

Determination of 39 polybrominated diphenyl ether congeners in sediment samples using fast selective pressurized liquid extraction and purification

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Abstract

In order to reduce time of analysis, a new pressurized liquid extraction (PLE) method that automatically and rapidly achieves quantitative and selective extraction of 39 polybrominated diphenyl ether (PBDE) congeners in sediment samples was optimized. It consists of on-line cleanup by inclusion of sorbents in the extraction cell. The new method was compared with a conventional method based on the use of Soxhlet extraction followed by solid-phase extraction (SPE) with cartridges. The instrumental determination was performed by GC–MS, using negative chemical ionization in the selected-ion monitoring mode. Recoveries from 47 to 82% were obtained for spiked tri- to hepta-PBDE congeners in sediment sample. The repeatability of replicate extractions was better than 15% relative standard deviation. The detection limits obtained with the new developed method were between 1 and 46 pg/g dry weight. The reduction in the sample preparation (extraction + cleanup) time (from days to 30 min) with a similar efficiency than that afforded by the conventional Soxhlet extraction–SPE cleanup technique indicates the suitability of this method. The method was applied to sediment samples where the analytes were detected in the range of 0.86–2.49 ng/g dry mass.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used in large quantities as flame-retardant additives in polymers, especially in the manufacture of a great variety of electrical appliances, including televisions and computers, building materials, and textiles [1]. Structural similarity to other environmental chemicals with known toxic effects (polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), dioxins) indicated that PBDEs can be harmful to health. The acute toxicity of PBDEs is low, however, there is concern for its long-term effects on the endocrine system [2,3]. Moreover, for many countries decreasing levels of organochlorine compounds have been reported recently in human milk [4] while levels for PBDEs increased continuously since 1972 [5]. Due to these findings, there is a growing tendency to analyze PBDEs in various environmental and biotic matrices.

The development of analytical methods to analyze PBDEs is a hard task. Several methods for analysis of PBDEs have been developed involving extraction with organic solvents or supercritical fluid extraction and further cleanup by adsorption chromatography [6] or by SPE [7]. Most of the analyses have concentrated on only a few specific major PBDE congeners. However, a simple and rapid method for the ultra-trace quantification of individual congeners is required to determine the extent of environmental exposure, the risk associated with specific congeners and their fate in the environment.

It is a well-known fact that pressurized liquid extraction (PLE) allows reduction of both extraction time and organic solvent consumption and increases sample throughput. Their uses have been reported for several studies in different applications. Recently, a review of the PLE applications for the extraction of moderately non-volatile organic pollutants from a variety of solid environmental matrices has been published [8]. In particular, there are studies on the analysis of different pesticides, polycyclic aromatic hydrocarbons (PAHs), PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) in sediments

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and sludge. However, in most of the reported applications of PLE, an exhaustive cleanup of the extracts prior to injection in the chromatographic system is necessary [9,10]. In an attempt to eliminate this time-consuming step, some authors proposed in-cell cleanup by packing the sample dispersed in an adsorbent, such as modified silica, Florisil or alumina [11,12], for PCB determinations. To our knowledge, there are no works concerning the PBDE extraction by PLE.

The aim of this study was to develop a rapid and simple method for the congener-specific determination of 39 different PBDEs, from mono- to hepta-BDE congeners, in sediment samples. An analytical method based in selective pressurized liquid extraction (SPLE) without further cleanup step was optimized. The quality parameters of the method are reported. In addition, the method was compared with conventional system using a Soxhlet extraction followed by a SPE cleanup. Different sediment samples from Catalonia (NE Spain) were analyzed using the developed method.

2. Material and methods

2.1. Standards and reagents

The Polybrominated Diphenyl Ether Analytical Standard Solution EO-5099 and the Decabrominated Diphenylether (BDE-209) were purchased from Cambridge Isotope Labs. (MA, USA). The components of EO-5099 solution were: 3 mono-BDEs, 7 di-BDEs, 8 tri-BDEs, 6 tetra-BDEs, 7 penta-BDEs, 5 hexa-BDEs and 3 hepta-BDEs (see Table 1). Moreover, the mixture also contains 11 ¹³C-labeled BDE congeners: 1 mono-BDE (¹³C]BDE-3), 1 di-BDE (¹³C]BDE-15), 1 tri-BDE (¹³C]BDE-28), 2 tetra-BDEs (¹³C]BDE-47 and ¹³C]BDE-77), 4 penta-BDEs (¹³C]BDE-99, ¹³C]BDE-100, ¹³C]BDE-118 and ¹³C]BDE-126), 1 hexa-BDE (¹³C]BDE-153) and 1 hepta-BDE (¹³C]BDE-183). The concentrations of each compound ranged from 100 pg/μl for the mono congeners to 250 pg/μl for the hepta congeners. The decachlorinated biphenyl (PCB-209) was purchased from Lab. Dr. Ehrenstorfer (Augsburg, Germany).

