Journal of Chromatography Open 8 (2025) 100245

Contents lists available at ScienceDirect

Journal of Chromatography Open

journal homepage: www.elsevier.com/locate/jcoa

Multitargeted analysis for the simultaneous determination of organochlorine pesticides and polychlorinated biphenyls in sediments exploiting comprehensive two-dimensional gas chromatography coupled to mass spectrometry☆

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ARTICLE INFO

Keywords:
PCBs
OCPs
POPs
GC×GC-MS

ABSTRACT

Persistent organic pollutants (POPs), including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), remain a significant environmental concern due to their persistence, bioaccumulation, and toxicity. Accurate quantification of these contaminants in sediment matrices remains analytically challenging due to the complexity of the matrix and the need for detection at trace levels to meet regulatory standards. This research focused on the development and application of an analytical protocol for the simultaneous determination of OCPs and PCBs in sediments using solid-phase extraction (SPE) followed by comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS). The developed method was validated, achieving low limits of detection (0.4 to 14 ng kg^{-1}) and quantification (1.1 to 41 ng kg^{-1}), with satisfactory linearity ($r^2 > 0.99$), accuracy (90–110%), and precision (RSD < 5%) for all target analytes. Validation with certified reference material confirmed the agreement between experimental and certified concentrations for most compounds. The protocol was applied to environmental sediment samples, detecting multiple PCBs and DDT-related compounds at concentrations below international guideline values. These results confirm the method's suitability for trace-level determination of OCPs and PCBs in sediments, addressing the analytical demands of environmental monitoring and regulatory compliance. The established protocol enables sensitive and reliable assessment of sediment contamination, supporting a simultaneous ongoing surveillance and risk assessment of such classes of persistent organic pollutants in the same analytical run.

1. Introduction

Persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), continue to raise environmental and public health concerns despite decades of regulatory control [1–4]. Both classes comprise semivolatile, halogenated compounds that exhibit chemical stability, hydrophobicity, and resistance to environmental degradation processes, enabling their long-term persistence in soils and sediments and facilitating their atmospheric transport over distances [1,5]. OCPs, including dichloro-diphenyl-trichloroethane (DDT), benzene hexachloride (BHC) isomers, aldrin, dieldrin, endosulfan, and related compounds, were extensively used worldwide from the 1940s for pest control in agriculture and vector management. In contrast, PCBs, comprising 209 possible congeners, were manufactured on a large scale for use as dielectric and coolant fluids, plasticizers, and building materials [3].

Although the European Union (EU) and many other regions banned or severely restricted the use of PCBs and many OCPs in the late 1970s and 1980s, their historical usage and persistence have led to their detection in environmental compartments, especially in soils and sediments, where they act as long-term reservoirs and secondary sources to the environment. PCBs and legacy pesticides remain regularly detected

☆ Manuscript prepared for submission to Journal of Chromatography Open (Elsevier), SI "Advances in Multidimensional Chromatographic Techniques".

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https://doi.org/10.1016/j.jcoa.2025.100245
Received 27 June 2025; Received in revised form 4 August 2025; Accepted 7 August 2025
Available online 7 August 2025

across Europe, sometimes exceeding regulatory thresholds for ecological and human health protection [4,6].

The risks posed by OCPs and PCBs are well established, with documented adverse effects including endocrine disruption, neurotoxicity, immunotoxicity, and carcinogenicity in both humans and wildlife. Their bioaccumulative nature facilitates trophic transfer and biomagnification, including both substance groups in Annexes A and B of the Stockholm Convention on Persistent Organic Pollutants [2]. The Water Framework Directive (2000/60/EC), Directive 2013/39/EU, and Environmental Quality Standards Directive (2008/105/EC) further establish environmental quality standards (EQS) for priority hazardous substances, including PCBs and several OCPs [7,8]. Similarly, the REACH Regulation (EC 1907/2006) requires monitoring, reporting, and remediation measures for contaminated sites and restricts the use of these substances on the market [9].

Analytical determination of OCPs and PCBs in soils and sediments is fundamental for regulatory compliance, environmental monitoring, and risk assessment. However, such analysis remains analytically demanding due to the complexity of environmental matrices and the low levels at which these contaminants are present, often requiring detection at trace levels to meet legal requirements and international guidelines [6,10]. Soil and sediment matrices are inherently heterogeneous and may contain large amounts of natural organic matter, sulfur compounds, and other co-extracted interferents that can impair extraction efficiency, cause matrix effects, and challenge accurate quantification [10,11].

Classical sample preparation approaches such as Soxhlet extraction, liquid-liquid extraction (LLE), and QuEChERS have been employed to isolate OCPs and PCBs [12,13]. While effective, these methods are laborious and solvent-intensive and may suffer from limited selectivity or efficiency in multi-residue analysis. Solid-phase extraction (SPE) is one of the preferred techniques for sample cleanup and pre-concentration, mainly due to its accessibility and ease of use [12,14,15].

