

Original Research

AN ASSESSMENT OF THE PRESENCE OF DIBENZ(a,h)ANTHRACENE, A PROBABLE HUMAN CARCINOGEN, IN THE BOR REGION, ON THE BASIS OF ITS CONTENT IN STEMS AND LEAVES OF COMMON IVY, LILAC, AND FIG

DOI: 10.5937/EcoTER26051P

**Aleksandra Papludis^{1,a*}, Slađana Alagić^{1,b}, Snežana Milić^{1,c}, Dragana Medić^{1,d},
Jelena Nikolić^{2,e}, Vesna Stankov Jovanović^{2,f}, Gordana Stojanović^{2,g}**

¹ University of Belgrade, Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, SERBIA

² University of Nis, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33,
18000 Niš, SERBIA

^a <https://orcid.org/0000-0002-5388-2428>

^b <https://orcid.org/0000-0002-2893-9285>

^c <https://orcid.org/0000-0002-5000-9156>

^d <https://orcid.org/0000-0001-9980-5949>

^e <https://orcid.org/0000-0002-9351-331X>

^f <https://orcid.org/0000-0001-7885-0476>

^g <https://orcid.org/0000-0002-3128-6510>

Abstract

In this work, the capacity of unwashed aerial parts of plant species: common ivy (CI), lilac (CL), and fig (CF), for DhA detection in biomonitoring purposes was investigated, using GC/MS, and the Pearson's correlation analysis. Additionally, the detected DhA concentrations were compared with the interrelated lawmaking. GC/MS detected many considerable DhA quantities and documented different capacity of the investigated species for DhA deposition/bioaccumulation, where CI, and CF, showed a better ability for the atmospheric dust retention than CL. However, the highest DhA concentrations were detected in CL parts: 1200.9 µg/kg for stems, and 174.5 µg/kg for leaves, which is even higher than the related USEPA limit values (LVs) for residential soils. Simultaneously, for CL parts, the highest number of locations lacking in DhA was found. Other species showed that almost all selected locations had measurable DhA concentrations, often at the levels that surpassed mentioned USEPA LVs. This means that all locations with such levels may signify possible dermal risks from direct contacts with aerial parts. The results of the Pearson's analysis confirmed that the industrial center in Bor, with the heating plant and the mining-metallurgical complex, can be one of significant but not the main source of DhA.

Keywords: Dibenz(a,h)anthracene, common ivy, lilac, fig, biomonitoring.

INTRODUCTION

Dibenz(a,h)anthracene (DhA) is a polycyclic aromatic hydrocarbon (PAH) consisting of five aromatic rings. It is mainly used for research purposes. In the environment, it occurs as a

* apapludis@tfbor.bg.ac.rs

result of the incomplete combustion of organic materials [1], and DhA it is primarily present in emissions produced during the combustion of gasoline, wood, and coal [2].

Some of the most important chemical and physical properties of DhA are as follows: form (at the room temperature) – solid, colorless, with a "bay-region" structure (Figure 1), formula – $C_{22}H_{14}$ [3], molecular weight - 278.35, solubility - 0.5 $\mu\text{g/L}$, vapor pressure - $1.0 \cdot 10^{-10}$ mm Hg, Henry's Law Constant - $7.30 \cdot 10^{-08}$ atm m^3/mol , Log K_{ow} - 6.84, and Log K_{oc} - 6.52 [4]. The reported values proves high lipofility of this compound, which normally enables an easy infiltration through biological membranes of various living organisms.

