UNIVERSITY "UNION - NIKOLA TESLA"

THE FOURTH INTERNATIONAL CONFERENCE ON SUSTAINABLE ENVIRONMENT AND TECHNOLOGIES

PROCEEDINGS

"Creating sustainable commUNiTy"

INTERNATIONAL CONFERENCE ON SUSTAINABLE ENVIRONMENT AND TECHNOLOGIES

27-28 SEPTEMBER 2024

CARA DUŠANA 62-64, BELGRADE, SERBIA

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Nikola Tesla

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CONTENTS

POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SOIL AROUND THE COPPER MINING AND SMELTING COMPLEX BOR

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Abstract: The presence of polycyclic aromatic hydrocarbons (PAHs) poses a significant risk to the environment due to their mutagenic and carcinogenic properties. In this paper a characterization of occurrence and levels of PAHs in 25 soils samples around Copper Mining and Smelting Complex Bor has been presented. Furthermore, the paper includes a characterization of source and carcinogenic potency of PAHs in analyzed soils. The diagnostic ratio of LPAHs/HPAHs was employed to differentiate between petrogenic and pyrogenic PAH sources. The results primarily indicated petrogenic PAH sources, with pyrogenic PAH sources identified at only three locations (with higher PAH concentrations). Overall, the PAH concentrations in these soils showed a low environmental risk, except at one location where the sum of 10PAH compounds exceeded the target value for hazardous and harmful contaminants.

Keywords: PAH, mining, environmental, carcinogenic risk

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants of significant environmental and public health concern due to their toxic, genotoxic, mutagenic, and/or carcinogenic properties. PAHs are hydrophobic, semi-volatile organic contaminants comprising at least two fused aromatic rings made up of carbon and hydrogen arranged in various structural configurations, simple to complex, including linear, angular, or clustered arrangements (Aralu et al., 2022). PAHs exhibit varying physicochemical and toxicological characteristics depending on their molecular weight. PAHs with two or three aromatic rings, due to their lower molecular weight, are typically referred to as light PAHs

(LPAHs). In contrast, PAHs with four or more aromatic rings are known as heavy PAHs (HPAHs). Heavy PAHs are more stable and more toxic than the light PAHs.

Polycyclic aromatic hydrocarbons are widely distributed in soils, sediments, groundwater, and the atmosphere. They are present around the globe and have been found to contaminate the soil. They are hydrophobic with low water solubility, so they have a tendency to bind with organic matter present in the soil (Škrbić et al., 2021). PAHs are relatively stable contaminants showing a recalcitrant nature in soils, making them more challenging to degrade when compared to many other organic contaminants.

Both natural and anthropogenic activities contribute to the widespread environmental occurrence of PAHs. While natural phenomena such as accidental forest fires and volcanic eruptions are significant sources, most of the PAH contamination originates from anthropogenic sources. They are easily deposited onto soil surfaces and can persist in the soil for several decades. They are formed and released into the environment through the combustion of fossil fuels and biomass in industries, power plants, gas production sites, traffic, household activities, municipal activities, and the burning of agricultural waste (Škrbić et al., 2021). Besides being present in liquid and solid fossil fuels such as coal, crude oil, and refined petroleum, PAHs are also produced by high-temperature industries such as melting and metal processing. Heavy industries, including metal mining and smelting, are operated in resource-rich areas. One prominent example is the Copper Mining and Smelting Complex, located in the city of Bor in Eastern Serbia.

The aim of this study was to analyze the concentration and distribution of individual PAH compounds in soils around the Copper Mining and Smelting Complex Bor. The main objectives of this study were to: 1) Determine the distribution and levels of PAHs; 2) Identify the sources of PAHs; and 3) Determine the carcinogenic potency of PAHs in the analyzed soil samples.

MATERIALS AND METHODS

Description of the study site

The city of Bor (coordinates: 44°05'N, 22°06'E), located on the Balkan Peninsula, belongs to the Bor district and covers an area of 856 km^2. The copper deposit in Bor is one of the largest European copper deposits. The Mining and Smelting Complex Bor is the only manufacturer of copper in Serbia. Due to mining operations over the last century, the topography has changed significantly, characterized by large surface mines.

