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VALIDATED UAE-GC-MS-SIM ANALYSIS OF PCBs IN SOILS: FROM METHOD PERFORMANCE TO HOMOLOGUE AND CONGENER PATTERNS

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ABSTRACT. Polychlorinated biphenyls (PCBs) are persistent organic pollutants that accumulate in soils, making their reliable determination in this complex matrix analytically challenging. This study presents the validation of a method based on ultrasound-assisted extraction (UAE) coupled with gas chromatography–mass spectrometry operating in selected ion monitoring mode (GC-MS-SIM) for the determination of 19 PCB congeners in soil samples. Method performance was evaluated in terms of selectivity, linearity, limits of detection and quantification, precision, and accuracy, demonstrating robust analytical performance for trace-level PCB determination. The obtained LODs ranged from 0.05 to 0.78 ng•g^{-1}. The validated method was applied to 92 soil samples collected from the Copșa Mică area (Romania) at two depth intervals (0–5 cm and 5–20 cm). Comparable ΣPCB concentrations were observed between the two soil layers, indicating a relatively uniform vertical distribution. Congener-specific analysis revealed the predominance of PCB 118 and PCB 187, while homologue distribution patterns were dominated by penta- and hepta-CBs. These results confirm the suitability of the validated method for PCB determination in soils and provide insight into congener- and homologue-level compositional patterns in real environmental samples.

Keywords: *polychlorinated biphenyls, soil, ultrasound-assisted extraction, GC-MS-SIM, method validation, homologue distribution, congener profile*

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of persistent organic pollutants characterised by high chemical stability, a hydrophobic nature, and resistance to degradation. These characteristics have contributed to their widespread accumulation in the environment, even after most countries banned their production and use [1,2]. Although their industrial applications were progressively phased out since the 1970s and 1980s, PCBs continue to be detectable in environmental matrices due to their long-lasting persistence and their ability to redistribute through atmospheric and pedological processes [1]. Consequently, soils serve as important environmental reservoirs and potential secondary sources of PCB contamination [3], where these chemicals may occur across a wide range of concentrations and degrees of chlorination. The complexity of the soil matrices, along with the presence of PCB congeners with varying physicochemical characteristics and the typically low concentrations at which these compounds occur, presents considerable analytical challenges. That's why efficient extraction procedures combined with advanced and sensitive instrumental techniques that ensure reliable quantification in intricate solid matrices are necessary.

The precise identification of PCBs in soils depends on efficient extraction and purification techniques, as well as rigorously validated experimental methods that guarantee adequate sensitivity, linearity, precision, and selectivity over wide concentration ranges. Gas chromatography coupled with mass spectrometry in selected ion monitoring mode (GC–MS–SIM) represents one of the most widely applied techniques for PCB determination in environmental samples due to its high selectivity and sensitivity [4-6]. Nevertheless, thorough method validation is crucial, especially when addressing several congeners with varying degrees of chlorination and inconsistent instrumental responses. In addition, ultrasound-assisted extraction (UAE) has been increasingly employed for the extraction of organic contaminants from solid matrices, offering advantages such as reduced solvent consumption, shorter times, and good extraction efficiency [7,8].

Although numerous studies have investigated the occurrence and distribution of PCBs in soils, most research has focused primarily on concentration levels or spatial contamination patterns [9,10]. However, relatively few studies combine a thoroughly validated UAE–GC–MS–SIM analytical approach for the simultaneous determination of multiple PCB congeners with a detailed evaluation of PCB compositional patterns at both the congener and homologue levels in real soil samples. In addition, information regarding PCB compositional profiles in soils from Copșa Mică area remains limited. Such an integrated approach is important because the distribution of individual congeners and homologue groups can provide additional information regarding contamination characteristics, environmental behaviour, and potential transformation processes of PCBs. The Copșa Mică area (Romania) represents a historically industrialised region affected by long-term metallurgical activities, making it a relevant site for investigating the occurrence and distribution of persistent organic contaminants in soils.

In this context the aim of this study was to validate and apply an ultrasound-assisted extraction combined with gas chromatography-mass spectrometry operating in selected ion monitoring mode (UAE–GC–MS–SIM) method for the simultaneous determination of 19 PCB congeners in complex soil matrices. The validated method was subsequently applied to soil samples collected from the Copsa Mica area, specifically from two depth intervals (0-5 cm and 5-20 cm). This application aimed to evaluate PCB concentrations and assess their compositional patterns based on congener and homologue distributions in accordance with the degree of chlorination. The selected congeners include indicator PCBs and compounds representative of several homologue groups (di-deca PCBs). This selection facilitates the characterisation of PCB profiles in soils while ensuring a focused analytical approach that is suitable for routine environmental analysis.

RESULTS AND DISCUSSION

Validation of GC-MS-SIM method parameters

The analytical method for quantifying polychlorinated biphenyls (PCBs) in soil samples was validated in accordance with international guidelines for persistent organic pollutant analysis (US EPA Method 8082A, US EPA Method 3550C, and US EPA Method 3630C) and involved a specific PCB standard mixture. The parameters evaluated included detection limits (LOD), quantification limits (LOQ), linearity, precision, selectivity and recovery.