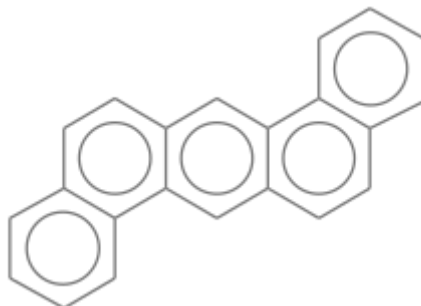


Figure 1 Molecular structure of DhA [3]

This compound can enter the human body through skin absorption or inhalation lung, after which it is dissolved in blood and distributed further to various target organs. In the body of experimental animals, more precisely, in their liver, it is metabolized by mixed-function oxidase enzymes, forming and transformed into dihydrodiols. Further epoxidation of the intermediate: 3,4-dihydrodiol, can lead to the formation of a diol-epoxide, which is considered the ultimate carcinogenic metabolite of dibenz(a,h)anthracene DhA [1]. Studies showed that the exposure to DhA has been closely linked to a higher risk of various respiratory illnesses, including asthma, obstructive lung diseases, and respiratory infections [2]. However, there are no studies evaluating its toxicity in humans. Based on confirmed evidence of carcinogenicity in animals, the United States Environmental Protection Agency (USEPA) has classified dibenz(a,h)anthracene this PAH compound as a B2 substance, meaning it is which means that it can be considered a probable human carcinogen [1].

From this reason, USEPA included DhA into the list of 16 priority PAHs that are the most dangerous for all living organisms [4–6]. They all can be found in USEPA Risk-Based Screening Tables, which contain the defined limit values (LVs) for each of 16 PAHs in tap water as well as in residential and industrial soil. A particular attention of this Agency was paid to the soil because it represents a very slowly renewable natural resource [7], which serves as a main environmental sink for PAHs [8]. In the case of this environmental sphere, when concentrations of PAHs are equal to or surpass the related LVs, further evaluations are required for the potential remediation. USEPA LVs are calculated on the basis of the target cancer risk (TR) of $1 \cdot 10^{-6}$ and 2 standards of the target hazard quotients (THQ): 1.0 and 0.1. The defined LVs for both standards for DhA in residential and industrial soils are: 0.11 and 2.1 mg/kg, respectively [5,6,9].

Unfortunately, there are still no defined toxicity LVs for DhA in plants, and also, in the scientific literature data, there are no any suggestions regarding this issue.

In this paper, the content of DhA is detected to establish, for the very first time, its concentrations in the above ground parts of the selected plants from the Bor region, as a well known highly polluted region but chiefly by heavy metals. The selected plants were: common ivy (CI), lilac (CL), and fig (CF) var. crna Petrovača, due to the fact that these plants were not investigated earlier with regard to PAH biomonitoring. Also, there was a hope that the detected DhA concentrations in the above ground parts of these plants can point to the environmental quality of the investigated region, primarily considering DhA pollution that comes from the atmosphere, and perhaps from the emissions of the city heating plant and the mining-metallurgical complex, as possible main sources.

MATERIALS AND METHODS

The contents of DhA were evaluated in the unwashed stems and leaves of CI, CL, and CF assembled at 9 locations from urban-industrial (UI), rural (R) and 1 touristic (T) zone from the Bor region. Touristic zone was a location next to the Borsko jezero (BJ), (eng. Bor Lake), while the locations from R zone were settlements: Oštrelj (O), Slatina (S), Krivelj (K), and Gornjane (G); sites from UI zone were: Flotacijsko jalovište (FJ), Bolničko naselje (BN), Slatinsko naselje (SN), and Naselje Sunce (NS). The distances of the mentioned sites from the city heating plant and the copper smelter in the industrial zone of the town of Bor are as follows: 0.7 km for FJ – flotation tailings pond out of use, 1.3 km for the site BN, near the city hospital, then for the two sites at the periphery of the town - 3.2 km for SN, and 3.6 km for NS. The sites in R zone are located as follows: 4.5 km for O, 6.5 km for S, 8 km for K, and 19 km for G. The distance for BJ site is 7 km.