Soil sampling

To assess PAH concentration levels, soil samples were collected during April 2023. Figure 1 shows the geographical position of the soil sampling sites (25 measuring points - locations).

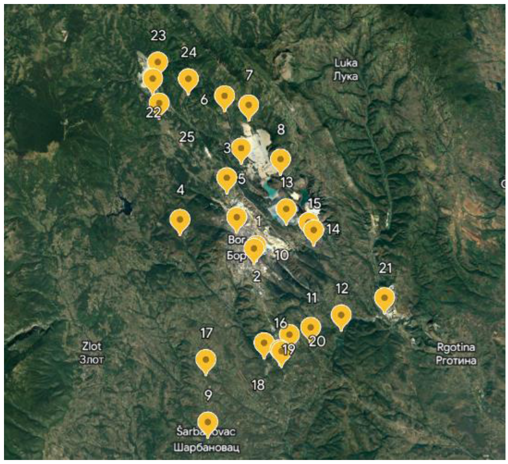

Figure 1 *The map of locations*

PAH analysis of samples was performed using a gas chromatograph with mass selective detector (GC/MS), according to ***EPA*** 8270D:2007, EPA 3540C:1996 and EPA 3630C:1996 methods. All GC/MS analyses were conducted by accredited chemical laboratory at the Mining and Metallurgy Institute Bor (Serbia).

RESULTS AND DISCUSSION

The descriptive statistical results (including abbreviations and the number of rings) of PAH compounds in soil samples are summarized in Table 1.

Table 1 *The concentration (μg/kg) of individual PAH compounds in soil samples*

PAH Compounds	Abbr.	Rings	Min	Max	Mean	SD
Naphthalene	Nap	2	20	46	31.2	6.1
Acenaphthylene	Acy	3	n.d.	n.d.	0.0	0.0

Acenaphthene	Ace	3	n.d.	21	7.4	5.0
Fluorene	Fl	3	11	34	17.9	4.5
Phenanthrene	Phe	3	30	393	57.3	70.4
Anthracene	Ant	3	n.d.	10	0.4	2.0
Fluoranthene	Flu	4	6	396	28.6	77.0
Pyrene	Pyr	4	23	304	43.8	54.7
Benzo(a)anthracene	BaA	4	n.d.	90	8.6	18.6
Chrysene	Chr	4	6	131	16.2	24.8
Benzo(b+k) fluoranthene	BbkF	5	n.d.	301	18.5	63.0
Benzo(a)pyrene	BaP	5	n.d.	68	6.7	15.3
Indeno(1,2,3-cd) pyrene	IcdP	6	n.d.	95	3.8	19.0
Dibenzo(a,h) anthracene	DahA	6	n.d.	62	3.0	12.4
Benzo(g,h,i)perylene	BghiP	6	n.d.	70	4.4	15.3

It is known that 16PAHs have been identified by the United States Environmental Protection Agency (USEPA) as priority contaminants due to their mutagenic, carcinogenic and teratogenic properties. Additionally, 7PAHs (benzo(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene) are classified as carcinogenic compounds (Carc PAHs).

Serbia has established the Directive on systematic soil quality control program, indicators for soil degradation risk assessment and methodology for remediation programs (Directive 30/2018). This directive sets target and intervention values for regulating the occurrence of a sum of 10PAHs (i.e. sum of anthracene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, phenanthrene, fluoranthene, indeno(1,2,3-c,d)pyrene, naphthalene and benzo(g,h,i)perylene) in soil. The Serbian Directive sets a target value of 1 mg/kg (1000 μg/kg) for 10PAHs, while the intervention value is 40 000 μg/kg. The concentration of total PAHs, the 10PAH and the carcinogenic 7PAH compounds at different locations are presented in Figure 2. The concentration of the 10PAHs is significantly below this target value at all locations except one - location 3 (Brezonik in the northern part of the Bor region). The high PAH concentrations at this location could be attributed to the nearby smelter, wich is surrounded by mining tailings, a quarry and underground pit exploitation.