Our study utilised selected ion monitoring (SIM) mode, using one target ion and two or three qualifier ions for confirmation alongside the retention times relative to calibration standards, thereby ensuring the *selectivity* of the method. These ions were identified using mass spectrometry analysis, and the validation of PCBs relied on retention times, qualifier ions, and target ions based on qualifier/target ion ratio. For increased reliability, this ratio must be within ±20% [11] in accordance with established GC-MS identification criteria (Table 1).

Table 1. Selected ion monitoring method parameters for PCB congeners

Analyte	t_R (min)	TI	QI^1	QI^2	QI^1/TI (%)	QI^2/TI (%)
PCB 8	16.383	222	152	186	7.3	8.6
PCB18	18.645	186	256	221	68.5	35.5
PCB 28	20.907	256	186	150	63.9	23.6
PCB 44	22.773	292	220	255	91.8	27.5
PCB 52	24.243	220	292	257	91.9	38.8
PCB 66	26.011	292	220	150	54	15.8
PCB 101	26.816	326	254	184	69.4	26.5
PCB 77	28.844	292	220	110	46.2	17.9
PCB 118	29.617	326	254	184	38	16.3
PCB 153	30.285	360	290	145	65	28.1
PCB 126	31.155	326	254	184	41.1	18.3
PCB 138	31.829	360	290	145	70.6	32.5
PCB 170	32.074	326	394	254	45.3	42.6
PCB 128	33.307	360	290	145, 218	90	35.5, 35.5
PCB 180	34.048	396	324	162	73.2	29.2
PCB 187	35.552	394	324	162	80.2	38.9
PCB 195	37.089	430	358	179	74.6	45.5
PCB 206	38.666	464	392	207	61.2	40.9
PCB 209	39.868	498	428	207	43.7	40
Standards						
IS	36.827	486	207	163	41	37.5
PCB 155	26.243	360	290	145	51	23.5
PCB 198	35.165	430	358	179	75.9	38.7

t^R – retention time; TI – target ion; QI^1, QI^2 – qualifier ions; IS – internal standard

The method *selectivity* is illustrated in Figure 1, which compares the chromatogram of the PCB standard mixture with the chromatograms of real soil samples. The chromatographic separation demonstrates good selectivity, with the target PCB congeners being efficiently separated and with no significant interferences observed at the retention times of the target congeners. A slight asymmetry was observed for the chromatographic signal at RT 20.91 min, which may be attributed to minor matrix-related co-elution effects without significantly affecting the identification and quantification of the target PCB congener.

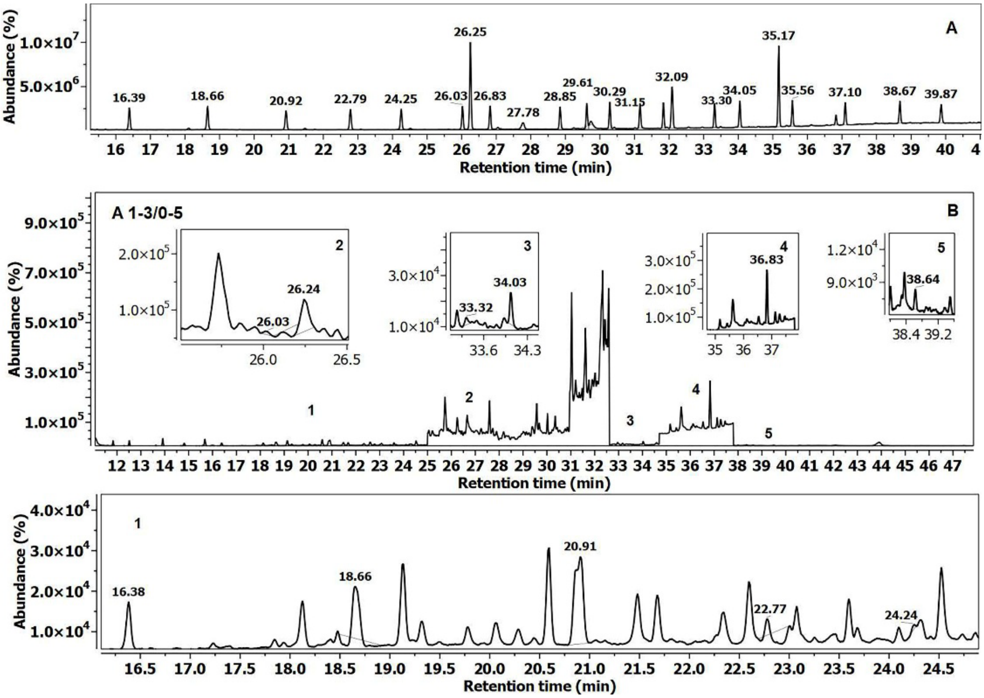

Figure 1. Selectivity assessment for PCB congeners by GC-MS (SIM mode): **(A)** chromatogram of PCB standard mixture; **(B)** soil sample extract with enlarged chromatographic zones (1-5), including a detailed view of zone 1

Given the significant differences in instrumental response and the extensive variation of PCB concentrations documented in Romanian soils [12,13], the *linearity* of the method was assessed by constructing calibration curves across two separate concentration ranges (0.125–12.5 and 12.5–1000 ng·mL⁻¹) (Table 2) to guarantee precise quantification at both low and high concentration levels. Calibration curves were constructed using the mean peak area ratio ($A_{analyte}/A_{IS}$) of multiple injections at each calibration level. A PCB stock solution mixture was utilised to create each calibration curve at six concentration levels. The correlation coefficients (R^2) exceeded 0.99 for all investigated congeners across both calibration ranges, indicating good linear relationships throughout the operating range.