On the instrumental side, the physicochemical properties of these contaminants make gas chromatography (GC) the preferred separation technique. Electron capture detection (ECD) remains widely used for routine monitoring due to its high sensitivity for halogenated compounds, while coupling GC with tandem mass spectrometry (GC–MS/MS) offers enhanced selectivity and confirmatory capability, particularly in complex matrices [3,4,13,16,17].

Alternatively, comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) has enhanced the ability to resolve complex mixtures and achieve lower detection limits. Over the last decade, thanks to the evolution of hardware and software, which has made the technology more robust and user-friendly, GC×GC has been increasingly exploited for environmental applications [6,10,18].

In this context, the present study aimed to develop and validate an analytical protocol for determining 22 organochlorine pesticides and 27 polychlorinated biphenyls in sediment samples in the same analytical run. The protocol combines SPE-based sample purification and enrichment with high-resolution chromatographic separation and detection by GC×GC-TOFMS. The method performance was evaluated in terms of sensitivity, linearity, accuracy, and precision, with validation performed using certified reference materials and real sediment samples.

2. Experimental section

2.1. Chemicals, supplies, and samples

All solvents used in this study were of analytical grade or higher purity. Acetone, hexane, and isopropanol were purchased from VWR International. PBI S.R.L. (Pestinorm grade). Organic-free water was prepared by liquid-liquid extraction of ultrapure water (Milli-Q® system, Millipore, Bedford, MA, USA) with hexane. Florisil 1 g SPE cartridges were obtained from Supelco (Bellefonte, PA, USA).

Certified standards used for calibration included 49 organochlorine compounds (22 OCPs and 27 PCBs) (**Table S1**), acquired from Ultra Scientific Italia S.R.L. (PCB 10 μg mL^{-1}, in isooctane, pesticides mixture 100 μg mL^{-1}, in acetone). The internal standard solution (decachlorobiphenyl, 1000 μg mL^{-1} in hexane) was purchased from Agilent Technologies (RPC-060S; Santa Clara, CA, USA). Tetra-n-butylammonium (TBA) sulfite and sodium sulfite (Na_2SO_3) used for sulfur cleanup were acquired from Sigma-Aldrich (St. Louis, MO, USA).

Certified reference sediment (CNS391–50 G, lot LRAC1441), containing known concentrations of OCPs and PCBs, was obtained from Sigma-Aldrich. Additional sediment samples (S1, S2, and S3) analyzed in this study were collected in the northern Adriatic Sea. The sediments were collected using a Van Veen grab sampler with a sampling area of 0.1 m^2. Once brought on board the support vessel, each sample was diluted with seawater and passed through a 1 mm mesh sieve. All samples were then placed in amber glass containers and stored at −18 °C (±2 °C) prior to lyophilisation and then stored at 4 °C before extraction. The fractions containing the analytes of interest were analyzed in the days following the extraction.

2.2. Solid phase extraction (SPE)

The extraction and cleanup of organochlorine pesticides and PCBs from sediment samples were based on a combination of EPA methods 3550B, 3660, and 3620C, with minor modifications [19–21].

For extraction, 5 g of lyophilized sediment was weighed and transferred into a glass vial. Samples were extracted three times consecutively by sonication for 10 min each with 20 mL of a 1:1 (v/v) acetone:hexane mixture. After each extraction, the mixture was allowed to settle, and the supernatant was centrifuged at 3000 rpm for 5 min. Supernatants from all three extractions were pooled, yielding a total extract volume of 60 mL. The pooled extract was concentrated under a gentle stream of nitrogen at 30 °C to a final volume of approximately 1 mL, avoiding dryness to prevent loss of semivolatile analytes [21].

Sulfur interferences were removed according to EPA Method 3660. One milliliter of the concentrated extract was transferred to a glass vial with 1 mL of clean hexane. Subsequently, 1 mL of TBA sulfite solution and 2 mL of isopropanol were added, and the mixture was vortexed for 1 min. Then, 5 mL of organic-free water was added, followed by an additional 1-minute vortex and a resting phase of 5–10 min to allow phase separation. The upper hexane layer was recovered for cleanup [21].

Cleanup was performed using SPE on 1 g Florisil cartridges. Cartridges were conditioned with 4 mL of hexane without drying. The recovered hexane extract (1 mL) was loaded onto the cartridge and eluted with 9 mL of a 10:90 (v/v) acetone:hexane mixture. The eluate was evaporated under nitrogen at 30 °C to near dryness, reconstituted to exactly 1.0 mL with hexane, and spiked with 20 μL of internal standard solution (decachlorobiphenyl, 1000 μg mL^{-1} in hexane) [19].

