Original Research

Polycyclic Aromatic Hydrocarbons in Different Layers of Soil and Groundwater - Evaluation of Levels of Pollution and Sources of Contamination

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Abstract

This study examined the concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) in soil and groundwater at a former cellulose factory in the city of Banja Luka, Republic of Srpska, Bosnia and Herzegovina. The objective of the study was to determine the concentrations of 16 PAHs in soil and groundwater at the site. The research area consisted of four representative locations in the industrial complex where the soil was sampled at depths of 0.3, 1, 2, 3, and 4 m and groundwater was sampled at 3.10, 2.50 and 3 m for two samples. In addition to the 16 PAHs, soil organic matter content and pH were also measured. The sum of the 16 PAHs (Σ16PAHs) in soil ranged from 0.99 to 2.24, 0.34 to 0.46, 0.24 to 0.32, 0.13 to 0.27 and 0.13 to 0.47 mg/kg for the 0.3, 1, 2, 3, and 4 m depths, respectively. Mean values were 1.70, 0.40, 0.28, 0.20 and 0.26 mg/kg, respectively. The Σ16PAHs in groundwater ranged from 0.23 to 4.50 mg/m³, with a mean value of 1.42 mg/m³. The concentrations of all 16 PAHs in the soil decreased with depth and there was no significant correlation between the concentrations of PAHs in the soil and groundwater. The concentrations of PAHs in the soil surface (0.3 m) and groundwater indicate that this industrial site is heavily contaminated and might need remedial action. Factor analysis indicates three sources of contamination, i.e. principal component (PC) PC1 (pyrogenic), PC2 (petrogenic) and PC3 (biomass), with 52.39%, 26.14% and 8.46% of the total variance, respectively. 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.

Keywords: soil, groundwaters, polycyclic aromatic hydrocarbons (PAHs), industrial complex, source of contamination

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**Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds containing two or more benzene rings in their structure. Polycyclic aromatic hydrocarbons (PAHs) result from anthropogenic activities, i.e. industrial emissions, incomplete combustion of petroleum, coal and other fossil fuels and other industrial and domestic activities [1-6]. Natural sources of PAHs are volcanoes, bacterial and algal synthesis, forest fires, petroleum seeps, erosion of sedimentary rocks containing petroleum hydrocarbons and decomposition of vegetative litterfall [7]. These compounds are widely present in the air, water, aquatic system, soils and sediments [8]. Although there are more than 100 different types of PAHs, [9] most analyses and data reports typically focus on 14 and 20 individual PAHs on average. PAHs can be divided into two categories: low molecular weight compounds are 2- and 3- rings (molecular weight <200 g/mol) and high molecular weight compounds are 4-, 5-, 6-ring PAHs (molecular weight >200 g/mol). Pure PAHs are usually colored, crystalline solids at ambient temperature [10], and they have high melting and boiling points, low vapor pressure and very low aqueous solubility. These compounds are very soluble in organic solvents and are lipophilic [11-12].

There is a large number of studies of PAHs in soils of different countries, namely Germany [13], France [14], Austria [15], China [16], USA [17], South Africa [18], Antarctic [19]. In their study, Brindha & Elango [20] have identified the presence of PAHs in groundwater in Chennai, Tamil Nadu, India. Li et al. [21] have researched the behavior of PAHs in surface and groundwater of the Yellow River, China, while Sun et al. [22] study focused on vertical migration of PAHs from surface soils to groundwater.

Systematic studies on PAHs contamination in surface soil in Bosnia and Herzegovina have been rare, and the research of PAHs at different soil depths was never conducted. Still, some analyses of PAHs in soil, air and sediment were carried out. One such analysis was of playground soil in the city of Sarajevo [23]. An investigation of POPs and PAHs in ambient air in the Central and Eastern Europe was also conducted in Bosnia and Herzegovina [24], as well as analyses of POPs and PAHs in sediments of the Neretva River [25]. A study of air PAHs in urban and rural areas was done in the city of Banja Luka in 2008 [26, 27]. The results of this study show that the value of PAHs in the urban area was much higher than in the rural area.

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, while in other studies, the greatest sampling depths were up to 20 cm [28], 40 cm [6], 50 cm [3] and 100 cm [22].

This study examined the concentrations of 16 PAHs in soil and groundwater in an industrial complex (locality Incel) (former Cellulose Factory) in the city of Banja Luka, Republic of Srpska, Bosnia and Herzegovina. The main objective of the paper is to determine the concentration levels, evaluate contamination of soil and groundwater in locations with high pollution in the city of Banja Luka and to assess the probable sources of PAHs contamination in soil and groundwater in locations.