Table 2. Calibration curves and linearity parameters (R^2) for PCB congeners between two concentration ranges

Analyte	**Low Range**		**High Range**	
	Equation of calibration	**R^2**	**Equation of calibration**	**R^2**
PCB 8	$y = 0.0171x + 0.0054$	0.9964	$y = 0.0136x + 0.0929$	0.9983
PCB18	$y = 0.0195x + 0.0017$	0.9965	$y = 0.0152x + 0.0532$	0.9993
PCB 28	$y = 0.0198x + 0.0028$	0.9936	$y = 0.0165x + 0.0635$	0.9994
PCB 44	$y = 0.0197x + 0.0026$	0.9973	$y = 0.0158x + 0.1047$	0.9993
PCB 52	$y = 0.0189x + 0.002$	0.9986	$y = 0.0144x + 0.1304$	0.9994
PCB 66	$y = 0.0171x + 0.0019$	0.9988	$y = 0.0137x + 0.1267$	0.999
PCB 101	$y = 0.0144x + 0.0023$	0.9951	$y = 0.0117x + 0.0057$	0.9991
PCB 77	$y = 0.0098x + 0.0009$	0.9989	$y = 0.0089x + 0.0631$	0.9994
PCB 118	$y = 0.0129x + 0.0016$	0.9979	$y = 0.0112x + 0.0106$	0.9995
PCB 153	$y = 0.0109x + 0.0017$	0.9978	$y = 0.0087x + 0.0866$	0.998
PCB 126	$y = 0.0128x + 0.0027$	0.9975	$y = 0.0111x + 0.0394$	0.9985
PCB 138	$y = 0.0079x + 0.0008$	0.9977	$y = 0.0065x + 0.0346$	0.9994
PCB 170	$y = 0.0158x - 0.0006$	0.9989	$y = 0.0137x + 0.0548$	0.9997
PCB 128	$y = 0.0105x + 0.0013$	0.9991	$y = 0.0089x + 0.0078$	0.9994
PCB 180	$y = 0.0106x + 0.0051$	0.9985	$y = 0.0083x + 0.086$	0.9995
PCB 187	$y = 0.0025x - 0.0028$	0.9995	$y = 0.0018x + 0.0113$	0.9996
PCB 195	$y = 0.0064x + 0.0004$	0.9956	$y = 0.0054x + 0.0297$	0.9995
PCB 206	$y = 0.0064x - 0.0003$	1	$y = 0.0055x + 0.0276$	0.9994
PCB 209	$y = 0.0071x + 0.0001$	0.9987	$y = 0.0057x + 0.0463$	0.9993
Standards	**Range 0.0125-0.2 $\mu g \cdot mL^{-1}$**			
PCB 155	$y = 12.088x + 0.0436$		$R^2 = 0.994$	
PCB 198	$y = 4.7607x + 0.0211$		$R^2 = 0.9942$	

R^2 - regression coefficient of calibration curve

Method *sensitivity* was expressed by the limits of detection (*LOD*) and quantification *(LOQ)*, using the formulas $LOD = 3.3 \times \sigma/S$ and $LOQ = 10 \times \sigma/S$ (where σ is the standard error of the intercept from linear regression and S represents the slope of the calibration curve), calculated in accordance with IUPAC guidelines [14]. These limits correspond to signal-to-noise ratios of approximately 3 and 10, respectively, demonstrating the high detection capacity of the PCB congeners. Therefore, the limit of detection and quantification were calculated only for the lower calibration range (0.125–12.5 $ng \cdot mL^{-1}$), as they reflect the method sensitivity at low concentrations. The obtained LOD and LOQ values are summarised in Table 3 and indicate a high sensitivity of the analytical method for PCB determination. The high-range calibration curve was used for quantification of higher levels.

Precision was evaluated in terms of repeatability and expressed as relative standard deviation (*RSD, %),* calculated using back-calculated concentrations obtained through repeated measurements. For some analytes, RSD was evaluated across the full low range (0.125–12.5 ng·mL^{-1}), whereas for others it was evaluated over reduced ranges (0.25–12.5 ng·mL^{-1}, 0.5–12.5 ng·mL^{-1}, and 2.5–12.5 ng·mL^{-1}). When the lowest levels (0.125 and/or 0.25, 0.5 ng·mL^{-1}) yielded negative back-calculated concentrations (below the quantifiable range), these values were excluded from RSD calculations (Table 3).