2.3. Instrumental experimental conditions

GC×GC-TOFMS analyses were performed on an Agilent 8890 GC, equipped with a quad-jet dual-stage cryogenic modulator (LECO Corporation, Mönchengladbach, Germany) and a PAL System device (CTC Analytics AG, Zwingen, Switzerland), coupled to a Pegasus BTX time-of-flight mass spectrometer (LECO Corporation). Chromatographic separation was achieved using an HP-5 ms Ultra Inert column (30 m × 0.25 mm × 0.25 μm d_f) as the primary dimension and an Rxi-17SilMS column (1.3 m × 0.25 mm × 0.25 μm d_f) as the secondary dimension. Ultra-high-purity helium gas was used as the carrier gas (1.40 mL min^{-1}).

The GC oven temperature program began at 45 °C (held for 1.25 min), followed by a ramp of 5 °C min^{-1} to 330 °C (held for 5 min). Temperature offsets for the secondary oven and modulator were set at +10 °C and +15 °C, respectively, with respect to the main oven temperature. A 2.8-second modulation period was employed, with a hot jet

duration of 0.84 s. The transfer line and electron ionization ion source temperatures were set at 330 °C and 250 °C, respectively, with an ionization energy of 70 eV. A mass range of 29 to 600 *m/z* was collected, with an acquisition delay of 180 s and an acquisition frequency of 150 Hz. The data were collected and processed using ChromaTOF software version 5.56 (LECO Corporation). The quantification ion for each analyte was selected based on the mass providing the highest selectivity, with a mass tolerance of 500 mDa.

2.4. Calibration, quality assurance (QA), and quality control (QC)

Quality assurance and quality control (QA/QC) procedures were applied throughout the study to ensure the reliability of analyses. These procedures, including calibration strategies, instrumental performance checks, and contamination control, were adapted from established analytical methodologies commonly employed in chromatographic analyses [22,23].

Multiple blank samples were analyzed during the study to assess potential contamination. Instrumental performance was continuously monitored through daily mass calibration, ensuring accurate mass assignments throughout the analyses. Leak tests were performed before each batch.

An external calibration method was developed and validated for each target compound. Calibration solutions at concentrations ranging from 0.10 to 1.96 μg kg^{-1} were prepared from certified standards Ultra PPM-5090–1 (100 μg mL^{-1} in acetone) and Ultra RPCM-240–1 (10 μg mL^{-1} in isooctane), along with an internal standard (0.98 μg kg^{-1}). These solutions were then analyzed using GC×GC-TOFMS. Calibration curves were constructed by dividing the peak area of each analyte by the internal standard peak area (decachlorobiphenyl) and plotting this ratio against concentration. The analyte concentrations in the sediment extracts were subsequently determined by interpolation from these calibration curves.

Calibration curves were fitted using the least squares method, with a minimum correlation coefficient (r^2) of 0.9. Method validation also included the evaluation of accuracy (determined in triplicate at 0.10 μg L^{-1}, expressed as the percentage difference between the expected and measured concentrations), precision (expressed as the relative standard deviation (RSD %) at the lowest level of the calibration curve), limit of detection (LOD), and limit of quantitation (LOQ). LOD and LOQ were estimated based on the calibration curve, using the standard deviation of the response (σ) and the slope of the curve (S), according to: LOD = 3.3 × (σ/S) and LOQ = 10 × (σ/S) [24].

The analytical method was further validated by analyzing a certified reference material (CNS391–50 G, lot LRAC1441, Sigma-Aldrich), consisting of sediment fortified with known concentrations of pesticides and PCBs. Compound identification in both the reference material and environmental samples was based on retention time verification in both chromatographic dimensions (^1t_R and ^2t_R), combined with spectral matching. The experimental results were then compared with the certified values to confirm the accuracy and reliability of the method.

3. Results and discussion

3.1. Method development and validation

The chromatographic separation achieved by GC×GC-TOFMS is illustrated in Fig. 1, demonstrating the system's capacity to resolve the 49 target analytes (22 OCPs and 27 PCBs). The separation was carried out by exploiting non-polar and relatively polar primary and secondary dimensions, respectively. This high resolving power is critical for the trace-level quantification of OCPs and PCBs in heterogeneous sediment samples.

The performance of the developed SPE-GC×GC-TOFMS method was evaluated using external calibration standards and a set of analytical quality parameters. Table 1 summarizes the key figures of merit obtained for the target compounds, while full calibration curve parameters are provided in the Supplementary Material (**Table S2**).