**Material and Methods**

**Location Sampling**

The subject of the research in the study was to measure the PAHs concentration in the soil and groundwater in the industrial complex in Banja Luka. Banja Luka is the second largest city in the Republic of Srpska, Bosnia and Herzegovina, with a population of 185,000. The city is situated in a basin 164 m above sea level. The average annual temperature reaches 10.7°C. The lowest temperatures range between -5.6°C and -27°C and the highest between 31.4°C and 41.4°C.

The former industrial complex originally manufactured cellulose, viscose and paper products. Established in 1954, it was a major industrial conglomerate during the Socialist Era, employing up to 6,500 workers. Following a period of decline in the 1980s and the War in Bosnia and Herzegovina in 1990s, the factory building was destroyed, and the manufacturing itself was subsequently split into several smaller enterprises. This industrial complex is situated 3 km from the city centre. Incel factory was heavily damaged which resulted in the emission of various toxic substances into the neighboring environment. Location is categorized as a hotspot (waste from cellulose and viscose factory) [29, 30]. This location was selected for research due to earlier studies that discovered high contamination with heavy metals (Cd, Pb, Ni, Cu, and Hg) and organic pollutants (Polychlorinated Biphenyls (PCB) and Total Petroleum Hydrocarbons (TPH)) [29] and PAH [30]. Soil and groundwater analyses were carried out at multiple spots and wells (piezometers) dug out and specially installed for this, as well as the future groundwater research (S1, S2, S3, and S4) (Fig. 1).

**Analysis**

A total of 16 soil and 4 groundwater samples were collected from four locations in the industrial complex, from different layers of soil (at a depth of 30 cm, 100 cm, 200 cm, 300 cm, and 400 cm) and groundwater was sampled at 3.10, 2.50 and 3 m for two samples from saturated zone. The depth of the wells is 3 m in one location and 4 m in three locations.

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
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The physical analyses conducted in the soil were: acidity (pH) measured in deionized water, and organic matter (humus) content applying Tyurin’s method [31]. Components of PAHs that were analysed 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). 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 [32, 33] and accredited standard method EPA 8270D/3550C:2007 for soil and EPA 8270D/EPA 3510 for water [34]. Accredited quantification limit for PAH in soil is 0,02 mg/kg and for water 0,03 ug/l.

Statistical Analysis

Descriptive statistical operations like mean, median (med), minimum (min), maximum (max), and Skewness test were applied for the analysis of the measured data. Pearson’s correlation with significance level of p-value: p<0.05, p<0.01, and p<0.001 was used. Excel 2016 and JASP v0.8.5.1 software tools were used for statistical data processing.

Results and Discussion

Basic Characteristics of PAHs Concentrations in Soils and Groundwater

Table 1 shows the descriptive statistics of the 16 priority PAHs compounds in contaminated soils (at a depth of up to 30 cm (surface layer), 100 cm, 200 cm, 300 cm, and 400 cm) and groundwater environmental samples in four locations of the examined area. In this research, the ∑16PAHs in the soil (at a depth of up to 30 cm, 100 cm, 200 cm, 300 cm, 400 cm) ranged from 0.99 to 2.24 mg/kg, from 0.34 to 0.46, from 0.24 to 0.32, from 0.13 to 0.27 and from 0.13 to 0.47, with mean values of 1.70 mg/kg, 0.40 mg/kg, 0.28 mg/kg, 0.20 mg/kg and 0.26 mg/kg, respectively. The ∑16PAHs in groundwater ranged from 0.23 to 4.50 mg/m³, with a mean value of 1.42 mg/m³. According to the national standards [32], the concentrations of ∑16PAHs found in this study are higher in one location and lower in other locations than the permissible value of 2 mg/kg in agricultural soils. The soil is heavily contaminated (heavily polluted) according to permissible limits of 1 mg/kg [35] in a surface layer of soil (0-30 cm) and contamination in soils was 1-2.24 times higher than limits.

The ∑16PAHs in groundwater ranged from 0.23 to 4.50 mg/m³, with a mean value of 1.41 mg/m³. The measured value indicates that groundwater is highly polluted and classified in the fifth class of water quality, and those are heavily polluted waters that can be used for almost no purpose [33]. Among the ∑16PAHs, the three most abundant were Phe (0.87 mg/m³), Nap (0.64 mg/m³) and BaA (0.62 mg/m³).