Table 3. Analytical performance for the determination of PCBs in soil samples using GC-MS-SIM

Analyte	**Range 0.125–12.5 ng·ml^{-1}**			**Range 25–1000 ng·ml^{-1}**
	LOD	**LOQ**	**RSD$_{mean}$ (min-max) (%)**	**RSD$_{mean}$ (min-max) (%)**
PCB 8^{a}	0.46	1.40	5.64 (2.46-9.90)	4.84 (0.68-15.19)
PCB18^{a}	0.46	1.39	15.14 (0.42-73.05)	4.54 (0.8-13.47)
PCB 28^{a}	0.62	1.87	5.31 (3.72-6.5)	8.04 (1.78-23.10)
PCB 44^{a}	0.40	1.21	5.03 (3.32-6.83)	3.09 (0.08-5.92)
PCB 52^{a}	0.29	0.87	5.80 (1.46-9.83)	3.67 (0.49-9.16)
PCB 66^{a}	0.27	0.82	6.17 (2.43-12.74)	5.63 (0.18-13.89)
PCB 101^{a}	0.54	1.62	11.61 (2.82-27.34)	5.44 (0.59-12.40)
PCB 77^{a}	0.25	0.76	5.46(1.56-13.28)	3.86 (1.03-7.59)
PCB 118^{a}	0.35	1.06	5.65 (1.01-14.80)	4.54 (1.07-8.69)
PCB 153^{a}	0.36	1.08	5.30 (2.16-10.78)	4.95 (0.28-15.06)
PCB 126^{a}	0.38	1.17	8.50 (1.35-21.36)	8.69 (0.09-39.35)
PCB 138^{a}	0.37	1.11	10.92 (2.40-19.23)	5.83 (2.03-12.27)
PCB 170^{a}	0.25	0.76	6.47 (2.81-8.58)	4.08 (0.29-8.12)
PCB 128^{a}	0.24	0.71	4.61 (1.44-9.05)	5.13 (0.41-12.87)
PCB 180^{b}	0.35	1.07	7.89 (3.87-12.35)	5.01 (0.08-11.66)
PCB 187^{d}	0.57	1.73	12.53 (4.13-18.75)	3.87 (1.08-7.50)
PCB 195^{c}	0.78	2.36	16.37 (0.22-51.89)	4.24 (1.64-7.50)
PCB 206^{a}	0.05	0.15	16.94 (1.53-55.11)	4.56 (0.36-10.49)
PCB 209^{b}	0.34	1.03	7.06 (2.28-14.83)	5.14 (0.51-12.78)

Standards	**Range 0.0125–0.2 µg·ml^{-1}**	
	LOD	**LOQ**
PCB 155	0.02	0.02
PCB 198	0.05	0.05

12.5 ng·mL^{-1} was used as an overlap point in both calibration ranges; for precision, it was included only in the low range; mean - average of multiple determinations

a–d indicate the low-range concentration intervals used for RSD calculation (ng·mL^{-1}), depending on the analyte quantifiability (**a**: 0.125–12.5 ng·mL^{-1}; **b**: 0.25–12.5 ng·mL^{-1}; **c**: 0.5–12.5 ng·mL^{-1}; **d**: 2.5–12.5 ng·mL^{-1})

The method's *accuracy* was assessed by determining the recovery rates for procedural recovery standards (PCB 155 and 198) and PCB congeners in the certified reference material (CRM) and is summarised in Table 4. The recovery control compounds were added prior to extraction to assess procedural performance; they were not included as target analytes and were not used for quantification. The recovery rates ranged from 78.7% to 129.1%, and all measured PCB concentrations fell within the recommended acceptance windows of the CRM, confirming the accuracy and reliability of the method used.

Table 4. Accuracy of the GC-MS(SIM) method based on recoveries of PCB congeners determined in a CRM

Analyte	Certified value (ng·g^{-1})	Suggested Acceptance Windows (ng·g^{-1})	Recovery (%)
PCB 28	58.8 ± 4.9	17.6 to 100.0	97.6
PCB 52	107.0 ± 8.2	32.1 to 181.9	78.7
PCB 101	58.3 ± 4.4	17.5 to 99.1	127.4
PCB 118	40.1 ± 3.3	12.0 to 68.2	83.5
PCB 138	38.5 ± 1.8	11.6 to 65.5	107.1
PCB 153	52.9 ± 2.7	15.9 to 89.9	115.8
PCB 180	59.6 ± 3.2	17.9 to 101.3	103.1
Recovery standards			
PCB 155	80	na	103.9
PCB198	80	na	129.1

na - not assessed

"Suggested acceptance windows" – represent the acceptance ranges provided in the certificate of the CRM and were used as reference criteria for method performance evaluation.

Application of the validated method to soil samples

To assess the level of PCB contamination in real soil samples collected from Copșa Mică, we investigated the ∑PCB concentrations in two soil depth layers (0–5 cm and 5–20 cm). The selected congeners include indicator PCBs and compounds representative of several homologue groups commonly monitored in environmental studies. This selection facilitates the characterisation of PCB profiles in soils while ensuring a targeted analytical approach that is suitable for routine environmental analysis. The total PCB concentrations (∑PCB) obtained for the analysed samples are presented in Table 5. The results indicate comparable concentration levels between the two investigated depth intervals with a mean value slightly higher in the 5–20 cm intervals, compared to the 0-5 cm layer. Both layers exhibited moderate variability.

Table 5. Concentrations of total PCB (∑PCB) in soil samples from Copșa Mică area, from two depth intervals (ng·g^{-1} dw)

Depth (cm)	∑PCB (ng·g^{-1} dw)		
	min-max	mean ± SD	median
0-5	2.98-35.64	15.36 ± 8.31	14.39
5-20	2.08-46.15	16.94 ± 10.01	15.49

Congener distribution

The distribution of $\sum_{17}$PCB concentrations across the two investigated soil layers is presented in Figure 2 as a boxplot, providing a graphical representation of the variability of concentrations of individual values. Slightly higher median and mean values were observed in the 5-20 cm layer compared to the surface horizon (0–5 cm). However, the Mann-Whitney U test indicated no statistically significant differences between the two depth intervals (U = 994, p = 0.62). These results suggest a relatively uniform vertical distribution of total PCBs within the investigated soil profile.