The method exhibited high linearity ($r^2 > 0.99$ for the majority of analytes), accuracy usually within the 90–110 % range, and precision with relative standard deviations below 5 % for most target compounds. LOD and LOQ were exceptionally low, ranging from 0.4 to 14 ng kg^{-1} and 1.1 to 41 ng kg^{-1}, respectively. These limits are substantially lower than the sediment guideline values adopted by national and international bodies. For instance, the Netherlands target values for sediment are 20 μg kg^{-1} for the sum of seven indicator PCBs, 10 μg kg^{-1} for total DDT (sum of DDT, DDE, and DDD), 0.09 μg kg^{-1} for hexachlorobenzene, 0.03 μg kg^{-1} for chlordane, and 5 μg kg^{-1} for the sum of "drins" (aldrin, dieldrin, and endrin) [25]. OSPAR background assessment criteria (BACs) for individual PCB congeners in sediment range from 0.10 to 0.22 μg kg^{-1}, while environmental assessment criteria (EACs) extend up to 40 μg kg^{-1}, depending on the congener [26]. Canadian sediment quality guidelines (CCME) specify interim sediment quality guidelines of 34.1 μg kg^{-1} for total PCBs and 1.19 μg kg^{-1} for total DDT [27].

For 4,4′-DDT and related isomers, international sediment guidelines generally fall within the 1 to 20 μg kg^{-1} range, while the LOQs achieved for 4,4′-DDT and 4,4′-DDE were 9.4 ng kg^{-1} and 15 ng kg^{-1}, respectively. For individual PCB congeners, such as PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, and PCB-180, the LOQs (2.5 to 13 ng kg^{-1}) resulted below the BACs and far below the EACs established by OSPAR, as well as the target values used by the Netherlands and the guidelines in North America. For other OCPs, including aldrin, dieldrin, endrin, and

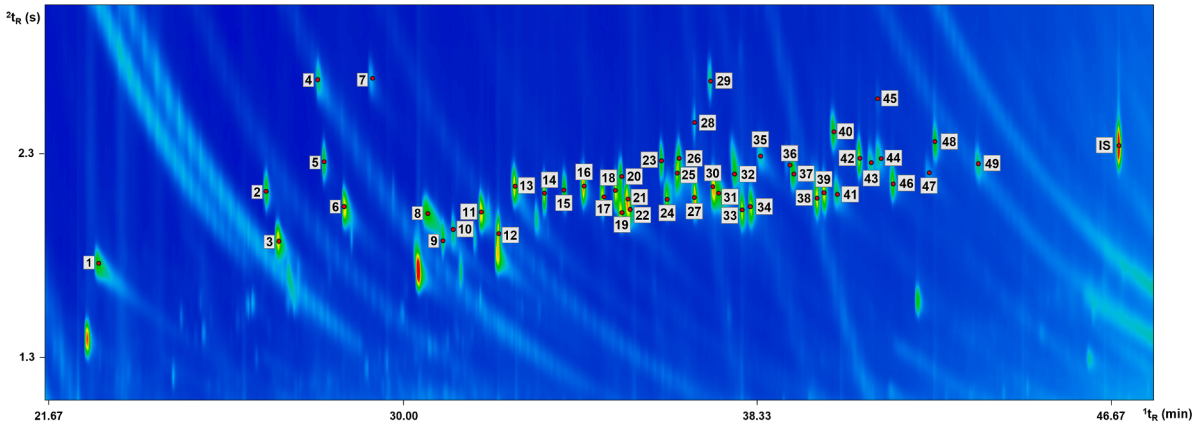

Fig. 1. GC×GC-TOFMS 2D plot of the calibration standard mixture at 0.10 μg kg^{-1}. Target OCPs and PCBs are labeled by number (refer to Table 1 for the identification), and the internal standard (decachlorobiphenyl) is indicated.

Table 1
Analytical parameters for the calibration curves of target organochlorine compounds analyzed by GC×GC-TOFMS. LOD and LOQ were estimated based on the calibration curve, using the standard deviation of the response (σ) and the slope of the curve (S), according to: LOD = 3.3 × (σ/S) and LOQ = 10 × (σ/S) [24].