The ∑16PAHs are the highest in the surface layer of...
Table 1. Descriptive statistics of the PAHs in different layers of soils and groundwater.

| PAHs | Soil (mg/kg)  | Groundwater (mg/m³) |
|------|---------------|----------------------|
|      | 30 cm | 100 cm | 200 cm | 300 cm | 400 cm | Mean | Med | Range | Mean | Med | Range | Mean | Med | Range | Mean | Med | Range |
| BbF  | 0.14  | 0.14  | 0.08-0.20 | 0.04  | 0.04  | n.d.-0.7 | 0.02  | 0.01  | n.d.-0.06 | 0.02  | 0.01  | n.d.-0.05 | 0.01  | 0.02  | 0.00-0.03 | -    | -    | n.d.-n.d. |
| BkF  | 0.24  | 0.28  | 0.07-0.32 | 0.01  | 0.01  | 0.01-0.02 | 0.01  | 0.00  | n.d.-0.03 | 0.01  | 0.01  | n.d.-0.01 | 0.01  | 0.00  | n.d.-0.04 | -    | -    | n.d.-n.d. |
| BaP  | 0.09  | 0.05  | 0.02-0.24 | 0.06  | 0.06  | 0.05-0.06 | 0.03  | 0.03  | 0.01-0.04 | 0.02  | 0.01  | n.d.-0.04 | 0.03  | 0.04  | 0.01-0.04 | -    | -    | n.d.-n.d. |
| BghiP| 0.15  | 0.15  | 0.03-0.28 | 0.01  | 0.01  | n.d.-0.01 | 0.01  | 0.00  | n.d.-0.02 | 0.00  | 0.00  | n.d.-0.01 | 0.03  | 0.02  | n.d.-0.06 | 0.02  | 0.00  | n.d.-0.09 |
| IcdP | 0.02  | 0.02  | n.d.-0.05 | 0.01  | 0.01  | n.d.-0.02 | 0.01  | 0.01  | n.d.-0.02 | 0.01  | 0.01  | 0.01-0.02 | 0.04  | 0.02  | n.d.-0.09 | -    | -    | n.d.-n.d. |
| Ant  | 0.20  | 0.25  | 0.01-0.30 | 0.02  | 0.02  | 0.02-0.03 | 0.02  | 0.02  | n.d.-0.04 | 0.01  | 0.01  | n.d.-0.03 | 0.03  | 0.02  | 0.02-0.07 | 0.02  | 0.00  | n.d.-0.07 |
| Chr  | 0.06  | 0.05  | 0.03-0.09 | 0.03  | 0.03  | 0.02-0.03 | 0.02  | 0.02  | 0.01-0.03 | 0.02  | 0.02  | 0.01-0.03 | 0.03  | 0.02  | 0.01-0.04 | 0.07  | 0.01  | n.d.-0.26 |
| DahA | 0.38  | 0.38  | 0.29-0.48 | -    | -    | n.d.-n.d. | 0.00  | 0.00  | n.d.-0.01 | -    | -    | n.d.-n.d. | 0.01  | 0.01  | n.d.-0.03 | 0.15  | 0.03  | n.d.-0.57 |
| Acy  | 0.11  | 0.10  | 0.02-0.21 | 0.01  | 0.01  | n.d.-0.03 | 0.04  | 0.04  | n.d.-0.06 | -    | -    | n.d.-n.d. | 0.00  | 0.00  | n.d.-0.01 | 0.17  | 0.12  | 0.02-0.44 |
| Pyr  | 0.03  | 0.02  | 0.01-0.08 | -    | -    | n.d.-n.d. | 0.02  | 0.02  | n.d.-0.04 | 0.00  | 0.00  | n.d.-0.01 | 0.01  | 0.00  | n.d.-0.02 | 0.13  | 0.01  | n.d.-0.50 |
| BaA  | 0.06  | 0.07  | n.d.-0.10 | 0.03  | 0.03  | 0.02-0.05 | 0.02  | 0.02  | n.d.-0.04 | 0.03  | 0.03  | 0.01-0.05 | 0.00  | 0.01  | n.d.-0.01 | 0.17  | 0.03  | 0.01-0.62 |
| Phe  | 0.04  | 0.04  | n.d.-0.09 | 0.05  | 0.05  | 0.03-0.07 | 0.05  | 0.05  | 0.04-0.06 | 0.03  | 0.02  | 0.01-0.06 | 0.03  | 0.02  | n.d.-0.07 | 0.23  | 0.02  | n.d.-0.87 |
| Flo  | 0.11  | 0.06  | 0.01-0.30 | 0.04  | 0.04  | 0.04-0.04 | 0.02  | 0.02  | 0.01-0.04 | 0.02  | 0.02  | n.d.-0.03 | 0.01  | 0.01  | 0.01-0.02 | 0.16  | 0.05  | n.d.-0.56 |
| Nap  | 0.03  | 0.03  | 0.01-0.07 | 0.03  | 0.03  | 0.03-0.03 | 0.01  | 0.01  | n.d.-0.02 | 0.00  | 0.00  | n.d.-0.01 | 0.01  | 0.00  | n.d.-0.02 | 0.19  | 0.06  | 0.02-0.64 |
| Ace  | 0.02  | 0.02  | 0.01-0.03 | 0.01  | 0.01  | 0.01-0.01 | 0.01  | 0.01  | n.d.-0.02 | 0.00  | 0.00  | n.d.-0.01 | 0.00  | 0.00  | n.d.-0.01 | 0.07  | 0.03  | 0.02-0.20 |
| Fluo | 0.02  | 0.02  | n.d.-0.02 | 0.05  | 0.05  | 0.05-0.05 | 0.01  | 0.00  | n.d.-0.02 | 0.02  | 0.00  | n.d.-0.05 | 0.00  | 0.01  | n.d.-0.01 | 0.04  | 0.01  | n.d.-0.16 |
| ∑ 16 PAHs | 1.70 | 1.79 | 0.99-2.24 | 0.40  | 0.40  | 0.34-0.46 | 0.28  | 0.28  | 0.24-0.32 | 0.20  | 0.19  | 0.13-0.27 | 0.26  | 0.19  | 0.13-0.47 | 1.42  | 0.69  | 0.23-4.50 |
| pH   | 6.45  | 6.25  | 5.60-7.70 | 7.66  | 7.66  | 7.37-7.94 | 7.72  | 7.73  | 7.43-7.99 | 7.82  | 7.87  | 7.51-8.08 | 7.95  | 7.91  | 7.87-8.07 | -    | -    | -    |
| Hum. | 1.65  | 1.30  | 0.00-4.00 | 1.53  | 1.53  | 0.82-2.24 | 1.11  | 0.74  | 0.53-2.42 | 0.83  | 0.82  | 0.75-0.93 | 0.74  | 0.75  | 0.72-0.76 | -    | -    | -    |
soil, and with increasing the depth it decreases. Similar results were also observed in Shenyang City in China, where the PAH concentrations decreased with the depth of the soil [36]. Jiao et al. [37] came up with a similar result of decreasing concentration of \( \sum_{16} \text{PAHs} \) by increasing the depth in the study (Shanxi, China) and explained that PAHs come from pyrolysis inputs due to industrial emissions formed and released during industrial activities and also shows the migrate trend of PAHs in the vertical section of the soils [37]. Comparing the concentrations of \( \sum \text{PAHs} \) in soils in the Loess Plateau, China, similar values were obtained in the surface layer of soil [3], in an urban location in China [6], 6 times higher than values in the Hunpu region, a wastewater-irrigated area, Shenyang City, China [36]. Values of PAHs in these locations are higher than values along the Govan to Clydebank corridor, the area with a history of heavy industry (concentrations range from 86.9–653 mg/kg) [38], similar as in examined locality. Values are 10 times lower than values in Glasgow soils and 2 times higher than values in Ljubljana and Torino soils [4].