The samples of the chosen plant parts were taken at the selected sites in September 2020, and analyzed as dried, unwashed material, in the same way as explained in Papludis *et al.* [5], and Papludis *et al.* [10] for (washed) roots and the corresponding soils of the same plant species. Leaves and stems of CI, CL, and CF, were used as unwashed, given that in this way they can reflect an actual state of seasonal pollution in the Bor region. Namely, unwashed aerial parts reflect the sum of an atmospheric deposition, and bioaccumulation of contaminants in these parts. Most importantly, for DhA isolation, the partially modified QuEChERS (Quick, Effective, Cheap, Easy, Rugged, Safe) technique was used [5,8], while for its identification and quantification, gas chromatographic-mass spectrometric (GC/MS) method was performed. The results are given in µg/kg DW (dry weight).

Additionally, the results of chemical analysis were subjected to the Pearson correlation analysis as a statistical method that may help in biomonitoring procedures, pointing to main sources of the pollutant, i.e., DhA, on the basis of correlations between the detected DhA contents and the parameter: distance (D). In the concrete study, this parameter denotes the distance of the sampling sites from the industrial center in the town of Bor as the possible main source of DhA pollution.

RESULTS AND DISCUSSION

The results of GC/MS analysis for DhA contents in leaves and stems of CI, CL, and CF are given in Table 1.

Table 1 The content of DhA ($\mu\text{g/kg}$, dw) in the leaf and stem samples of CL, CF, and CI

Location / Plant species and their parts	CL		CF		CI	
	Leaf	Stem	Leaf	Stem	Leaf	Stem
FJ	nd	nd	128 ± 0.5	161 ± 8	130.7 ± 3.5	170.6 ± 2.5
BN	nd	1200.9 ± 88.5	87 ± 3	230 ± 0.5	112 ± 4	87 ± 4
SN	nd	nd	72.7 ± 3.5	190 ± 5	59.96 ± 3.66	nd
NS	174.5 ± 6.8	nd	89.4 ± 2.6	73.4 ± 1.6	110 ± 7	72.7 ± 7.1
O	nd	nd	96.2 ± 1.5	149.2 ± 4.5	111 ± 3.8	117 ± 18
S	nd	nd	27.46 ± 2.15	98 ± 9	28 ± 2.3	95.11 ± 4.27
BJ	47.3 ± 3.6	950.3 ± 41.7	40.3 ± 3.5	142.56 ± 2.39	58 ± 10	69 ± 4
K	84 ± 1	nd	53.2 ± 3.5	nd	45.4 ± 1.7	124 ± 1.9
G	35.7 ± 3.5	nd	13.8 ± 0.8	nd	76 ± 2	99 ± 7

Based on the obtained results, it can be said that the concentrations of DhA varied among plant species but also among plant parts, as well as among locations and there were no any rules that can be defined. The highest DhA concentration was detected in the case of CL stems, at the U/I site BN: $1200.9 \mu\text{g/kg}$. The highest DhA concentration for leaves was found in the same plant species, at the site NS: $174.5 \mu\text{g/kg}$ (also in U/I zone). However, at the same time, this plant species had the highest number of locations with DhA level: nd (in comparison with CF, and CI). In the case of CF, and CI above ground parts, DhA was detected at almost all locations, mostly in significant concentrations (Table 1), which may suggests a better tendency of their aerial organs for atmospheric dust capturing. This situation, namely, the variability in DhA presence and its quantities in plant parts at the selected locations may also represent a first signal of the existence of different sources of DhA in the investigated region.

Interestingly, in many cases, the obtained DhA values were higher than the corresponding USEPA LVs for residential soil, considering both defined standards for THQ [6]. This further indicates that, similarly to the case with soil, a direct contact with the stems and leaves of the investigated plants at some locations could pose a risk from DhA, primarily regarding the human skin (at points of direct contacts). These locations (given in bold in the Table 1) are as follows:

- 1) site NS for CL leaves, and sites BN, and BJ, for CL stems;
- 2) site FJ for CF leaves, and sites FJ, BN, SN, O, and BJ for CF stems, and
- 3) sites FJ, BN, NS, O, and K for CI leaves, and sites FJ, O, and K for CI stems.

Almost all other DhA values for its deposition/bioaccumulation in the investigated plant parts were below the detection limits (marked as: nd) and only at few locations, some measurable values were recorded.

