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# Application of ultrasound-assisted liquid-solid extraction for the isolation of PAHs from organic-rich soil samples

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**Abstract:** Polycyclic aromatic hydrocarbons (PAHs) occur in soils at concentrations of  $\text{ng}\cdot\text{g}^{-1}$  or less, and their levels are influenced by a number of factors, including the content of organic matter. Extraction of PAHs from soils, enriched in organic fraction, can be problematic, time-consuming and cost-intensive. The aim of this study was to modify an ultrasound-assisted solid-liquid extraction method, used for the isolation of 16 priority PAHs from forest soils collected from soil (sub)horizons with different organic matter content. The following parameters were considered: (i) the type and volume of solvent, (ii) the time of extraction and (iii) the purification of extracts by the SPE method. The final qualitative and quantitative determination of 16 PAHs was performed by the GC-MS method. The following results were obtained: recovery 71-107%,  $R^2 = 0.993-0.999$ ,  $\text{LOD} = 0.008-0.026 \mu\text{g}\cdot\text{ml}^{-1}$  and  $\text{LOQ} = 0.024-0.078 \mu\text{g}\cdot\text{ml}^{-1}$ . The above method was successfully applied for the extraction of selected PAHs from organic soil samples collected from forest complexes located in south-central Poland.

## Introduction

Environmental monitoring plays a crucial role in assessing the quality of the environment. It involves the systematic collection of data on various environmental components, including soil, air and water, to identify changes and trends over time. Monitoring programs often require chemical analyses to meet standards set by environmental authorities. These studies aim to estimate the level of contamination by a range of compounds, including trace elements (e.g., Hg, Pb, Cd), pesticides, polycyclic aromatic hydrocarbons (PAHs), and other hazardous substances (Dołęgowska et al. 2024, Kostecki 2022, Pohl and Kostecki 2020, Seyfi et al. 2021).

PAHs are a class of organic compounds characterized by the presence of at least two benzene rings in their structure. They are common in the environment and tend to accumulate in plants and soils (Patel et al. 2020, Premnath et al. 2021). Routine environmental monitoring usually involves the identification of 16 PAHs - acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, perylene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene which have been recognized by the United States Environmental Protection Agency (US EPA) as priority pollutants due to their mutagenic and carcinogenic properties (Mogashane et al. 2024, Saeedi et al. 2020, Venkatraman et al. 2024). PAH properties are determined by the molecular weight

of the compound. Heavy PAHs, containing 5- and 6-aromatic rings, are more stable, less polar and less soluble than low-molecular-weight (LMW) PAHs, which consist of 2, 3, and 4 benzene rings (Patel et al. 2020, Premnath et al. 2021). These properties influence how PAHs behave in the environment, in the atmosphere, in water, and in soil (Mogashane et al. 2024, Pohl and Kostecki 2020, Ukalska-Jaruga et al. 2019, Venkatraman et al. 2024).

PAHs can be formed through natural processes such as volcanic eruptions, natural fires, or soil-forming processes (Patel et al. 2020, Pohl and Kostecki 2020, Ukalska-Jaruga and Smreczak 2020). However, the main source of these compounds is anthropogenic activity. They are released into the atmosphere as a result of the incomplete combustion of fossil fuels, petroleum, biomass (e.g., grass, wood), as well as a by-product of several industrial processes, including the production of aluminum, cement, iron, rubber and steel (Gholami et al. 2024, Mogashane et al. 2024, Patel et al. 2020, Premnath et al. 2021, Ukalska-Jaruga et al. 2020). In the atmosphere, they can be transported over long distances (LMW PAHs) or deposited near their sources of formation (HMW PAHs) (Venkatraman et al. 2024).

In the environment, PAHs can accumulate in their two natural reservoirs: plants and topsoils (Sushkova et al. 2020). In temperate climate zones, the uppermost part of forest soils is the organic soil horizon (O), which consists of various, more or less developed, soil subhorizons – for example the organic litter subhorizon (OI) or the organic fermentative-humic subhorizon

(Ofh) (Hartemink et al. 2020). Organic (sub)horizons are rich in organic matter, which binds PAHs tightly, making their extraction more difficult. Furthermore, organic matter can interfere with chromatographic analysis by producing signals similar to those of the target compounds (Ukalska-Jaruga et al. 2019). The extraction efficiency of PAHs from organic-rich soils can also be affected by soil texture and composition, as well as the presence of heavy metals. However, their role is less significant compared to that of organic matter, which acts as a key binding agent for PAHs (Saeedi et al. 2020, Ukalska-Jaruga et al. 2019, Zuloaga et al. 2000).

The determination of PAHs in solid environmental samples requires their prior transfer into a liquid solvent. This step often represents a bottleneck in both the qualitative and quantitative analysis of these compounds due to their diverse properties, including solubility, volatility, adsorption capacity, and biodegradability. Therefore, during the extraction process, special attention should be paid to both the characteristics of PAHs and the properties of the sample, such as pH and organic matter content, as these factors affect PAH sorption and accumulation (Gholami et al. 2024, Saeedi et al. 2020, Ukalska-Jaruga et al. 2019).