The distribution of the 2 and 3-ring (low molecular) and 4, 5, 6-ring (high molecular) PAHs are shown in Fig. 2. The PAHs frequency in surface soils (0-30 cm) was detected as 2 and 3- rings (28%) and 4, 5 and 6-ring (72%). High percentages of high molecular PAHs (4, 5, 6-rings) are found at all depths in the soil, and in lesser quantities in the water. The percentage representation of low molecular PAHs (2, 3, 4-rings) was highest in groundwater.

**Correlation Analysis of PAHs and Soil Properties**

Tables 2 and 3 present the correlation analysis (Pearson correlation test). Table 2 shows correlations between the determined PAHs values in the surface layer of soil in each location and PAHs values per different soil layers and groundwater. Table 3 displays the correlation analysis for PAHs components (p<0.05, p<0.00) (p - Pearson’s rank correlation). Bolded numbers indicate a statistically significant correlation (r>0.5).

**Table 2. Correlation per layers of soil and groundwater.**

|                           | Pearson’s correlation |
|---------------------------|-----------------------|
|                           | r   | p       |
| S1 Surface layer - S1 100 cm | 0.977*** | <.001 |
| S1 Surface layer - S1 200 cm | 0.922*** | <.001 |
| S1 Surface layer - S1 300 cm | 0.931*** | <.001 |
| S1 Surface layer - S1 400 cm | 0.921*** | <.001 |
| S1 Surface layer - S1 Groundwater | 0.143 | 0.598 |
| S2 Surface layer - S2 100 cm | 0.991*** | <.001 |
| S2 Surface layer - S2 200 cm | 0.995*** | <.001 |
| S2 Surface layer - S2 300 cm | 0.993*** | <.001 |
| S2 Surface layer - S2 Groundwater | 0.619* | 0.011 |
| S3 Surface layer - S3 200 cm | 0.949*** | <.001 |
| S3 Surface layer - S3 300 cm | 0.992*** | <.001 |
| S3 Surface layer - S3 400 cm | 0.993*** | <.001 |
| S3 Surface layer - S3 Groundwater | -0.061 | 0.824 |
| S4 Surface layer - S4 200 cm | 0.966*** | <.001 |
| S4 Surface layer - S4 400 cm | 0.965*** | <.001 |
| S4 Surface layer - S4 Groundwater | -0.329 | 0.214 |

* p<0.05, *** p<0.001.

![Fig. 2. Frequency of PAHs per ring in soil and groundwater for low and high molecular PAHs.](image-url)
Table 3. Correlation per PAHs components of soil and groundwater.

| Pearson’s correlation test (r and p values) | Nap-Acy | < .001 | Ace-DahA | -0.145 | 0.543 | Fluo-BaP | 0.862*** | < .001 |
|-------------------------------------------|---------|--------|----------|--------|-------|----------|----------|--------|
| Nap-Ace                                   | 0.679***| < .001 | Ace-BghiP| 0.005  | 0.982 | Fluo-IcdP| 0.919*** | < .001 |
| Nap-Flo                                   | 0.761***| < .001 | Flo-Phe  | 0.490* | 0.028 | Fluo-DahA| 0.900*** | < .001 |
| Nap-Phe                                   | 0.249   | 0.290  | Flo-Ant  | 0.775***| < .001 | Fluo-BghiP| 0.852*** | < .001 |
| Nap-Ant                                   | 0.696***| < .001 | Flo-Fluo | 0.414  | 0.070 | Pyr-BaA  | 0.133    | 0.575  |
| Nap-Fluo                                  | 0.155   | 0.514  | Flo-Pyr  | 0.453* | 0.045 | Pyr-Chr  | -0.011   | 0.964  |
| Nap-Pyr                                   | 0.556*  | 0.011  | Flo-BaA  | 0.431  | 0.058 | Pyr-BbF  | 0.017    | 0.943  |
| Nap-BaA                                   | 0.120   | 0.613  | Flo-Chr  | 0.270  | 0.249 | Pyr-BkF  | -0.080   | 0.738  |