Five different solutions were prepared in order to check the linearity of the method. These solutions contained 39 PBDE congeners as well as the BDE-209, at different

concentrations ranging between 5 and 200 pg/μl, and the PCB-209 always at 100 pg/μl.

Solvents (dichloromethane and hexane) for organic trace analysis were purchased from Merck (Darmstadt, Germany). Alumina and Florisil cartridges were obtained from IST. Alumina (0.063–0.200 mm) and copper (<63 μm) were obtained from Merck, and Hydromatrix (pelletized diatomaceous earth) from Varian.

2.2. Sample collection

Samples analyzed in this study were river and marine sediments (RS and MS, respectively) collected using a Van Veen grab. The samples were transferred to the laboratory at a temperature of 4 °C, then frozen at –20 °C before being freeze dried. The lyophilized samples were grounded and homogenized by sieving through a stainless steel 2-mm sieve, and stored in sealed containers at –20 °C until analysis.

For the optimization studies, a river sediment control obtained from river receiving domestic wastewater mixed with wastewater originating from the rubber industry was used.

2.3. Selective PLE

Before extraction, 10 μl of surrogate standard were added to 1 g dry mass of each sample. Spiked samples were kept overnight to equilibrate. PLE was carried out using a fully automated ASE 200 system (Dionex, Sunnyvale, CA, USA). The PLE conditions were optimized for the extraction of PBDE congeners from sediment samples as discussed in Section 3. Alumina was selected as sorbent in the extraction cell. The final optimized method was as follows: a 22 ml extraction cell was loaded by inserting two cellulose filters into the cell outlet, followed by 6 g of alumina. Spiked samples of 1 g were ground with alumina and cooper (1:2:2). The mixture was loaded into the extraction cell on top of alumina. The dead volume was filled with hydromatrix, and the cell was sealed with the top cell cap. The extraction cell was filled with a hexane–dichloromethane (1:1) mixture until the pressure reached 1500 psi, and heated to 100 °C (1 psi = 6894.76 Pa). After an oven heat-up time of 5 min under these conditions, two static extractions of 10 min at constant pressure and temperature were developed. After this static period, fresh solvent was introduced to flush the lines

Table 1
PBDE congeners involved in the present study

Mono-BDEs	Di-BDEs	Tri-BDEs	Tetra-BDEs	Penta-BDEs	Hexa-BDEs	Hepta-BDEs
BDE-1	BDE-7	BDE-17	BDE-47	BDE-85	BDE-138	BDE-181
BDE-2	BDE-8	BDE-25	BDE-49	BDE-99	BDE-153	BDE-183
BDE-3	BDE-10	BDE-28	BDE-66	BDE-100	BDE-154	BDE-190
	BDE-11	BDE-30	BDE-71	BDE-116	BDE-155	
	BDE-12	BDE-32	BDE-75	BDE-118	BDE-166	
	BDE-13	BDE-33	BDE-77	BDE-119		
	BDE-15	BDE-35		BDE-126		

and cell, and the extract was collected in the vial. The flush volume amounted to 100% of the extraction cell. The extraction was cycled twice. The volume of the resulting extract was about 35 ml. Extracts were finally concentrated to incipient dryness and re-dissolved with 10 μl of the recovery standard (PCB-209, 100 $\text{pg}/\mu\text{l}$) and 40 μl of isooctane prior to the analysis by GC–negative chemical ionization (NCI)–MS.

In order to estimate the repeatability of the SPLE method, triplicate analyses were carried out with the river sediment control spiked with PBDE congeners at levels between 1 and 3 ng/g .

2.4. Soxhlet extraction

Soxhlet extraction for comparison of the SPLE results was accomplished in cellulose thimbles containing 1 g sediment control. Two grams of copper was added to sediment to remove sulfur interference. Triplicate extractions were done using 75 ml of a mixture of hexane–dichloromethane (1:1) for 24 h. In order to test the efficiency of the Soxhlet extraction, a subsequent extraction was performed. After extraction, the extracts and the rinses of the Soxhlet were combined, concentrated to a few milliliter by rotary evaporation and then subjected to the cleanup procedure.