#	Target	^1t_R (min)	^2t_R (s)	Quantifier ion (*m/z*)	r^2	LOD (ng kg^{-1})	LOQ (ng kg^{-1})	Accuracy (%)[a]	Precision (%)[b]
1	Pentachlorobenzene	22.7	1.79	250	0.9999	4.0	12	97	2.7
2	α-BHC	26.7	2.13	181	0.9984	3.0	9.1	102	2.7
3	Hexachlorobenzene	27.0	1.89	282	0.9996	6.1	18	106	3.5
4	ß-BHC	27.9	2.68	219	0.9988	4.3	12	96	3.1
5	γ-BHC	28.1	2.26	219	0.9956	1.8	5.4	98	1.7
6	PCB-18	28.6	2.04	256	0.9997	3.0	9.0	99	1.9
7	δ-BHC	29.2	2.69	219	0.9982	2.3	6.8	114	1.7
8	PCB-28	30.7	1.98	256	0.9994	4.1	13	98	2.8
9	Heptachlor	30.9	1.88	272	0.9920	4.1	12	109	4.5
10	Alachlor	31.2	1.94	146	0.9986	0.9	2.6	99	1.8
11	PCB-52	31.8	2.04	292	0.9980	4.4	13	103	2.8
12	Aldrin	32.3	1.90	263	0.9998	1.0	3.2	102	0.6
13	PCB-44	32.6	2.16	292	0.9996	2.7	8.3	97	1.9
14	Isodrin	33.3	2.11	193	0.9998	2.3	7.0	107	1.4
15	Heptachlor epoxide	33.8	2.12	353	0.9947	3.7	11	110	3.1
16	PCB-95	34.2	2.13	326	0.9993	0.9	2.7	103	0.6
17	*trans*-Chlordane	34.7	2.10	373	0.9995	7.4	23	100	4.0
18	2,4′-DDE	35.0	2.12	318	0.9990	5.2	16	99	3.4
19	PCB-101	35.1	2.03	326	0.9929	4.1	12	114	3.3
20	Endosulfan I	35.1	2.18	195	0.9996	2.1	6.3	96	2.2
21	*cis*-Chlordane	35.2	2.09	373	0.9983	1.0	3.1	108	0.8
22	PCB-99	35.3	2.03	326	0.9994	3.2	9.8	99	1.9
23	Dieldrin	36.1	2.26	79	0.9997	0.4	1.2	98	0.2
24	4,4′-DDE	36.2	2.09	318	0.9991	4.9	15	100	3.4
25	PCB-110	36.4	2.21	326	0.9953	1.8	5.6	108	1.4
26	2,4′-DDD	36.5	2.27	235	0.9926	1.1	3.4	106	1.0
27	PCB-151	36.9	2.08	360	0.9994	3.1	9.3	102	2.2
28	Endrin	36.9	2.45	263	0.9995	7.2	22	95	2.9
29	Endosulfan II	37.2	2.67	195	0.9972	0.4	1.1	104	0.8
30	PCB-149	37.3	2.15	360	0.9998	3.5	11	100	2.1
31	PCB-118	37.4	2.13	254	0.9986	0.8	2.5	90	1.1
32	PCB-114	37.7	2.23	326	0.9989	2.2	6.7	106	3.2
33	PCB-146	37.9	2.03	360	0.9955	1.2	3.5	105	0.9
34	PCB-153	38.2	2.05	360	0.9992	2.3	6.8	104	1.7
35	PCB-105	38.3	2.33	326	0.9979	0.9	2.7	96	2.2
36	4,4′-DDT	39.0	2.27	235	0.9154	3.1	9.4	139	3.7
37	PCB-138	39.1	2.23	360	0.9977	2.5	7.5	102	1.8
38	PCB-187	39.7	2.08	396	0.9976	3.4	10	105	2.0
39	PCB-183	39.9	2.11	396	0.9995	2.5	7.6	102	1.7
40	PCB-128	40.1	2.43	360	0.9974	2.1	6.3	98	1.8
41	PCB-167	40.1	2.14	360	0.9994	2.3	6.9	102	2.0
42	PCB-177	40.7	2.27	394	0.9984	1.4	4.4	104	1.0
43	PCB-156	40.9	2.30	360	0.9902	1.7	5.1	107	1.7
44	PCB-157	41.1	2.32	360	0.9950	2.1	6.3	110	2.4
45	Methoxychlor	41.1	2.59	227	0.9063	14	41	136	24
46	PCB-180	41.5	2.17	394	0.9986	1.9	5.7	99	1.3
47	PCB-169	42.2	2.25	360	0.9997	3.3	9.8	100	3.9
48	PCB-170	42.5	2.36	394	0.9988	1.1	3.2	102	0.8
49	PCB-189	43.5	2.27	394	0.9974	4.3	13	95	2.7

[a] : 0.20 μg kg^{-1}, $n = 3$.
[b] : 0.10 μg kg^{-1}, $n = 3$.

chlordane, national and international sediment guidelines usually range from 0.01 to 5 μg kg^{-1}, with the LOQs in this study (e.g., 1.2 ng kg^{-1} for dieldrin, 2.6 ng kg^{-1} for alachlor, and 3.1–23 ng kg^{-1} for chlordane isomers) demonstrating analytical sensitivity that meets or exceeds regulatory requirements [25–27].