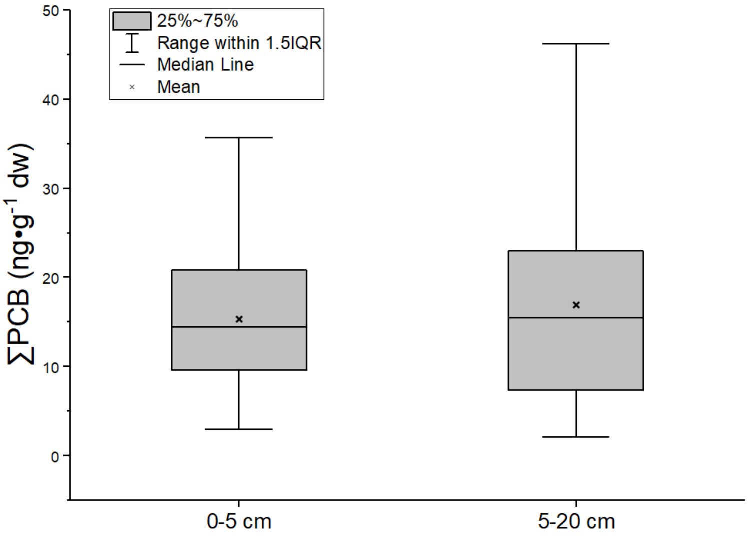

Figure 2. Distribution of $\sum_{17}$PCB concentrations (ng·g^{-1}) in soils from Copșa Mică at two depth intervals (0–5 cm and 5–20 cm). Boxes represent the interquartile range (25–75%); whiskers indicate values within 1.5 IQR; the horizontal line denotes the median; and the symbol (x) represents the mean

To determine the individual contributions of congeners to the PCB concentration shown in Figure 2, Table 6 provides the mean values (± SD) for each congener identified in two analysed depth intervals.

The distribution of the PCB congeners revealed that PCB 118 and PCB 187 were the most prevalent in both soil depth intervals, exhibiting the highest concentrations among the analysed congeners. In the 0-5 cm layer, PCB 118 accounted for 30% of ∑PCB (216 out of 706 ng·g^{-1} dw) and displayed similar mean concentrations across both soil depths, while PCB 187 represented 20% of the total concentration. In contrast, in the 5-20 cm layer, PCB 187 became the dominant congener, accounting for 28% of ∑PCB (215 out of 780 ng·g^{-1} dw), whereas PCB 118 represented 24% of total concentration. The predominance of PCB 118 observed in the analysed samples is consistent with previous studies on PCB distribution in soils. PCB 118, a dioxin-like congener known for its toxicological properties, is commonly detected in environmental matrices due to its persistence and occurrence in technical mixtures utilised in electrical devices (capacitors, transformers) [15,16]. Higher chlorinated congeners, such as PCB 187, exhibit strong hydrophobicity and high affinity for soil organic matter, leading to their accumulation and persistence in soils [16,17].

Table 6. Distribution of PCB congeners in soil samples at two depth intervals (ng·g^{-1} dw)

Congener	0-5 cm (mean ± SD)	5-20 cm (mean ± SD)
PCB 8	0.9 ± 0.65	0.84 ± 0.42
PCB18	1.68 ± 1.27	1.80 ± 1.92
PCB 28	2.57 ± 1.94	3.09 ± 3.66
PCB 44	0.4 ± 0.47	0.37 ± 0.29
PCB 52	0.16 ± 0.49	0.16 ± 0.17
PCB 66	0.25 ± 0.23	0.31 ± 0.30
PCB 101	0.47 ± 0.88	0.56 ± 0.79
PCB 77	0.14 ± 0.14	0.14 ± 0.09
PCB 118	6.97 ± 3.81	6.87 ± 3.27
PCB 153	0.58 ± 0.89	0.49 ± 0.51
PCB 126	nd	nd
PCB 138	nd	nd
PCB 170	0.03 ± 0	0.16 ± 0.14
PCB 128	0.17 ± 0.22	0.17 ± 0.35
PCB 180	1.24 ± 1.04	1.07 ± 0.64
PCB 187	5.99 ± 4.60	7.96 ± 6.09
PCB 195	2.78 ± 0	1.93 ± 1.77
PCB 206	0.13 ± 0.07	0.51 ± 0.50
PCB 209	0.07 ± 0	0.11 ± 0.06

nd - not detected

The congeners PCB 28 and PCB 180 also presented relatively elevated mean concentrations compared to most other congeners, while PCB 195 showed higher values in the surface layer. The remaining congeners were characterised by lower mean concentrations (< 1 ng·g^{-1} dw) and a moderate distribution across the two investigated soil depth intervals.

Neither PCB 126 nor PCB 138 was detected in the analysed soil samples. Overall, the PCB congener profile is similar across the two soil layers with specific differences for certain compounds, without indicating a major change in the contamination structure based on depth.