As explained, in terms of obtaining safe information on plants' parts usability in the detection of assumable DhA major sources, the Pearson correlation analysis was applied to the detected concentrations and the parameter D. The results showed that the Pearson's

correlation coefficients mostly had negative character, which points that the concentrations of DhA decreased with D increasing. This is normally to expect in the case of point sources, which may signalize that DhA had an origin that can be connected with the industrial center in Bor. However, given that the computed values were very low, it can be concluded that the supposed connection was at the very low level, too, and finally that - the city heating plant and mining-metallurgical complex cannot be considered as the main and sources of DhA. Only the detected concentrations in stems and leaves of CF were in statistically significant correlations with D ($p = -0,755^*$, and $p = -0,804^{**}$, respectively). These facts represent one more proof that the industrial center can be one of significant but not the main source of DhA. Its other sources can be: traffic, heating in individual households based on wood and coal, controlled combustions in agricultural fields in autumn, spontaneous forest fires, as well as spontaneous ignitions in the city landfill, etc.

CONCLUSION

The results of chemical analysis in this work provided evidence of many cases with considerable DhA concentrations, and revealed different capacity of the investigated plant species for DhA deposition/biaccumulation, where CF, and CI, showed a better capability for the atmospheric dust retention in comparison with CL. However, the highest DhA concentrations were detected in CL aerial parts: 1200.9 $\mu\text{g/kg}$ for stems (at the site BN), and 174.5 $\mu\text{g/kg}$ for leaves (at the site NS), which are higher values than the proscribed USEPA LVs for residential soils. At the same time, this plant species showed the highest number of locations, which were without the detected DhA. The other plant species showed that almost all selected locations had measurable DhA concentrations, in many cases even at the levels that surpassed the related USEPA LVs. It can be concluded that all locations with these levels may represent a signal on possible dermal risks from a direct contact with plant parts considering all investigated species.

The results of statistical analysis pointed that the industrial center in Bor, with the heating plant and the mining-metallurgical complex, can be one of significant but not the main source of DhA. The other sources can be: traffic, domestic heating, controlled combustions in rural zone, spontaneous forest combustions, as well as spontaneous ignitions in the city landfill, etc.

ACKNOWLEDGEMENTS

The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, for all the financial support of this work, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor (contract number 451-03-34/2026-03/200131), and at the University of Niš, Faculty of Science and Mathematics in Niš (451-03-34/2026-03/200124).

REFERENCES

- [1] Bhattacharya, S., Chakraborty, P., Roy, S. Dibenz[a,h]anthracene, Editor: Philip Wexler, Encyclopedia of Toxicology (Third Edition), 2014, p. 62–66.

- [2] Xie, Y., Guo, Z., Liu, J. *et al.* Environ. Hlth. Adv. 2025, 13, 100120, 1–8.
- [3] Available from: <https://webbook.nist.gov/cgi/cbook.cgi?ID=53-70-3>
- [4] Alagić, S., Maluckov, B., Radojičić, V. Clean Technol. Environ. Res. 2015, 17, 597–614.
- [5] Papludis, A., Alagić, S., Milić, S. *et al.* Environments 12(8), 256.
- [6] USEPA, 2024. United States Environmental Protection Agency (2024): Risk-Based Screening Tables — Generic Tables; Regional Screening Levels, RSLs, Summary Tables (TR=1x10⁻⁶ and THQ=1.0, and THQ=0.1) May 2024. Available from: <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>
- [7] Petruzzelli, G., Pezzarossa, B. Pedron, F. Environments 2025, 12, 183.
- [8] Cvetkovic, J., Mitic, V., Stankov-Jovanovic, V. *et al.* Anal. Methods. 2016, 8, 1711–1720.
- [9] Alagić, S., Stankov-Jovanović, V., Mitić V. *et al.* Sci. Total Environ. 2016, 562, 561–570.
- [10] Papludis, A., Alagić, S., Milić, S. *et al.* Materials protection 2023, 64(1), 13–21.