The performance of SPE-based sample preparation observed in this study is consistent with the literature, which demonstrates its effectiveness for the cleanup, enrichment, and automation of trace organic pollutants in environmental analysis. For instance, Tomazini et al. employed ultrasound-assisted extraction (UAE) combined with SPE cleanup using Florisil® and GC-ECD, achieving recoveries between 81 % and 108 % with RSDs below 6 %, and LODs between 2 and 6 μg kg^{-1} [11]. Yang et al. developed an SPE method for the enrichment of 23 PCB congeners in wastewater, followed by GC–MS analysis, obtaining recoveries of 70.6–92.4 % and LODs between 0.05–0.22 ng l^{-1} [15]. Zeng et al. compared multiplug filtration cleanup (m-PFC) and SPE methods for pesticide residue analysis in fruits and vegetables by GC-ECD and GC-FPD, achieving recoveries from 67 % to 112.8 % and RSDs between 0.2 % and 15.2 % [16]. A broader compilation of relevant analytical methods is summarized in Supplementary Material (**Table S3**).

Overall, the developed method meets and surpasses the regulatory and guideline values established for sediment monitoring. The combination of low LOQs and high selectivity enables reliable compliance assessment, effective surveillance of contaminated and background sites, and early detection of contamination events. In addition, these figures of merit ensure comparability with international datasets, as many published studies report higher LOQs, often in the 0.1–1.0 μg kg^{-1} range, for similar analytes. The SPE-GC × GC-TOFMS method, therefore, provides robust analytical performance suitable for routine monitoring of OCPs and PCBs in sediments under European and international standards.

Validation of the method was further assessed through the analysis of a certified reference sediment (CNS391–50 G, Sigma-Aldrich, lot LRAC1441) containing known concentrations of multiple OCPs and

PCBs. Fig. 2 presents a comparison between the concentrations determined experimentally and the certified values for each target analyte, with tolerance intervals indicated for reference.

As can be observed, the experimental results fell within the certified tolerance ranges, demonstrating satisfactory trueness and precision of the method. For instance, compounds such as δ-BHC, aldrin, dieldrin, endrin, 2,4′-DDD, PCB-153, and PCB-138 exhibited measured concentrations that were within the lower and upper certified limits. The standard deviations associated with these measurements were generally low, supporting the method's reliability for quantification in complex matrices.

Overall, such agreement between the experimental and certified values across the majority of target analytes confirms the accuracy of the entire analytical workflow, including extraction, cleanup, and quantification procedures. These results provide strong evidence of the method's suitability for analyzing OCPs and PCBs in sediment matrices, fulfilling the requirements for trace-level determination in environmental monitoring.

3.2. Application to real-world samples

The validated method was then applied to analyze environmental sediment samples (S1, S2, and S3), resulting in the quantified analytes and quantities summarized in Fig. 3.

The concentrations of the target organochlorine compounds varied among samples, ranging from below the quantification limit to approximately 0.17 μg kg^{-1}. Among the PCBs, PCB-28, PCB-44, PCB-52, PCB-101, and PCB-110 were detected in all samples, with the highest concentrations generally observed for PCB-28 (0.13 to 0.17 μg kg^{-1}), PCB-101 (0.12 to 0.13 μg kg^{-1}), and PCB-110 (0.11 to 0.15 μg kg^{-1}). Other congeners, such as PCB-138, PCB-153, and PCB-95, were also present at levels ranging from 0.06 to 0.12 μg kg^{-1}. For OCPs, 4,4′-DDE was detected in all three samples at concentrations ranging from 4.6E-02 to 6.7E-02 μg kg^{-1}. Pentachlorobenzene (PeCB) was only quantifiable in two samples at low levels (7.0E-03 to 8.0E-03 μg kg^{-1}).

The concentration ranges observed are consistent with recent environmental monitoring studies in Europe and elsewhere, which have reported similar or slightly higher levels of legacy PCBs and OCPs in sediments, reflecting the ongoing persistence of these pollutants despite regulatory restrictions [3,4,10].

All measured concentrations were below sediment guideline values, which generally range from 0.2 to 1 μg kg^{-1} for individual PCBs and up to 1 μg kg^{-1} for OCPs [25–27]. The low levels observed reflect both the high sensitivity of the method and the effectiveness of historical regulatory restrictions on these substances. Standard deviations were low, attesting to the method's reproducibility even at trace levels.

These findings confirm the continued environmental relevance of legacy POPs in sediment matrices while also demonstrating the method's suitability for ultra-trace quantification in routine environmental surveillance and risk assessment.

Fig. 4 shows the total ion chromatogram (TIC) of a sediment sample, in which the 12 target analytes are highlighted. The value of the GC×GC separation is further evidenced in real-world samples, where the complexity of the sediment sample extract is evident. Numerous additional compounds, mainly phenolic compounds and aliphatic and aromatic hydrocarbons, are present and could potentially interfere with the determination of the target contaminants if sufficient selectivity is not achieved. Although outside the scope of this study, the comprehensive information provided by GC×GC-TOFMS also enables non-targeted analysis, allowing the identification of additional analytes or contaminants that might be overlooked by targeted techniques such as GC–MS/MS.