PAHs are commonly found in the environment; therefore, there is a growing need to develop new, more environmentally friendly extraction methods. According to the principle of green chemistry, such methods should be simple, fast, efficient, environmentally friendly and require low volumes of reagents. Several techniques are available for the extraction of PAHs from solid samples, including soil. These include Soxhlet extraction (Famiyeh et al. 2021, Mogashane et al. 2024, Silalahi et al. 2021) and mechanical shaking (Famiyeh et al. 2021, Mogashane et al. 2024, Silalahi et al. 2021, Sushkova et al. 2020), both of which are time-consuming and require large volumes of solvent. Faster and more efficient, but more expensive, alternatives include supercritical fluid extraction (SFE) (Famiyeh et al. 2021, Mogashane et al. 2024), pressurized liquid extraction (PLE) (Mogashane et al. 2024), subcritical water extraction (SWE) (Kariyawasam et al. 2023, Sushkova et al. 2020), and microwave assisted extraction (MAE) (Famiyeh et al. 2021, Kariyawasam et al. 2023, Mogashane et al. 2024). An alternative method that is similarly fast and easy, but less expensive, is ultrasound-assisted extraction (sonication) (Dołęgowska et al. 2025, Famiyeh et al. 2021, Mogashane et al. 2024, Silalahi et al. 2021, Sun et al. 1998). Therefore, the aim of this work was to modify an ultrasound-assisted extraction procedure for isolating 16 priority PAHs from soil samples with varying organic matter content. A similar methodology was used by Ozcan et al. (2009) and by Baran and Oleszczuk (2002). However, in the study by Ozcan et al. (2009), the soil samples used had low organic matter content (~1.8%), whereas organic horizons (e.g. Ofh) may contain up to 80% organic matter (Dołęgowska et al. 2024). In contrast, Baran and Oleszczuk (2002) analyzed sewage sludge using a different solvent mixture.

In this study, the optimization process involved evaluating the following parameters: (i) the type and volume of solvent, (ii) the extraction time, and (iii) the purification of extracts using the SPE method. The final qualitative and quantitative determination of PAHs was performed using the GC-MS method. To test the hypothesis that the modified procedure can

be used in routine monitoring programs, PAHs were analyzed in 12 soil samples collected from two pine forest areas located in south-central Poland.

## Materials and methods

### *Fieldworks and sample preparation*

Twelve soil samples were collected from two pine forest areas with dense tree cover and abundant mosses, located in south-central Poland. Area 1 is situated approximately 40 km from the city of Kielce, near the villages of Zajączków and Wesoła. In contrast, area 2 is located within the administrative boundaries of the city, in proximity to a local cemetery and single-family houses.

Area 1 was defined as an unpolluted site, as the concentrations of trace elements, such as cadmium, in soil samples from this area were up to twenty times lower than those in samples collected near Kielce (Dołęgowska et al. 2024).

The soils in both areas are predominantly podzolic, characterized by a well-developed organic soil horizon transitioning into a humus-eluvial horizon. Samples were collected from individual soil (sub)horizons with distinct compositions and structures: the organic fermentative-humic subhorizon (Ofh) and the humic-eluvial (AE) horizon. Two samples were collected from area 1, while ten samples from area 2. The thickness of the Ofh subhorizon ranged from 2 to 5 cm. After collection, the soil samples were placed in dark glass jars and transported to the laboratory. There, the samples were dried in a dark room at room temperature, sieved ( $\varnothing < 2$  mm, Analysette 3 Spartan, FRITTSCH, Germany), and milled (Pulverisette 2 Fritsch, FRITTSCH, Germany).

### *Short characteristics of soil samples*

Soil samples taken from the Ofh-subhorizon and the AE horizon revealed significant differences in their physicochemical parameters, including pH, electrolytic conductivity (EC), soil organic matter content, as well as concentrations of major and trace elements. The average pH of samples from the Ofh-subhorizon was 4.6, nearly one unit lower than that of the horizon AE. Furthermore, the EC levels differed fivefold between the two horizons. It is noteworthy that the organic matter content was significantly greater in the Ofh-subhorizon, with an average value 17 times higher than that observed in the AE horizon, and a recorded maximum of 81%. A similar trend was observed for the concentrations of trace and major elements (Cd: Ofh 0.947 mg·kg<sup>-1</sup>, AE 0.205 mg·kg<sup>-1</sup>; Hg: Ofh 0.191 mg·kg<sup>-1</sup>, AE 0.055 mg·kg<sup>-1</sup>; Pb: Ofh 50.0 mg·kg<sup>-1</sup>, AE 31.0 mg·kg<sup>-1</sup>; S: Ofh 1929 mg·kg<sup>-1</sup>, AE 823 mg·kg<sup>-1</sup>; Fe: Ofh 3734 mg·kg<sup>-1</sup>, AE 2559 mg·kg<sup>-1</sup>) (Dołęgowska et al. 2024).

### *Chemicals and materials*

To optimize the procedure of PAH extraction, the following reagents were used:

- A standard solution of 16 PAHs: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene (124812X, VWR

BDH CHEMICALS®). The concentration of each PAH in the standard solution was 0.1 mg·ml<sup>-1</sup>.

- Pure methanol, dichloromethane (Chempur®), acetone, n-hexane (Merck®), and ethyl acetate (VWR BDH CHEMICALS®).
- Certified reference material (CRM): contaminated soil containing PCBs and PAHs (LGC6115, LGC Standards).