2.5. Cleanup

After extraction with Soxhlet, crude extracts were subjected to a purification step. Amount of 2 and 6 g of alumina and Florisil SPE cartridges were tested and compared. The conditioning parameters, sample loading volume and elution parameters were optimized. SPE cartridges were conditioned with 20 ml hexane. The sample volume loaded was ~ 1 ml, and the elution step was performed with 30 ml hexane–dichloromethane (1:2). Samples were finally concentrated to incipient dryness and re-dissolved with 10 μl of the recovery standard (PCB-209, 100 $\text{pg}/\mu\text{l}$) prior to the analysis by GC–NCI–MS.

2.6. Gas chromatography/mass spectrometry

GC–NCI–MS analyses were performed on a gas chromatograph Agilent 6890 connected to a mass spectrometer Agilent 5973 Network (Agilent). A HP-5 ms (30 m \times 0.25 mm i.d., 0.25 μm film thickness) containing 5% phenyl-methylsiloxane (model HP 19091S-433) capillary column was used for the determination of congeners from mono- to hepta-BDEs. The temperature program was from 110 $^{\circ}\text{C}$ (held for 1 min) to 180 $^{\circ}\text{C}$ (held for 1 min) at 8 $^{\circ}\text{C}/\text{min}$, then from 180 to 240 $^{\circ}\text{C}$ (held for 5 min) at 2 $^{\circ}\text{C}/\text{min}$, and then from 240 to 265 $^{\circ}\text{C}$ (held for 6 min) at 2 $^{\circ}\text{C}/\text{min}$, using the splitless injection mode during 1 min. The operating conditions were as follows: ion source temperature = 250 $^{\circ}\text{C}$, ammonia as chemical ionization moderating gas at an ion source pressure of 1.9×10^{-4} Torr

[13] (1 Torr = 133.322 Pa). The experiments were carried out monitoring the two most abundant isotope peaks from the mass spectra corresponding to $m/z = 79$ and 81 ($[\text{Br}]^{-}$).

Confirmation criteria for the detection and quantification of PBDEs should include the following: (a) retention time for all m/z monitored for a given analyte should maximize simultaneously ± 1 s, with signal-to-noise ratio ≥ 3 for each; (b) the ratio between the two monitored ions should be within 15% of the theoretical. Quantification was carried out by internal standard procedure with the PCB-209 as internal standard.

3. Results and discussion

3.1. Investigation of selective PLE

The PLE is a system accepted by the US Environmental Protection Agency (EPA) and other environmental agencies for the extraction of organic compounds from solid matrices. It has been widely applied for the extraction of contaminants like PCBs, pesticides, PAHs from different solid samples. The advantage of this system is that the extraction time is very much reduced and it is automated.

Preliminary studies were carried out in order to select the adsorbent for the selective PLE method. A mixture of 39 PBDE congeners selected for this study, as well as the BDE-209, was loaded in different SPE cartridges: 2 and 6 g of alumina and Florisil. Table 2 shows the different recoveries obtained using these cartridges. As can be seen, both sorbents give acceptable recoveries for the mono- to hepta-BDE congeners. Recoveries were more than 54% (with the exception of mono-BDEs), with values increasing with the degree of bromination. However, the BDE-209 was completely lost with Florisil, whereas the use of alumina cartridges resulted in a good BDE-209 recovery (59–73%). These differences on BDE-209 recoveries could be attributed to the lower polarity of this compound, compared with lower brominated BDE congeners. For this reason, and in order to obtain a methodology to analyze all the degree of bromination, the use of Florisil was rejected and alumina was selected as the sorbent for the SPLE method.

A river sediment control was subjected to SPLE with the aim of finding conditions under which this extraction technique would achieve both an extraction efficiency comparable with the Soxhlet extraction, and an extract ready for injection into the GC–MS system. To optimize the SPLE method, an amount of 1 g of sample spiked with 1–3 ng (depending on the degree of bromination) of the PBDE congeners was dispersed with 2 g of alumina as well as with 2 g of cooper. The extraction cell was charged, and different temperatures (40, 70, 100, and 150 $^{\circ}\text{C}$) were tested using a pressure of 1500 psi and a flush volume of 85% of the cell volume. The effect of the temperature on the recovery is presented in Fig. 1a. One congener of each degree of bromination was selected for the representation. However, similar

Table 2
PBDE recoveries obtained using different SPE cartridges in the purification step