Homologue distribution

To better understand the compositional characteristics of PCB contamination in the investigated soils, the analysed congeners were grouped according to their degree of chlorination into homologue groups: PCB 8 (di-CB); PCB 18 and PCB 28 (tri-CBs); PCB 44, PCB 52, PCB 66, and PCB 77 (tetra-CBs); PCB 101 and PCB 118 (penta-CBs); PCB 128 and PCB 153 (hexa-CBs); PCB 170, PCB 180 and PCB 187 (hepta-CBs); PCB 195 (octa-CB); PCB 206 (nona-CB); and PCB 209 (deca-CB). The relative contribution of each homologue group to the total PCB concentration is illustrated in Figure 3. The results showed that *penta-CBs* were the dominant group in the surface layer, accounting for the largest proportion of ∑PCB. In contrast, in the 5-20 cm layer, the contribution of hepta-chlorinated biphenyls increased, while tri-CBs also represented an important fraction of the total PCB burden in both soil depth intervals.

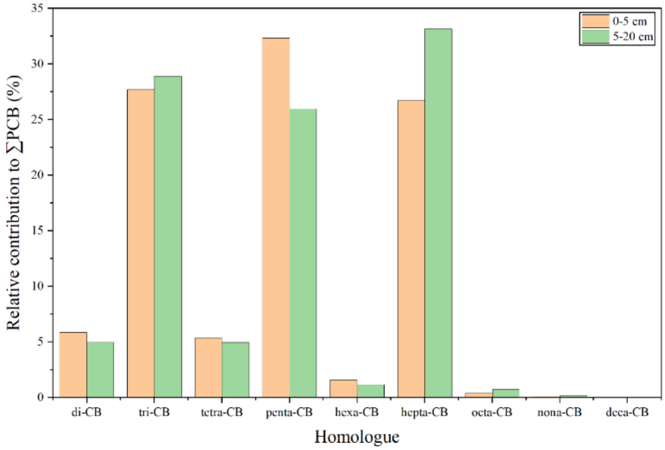

Figure 3. Homologue distribution of PCBs in soils from Copsa Mica at two depth intervals (0-5 cm and 5-20 cm), expressed as the relative contribution (%) to ∑PCB.

These results contrast with previous studies where penta-CBs were recorded among dominant homologues in soils from Midway Atoll (North Pacific Ocean) [18], as well as in pine needle samples and soil samples from an industrial area in Ulsan, South Korea [19]. Similar homologue patterns, dominated by penta- and hepta-CBs, have been reported in other regions as well [20,21].

The remaining homologue groups occurred in a comparatively lower proportion in both investigated soil intervals.

CONCLUSIONS

A robust analytical method based on ultrasound-assisted extraction coupled with gas chromatography–mass spectrometry operating in selected ion monitoring mode (UAE–GC–MS–SIM) was successfully validated for the determination of 19 PCB congeners in soil samples. The validation results demonstrated satisfactory selectivity, linearity over the investigated calibration ranges, low limits of detection and quantification, as well as good precision and accuracy, confirming the suitability of the method for trace-level PCB determination in complex soil matrices. The validated procedure was subsequently applied to 92 soil samples collected from the Copșa Mică area (Romania), from two depth layers (0–5 cm and 5–20 cm), enabling the evaluation of both concentration levels and compositional patterns of PCBs in real soils. The obtained results showed comparable ΣPCB concentrations between the two soil layers, and statistical analysis using the Mann–Whitney U test indicated no significant differences between the investigated depth intervals, suggesting a relatively uniform vertical distribution within the analysed soil profile. At the congener level, PCB 118 and PCB 187 were identified as the dominant compounds in both soil layers, while the remaining congeners generally occurred at lower concentrations. Evaluation of the homologue distribution revealed the predominance of penta- and hepta-chlorinated biphenyls, highlighting characteristic compositional patterns of PCBs in the studied soils. Overall, the validated UAE–GC–MS–SIM approach proved to be a reliable analytical tool for PCB determination in soils and for supporting detailed compositional assessment based on congener and homologue distributions in real environmental samples. By combining method validation with the compositional evaluation of PCB congeners and homologues in real soil samples, the present study provides a reliable analytical framework for the characterisation of PCB occurrence and distribution in soil matrices.

EXPERIMENTAL SECTION

The study area and sample collection

Copșa Mică is located along a lowland corridor of the Târnava Mare River in northern Sibiu County, Transylvania, Romania. Historically, this town was recognised as one of Europe's most polluted cities [22], primarily due to its persistent industrial emissions. The pollutants originated from two major industrial facilities in the area: Carbosin, which produced carbon black from 1936 to 1993, and Sometra, which specialised in non-ferrous metallurgy.

Soil samples were obtained from two depth levels (0-5 cm and 5-20 cm) across 46 locations, yielding a total of 92 samples. Figure 4 illustrates the study area around Copșa Mică industrial platform; samples were collected from locations at different distances from the former Sometra and Carbosin industrial sites, which were historically the primary sources of pollution in the region. Prior to extraction, the samples were homogenised, air-dried, ground and sieved (≈ 1-2 mm) and subsequently stored in a dark and dry environment.