Ultrasound-assisted extraction was done using an ultrasonic bath (Bandelin Sonorex™). The extracts were purified using PTFE syringe filters (25 mm, 0.22 µm, GILSON), and solid-phase extraction (SPE) was carried out with 3 ml/500 mg C18 glass cartridges.

### GC-MS analysis

Sixteen PAHs were determined using a gas chromatograph coupled with a mass spectrometer (Clarus 600T, Perkin Elmer, USA). PAHs were separated on Elite 5-MS capillary column (l: 30 m, i.d.: 0.25 mm, film: 0.25 µm). The GC-MS method parameters were as follows: the temperature was initially set at 70°C and held for 2 min, then increased to 150°C at a rate of 20°C·min<sup>-1</sup>, followed by an increase to 300°C at 10°C·min<sup>-1</sup>, where it was held for 10 min. A 5 µl sample was injected in split mode (1:10). Helium (purity ≥99.9999%) was used as the carrier gas, with a constant flow rate of 1 ml·min<sup>-1</sup>. The ion

source and transfer line temperatures were set at 250°C. The MS analysis was performed in both SCAN and SIM modes. The total run time was 30 min.

### Calibration curves and linearity

Standard solutions of 16 PAHs in pure methanol (Chempur®) were prepared in the concentration range of 0.008–20.0 µg·ml<sup>-1</sup>. Each solution was analyzed in triplicate. The linear range was established between 0.020–5.000 µg·ml<sup>-1</sup> with R<sup>2</sup> ranging from 0.993 to 0.999 and relative standard deviations (RSD) between 2.76 to 8.38% (n=3). Limits of detection (LOD), determined as a signal-to-noise ratio of 3:1, ranged from 0.008–0.026 µg·ml<sup>-1</sup>. Limits of quantification (LOQ), calculated as LOQ = 3·LOD, ranged from 0.024 to 0.078 µg·ml<sup>-1</sup>. Detailed data on the analyzed PAHs and corresponding calibration curves are presented in Table 1.

### Extraction parameters

The ultrasound-assisted liquid-solid extraction method proposed by Sun et al. (1998) was modified in following aspects: (i) type of solvent, (ii) solvent volume, and (iii) extraction time (Fig. 1). The procedure was optimized using a soil sample from area no 1. Details of the optimized parameters are summarized in Fig

**Table 1.** Data on the tested PAHs and the calibration curves.

PAHs	Regression coefficient	Linearity range [µg·ml <sup>-1</sup> ]	RSD [%]	LOD [µg·ml <sup>-1</sup> ]	LOQ [µg·ml <sup>-1</sup> ]
Acenaphthylene	0.999	0.020–5.000	6.36	0.009	0.027
Acenaphthene	0.999		4.57	0.026	0.078
Fluorene	0.999		8.38	0.009	0.027
Phenanthrene	0.999		6.08	0.008	0.024
Anthracene	0.999		3.23	0.008	0.024
Fluoranthene	0.999		4.49	0.013	0.039
Pyrene	0.999		4.63	0.008	0.024
Benzo[a]anthracene	0.999		2.87	0.009	0.027
Chrysene	0.999		3.37	0.008	0.024
Benzo[b]fluoranthene	0.999		4.95	0.009	0.027
Benzo[k]fluoranthene	0.993		3.74	0.009	0.027
Benzo[a]pyrene	0.999		2.76	0.011	0.033
Perylene	0.997		6.68	0.013	0.039
Indeno[1,2,3-cd]pyrene	0.998		3.82	0.013	0.039
Dibenzo[a,h]anthracene	0.998		3.45	0.026	0.078
Benzo[ghi] perylene	0.999		4.41	0.013	0.039

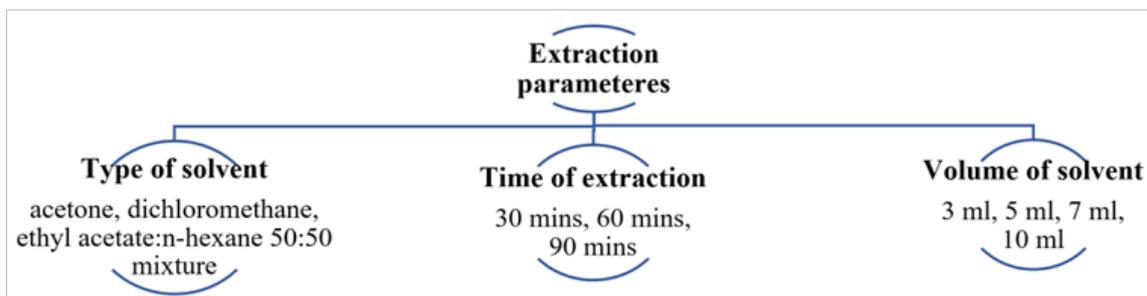


Fig. 1. Scheme of optimised extraction parameters.

### Type of solvent and extraction time

1 g of the sample was placed in each of screw-cap glass tubes and spiked with 200  $\mu\text{l}$  of PAH standard solution ( $0.156 \mu\text{g}\cdot\text{ml}^{-1}$ ). Subsequently, 10 ml of (i) acetone, (ii) dichloromethane, or (iii) a 50:50 mixture of ethyl acetate and n-hexane was added to the samples, which were then subjected to ultrasound-assisted liquid-solid extraction at a constant temperature of  $30^\circ\text{C}$ . The extraction was carried out for (i) 30 min, (ii) 60 min, and (iii) 90 min. After this time, the extracts were filtered through syringe filters and evaporated to dryness in a water bath at  $70^\circ\text{C}$ . Finally, the residues were dissolved in 200  $\mu\text{l}$  of solvent and analyzed using the GC-MS method. The procedure was repeated three times. It was observed that dichloromethane produced a mixture that flowed spontaneously out of the test tube during extraction and was therefore excluded from further steps.

