

DISTRIBUTION OF PAHs IN SOILS FROM THE BOR REGION, TAKEN FROM THE ROOTING ZONE OF POISON IVY

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Abstract

In this work, the distribution of polycyclic aromatic hydrocarbons (PAHs) was examined in the soil from the Bor region, sampled from the rooting zones of poison ivy. The samples were taken from different locations in the Bor town and its surroundings and analyzed using gas chromatographic-mass spectrometric method, and hierarchical cluster analysis with the average linkage between groups as an appropriate statistical method. The obtained results soundly illustrated the distribution of individual PAHs in soil and simultaneously, they indicated probable PAH sources, i.e., anthropogenic or natural. In accordance with the obtained hierarchical dendrogram, it can be supposed that only benzo(a)pyrene had a natural origin (from different processes in the soil), whereas all other PAHs had anthropogenic, i.e. atmospheric origin. The grouping of the latest compounds showed that they were kept in soil for different - longer or a shorter time.

Keywords: HCA, distribution, soil PAHs

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants with complicated aromatic structures in their molecules. Their lipophilic features (Table 1), coming from the present benzene molecules, allow an easy connection to soil particles, i.e., soil organic matter, where they can stay for a very long time [1, 2, 3]. In addition, they can be generated in soils from different diagenetic, and biogenic sources [2, 4]. The most important PAH compounds, together with their main characteristics are given in Table 1.

The main problem with these dangerous pollutants is their persistence in soil (the so called “ageing” with time), and generally – persistence in the complete environment; their toxicity, and in some cases, even carcinogenicity is also of concern (Table 1). For example, PAHs that contain 3 to 5 benzene rings, can survive in the atmosphere for a few hours or days, while in soil, they can be present for decades [6]. Decades ago, at the beginning of industrial period, most kinds of soils (without a direct exposition to PAH sources), had low concentrations of individual PAHs: 1–10 µg/kg; however, at the beginning of 21st century, this range extended to 100 µg/kg [3]. Recently, as informed by Gasecka et al. [7], some studies found that the concentrations of individual PAHs in soils can vary from “not detected” (nd) to several hundred of µg/kg. For instance, Awere et al. [8] reported that in Ghana, near an e-waste recycling site, it was detected 390–710 ng of PAHs in a 1 g of soil.

Table 1 - Polycyclic aromatic hydrocarbons with their physical and chemical properties^a

Compound / Abbreviation	Molecular Weight	Solubility (µg/L)	Vapor Pressure ^c (mm Hg)	Henry's Law Constant ^c (atm·m ³ /mol)	Log K _{ow} ^d	Log K _{oc} ^e
LMW (Low Molecular Weight: 2–3 rings)						
Naphtalene / Nap	128.19	31.69	0.087	4.83·10 ⁻⁰⁴	3.36	2.97
Acenaphthylene / Acy	152.20	3.930	2.9·10 ⁻⁰²	1.45·10 ⁻⁰³	4.07	1.40
Acenaphthene / Ace	154.21	1.930	4.5·10 ⁻⁰³	1.91·10 ⁻⁰⁵	3.98	3.66
Fluorene / Flr	166.20	1.680–1.980	3.2·10 ⁻⁰⁴	1.00·10 ⁻⁰⁴	4.18	3.86
Anthracene / Ant	178.20	76	1.7·10 ⁻⁰⁵	1.77·10 ⁻⁰⁵	4.45	4.15
Phenanthrene / Ant	178.20	1.200	6.8·10 ⁻⁰⁴	2.56·10 ⁻⁰⁵	4.45	4.15
MMW (Medium Molecular Weight: 4 rings)						
Fluoranthene / Flt	202.26	200–260	5.0·10 ⁻⁰⁶	6.50·10 ⁻⁰⁶	4.90	4.58
Pyrene / Pyr	202.30	77	2.5·10 ⁻⁰⁶	1.14·10 ⁻⁰⁵	4.88	4.58
Benzo(a)anthracene ^b / BaA	228.29	10	2.2·10 ⁻⁰⁸	1.00·10 ⁻⁰⁶	5.61	5.30
Chrysene ^b / CHR	228.30	2.8	6.3·10 ⁻⁰⁷	1.05·10 ⁻⁰⁶	5.16	5.30
HMW (High Molecular Weight: ≥ 5 rings)						
Benzo(a)pyrene ^b / BaP	252.30	2.3	5.6·10 ⁻⁰⁹	4.90·10 ⁻⁰⁷	6.06	6.74
Benzo(b)fluoranthene ^b / BbF	252.30	1.2	5.0·10 ⁻⁰⁷	1.22·10 ⁻⁰⁵	6.04	5.74
Benzo(e)pyrene / BeP	252.30	6.3	5.7·10 ⁻⁰⁹	NA	NA	NA
Benzo(k)fluoranthene ^b / BkF	252.30	0.76	9.6·10 ⁻¹¹	3.87·10 ⁻⁰⁵	6.06	5.74
Benzo(j)fluoranthene / BjF	252.32	6.76	1.5·10 ⁻⁰⁸	1.00·10 ⁻⁰⁶	6.12	4.7–4.8
Indeno(1,2,3-c,d)pyrene ^b / IcP	276.30	62	1.0·10 ⁻¹¹ –1.0·10 ⁻⁰⁶	6.95·10 ⁻⁰⁸	6.58	6.20
Benzo(g,h,i)perylene / BgP	276.34	0.26	1.0·10 ⁻¹⁰	1.44·10 ⁻⁰⁷	6.50	6.20
Dibenz(a,h)anthracene ^b / DhA	278.35	0.5	1.0·10 ⁻¹⁰	7.30·10 ⁻⁰⁸	6.84	6.52