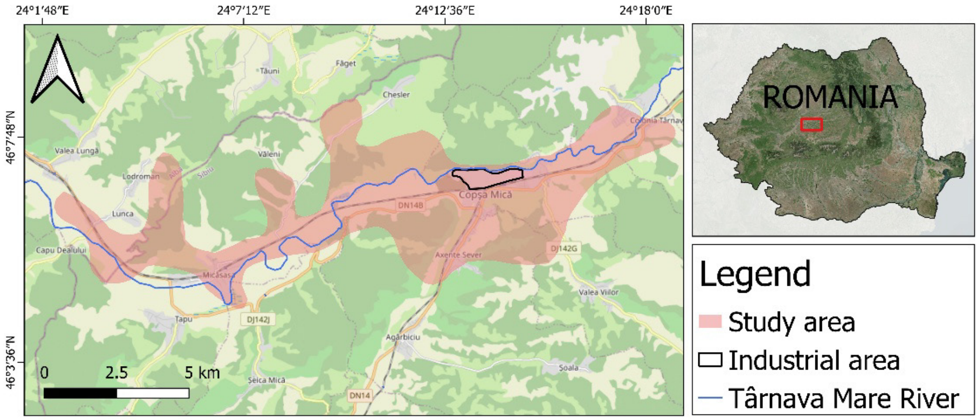

Figure 4. Location of the study area in the Copșa Mică region, Romania, including the industrial platform and the sampling zone along the Târnava Mare River

Chemicals and reagents

A standard stock solution mixture containing 19 PCBs (8, 18, 28, 44, 52, 66, 77, 101, 118, 126, 128, 138, 153, 170, 180, 187, 195, 206, 209, each at 100 $\mu g \cdot mL^{-1}$ in isooctane), was purchased from Restek (USA). The polychlorinated biphenyl-rich certified reference material (CRM) was purchased from Sigma-Aldrich, USA. PCB 155 (97% purity) and PCB 198 (97% purity) were used as recovery standards and purchased from LGC Labor GmbH (Germany), and as an internal standard, 3,3′,4,4′-tetrabromodiphenyl ether (BDE 77) (10 $\mu g \cdot mL^{-1}$ in isooctane) was used and purchased from CPAchem Ltd. (Bulgaria). Acetone, n-hexane, and dichloromethane (DCM) were purchased from Honeywell (Germany) and isooctane from VWR (France), all at HPLC grade. Anhydrous sodium sulfate (12-60 mesh) was purchased from J.T. Baker (Mexico), and silica gel was purchased from Merck (Germany); all of them were analytical grade and were baked at 420℃ for 4 h before use. The copper (< 425 μm, 99.5%, Sigma-Aldrich, USA) was activated using a 1N HCl solution, subsequently rinsed with water until a pH of 5 was attained, and finally washed with acetone and DCM. All the glassware was thoroughly washed and soaked in alkaline bath solution for 12 hours and oven-dried at 120℃ for 12 hours before use.

Extraction and purification of PCBs

The ultrasound extraction (UAE) method was used to extract PCBs from soil samples. Subsequently, the extract solutions underwent a cleanup protocol. UAE was performed using an ultrasonic water bath (Elma Transsonic T660/H) equipped with a generator operating at a frequency of 35 kHz and a nominal power output of 320 W. Ultrasonication was carried out in continuous mode. The extraction temperature was monitored and maintained approximately constant at room temperature by cooling the water bath during sonication. These procedures were conducted based on previous studies reported by Barhoumi [23], Adesina [24] and Güzel [25] with minor modifications. Prior to extraction, approximately 9 g of soil sample was spiked with 200 μL (0.08 $\mu g \cdot mL^{-1}$) recovery standard mixture to ensure the integrity of the extraction process. Then, 30 mL solvent mixture of hexane and acetone (v/v, 1:1) was added. The sample was placed in an ultrasonic bath and sonicated for 20 minutes. After the extraction process, the extract was centrifuged for 15 minutes at 4000 rpm and 10°C. These procedures were repeated two additional times using fresh solvent mixtures. The resulting extract was concentrated using a rotary evaporator to 2–3 ml and allowed to stand overnight on 0.5 g of activated copper for sulphur elimination. An additional 10 mL n-hexane was added to the flask and evaporated to 1 mL. This concentrated fraction was purified using thin-layer chromatography consisting of 4 g silica gel and 1 g sodium sulphate and eluted with a 40 mL mixture of n-hexane and dichloromethane (v/v, 4:1). Finally, the sample was concentrated to approximately 0.5 ml and spiked with 0.5 ml (1 $\mu g \cdot ml^{-1}$) of internal standard prior to GC analysis.

Instrument analysis

The analysis of PCBs was performed using an Agilent 7890 gas chromatograph, equipped with a mass spectrometer (MSD) model 5975. The Zebron ZB-PAH-EU capillary column measuring 30 m x 0.25 mm x 0.2 µm was provided by Phenomenex (USA). Helium (99.99%) is used as the carrier gas at a flow rate of 1 mL/min, and the injector temperature is set at 280°C. The analytical method used a column heating gradient that went from the column temperature being held at 70°C for 2 minutes, increasing to 150°C at a rate of 25°C/min, subsequently rising to 200°C at a rate of 3°C/min, and finally ramping up to 280°C at a rate of 5°C/min, maintained for 10 minutes. The mass spectrometer detector (MSD) operated in electron impact ionisation at an ionising energy of 70 eV, with the ion source temperature set at 300°C and a quadrupole temperature of 180°C. The study was conducted by selected ion monitoring (SIM) utilising one target ion and two or three qualifier ions. The identification of these ions was conducted using mass spectrometry analysis. The confirmation of PCBs relied on retention times (which should be ± 0.2-0.3 min), qualifier ions, and target ions according to the qualifier/target ion ratio; for enhanced reliability, this ratio must be at least 20%. The data acquisition was performed using ChemStation software No. 2.