### SPE for clean-up of the extraction solution

1 g of the sample was placed in each of three screw-cap glass tubes and spiked with 200  $\mu\text{l}$  of PAH standard solution. Next, 10 ml of (i) acetone, (ii) dichloromethane, or (iii) a 50:50 mixture of ethyl acetate and n-hexane was added to the samples, which were subjected to ultrasound-assisted liquid-solid extraction.

The extraction was carried out at  $30^\circ\text{C}$  for 30 mins. After this time, the extracts were injected into SPE cartridges (3 ml/500 mg C18 glass cartridges) at a flow rate of  $2 \text{ ml}\cdot\text{min}^{-1}$  through a previously conditioned cartridges (with 5 ml of appropriate solvent). The filtrates were discarded, and the columns were air-dried for 10 min. Adsorbed compounds were then eluted from the columns (2 x 1 ml with a suitable eluent), evaporated to dryness, and dissolved in 200  $\mu\text{l}$  of solvent. The extracts were analyzed by the GC-MS method. The entire procedure was repeated three times.

### Solvent volume

1 g of the sample was placed in each of eight screw-cap glass tubes and spiked with 200  $\mu\text{l}$  of PAH standard solution. Next, an appropriate volume of either acetone or a 50:50 mixture of ethyl acetate and n-hexane was added to the samples in the following volumes: (i) 3 ml, (ii) 5 ml, (iii) 7 ml, and (iv) 10 ml. The samples were then subjected to ultrasound-assisted liquid-solid extraction, carried out at  $30^\circ\text{C}$  for 60 mins. After this time, the samples were filtered, evaporated to dryness, re-dissolved in solvent, and analyzed using the GS-MS method. The entire procedure was repeated three times.

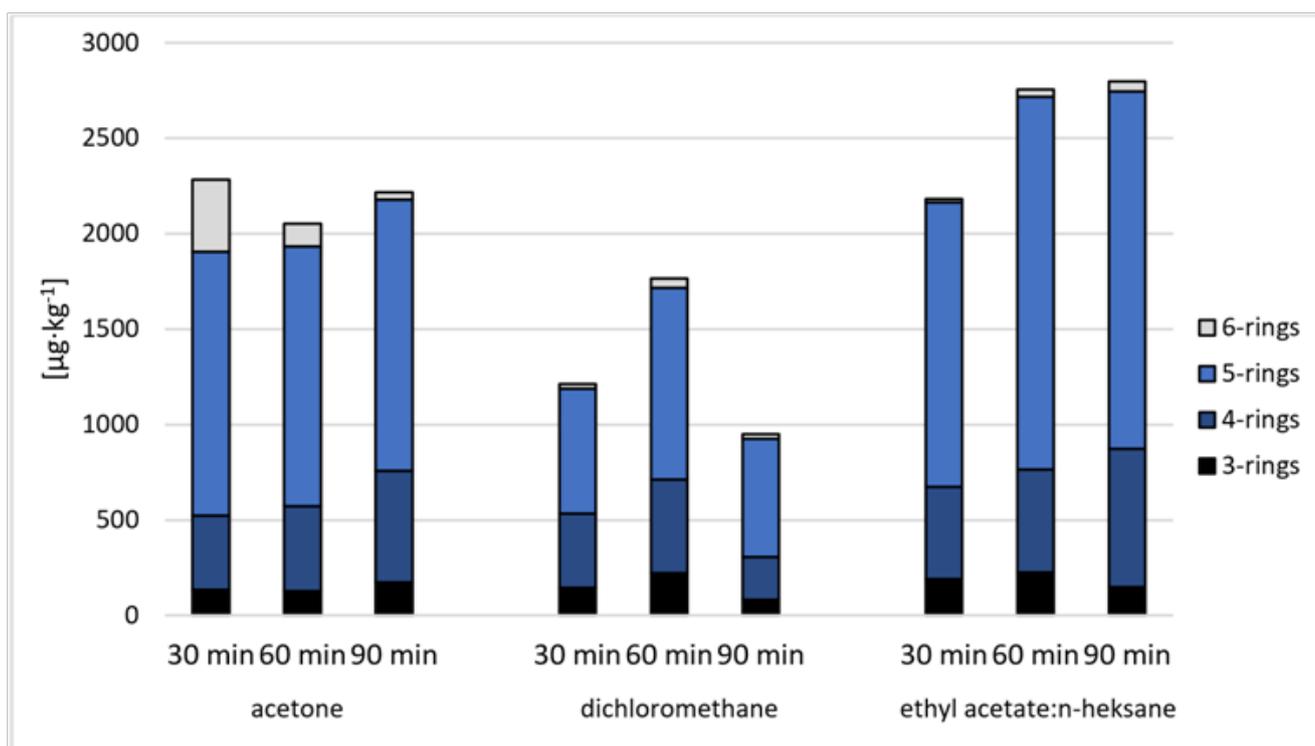


Fig. 2. Effect of solvent type and extraction time on PAH extraction efficiency.