| Nap-Chr                                   | -0.068  | 0.775  | Flo-BbF  | 0.297  | 0.203 | Pyr-BaP  | 0.205    | 0.386  |
| Nap-BbF                                   | -0.036  | 0.882  | Flo-BkF  | 0.142  | 0.551 | Pyr-IcdP | 0.017    | 0.944  |
| Nap-BkF                                   | -0.161  | 0.498  | Flo-BaP  | 0.476* | 0.034 | Pyr-DahA | 0.047    | 0.845  |
| Nap-BaP                                   | 0.103   | 0.664  | Flo-IcdP | 0.222  | 0.347 | Pyr-BghiP| -0.081   | 0.735  |
| Nap-IcdP                                  | -0.111  | 0.641  | Flo-DahA | 0.198  | 0.402 | BaA-Chr  | 0.841*** | < .001 |
| Nap-DahA                                  | -0.112  | 0.639  | Flo-BghiP| 0.203  | 0.390 | BaA-BbF  | 0.851*** | < .001 |
| Nap-BghiP                                 | -0.030  | 0.901  | Phe-Ant  | 0.380  | 0.098 | BaA-BKF  | 0.810*** | < .001 |
| Acy-Ace                                   | 0.171   | 0.470  | Phe-Fluo | 0.012  | 0.959 | BaA-BaP  | 0.780*** | < .001 |
| Acy-Flo                                   | 0.411   | 0.071  | Phe-Pyr  | 0.059  | 0.804 | BaA-IcdP | 0.835*** | < .001 |
| Acy-Phe                                   | 0.140   | 0.557  | Phe-BaA  | -0.098 | 0.680 | BaA-DahA | 0.873*** | < .001 |
| Acy-Ant                                   | 0.649***| 0.002  | Phe-Chr  | -0.090 | 0.706 | BaA-BghiP| 0.698*** | < .001 |
| Acy-Fluo                                  | 0.086   | 0.719  | Phe-BbF  | -0.105 | 0.659 | Chr-BbF  | 0.984*** | < .001 |
| Acy-Pyr                                   | 0.699***| < .001 | Phe-BkF  | -0.178 | 0.454 | Chr-BkF  | 0.978*** | < .001 |
| Acy-BaA                                   | 0.036   | 0.879  | Phe-BaP  | 0.007  | 0.976 | Chr-BaP  | 0.930*** | < .001 |
| Acy-Chr                                   | -0.047  | 0.843  | Phe-IcdP | -0.156 | 0.511 | Chr-IcdP | 0.983*** | < .001 |
| Acy-BbF                                   | -0.045  | 0.851  | Phe-DahA | -0.198 | 0.403 | Chr-DahA | 0.962*** | < .001 |
| Acy-BkF                                   | -0.097  | 0.683  | Phe-BghiP| -0.108 | 0.650 | Chr-BghiP| 0.858*** | < .001 |
| Acy-IcdP                                  | 0.116   | 0.625  | Ant-Fluo | 0.254  | 0.280 | BbF-BKF  | 0.975*** | < .001 |
| Acy-DahA                                  | -0.098  | 0.681  | Ant-Chr  | 0.135  | 0.569 | BbF-DahA | 0.968*** | < .001 |
| Acy-BghiP                                 | 0.162   | 0.056  | Ant-Flu  | 0.419  | 0.087 | BbF-IcdP | 0.986*** | < .001 |
| Acy-BghiP                                 | -0.098  | 0.681  | Ant-BaA  | 0.105  | 0.659 | BbF-BghiP| 0.879*** | < .001 |
| Acy-BghiP                                 | 0.144   | 0.545  | Ant-DahA | 0.105  | 0.659 | BbF-BghiP| 0.971*** | < .001 |
| Acy-Chr                                   | -0.100  | 0.675  | Fluo-Pyr | 0.039  | 0.871 | BaP-DahA | 0.897*** | < .001 |
| Acy-BghiP                                 | -0.047  | 0.844  | Fluo-BaA | 0.857***| < .001 | BaP-BghiP| 0.817*** | < .001 |
| Acy-BghiP                                 | -0.164  | 0.490  | Fluo-Chr | 0.935***| < .001 | IcdP-DahA| 0.982*** | < .001 |
| Acy-BghiP                                 | 0.012   | 0.960  | Fluo-BbF | 0.941***| < .001 | IcdP-BghiP| 0.884*** | < .001 |
| Acy-IcdP                                  | -0.109  | 0.646  | Fluo-Bkf | 0.919***| < .001 | Daha-BghiP| 0.865*** | < .001 |