4. Conclusions

This study presents the development and validation of an analytical

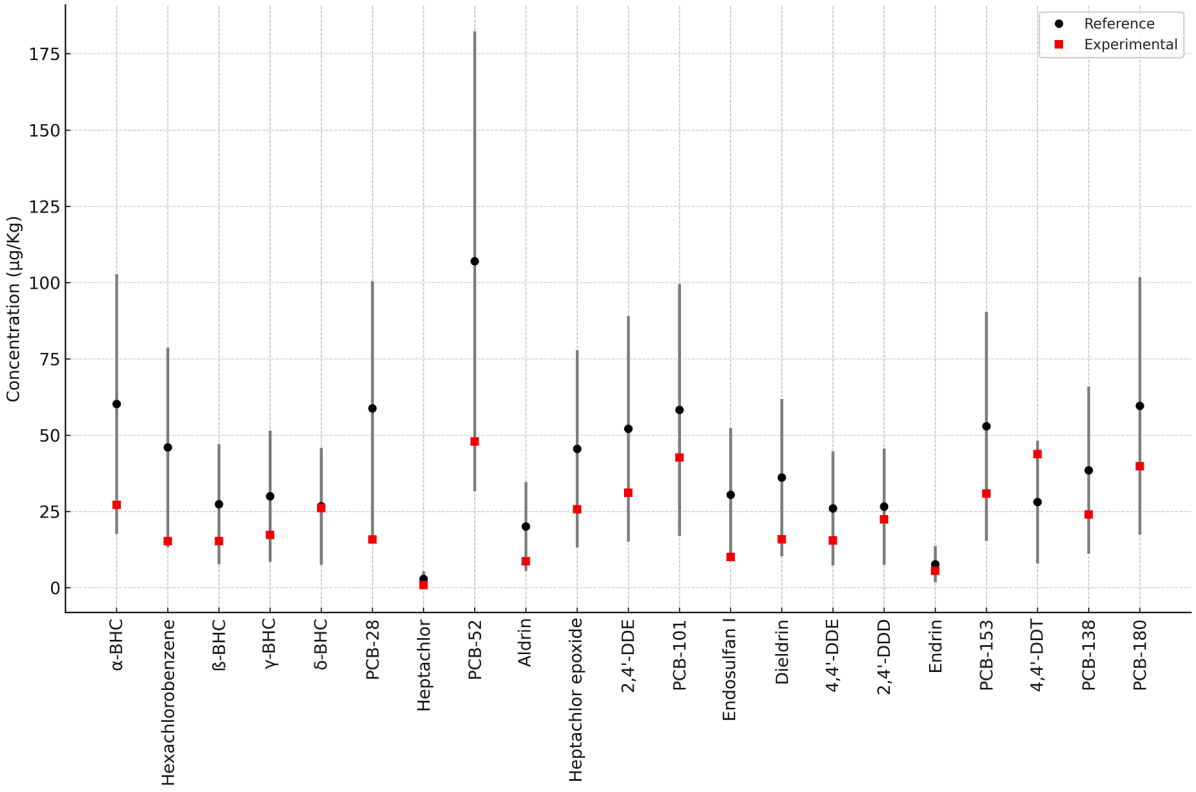

Fig. 2. Certified (black circles) and experimental (red squares) concentrations of pesticides and PCBs in the reference sediment sample. Vertical gray lines indicate the certified tolerance range for each compound.

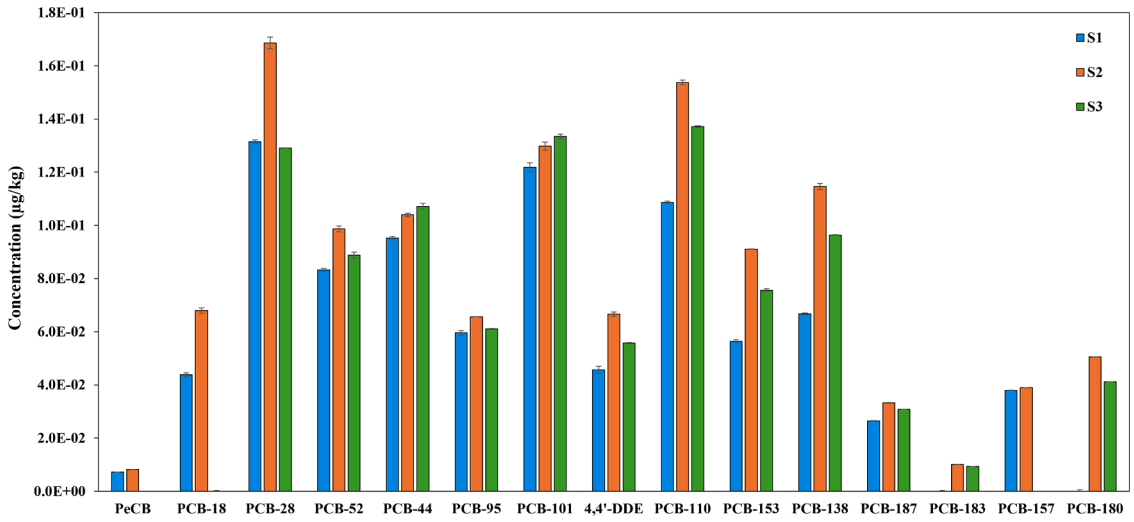

Fig. 3. Concentrations of target organochlorine compounds (µg kg^{-1}) detected in sediment samples S1, S2, and S3, collected from different sites in the northern Adriatic Sea.