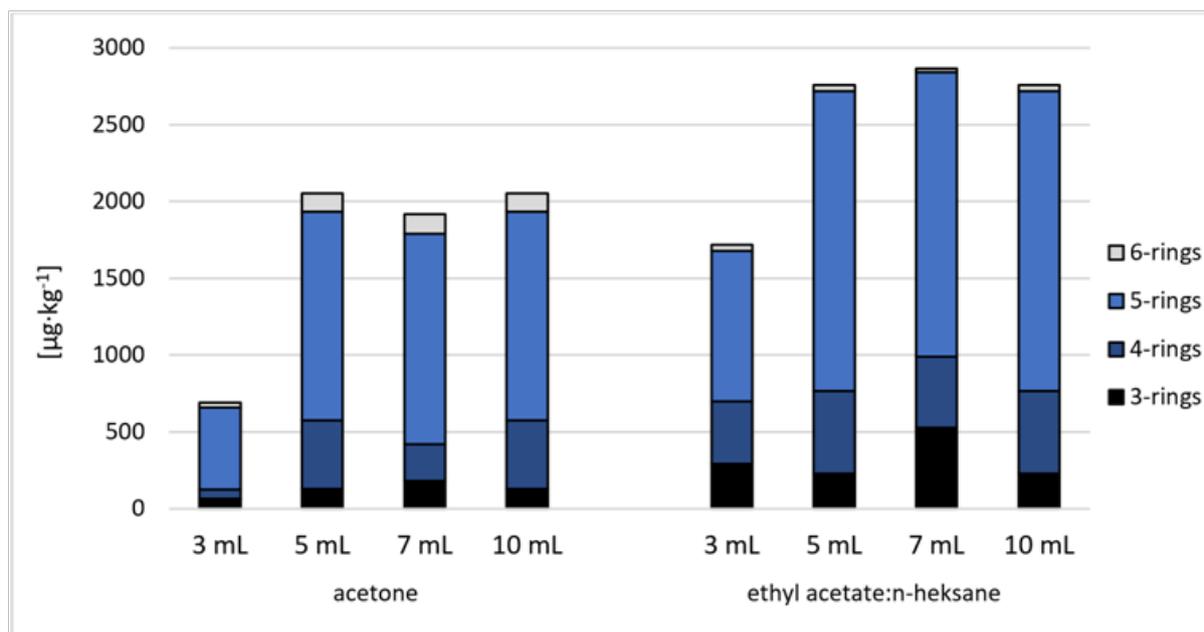


Fig. 3. Effect of solvent type and volume on PAH extraction efficiency.

## Results and discussion

### Extraction parameters and recoveries

The highest extraction efficiency of PAHs was observed using the ethyl acetate:n-hexane mixture at both 60 and 90 minutes (Fig. 2). As the differences between these times were not statistically significant, the shorter extraction time was selected. For solvent volumes of 5, 7, and 10 ml, the extracted amounts of PAHs from soil samples were comparable and higher than that obtained with 3 ml (Fig. 3). Therefore, a volume of 5 ml was selected for further extraction. The entire procedure was repeated three times.

The subsequent extraction parameters were selected based on the results obtained:

- solvent type: 50:50 mixture of ethyl acetate and n-hexane,
- solvent volume: 5 ml,
- extraction time: 60 min.

The application of the SPE method did not improve the separation of PAHs. Considering this, along with the fact that introducing additional steps increases both time and cost, and in light of the need for methodological alignment with the principles of green chemistry, the SPE method was ultimately