	Alumina		Florisil	
	2 g	5 g	2 g	5 g
Mono-BDEs				
BDE-1	19	27	20	35
BDE-2	24	36	23	39
BDE-3	20	29	22	42
Di-BDEs				
BDE-10	54	66	56	71
BDE-7	65	78	62	78
BDE-11	69	84	64	83
BDE-8	76	94	71	29
BDE-12 + 13	70	84	66	82
BDE-15	70	85	65	84
Tri-BDEs				
BDE-30	79	88	80	86
BDE-32	91	104	91	96
BDE-17	93	108	92	102
BDE-25	90	107	89	100
BDE-28 + 33	89	105	88	98
BDE-35	94	112	95	106
BDE-37	91	110	90	104
Tetra-BDEs				
BDE-75	95	108	99	103
BDE-71	97	113	102	107
BDE-49	97	113	94	108
BDE-47	100	116	105	112
BDE-66	99	116	101	113
BDE-77	106	134	110	123
Penta-BDEs				
BDE-100	103	119	110	114
BDE-119	101	120	111	112
BDE-99	104	122	109	115
BDE-116	96	118	101	108
BDE-118	106	128	112	121
BDE-85	110	132	116	124
Hexa-BDEs				
BDE-154	108	125	117	119
BDE-153	106	127	115	117
BDE-138	113	139	118	125
BDE-166	92	116	92	96
Hepta-BDEs				
BDE-183	106	126	108	107
BDE-181	105	128	93	87
BDE-190	112	135	99	93
Deca-BDE				
BDE-209 ^a	59	73	0	0

^a BDE-209 analyses were performed using a DB-5 ms (15 m × 0.25 mm i.d., 0.25 μm film thickness) column. The temperature program was from 140 °C (held for 1 min) to 325 °C (held for 10 min) at 10 °C/min [18].

behavior was observed for the rest of congeners. For all the temperatures tested (with the exception of mono-, di- and tri-BDEs at 40 °C), recoveries were between 40 and 120%, the range established in some EPA methods [14,15] as the minimum requirement of well accepted methods. However, the best results were achieved working at 100 °C, with re-

coveries ranging between 66 and 106%. This temperature was selected for further experiments.

The effect of the pressure on the recovery was studied in the range between 1000 and 2000 psi (1000, 1500, and 2000 psi), using a temperature of 70 °C and a flush volume of 115% of the cell volume. Results were presented in Fig. 1b, and no significant influence on the recoveries was observed. Acceptable recoveries were obtained for the three different pressures tested, with the exception of mono-BDE congeners. As pressure of 1500 psi is the default pressure of the system, this value was selected for further experiments. Other PLE studies [11,16] also showed that pressure is a parameter without significant effect on the extraction process. The main purpose of applying an increased pressure is to keep the liquid from boiling.

The influence of the solvent used to rinse the cell after the static extraction step (flush percentage) was also studied, modifying its value between 85 and 115% (85, 100, and 115%). These experiments were carried out at 70 °C and 1500 psi. No significant influence on the recoveries was observed (Fig. 1c); however, slightly better recoveries were obtained working at 100%. Thus, the optimal conditions for the SPLE analysis of PBDEs were: temperature of 100 °C, pressure of 1500 psi and 100% of flush volume. These optimal conditions differed from those obtained by Gómez-Ariza et al. [12] for the SPLE analysis of PCBs. They worked at 40 °C, pressure of 2000 psi and 150% of flush volume.

Finally, it should be pointed out that hexane–dichloromethane (1:1) was selected as the extraction solvent in the present work. However, hexane–dichloromethane (80:20) was also tested using the optimized conditions in the SPLE system (100 °C, 1500 psi, 100% flush volume). Similar recoveries were obtained with both extraction solvents (Table 3).

3.2. Comparison of SPLE and Soxhlet–SFE methods

Once the SPLE method was optimized, a study of the repeatability was carried out, analyzing by triplicate the same river sediment spiked with the different PBDE congeners. Results were compared with those obtained using the conventional system with Soxhlet extraction followed by a SPE cleanup with alumina cartridges. Previously, the efficiency of the Soxhlet extraction was tested carrying out a subsequent extraction. No PBDEs were detected in the re-extraction samples, concluding that the first Soxhlet extraction was virtually exhaustive.

Table 3 shows the mean values as well as the associated relative standard deviation of the two methods studied. Recoveries obtained using the optimized SPLE method ranged from 22 to 82%, whereas those obtained by conventional method were in the range of 42 and 81%. In general, the conventional method gives better recoveries for the mono- to tri-BDE congeners. For the rest of congeners (from tetra- to hepta-BDEs), similar results were obtained using both systems. The higher recoveries obtained by the conventional