^a Table adapted from [5]^b Classified by US EPA as a probable human carcinogen [9]^c Indicates the chemical's potential to volatilize^d Provides an indication of the potential for the organic compound to partition from water into lipids^e Indicates a compound's potential to bind to organic carbon in soils

NA = no data available

In Bor's region, the concentrations of soil PAHs were investigated mostly through examinations of plants' bioremediation and phytoremediation potentials [10, 11] and in this work, the spatial soil samples taken from the roots of poison ivy (PI), collected from different locations, were also used for the detection of present PAHs and a processing by the related statistical method that may help in illustration of PAH distribution in soil of the studied region.

2. EXPERIMENTAL

The concentrations of soil PAHs were determined in the related spatial soil samples of PI as described in Papludis et al. [12]. Shortly, the representative soil samples of PI were taken from the rooting zone, from 9 sites in Bor's municipality, in September 2020. Dried samples were homogenized, and then PAHs were isolated using a QuEChERS (Quick, Effective, Cheap, Easy, Rugged, Safe) method and analyzed by gas chromatographic-mass spectrometric (GC/MS) method. All samples were analyzed in triplicate and results are showed in µg/kg (dry weight, DW), in Papludis et al. [12].

Soils were collected from different sites in rural (R), and urban/industrial (UI) zone. The R zone encompasses 5 sites: Oštrej (O), Slatina (S), Borsko jezero (BJ), Krivelj (K), and Gornjane (G), whereas UI zone had 4 sites: Flotacijsko jalovište (FJ), Bolničko naselje (BN), Slatinsko naselje (SN) and Naselje Sunce (NS).

Hierarchical cluster analysis (HCA) with the average linkage between groups as an appropriate method (for the identification of homogenous groups of the examined PAHs) was conducted in terms of getting a picture of PAH distribution in the analyzed [13]. IBM SPSS Statistics 20 software (USA) was applied.

3. RESULTS AND DISCUSSION

The detected soil PAH concentrations ranged from nd (not detected) for Ant, CHR, BkF+BbF, and DhA at many sites to over 500 µg/kg for Flt at the sites FJ, and O [12]. On the basis of these

concentrations, which were treated as variables, the average linkage between groups was applied in HCA method and the following hierarchical dendrogram was computed (Fig. 1):