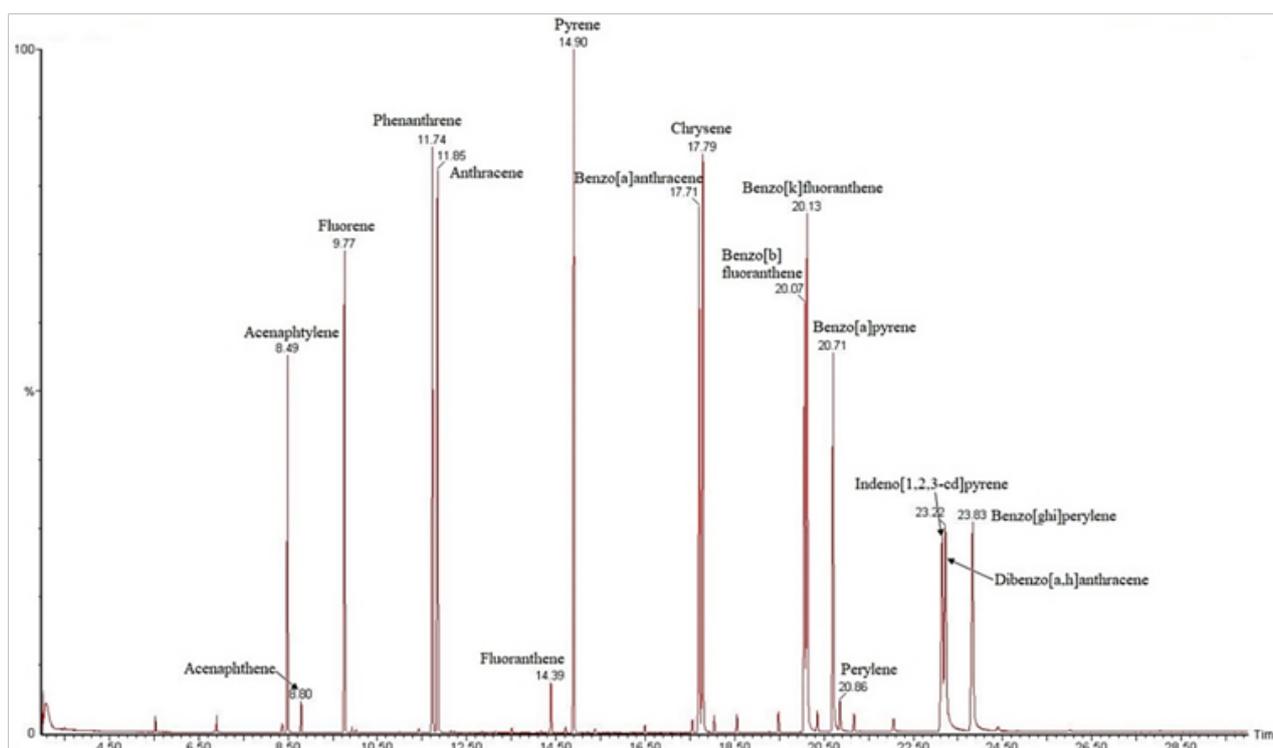
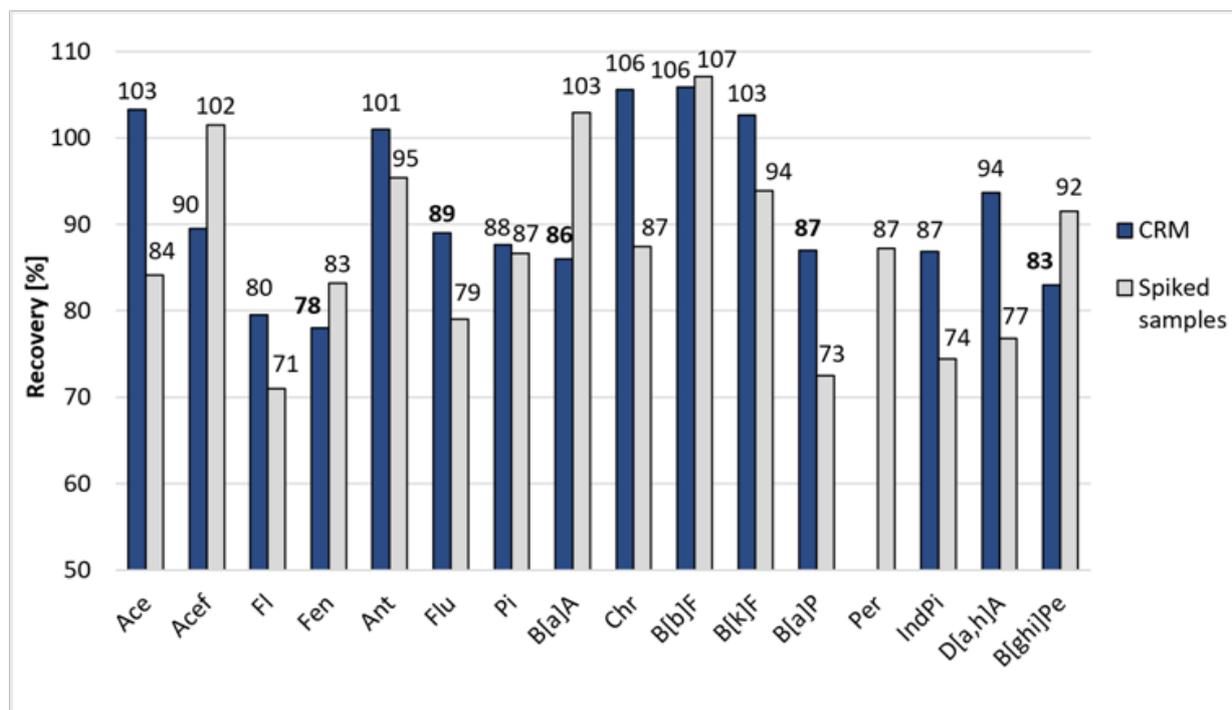


Fig. 4. Chromatogram of 16 PAHs obtained by the GC-MS method.