*p < 0.05, ** p < 0.01, *** p < 0.001.
The results of the correlation analysis between the PAHs values of surface soil in each location and PAHs values in soil layers and groundwater are considered to have a strong positive statistically significant correlation ($r>0.5$). Correlation with PAHs values in groundwater is weak, which confirms that the site soil is not the only cause of groundwater pollution. An additional source of pollution may arise from other polluted sites, which have reached the site via groundwater flow.

Correlations of Nap with Acy, Ace, Flo, Ant, and Pyr; Acy with Ant and Pyr; Ace with Flo and Ant; Flo with Ant; Ant with Pyr; Flu on with BaA, Chr, BbF and BkF; Flu on with BaP, IcdP, DahA and BghiP; BaA with Chr, BbF, BkF, BaP, IcdP, DahA and BghiP; Chr with BbF, BkF, BaP, IcdP, DahA and BghiP; BbF with BkF, BaP, IcdP, DahA and BghiP; BghiP with BkF, BaP, IcdP, DahA and BghiP; IcdP with DahA and BghiP; BaP with IcdP, DahA and BghiP; IcdP with DahA and BghiP; DahA with BghiP are strong positive correlations. These results suggest that these pollutant pairs might have similar sources or result from similar factors.

In location je type of soil is clay. pH values in H$_2$O are from 7.37 to 8.07 in samples. Organic matter (%) are from 0.53 to 2.42. Due to their hydrophobicity and non-polarity, PAHs merge with soil organic matter (SOM) or humus colloids in soil [38]. SOM plays the role of PAHs carrier for downward migration and protects PAHs from the degradation. Fine particle clays have a larger specific surface area or have more adsorption sites, showing a higher sorption capacity of PAH compared to fine or coarse sand [22].