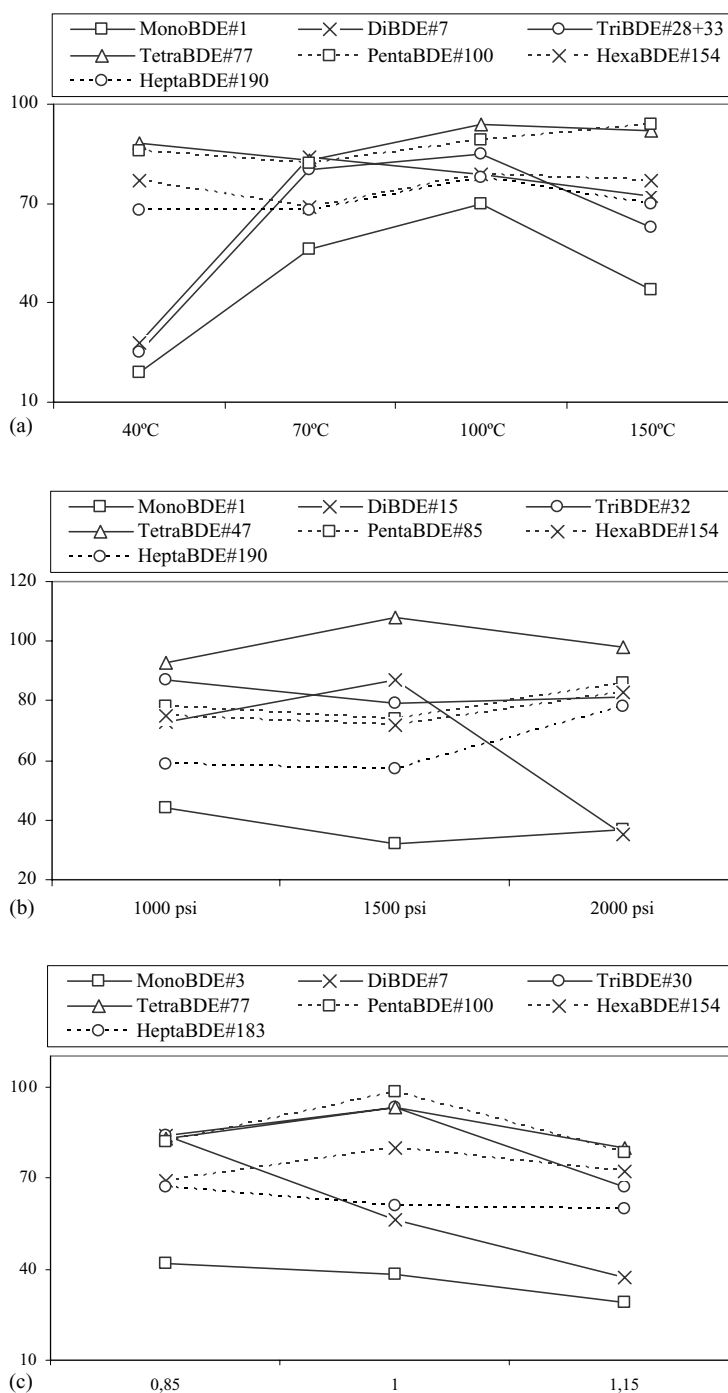


Fig. 1. (a) Influence of the temperature on the selective extraction of PBDEs (1500 psi and 85% of flush volume); (b) influence of the pressure on the selective extraction of PBDEs (70°C and 115% of flush volume); and (c) influence of the flush volume on the selective extraction of PBDEs (70°C and 1500 psi).

method for the lower brominated compounds could be attributed to the purification of the extracts. The chromatographic region where mono- through tri-BDEs eluted, presented a high degree of purification when conventional system was applied. However, relative standard deviations of the SPLE method were lower than those obtained using the conventional method, especially when the degree of bromination increased. For the major congeners de-

tected in sediment samples, tetra-BDE-47, penta-BDE-99, penta-BDE-100 and hexa-BDE-153, the optimized SPLE method achieved recoveries in the range of 60 and 75%, with relative standard deviation lower than 5%. The low standard deviations obtained with SPLE method could be the result of the automation of the system.

The method detection limits (LOD_{method}) obtained using SPLE followed by GC-NCI-MS in SIM mode are shown

Table 3

PBDE recoveries obtained using the conventional Soxhlet–SPE method as well as the optimized SPLE method