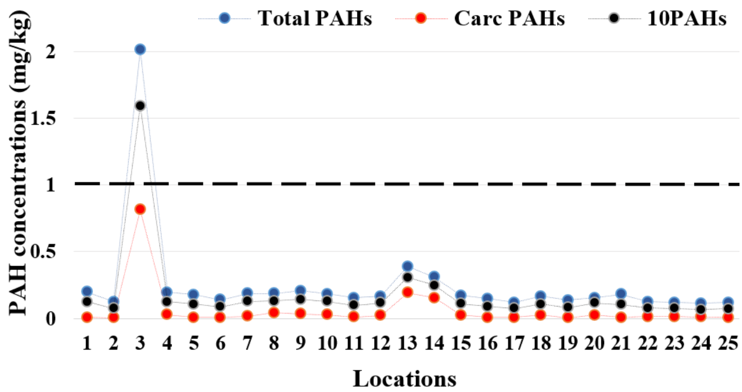

Figure 2 *PAH concentrations on different locations*

Based on the number of aromatic rings, 16 PAHs are categorized into 5 groups as: 2-rings PAHs, 3-rings PAHs, 4-rings PAHs, 5-rings PAHs and 6-rings PAHs. The distribution of PAHs in these soil samples indicates that 3-ring PAHs are the most dominant, followed by 4-ring PAHs and 2-ring PAHs (Figure 3).

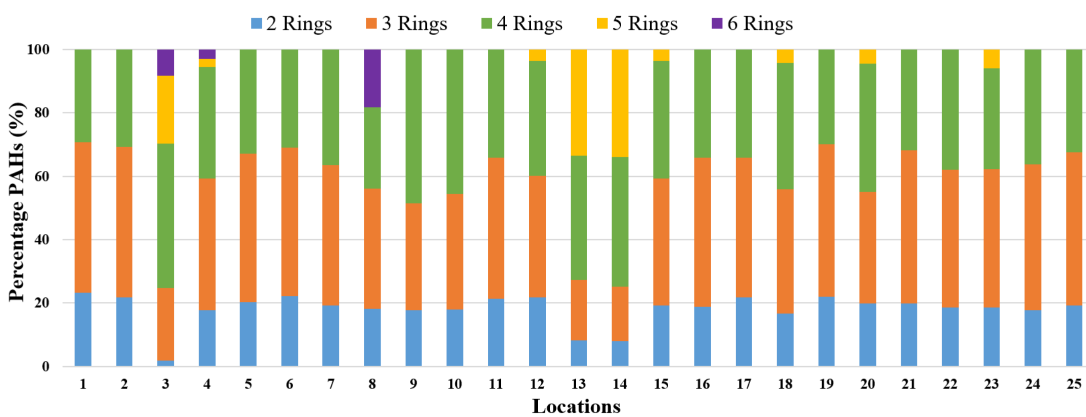

Figure 3 *Contribution of different ring numbers to the total PAHs depending on locations*

PAH source materials are generally classified as either petrogenic (derived from petroleum) or pyrogenic (derived from combustion). In order to characterize the sources of PAHs, the ratio of LPAHs/HPAHs was calculated. This ratio has been extensively used in literature to distinguish between petrogenic and pyrogenic PAH sources (Aralu et al., 2022). Generally, a LPAHs/HPAHs ratio greater than 1 indicates petrogenic sources, while a ratio less than 1 confirms pyrolytic PAH inputs. The results revealed that petrogenic source was dominant for most of the analyzed soil samples, while a pyrogenic source was confirmed for only three locations (Figure 4). It is interesting to note that these three locations with a dominant pyrogenic PAH source also have increased PAHs content. Petrogenic sources tend to be dominated by lower molecular weight LPAHs. Pyrogenic sources are associated with the incomplete combustion of organic matter. Some PAHs are characteristic for domestic heating or biomass burning (Flu, Pyr), while BghiP, BbF, IcdP were specific for car exhausts. The dominance of the LPAHs suggests a release of PAHs to the environment through the combustion of fossil fuels and their processing products. LPAHs are more biodegradable, less lipophilic and not to be sorbed as strongly as the HPAHs (Aralu et al., 2022). The increased PAHs content at location 3 could be attributed to the nearby smelter, as well as the operation of the mining machinery.