SOM has a high sorption capacity, limiting PAHs to the upper part of the soil profile thereby reducing the concentration of PAHs with the depth. Organic matter is of great importance for the sorption of hydrophobic organic compounds (among other things PAHs). Its content is higher than 8% while the combined effect of organic matter and clay mineral is manifested at its content below 6% [39].

The physical and chemical composition of the soil is responsible for retaining PAHs in soil. The quantities of organic C and hydrophobicity of organic matter in soil are estimated as the most important parameter for PAH retention in the environment [40, 41].

A correlation analysis between Σ16PAHs, humus (organic matter) and pH in soil was conducted in the present study. A statistically moderate negative correlation was found between Σ16PAHs and pH. The value of $r$ is -0.655 (p-value is <0.01). The significant correlation between Σ16PAHs and humus has not been determined in the study. There is probably a lasting input of fresh PAHs (from the biomass heating plant in close proximity as well as the traffic) which confirms the correlation. Nam et al. [42] obtained similar results.

Factor, Principal Components and Cluster Analysis

Factor and principal components analysis (FA and PCA) are multivariate statistical methods to identify the main factors that determine the variability of environmental quality [43]. The relationship between the components of PAHs levels in soils and groundwater with anthropogenic activities was examined, using FA. FA was employed to determine the effective variable factors (compounds). The varimax rotation was used for component loading for PAHs components in soil and groundwater (Table 4).

The aim of FA was to create a fewer number of factors by combining two or more variables. The primary output for a PCA shows the correlation between each variable of a principal component and the variable factors (PC1, PC2, and PPC3), i.e. elements in soil samples are affected by two major components. Three principal components (PC) have eigenvalues higher than 1 (PC1, PC2, and PC3).

The RC1 factor included BaA, BaP, BbF, BghiP, BkF, Chr, DahA, Flu and IcdP was identified according to their coefficients in the component matrix. The PC1 factor is in relation to coal combustion, i.e. burning and vehicular emissions and was indicative of the pyrogenic origin, especially Fla, Pyr, BaA, BbF, BkF, BaP, BghiP, IcdP [44]. According to Liu et al. [45], all components were strong positively loaded if values were >0.75, and moderately loaded if values were in the range from 0.75-0.5 (Table 4). Harrison et al. [46] reported that compounds Flu, BaA, and Chr were typical markers for coal combustion. The PC1 factor explained 52.39% of the total variance. Davis et al. [47] also reported that BghiP and IcdP sources were from the vehicular exhaust. According to Iwegbue et al. [48], Chr, BkF and DahA are indicators of diesel emissions and BghiP and IcdP originate through combustion of heavy oil.

The PC2 factor that includes Acy, Ant, Nap and Pyr was identified as well, and it explains 26.14% of the total variance. This factor is of petrogenic origin. Acy component was strong positively loaded (>0.75) [45] (Table 1). Furthermore, Davis et al. [47] pointed out that Acy is the main product of a petroleum source. Ant and Pyr were also strong positively loaded, if the value were >0.70 [49]. Nap acts as a marker for petroleum source. The PC2 factor is in relation to coal combustion, i.e. burning and vehicular emissions and was indicative of the pyrogenic origin, especially Fla, Pyr, BaA, BbF, BghiP, IcdP [44]. According to Liu et al. [45], all components were strong positively loaded if values were >0.75, and moderately loaded if values were in the range from 0.75-0.5 (Table 4). Harrison et al. [46] reported that compounds Flu, BaA, and Chr were typical markers for coal combustion. The PC1 factor explained 52.39% of the total variance. Davis et al. [47] also reported that BghiP and IcdP sources were from the vehicular exhaust. According to Iwegbue et al. [48], Chr, BkF and DahA are indicators of diesel emissions and BghiP and IcdP originate through combustion of heavy oil.

The PC3 factor includes components that were strongly positively loaded Ace, Flo (0.75) and Phe (0.70) [45, 49]. Ant and Nap were moderately loaded, as their values ranged from 0.75-0.5. This factor contains 3- and 4-ring PAH compounds of biomass origin and explains 8.46% of the total variance. Loadings of Phe and Ant were higher and represent low-temperature processes
of wood/biomass combustion, i.e. the incomplete combustion of wood/biomass [47]. Zeng et al. [6] explained that the Flo compounds were characteristic of coal combustion. The probable cause is a wood-burning plant nearby.