	Soxhlet–SPE method		Optimized SPLE method		SPLE, hexane–dichloromethane (4:1)
	Mean (<i>n</i> = 3)	RSD (%)	Mean (<i>n</i> = 3)	RSD (%) CV	
Mono-BDEs					
BDE-1	42	6	23	9	24
BDE-2	78	32	24	4	38
BDE-3	46	9	22	11	28
Di-BDEs					
BDE-10	53	3	41	4	38
BDE-7	57	2	40	9	39
BDE-11	51	2	34	5	34
BDE-8	51	2	34	5	34
BDE-12+13	58	1	41	7	39
BDE-15	61	7	34	13	30
Tri-BDEs					
BDE-30	64	1	53	10	56
BDE-32	65	1	54	8	57
BDE-17	71	3	56	6	57
BDE-25	64	4	56	6	57
BDE-28 + 33	68	2	62	6	63
BDE-35	70	3	67	7	70
BDE-37	70	4	70	10	72
Tetra-BDEs					
BDE-75	68	7	65	5	68
BDE-71	76	2	72	6	70
BDE-49	77	10	72	6	70
BDE-47	81	4	74	2	79
BDE-66	71	7	72	3	73
BDE-77	74	12	82	2	85
Penta-BDEs					
BDE-100	70	8	60	1	62
BDE-119	67	10	63	4	63
BDE-99	82	9	75	2	77
BDE-116	67	8	58	2	60
BDE-118	69	14	67	1	70
BDE-85	70	13	66	1	69
Hexa-BDEs					
BDE-154	67	9	61	3	63
BDE-153	63	13	68	5	71
BDE-138	64	16	65	5	70
BDE-166	64	16	65	5	70
Hepta-BDEs					
BDE-183	61	12	53	10	59
BDE-181	52	11	46	12	54
BDE-190	53	12	47	14	55

SPLE recovery results, using hexane–dichloromethane (4:1) as solvent extraction, were also included.

Table 4

PBDE detection limits (expressed as pg/g) obtained by SPLE–GC–NCI–MS and Soxhlet–SPE–GC–NCI–MS

	SPLE–GC–NCI–MS	Soxhlet–SPE–GC–NCI–MS
Mono-BDEs	18–26	16–50
Di-BDEs	1–19	4–21
Tri-BDEs	5–10	4–14
Tetra-BDEs	12–34	3–13
Penta-BDEs	6–46	7–27
Hexa-BDEs	8–24	13–36
Hepta-BDEs	6–13	5–15

in Table 4. The values were compared with those obtained using the conventional Soxhlet–SPE–GC–NCI–MS method. The LODs were based on the peak-to-peak noise of the baseline near the analyte peak obtained by analyses of a spiked sediment control, and on minimal value of signal-to-noise ratio of 3. The LOD_{method} obtained with the new developed method were between 1 and 46 pg/g, showing similar values to those found for Soxhlet–SPE followed by GC–NCI–MS (from 3 to 50 pg/g).

Fig. 2 shows the chromatograms obtained for spiked sediment using both system. Extracts were sufficiently clean,