Data handling

Data processing was performed using Microsoft Excel and OriginPro 2025 software. For statistical evaluation, descriptive parameters including mean, median, minimum, maximum and standard deviation were calculated for each depth interval. The distribution of ∑PCB concentrations was illustrated by boxplot representations. Differences between the two soil depth intervals were assessed using the Mann-Whitney U test, and statistical significance was considered $p < 0.05$.

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REFERENCES

1. K. Breivik, A. Sweetman, J. M. Pacyna, K. C. Jones; *Sci. Total Environ.,* **2007***, 377*, 296–307
2. A. A. Bhat; M. Ahmed; N. Elboughdiri; J. Singh; K. Kriaa; C.Maatki; B. Hadrich; A.K. Wani; *Microchem J.*, **2026**, 117041

3. J. M. Armitage; M. Hanson; J. Axelman; I. T. Cousins; *Sci. Total Environ.*, **2006**, *371(1–3)*, 344–352
4. K. Jia; X. Feng; K. Liu; Y. Han; Y. Xue; C. Xue; *J. Chromatogr. B*, **2013**, *923–924*, 37–42
5. T. Nenin; T. Mitrović; A. Petković; J. Čolić; *Microchem. J.*, **2024**, *207*, 111761
6. F. Ben Salem; O. Ben Said; R. Duran; M. Monperrus; *Bull. Environ. Contam. Toxicol.*, **2016**, *96(5)*, 678–684
7. V. A. Pănescu; V. Bocoș-Bințințanș; M. C. Herghelegiu; R.T. Coman; V. Berg; J. L. Lyche; M. S. Beldean-Galea; *Sustainability*, **2023**, *16(1)*, 232
8. G. Bianco; G. Novario; D. Bochicchio; G. Anzilotta; A. Palma; T. R. I. Cataldi; *Chemosphere*, **2008**, *73(1)*, 104–112
9. S. N. Meijer; W. A. Ockenden; E. Steinnes; B. P. Corrigan; K. C. Jones; *Environ. Sci. Technol.*, **2003**, *37(3)*, 454–461
10. S. A. Debela; I. Sheriff; J. Wu; Q. Hua; Y. Zhang; A. K. Dibaba; *Sci. Afr.*, **2020** *8*, e00329
11. C. Sánchez-Brunete; B. Albero; J. L. Tadeo; *J. Agric. Food Chem.*, **2004**, *52(6)*, 1445–1451
12. D. Dragan; S. Cucu-Man; A. C. Dirtu; R. Mocanu; L. V. Vaeck; A. Covaci; *Int. J. Environ. Anal. Chem.*, **2006**, *86(11)*, 833–842
13. A. Covaci; C. Hura; P. Schepens; *Sci. Total Environ.*, **2001**, *280(1–3)*, 143–152
14. M. Thompson; S. L. R. Ellison; R. Wood; *Pure Appl. Chem.*, **2002**, *74(5)*, 835–855
15. V. C. Eze; T. O. Maduka; C. I. Iheme; A.C. Chiedozie; H. O. Abugu; J. C. Egbueri; S. I. Ogbuefi; M. O. Muogbo; S. I. Abba; *Int. J. Environ. Anal. Chem.*, **2025**, *105(17)*, 5551–5577
16. https://www.atsdr.cdc.gov/toxprofiles/tp17.pdf, **2000**, Accession date: 02.02.2026-12:30
17. J. J. Nam; O. Gustafsson; P. Kurt-Karakus; K. Breivik; E. Steinnes; K. C. Jones; *Environ. Pollut.*, **2008**, *156(3)*, 809–817
18. J. Ge; L. A. Woodward; Q. X. Li; J. Wang; *PLoS ONE*, **2013**, *8(8)*, e71521
19. H.-K. Cho; S. N. Khuman; I.-G. Cho; M.-K. Park; S.-D. Choi; *Chemosphere*, **2024**, *369*, 143821
20. S. N. Meijer; W. A. Ockenden; E. Steinnes; B. P. Corrigan; K. C. Jones; *Environ. Sci. Technol.*, **2003**, *37(3)*, 454–461
21. B. Aichner; B. Bussian; P. Lehnik-Habrink; S. Hein; *Environ. Sci. Technol.*, **2013**, *47(22)*, 12703–12714
22. I. Rusu; *Eur. J. Sci. Theol.*, **2008**, *4(4)*, 33–40
23. B. Barhoumi; M. S. Beldean-Galea; A. M. Al-Rawabdeh; C. Roba; I. M. Martonos; R. Bălc; M. Kahlaoui; S. Touil; M. Tedetti; M. R. Driss; C. Baciu; *Sci. Total Environ.*, **2019**, *660*, 660–676
24. O. A. Adesina; I. Ezengwa; K. A. Abdulraheem; A. J. Adewole; O. B. Oyetunji; *Chem. Environ. Eng.*, **2023**, *7*, 100343
25. B. Güzel; O. Canlı; E. Aslan; *Mar. Pollut. Bull.*, **2022**, *175*, 113172