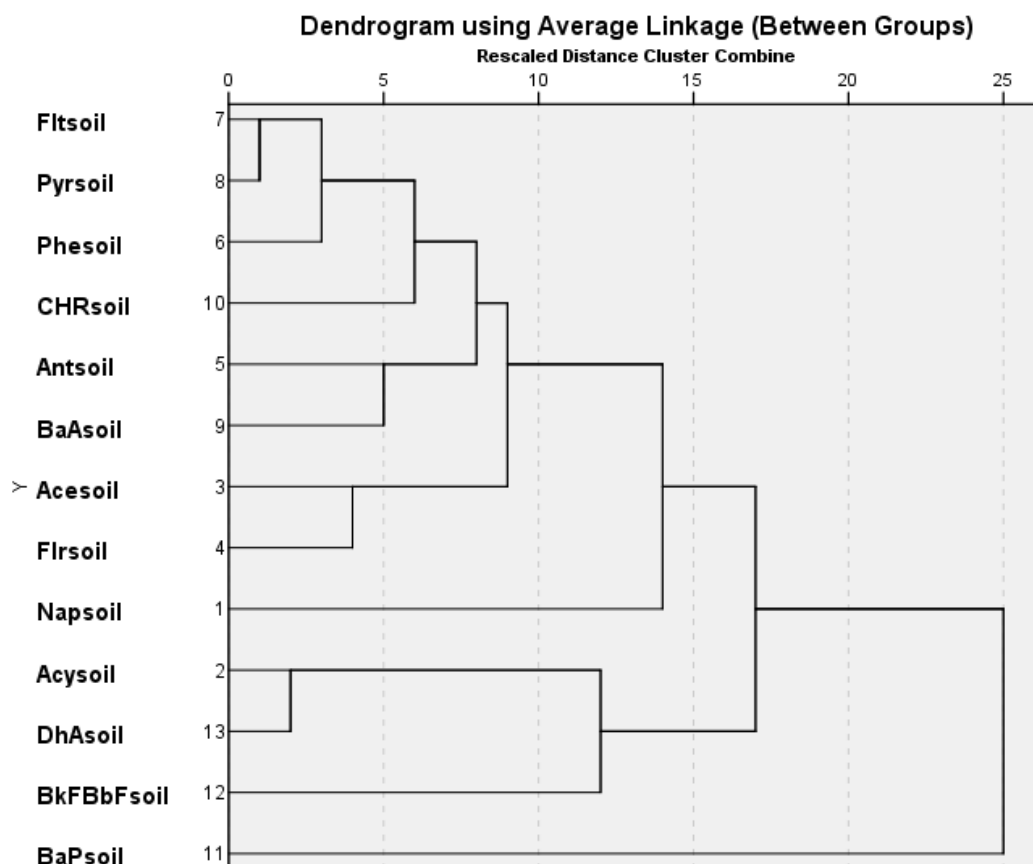


Figure 1. Homogenous groups of PAH compounds for the investigated soil in the region of Bor

The hierarchical dendrogram for the investigated soil PAHs of PI showed the two main clusters: an isolated cluster for BaP, and the other main cluster composed of all other compounds, represented in the form of numerous subclusters, in the arrangement as follows: the first main subcluster contained several subclusters such as: BbF+BkF/DhA-Acy, and the second main subcluster containing an isolated subcluster for Nap, and the other subcluster with the following groupings of compounds: Flr-Ace, BaA-Ant, and CHR/Phe/Pyr-Flt (Figure 1). This dendrogram clearly showed that the greatest distance occurred between the latest group of compounds (CHR/Phe/Pyr-Flt), and BaP (which formed an isolated cluster from all other compounds), which further pointed on its dissimilar origin; namely, it was probably mainly formed in the soil, during some natural processes [2, 4]; finally, the lowest concentrations of individual soil PAHs were found in this particular case, i.e., in the case of BaP. At the same time, it can be supposed that the latest mentioned group of compounds, i.e., CHR, Phe, Pyr, and Flt, had the most similar origin (which is the most dissimilar in comparison with the origin of BaP). This may signify that their origin can be connected with the influence of anthropogenic, practically, atmospheric pollution. More precisely, it can be say that this group of compounds “came” to soil the most recently, representing the “freshest” anthropogenic PAHs in the investigated soils. For all other compounds, it can be also assumed that they originated from the atmosphere but probably, they were not so “fresh”, i.e. it is very possible that, in some extent, they were subjected to different “ageing” processes.

4. CONCLUSION

The results obtained from the applied chemical, and statistical methods soundly reflected the distribution of individual PAHs in soil of the region of interest and at the same time, pointed on

probable PAH sources, i.e., anthropogenic or natural. According to the obtained hierarchical dendrogram, it can be said that only BaP originated from natural processes in soil, whereas all other PAHs originated from anthropogenic, i.e. atmospheric sources; these latest compounds were retained in soil for a longer or a shorter time.

ACKNOWLEDGEMENTS

The research presented in this paper was done with the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor (contract number 451-03-137/2025-03/200131), and at the University of Niš, Faculty of Science and Mathematics in Niš (contracts' numbers 451-03-137/2025-03/200124, and 451-03-136/2025-03/200124).

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