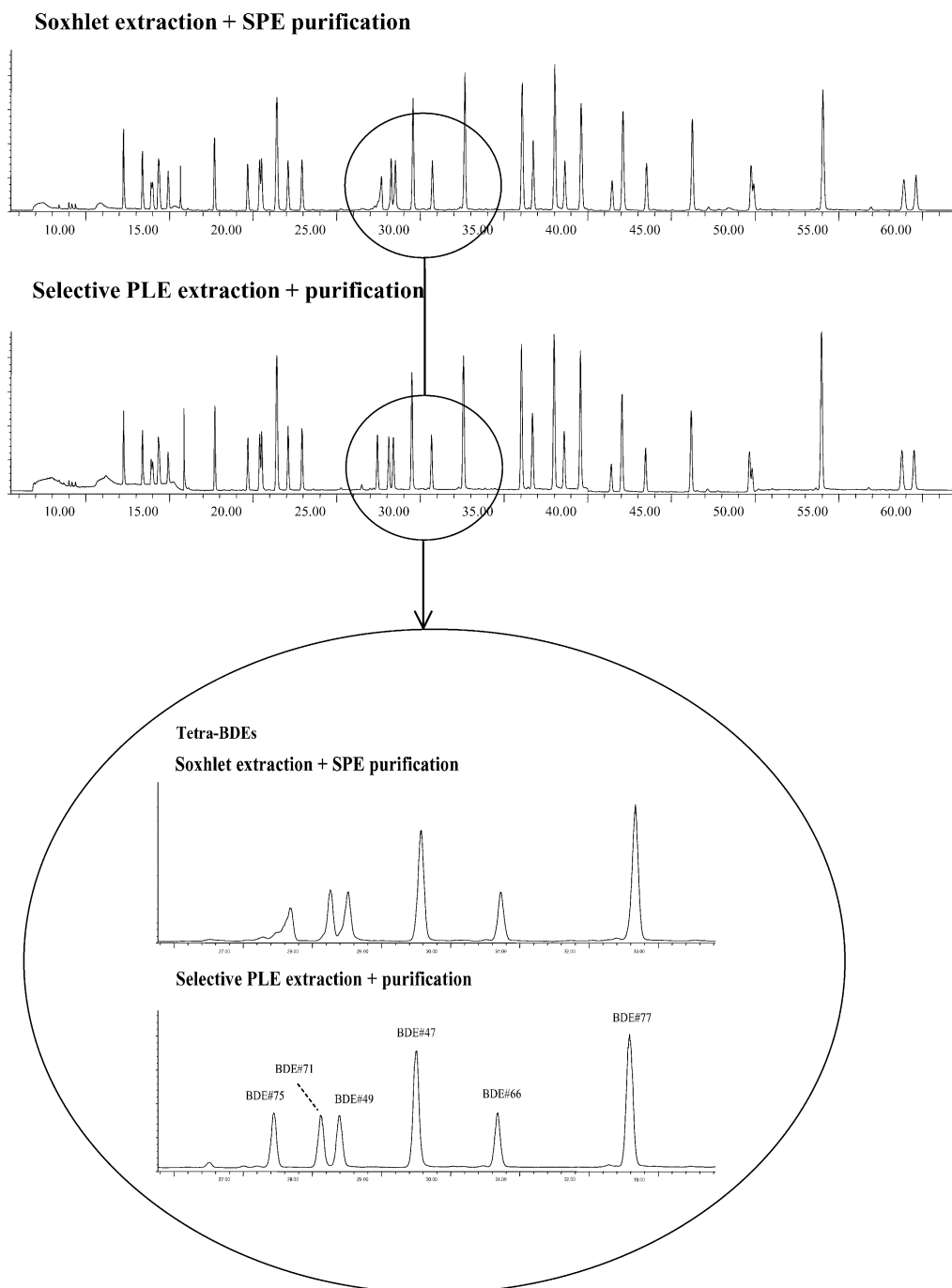


Fig. 2. m/z 79 chromatograms obtained for a spiked sediment sample using the SPLE and the conventional procedures. Tetra-BDEs window was magnified.

allowing the detection and quantification of different PBDE congeners; however, for some chromatographic regions, the purification obtained by SPLE method was better than those afforded using the conventional method. This is reflected for the tetra-BDE window, i.e. the BDE-75 coeluted with an interferent peak using the Soxhlet-SPE, whereas this interference was removed in the SPLE chromatogram.

In addition to extraction recoveries and reproducibility, it is interesting to compare the relative merits of each extraction technique. The relative consumptions of organic solvent

were ~ 75 ml for Soxhlet and ~ 35 ml for SPLE. However, for spent time the save was considerably when SPLE was used: 2 days for Soxhlet + SPE and 30 min for SPLE. The SPLE present a number of advantages, being less time consuming and more automated than the conventional method.

3.3. Application of SPLE method to sediment samples

The developed methodology was applied to the analysis of two river and five marine sediments. Table 5 shows the

Table 5
PBDE concentration levels (expressed in ng/g dry mass) of sediment samples

	RS1 ^a	RS2	MS1 ^b	MS2	MS3	MS4	MS5
BDE-47	0.30	0.09	0.07	0.09	0.10	0.13	0.09
BDE-100	0.17	0.14	nd	0.11	0.10	0.13	nd
BDE-99	0.52	0.65	0.14	0.16	0.16	0.22	0.16
BDE-118	nd ^c	0.24	nd	0.18	0.18	0.22	0.18
BDE-154	0.12	0.28	nd	nd	0.09	0.11	nd
BDE-153	0.28	0.51	0.24	0.24	0.24	0.32	0.27
BDE-183	0.44	0.59	0.40	0.41	0.44	1.22	0.62
Total PBDEs	1.83	2.49	0.86	1.19	1.32	2.34	1.32

^a RS = river sediment.

^b MS = marine sediment.

^c nd = not detected.

different PBDE congeners detected, as well as their concentration levels (concentrations were not corrected for the recoveries). Seven different PBDE congeners (BDE-47, -100, -99, -118, -154, -153 and -183) were detected, and total PBDE levels ranged from 0.86 to 2.49 ng/g. For sample RS1, BDE-47, -99 and -100 were the predominant peaks (Fig. 3). The sum of these three congeners represented the 54% of the total PBDE contamination. These results were in accordance with published environmental levels, where major congeners detected were BDE-47, -99, -100, -153 and -209. BDE-209 determination was not included in the present study. Analysis of this high brominated congener includes a number of additional difficulties. The compound is not stable at higher temperatures in the injector and at the GC column.