Three components accounted for 86.99% of the total variance, highlighting the major trends of the soil ecosystem. The source analysis of soil PAHs demonstrated that the main causes of PAHs are coal combustion (pyrogenic) (PC1 factor), petroleum sources (petrogenic) (PC2 factor) and biomass combustion (PC3 factor).

PCA provides information on the most significant parameters [51]. Fig. 3a) shows which PCA is done to combine measured variables in three components, PC1, PC2, and PC3. The direction of the arrows shows that variables, i.e. PAHs components (Ace, Acy, Ant, BaA, BaP, BbF, BghiP, BkF, Chr, DahA, Flo, Fluo, IcdP Nap, Phe, and Pyr) contribute to the three variable factors. The weights to emphasize are BaA, BaP, BbF, BghiP, BkF, Chr, DahA, Fluo and IcdP (for PC1), Acy, Nap and Pyr (for PC2) and Phe, Flo, and Ace (for PC3) variables that stand out more than others.

Fig. 3b) shows PCA scree plot (varimax rotation) with eigenvalues higher than one, as a criterion for evaluating the components required to explain the origin of variance in the data. Three factors explained 86.99% of the data in total variance.

Hierarchical cluster analysis (CA), an analytical technique for multivariate data analysis [21] was applied to the data, and the Paired group (UPGMA) method distance was chosen for calculation (Fig. 4). CA was performed to check the results of the PC analysis and provided details of similarities between groups of parameters [52].

The results of the CA yield a slightly similar result like PCA. From the results, three main groups can be identified. Acy and Pyr (Group 1) and Phe, Chr, IcdP, DahA, BghiP, Fluo, BbF and BkF (Group 2) and Ant, Nap, Ace, BaA, Flo and BaP (Group 3), indicating that the pollutants in the similar group might have similar sources (Fig. 4), which was also confirmed by PCA.
Conclusions

This research found that the \(\sum\)16PAHs in the soil (at a depth of up to 30 cm, 100 cm, 200 cm, 300 cm and 400 cm) ranged from 0.99 to 2.24 mg/kg, from 0.34 to 0.46, from 0.24 to 0.32, from 0.13 to 0.27 and from 0.13 to 0.47, with mean values of 1.70 mg/kg, 0.40 mg/kg, 0.28 mg/kg, 0.20 mg/kg and 0.26 mg/kg, respectively. The \(\sum\)16PAHs in groundwater ranged from 0.23 to 4.50 mg/m\(^3\), with a mean value of 1.42 mg/m\(^3\). According to the national standards, the concentrations of \(\sum\)16PAHs found in this study are higher in one location and lower in other locations than the permissible value of 2 mg/kg in agricultural soils. Soil and groundwater are heavily contaminated (heavily polluted) in the surface layer of soil (0-30 cm). The study indicated that PAHs concentration in the industrial complex and in different layers of soil and groundwater were high. The significantly higher values of \(\sum\)16PAHs in the surface soil layer compared to other soil layers indicate that there is a fresh intake of PAHs at the site, with pre-existing historical pollution. The measured value also indicates that groundwater is highly polluted and that groundwater is classified in the fifth class of water quality, and those are heavily polluted waters that can be used for almost no purpose. The flow of groundwater has a significant influence in PAH concentrations since a significantly higher concentration of PAHs is observed in groundwater compared to the soil at research sites. The \(\sum\)16PAHs is the highest in surface layer of soil, and with increasing the depth it decreases.

Maximum \(\sum\)16PAHs values were observed at 0-30 cm and PAH concentrations decreased with depth in the different soil layers, and PAHs were dominantly accumulated in the surface soil layer.

The relationship between the components of PAHs levels in soils and groundwater and anthropogenic activities was examined, using factor analysis (FA). Three components accounted for 86.99% of the total variance. The source analysis of soil PAHs demonstrated that the main causes of PAHs are coal combustion (pyrogenic) (PC1 factor included BaA, BaP, BbF, BghiP, BkF, Chr, DahA, Fluo, and IcdP), petroleum sources (petrogenic) (PC2 factor included Acy, Ant, Nap and Pyr) and biomass combustion (PC3 factor included Ace, Flo, and Phe). The results of the hierarchical cluster analysis (CA) yield a slightly similar result like principal components analysis. From the results, three main groups can be identified. Acy and Pyr (Group 1) and Phe, Chr, IcdP, DahA, BghiP, Fluo, BbF, and BkF (Group 2) and Ant, Nap, Ace, BaA, Flo, and BaP (Group 3).

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Conflict of Interest

The authors declare no conflict of interest.

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