RQ_{(NCs)}$ for ΣPAHs was less than 800, while values of $RQ_{(MPCs)}$ were higher than 1, indicating that the ΣPAHs in the surface layer of soils were assigned a moderate ecological risk 2 level. Moderate risk 2 level is also at depths of 100 and 200 cm. At depths of 300 and 400 cm values indicate low ecological risk. The value of $RQ_{(NCs)}$ for ΣPAHs in groundwater indicates high ecological risk (ΣPAHs $\geq$ 800 and $RQ_{(MPCs)} \geq 1$).

Conclusion

In the study, four specific diagnostic molecular ratios of PAHs were used for the identification of sources of PAHs pollution. The ratios indicate combination of several sources on location, that the most likely sources of PAHs related to emissions from pyrogenic (combustion) origin.

The ecological risk assessment in layers of soil and groundwater indicates that there is a high ecological risk of PAHs in the location studied. The mean values of ecological risk in soil and groundwater decreased with soil depth and groundwater.

The monitoring of PAHs in groundwater and soil in an industrial complex should be given greater attention, especially given the fact that there are plans to develop residential and commercial properties on its grounds. On the other hand, the alluvial character of the land and the proximity of the Vrbas River require more attention because arable land, as well as agricultural irrigation, are located near and downstream. It is still common for households to have their own wells used for drinking water, livestock and irrigation. Accordingly, continuous monitoring at a number of locations in the industrial complex is necessary to determine the spatial and temporal distribution of PAHs. The analysis of PAHs must be done in soil and groundwater, but also in the air and sediment of the Vrbas River, due to its close proximity to industrial complex. It is imperative to adopt regulations governing permissible limits in industrial soils and to initiate urgent remediation in the location. Measures should be implemented to quickly reduce and eliminate the pollution of PAHs in the location.

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