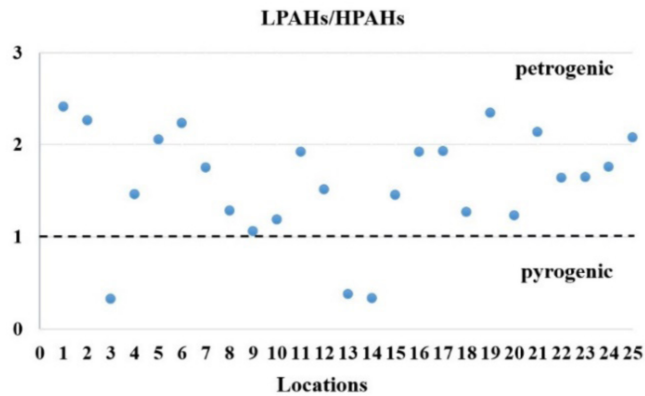

Figure 4 *Diagnostic ratio intended to identify PAHs sources in soils*

The PAH toxicities of soil samples were estimated using toxicity equivalency factors (TEF) as previously described (Škrbić et al., 2021). The TEF value indicates the toxicity and environmental risks of PAHs. As the most toxic PAH among 16 USEPA priority PAHs, benzo(a)pyrene BaP was used as the reference chemical with defined TEF value of 1. TEF values for other PAHs were assigned based on their carcinogenic level relative to that of BaP. The carcinogenic potency of each analysed soil sample was calculated as the toxicity equivalent quotient (TEQ) which is obtained as the sum of BaP equivalent concentrations (∑BaPeq) as follows:

$$TEQ = (\sum BaPeq) = \sum (TEF\ PAH_i \times PAH_i) \qquad (1)$$

where PAH_i represents the detected concentration of the *i*-PAH compound in analysed sample.

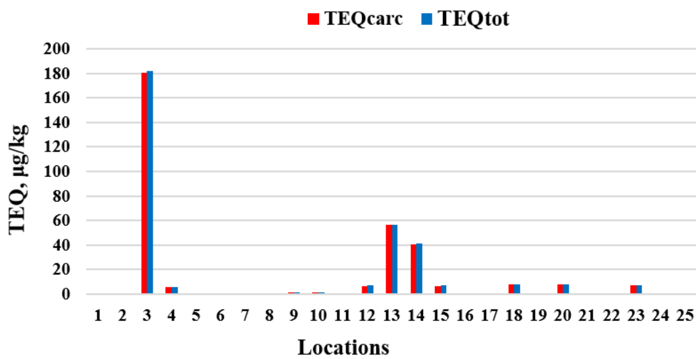

Figure 5 *The carcinogenic potency of analyzed soil samples*

The values of TEQ calculated for total PAHs (TEQtot) and carcinogenic PAHs (TEQcarc) were nearly identical (Figure 5). This implies that carcinogenic PAHs predominantly contributed to the total carcinogenic potency of the investigated soil samples. The risk from PAHs detected in soils was mainly affected by heavy compounds, i.e. PAHs with the highest TEF values (BaP and DahA with a TEF of 1; BaA, BbkF and IcdP with aTEF of 0.1).

TEQ values calculated for each location ranged from 0.02 µg/kg to 181 µg/kg. The carcinogenic potency of soil at the aforementioned three locations (especially location 3) was significantly higher compared to other locations. However, according to the Canadian soil quality guidelines for the protection of environmental and human health, TEQ values for these soil samples did not exceed the set value of ∑BaPeq of 600 µg/kg, which is considered a safe limit. Therefore, the concentration of PAHs in these soils might pose a low potential carcinogenic risk.

CONCLUSION

PAHs are a global concern for both environmental and human health. In this paper, PAH analysis was performed on 25 soil samples from around the Copper Mining and Smelting Complex Bor. The results showed that the examined area was not significantly affected by PAH contamination. Only at one location did the PAH concentration exceed the target value for the sum of 10 PAHs as prescribed by the Serbian Directive. Generally, the dominant PAHs detected in the soils were 3-ringed and 4-ringed PAHs. The diagnostic ratio of LPAHs/HPAHs was predominantly >1, indicating a mostly petrogenic PAH source in the study areas, while on only three locations this ratio was <1, which indicated a pyrogenic PAH source. TEQ values determined for all soil samples did not exceed the value of 600 µg/kg, which is considered a safe limit. This investigation provides valuable data on the PAHs presence in soils around the Copper Mining and Smelting Complex Bor and reveals a low environmental risk, except for one location.

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