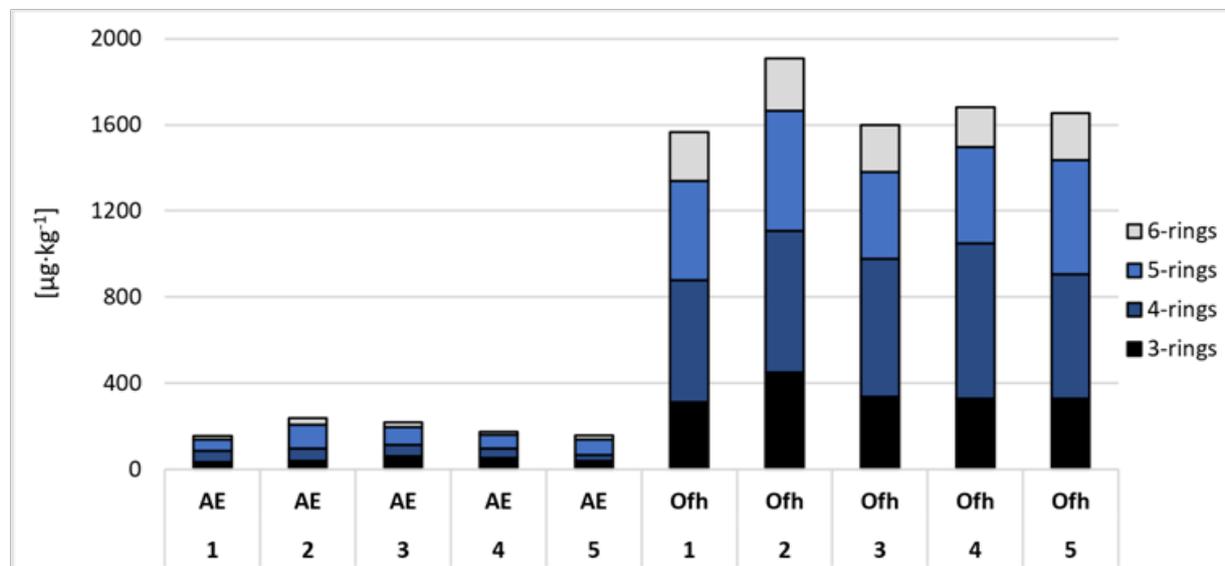


**Fig. 5.** Recoveries of PAHs obtained for the spiked samples and the CRM (contaminated soil – PCBs and PAHs LGC6115, LGC Standards), where: Ace – acenaphthylene, Acef – acenaphthene, Fl – fluorene, Fen – phenanthrene, Ant – anthracene, Flu – fluoranthene, Pi – pyrene, B[a]A – benzo[a]anthracene, Chr – chrysene, B[b]F – benzo[b]fluoranthene, B[k]F – benzo[k]fluoranthene, B[a]P – benzo[a]pyrene, Per – perylene, D[a,h]A – dibenzo[a,h]anthracene, IndPi – indeno[1,2,3-c,d]pyrene, B[ghi]Pe – benzo[g,h,i]perylene (certified values are indicated in bold).

excluded from the procedure. As shown in Figs. 2 and 3, neither longer extraction times nor larger solvent volumes led to improved PAH extraction efficiency from soil. The extraction efficiency was comparable for solvent volumes of 5 ml and 7 ml; therefore, the lower volume was selected in accordance with green chemistry principles. A representative chromatogram of the PAH determination using the selected extraction parameters is presented in Fig. 4. The soil sample was treated with 5 ml of a 50:50 ethyl acetate:n-hexane solution, and extraction was carried out in an ultrasonic bath at 30°C for 60 min. The calculated recoveries for spiked samples and the

certified reference material (PCBs and PAHs LGC6115, LGC Standards) ranged from 71 to 107% for the spiked samples and 78-106% for the CRM (Fig. 5).

The recovery results indicate that the modified method provide good accuracy for the determination of PAHs. The observed differences are due to the differing stability and binding affinities of PAHs in laboratory-enriched (spiked) samples compared to those present in natural environments. PAHs interact with soil components through various binding mechanisms, laboratory-prepared samples do not adsorb PAHs in the same way as samples under natural conditions.



**Fig. 6.** PAH content in soils collected from area 2.

**Table 2.** Concentration of PAHs in soils from different regions in Poland.

Region	Soil horizon	Min	Max	Mean	References
		[ $\mu\text{g}\cdot\text{kg}^{-1}$ ]			
North-eastern region of Poland	O	124	3145	681	Chaber and Gworek 2020
	A	12.6	194	85.6	
Central region of Poland	O	623	327	1946	
	A	30.8	1307	335	
Southern region of Poland	O	1226	9166	2526	
	A	120	4455	1050	
Southern region of Poland	Ofh	-	-	3805	Łyszczarz et al. 2022
	AE	-	-	651	
	Ofh	-	-	3087	
	AE	-	-	714	
	Ofh	-	-	2936	
	AE	-	-	2345	
South-central part of Poland	Ofh	-	-	1450	Migaszewski et al. 2002
	Ah	-	-	1051	
	Ofh	-	-	1887	
	AE	-	-	60.0	

Nevertheless, in both cases, the recoveries fell within ranges considered acceptable for environmental sample analysis. The most comparable values were obtained for pyrene and benzo[b]fluoranthene. For the remaining PAHs, differences in recovery ranged from 5% (phenanthrene) to 19% (acenaphthylene).

#### **Determination of PAHs in environmental samples prepared according to the modified extraction procedure**

The modified extraction procedure was used to determine 16 priority PAHs in soil samples taken from site 2, including 5 samples from the Ofh subhorizon and 5 from the AE horizon. Based on the physicochemical characteristics of the samples (see subsection *Short characteristics of soil samples*), it was anticipated that higher levels of soil organic matter (SOM) would correlate with elevated PAH concentrations, as suggested by previous studies (Dołęgowska et al. 2025, Ukalska-Jaruga et al. 2019, Ukalska-Jaruga and Smreczak 2020). This correlation was confirmed by the results obtained in the present study (Fig. 6). The total PAH concentration in the Ofh samples was up to twelve times higher than that in the AE samples ( $\Sigma 16$  PAHs – AE: 155-239  $\mu\text{g}\cdot\text{kg}^{-1}$ ; Ofh: 1566-1907  $\mu\text{g}\cdot\text{kg}^{-1}$ ). SOM is a key factor that affects the PAH sorption in organic-rich soils (Ukalska-Jaruga and Smreczak 2020, Gholami et al. 2024). Moreover, the strong binding of PAHs to SOM can hinder their extraction. High SOM content may also result in the co-extraction of other organic compounds, complicating both qualitative and quantitative PAH analysis (Ukalska-Jaruga and Smreczak 2020). Nevertheless, the modified extraction method presented in this study appears to fulfill the requirements for

efficient PAH extraction, as evidenced by the recovery results (Fig. 5).