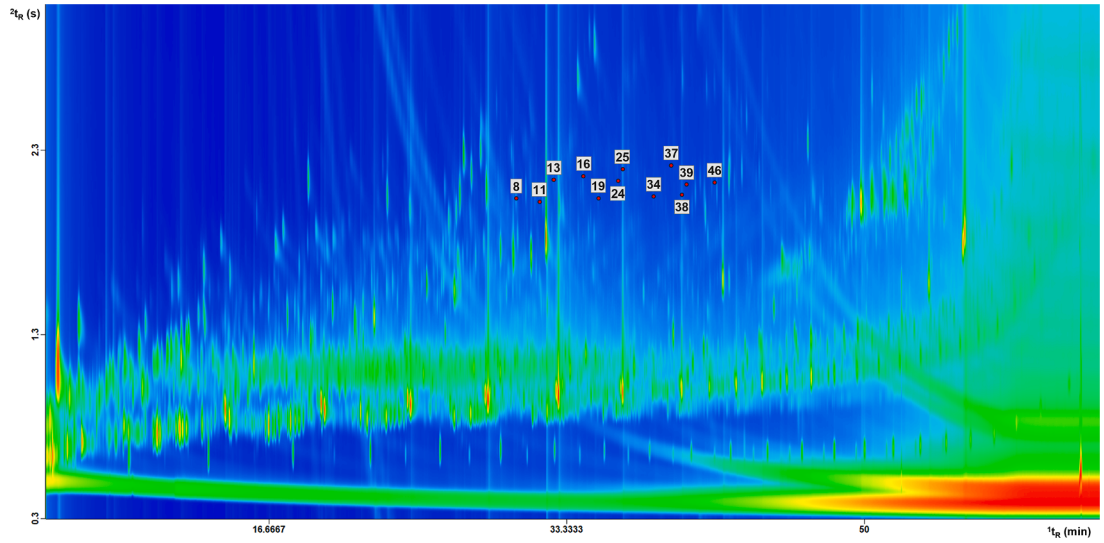

Fig. 4. Representative GC × GC-TOFMS 2D chromatogram of the environmental sediment sample S1. Detected OCPs and PCBs are annotated. For peak ID, please refer to Table 1.

protocol for the simultaneous determination of OCPs and PCBs in sediments, employing SPE-GC×GC-TOFMS. The developed workflow demonstrates the applicability of GC×GC-TOFMS for target determination of OCPs and PCBs in sediments.

The method provided detection and quantification limits in the sub-nanogram-per-gram range for all target analytes. Validation using certified reference material indicated agreement between experimental and certified values for most compounds, supporting the accuracy and reliability of the approach for complex environmental matrices.

Analysis of environmental sediment samples revealed the detection of multiple legacy POPs, including PCB congeners and DDT-related compounds. All measured values were lower than the guideline limits set by European and international authorities for sediments. The results indicate a predominance of historical contamination, consistent with restrictions implemented in the past decades. The method demonstrated sufficient sensitivity and selectivity for routine regulatory monitoring and environmental risk assessment of OCPs and PCBs. Additionally, the comprehensive chromatographic data output of GC×GC-TOFMS opens opportunities for non-targeted screening and the identification of emerging or unexpected contaminants.

CRediT authorship contribution statement

Allan Polidoro: Formal analysis, Data curation, Visualization, Writing – original draft. **Valentina Costa:** Investigation, Writing – original draft. **Monica Romagnoli:** Visualization, Writing – original draft. **Elena Sarti:** Investigation, Writing – original draft. **Claudia Stevanin:** Writing – review & editing. **Cinzia Fabbro:** Investigation, Writing – review & editing. **Luisa Pasti:** Resources, Project administration, Writing – review & editing. **Flavio A. Franchina:** Investigation, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank the National Recovery and Resilience Plan, Mission 4, Component 2, Investment 1.5 - NextGenerationEU, Call for Tender No. 3277 dated 30/12/2021; Award Number: 0001052 dated 23/06/2022. The authors would also like to thank Antonella Pagnoni for the fruitful discussions and assistance with sample preparation, and LECO Corporation for their support.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcoa.2025.100245.

Data availability

Data will be made available on request.

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