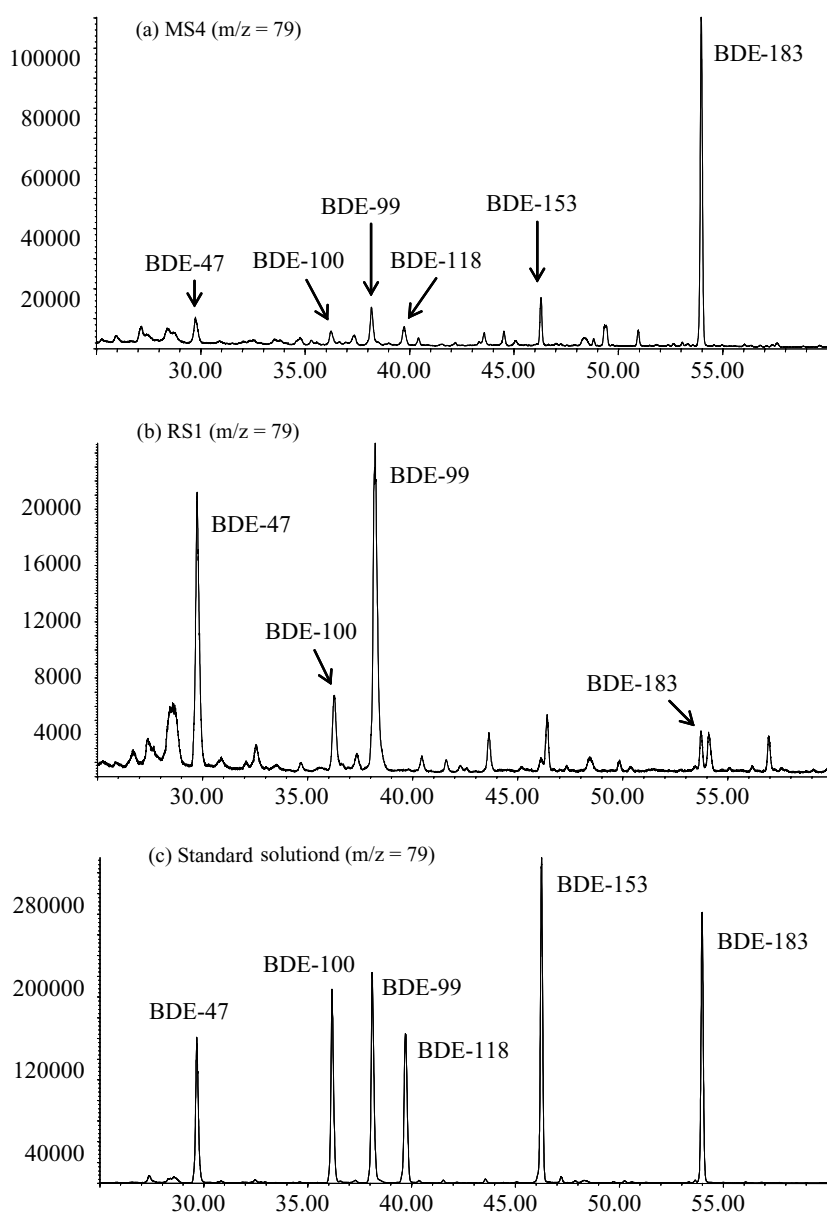


Fig. 3. m/z 79 chromatograms of (a) marine sediment, (b) river sediment, and (c) standard solution. Different BDE congeners were identified in the two sediment samples.

Moreover, the compound is sensitive for degradation by UV light and their behavior in the MS source is different from that of low brominated compounds. Further investigation will be made in order to determine BDE-209 in these samples.

Other samples analyzed (MS1, MS2, MS3, MS4 and MS5) showed a principal contribution from BDE-183, which was present at concentrations varying from 0.40 to 1.22 ng/g. In these cases, the hepta-brominated congener constituted between 33 and 52% of the total PBDE contamination. BDE-183 is often taken as indicative of the presence of the octa-BDE formulations [17]. The presence of BDE-183 could indicate the source of PBDE contamination in the studied area: the use of commercial formulations such as octa-BDE. These results indicated the need to apply analytical methods covering all the bromination degrees. Our methodology was able to determine from the mono-through hepta-BDE congeners, instead previous protocols focused only on the BDE-47, -99 and -100 determinations.

4. Conclusions

A simple and rapid method for the determination of mono- to hepta-BDE congeners in sediment samples has been developed using a selective PLE and GC-MS. Results demonstrated that this SPLE approach compares satisfactorily with traditional Soxhlet extraction methods. Applying the developed methodology gives increased possibilities of automation with no extra cleanup step needed, leading to substantial time savings as compared to classical methodologies.

The developed method was applied to PBDE determinations in sediment samples, where the analytes were detected in the range of 0.86–2.49 ng/g dry mass. Hepta-brominated congeners constituted between 33 and 52% of the total PBDE contamination in some of the samples analyzed, indicating the importance to cover all the bromination degrees in the analytical methodologies for PBDE determinations.

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