Our results were also compared with PAH concentrations in soils from other regions of Poland. Although absolute PAH levels vary regionally, a consistent pattern emerges higher soil organic matter content is associated with increased PAH concentrations. For example, Chaber and Gworek (2020) reported higher PAH levels in the A horizon, which contained more organic matter (4.6% TOC) than our AE samples (3.05% TOC), though still lower than those observed in the organic horizon ( $\Sigma 13$  PAHs – organic horizon (O): 623-3207  $\mu\text{g}\cdot\text{kg}^{-1}$ ; humic horizon (A): 30.8-1307  $\mu\text{g}\cdot\text{kg}^{-1}$ ). The AE horizon analyzed in this study, being a transitional horizon, exhibits characteristics of both the humic and eluvial horizons. As such, its lower PAH concentrations compared to the A horizon are consistent with this trend. A similar pattern was observed in samples from the Holy Cross Mountain area, analyzed by Migaszewski et al. (2002) using traditional Soxhlet extraction ( $\Sigma 17$  PAHs – AE: 60  $\mu\text{g}\cdot\text{kg}^{-1}$ ; Ofh: 1450-1887  $\mu\text{g}\cdot\text{kg}^{-1}$ ). Comparable findings were also reported by Łyszczarz et al. (2022), who used 2-propanol extraction combined with SPE. In their study, PAH concentrations were approximately twice as high ( $\Sigma 15$  PAHs – Ofh: 2936-3805  $\mu\text{g}\cdot\text{kg}^{-1}$ , AE: 651-2345  $\mu\text{g}\cdot\text{kg}^{-1}$ ), which can be attributed to substantial regional exposure to industrial emissions. Despite these differences, the overarching trend remains consistent across studies (Table 2).

This indicates that the modified procedure is effective for determining PAHs in organic-rich soils. Moreover, it requires smaller solvent volumes, and a shorter extraction time compared to traditional PAH extraction methods.

## Conclusions

In this study, the modified ultrasound-assisted liquid-solid extraction method was successfully applied to isolate 16 priority PAHs from forest soil samples with varying organic matter content. The use of a 5 ml ethyl acetate (50:50) mixture as solvent, with an extraction time of 60 min, was found to be the optimal condition for efficient PAH extraction. This method proved to be simpler, less time-consuming, and required smaller volumes of organic solvents compared to other extraction techniques.

The modified procedure demonstrated good accuracy for PAH determination, with recovery rates ranging from 71 to 107% for spiked samples and 78 to 106% for the certified reference material. These results confirm the method's reliability in providing consistent data. Its application to forest soil samples further validates its effectiveness. Overall, these findings highlight the method's potential as a valuable tool for PAH analysis in various soil types and underscore its suitability for routine environmental monitoring and pollution control.

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## Zastosowanie ekstrakcji ciecz-ciało stałe wspomaganą ultradźwiękami do izolacji WWA z próbek gleb bogatych w materię organiczną

**Streszczenie.** Wielopierścieniowe węglowodory aromatyczne (WWA) występują w glebach w stężeniach  $\text{ng}\cdot\text{g}^{-1}$  lub niższych, a na ich poziom wpływa szereg czynników, w tym zawartość materii organicznej. Ekstrakcja WWA z gleb wzbogaconych w materię organiczną może być problematyczna, czasochłonna i kosztowna. Celem tej pracy była modyfikacja metody ekstrakcji ciało stałe-ciecz wspomaganą ultradźwiękami, stosowanej do izolacji 16 priorytetowych WWA z gleb leśnych zebranych z (pod)poziomów glebowych o różnej zawartości materii organicznej. Podczas ustalania metodyki ekstrakcji wspomaganą ultradźwiękami z gleb leśnych bogatych w materię organiczną wzięto pod uwagę następujące parametry: (i) rodzaj i objętość rozpuszczalnika, (ii) czas ekstrakcji oraz (iii) oczyszczanie ekstraktów metodą SPE. Jakościowe i ilościowe oznaczenie 16 WWA wykonano metodą chromatografii gazowej sprzężoną ze spektrometrią mas (GC-MS). Uzyskano następujące wyniki: odzysk 71-107%,  $R^2 = 0,993-0,999$ ,  $\text{LOD} = 0,008-0,026 \mu\text{g}\cdot\text{ml}^{-1}$  i  $\text{LOQ} = 0,024-0,078 \mu\text{g}\cdot\text{ml}^{-1}$ . Powyższą metodę z powodzeniem zastosowano do ekstrakcji wybranych WWA z próbek gleb organicznych pobranych z kompleksów leśnych zlokalizowanych w środkowo-południowej Polsce.