Evaluation of Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples

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ABSTRACT

Three commonly applied extraction techniques for persistent organic chemicals, Soxhlet extraction (SE), accelerated solvent extraction (ASE) and microwave-assisted extraction (MAE), were applied on soil and fish samples in order to evaluate their performances. For both PCBs and PBDEs, the two more recent developed techniques (ASE and MAE) were in general capable of producing comparable extraction results as the classical SE, and even higher extraction recoveries were obtained for some PCB congeners with large octanol–water partitioning coefficients (K_{ow}). This relatively uniform extraction results from ASE and MAE indicated that elevated temperature and pressure are favorable to the efficient extraction of PCBs from the solid matrices. For PBDEs, difference between the results from MAE and ASE (or SE) suggests that the MAE extraction condition needs to be carefully optimized according to the characteristics of the matrix and analyte to avoid degradation of higher brominated BDE congeners and improve the extraction yields.

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1. Introduction

Polychlorinated biphenyls (PCBs) are industrial chemicals that have been used for more than half a century before a global ban was imposed in 2004. This group of contaminants has already been ubiquitously detected in the environment [1] and poses a threat to the health of animal and human [2,3]. Polybrominated diphenyl ethers (PBDEs), considered as emerging persistent organic pollutants (POPs), share similar chemical structure and environmental behavior with PCBs. They have been of increasing public concern in recent years since large quantities of these substances have been produced as additive flame retardants and might in turn be released into the environment and human body [4]. In order to study their environmental behaviors, it is imperative to develop sensitive and reliable analytical methods.

The conventional and classical method for extraction of PCBs and PBDEs from environmental samples is Soxhlet extraction (SE), which requires large amounts of solvent and more than 20 h to complete the extraction. As such, novel extraction techniques have been developed such as Soxtec, ultrasonic-assisted extraction (UAE), microwave-assisted extraction (MAE), supercritical fluid extraction

(SFE) and accelerated solvent extraction (ASE), which significantly decreased the extraction time and solvent consumption, and nowadays frequently used for the extraction of POPs from various matrices [5,6].

Analytical-scale MAE was firstly performed for the extraction of organic substances by Ganzler et al. [7] in 1986. It was considered as an appreciable technique superseding traditional SE. The main advantages are low temperature requirement, high extraction rate, automation and the possibility of simultaneously extracting different types of samples. MAE utilizes microwave energy to cause rotation of molecules with permanent dipole and disorganised movement, leading to rapid heating of the solvent and samples [6,8]. Pure alkanes cannot be used as solvents for the extraction of POPs from solid samples, and solvent mixtures with two different polarities such as *n*-hexane/acetone are often recommended. Many researches and applications of MAE have been carried out to extract organic pollutants from various matrices in recent years [9–18].

One of the latest contributions to the extraction techniques is ASE, which significantly streamlines sample preparation. Under elevated temperature and pressure, an extraction solvent can be used above its boiling point but still remains in the liquid state, increasing the kinetics of the extraction process. As a result, the extraction time and solvent consumption are significantly decreased. The first scientific publications on ASE appeared in 1995 [19,20], and this technique has thereafter

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gained wide acceptance for the extraction of organic contaminants [17,18,21–25].

Several studies have been conducted to compare the extraction efficiencies of different techniques in regard to various organic compounds in recent years. However, only a few of them were performed using different techniques to simultaneously extract different analytes, such as organochlorine pesticides (OCPs) and PCBs [12], OCPs and polycyclic aromatic hydrocarbons (PAHs) [17], OCPs, PAHs and PCBs [15], PCBs and polychlorinated dibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs) [24,25]. To our knowledge, only two previous studies focused on using different techniques to evaluate the extraction of both PCBs and PBDEs from biological matrices [26,27]. Furthermore, most of these studies were performed on spiked matrices or reference materials. As indicated by Abrha and Raghavan [28], contaminant recovery from spiked sample might not be comparable to the native matrix and only provides reliable benchmarks for further investigation. On the other hand, only few certificated reference materials (CRM) are available for PBDEs, which makes comparison of different extraction methods more difficult for this group of POPs.

This study aimed to investigate the extraction efficiencies of the classical SE and two “modern” techniques, MAE and ASE for the extraction of both PCBs and PBDEs from real soil and fish samples. The conditions have not been optimized individually for each extraction technique, but chosen from a comprehensive reference list which covers many of the most important articles published on PCBs and PBDEs extraction from various matrices [6,8,21–32].

2. Materials and methods

2.1. Chemicals

Acetone, *n*-hexane and dichloromethane (DCM) were purchased from Tedia Company Inc. (Fairfield, OH, USA) at pesticide grade and nonane was from Sigma (St. Louis, USA). Silica gel 60 (0.063–0.100 mm) was obtained from Merck, and basic alumina was from Aldrich. Anhydrous sodium sulfate (Na_2SO_4), concentrated sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were guaranteed reagent (purity 99.8% up) from domestic manufacturers. Prior to use, silica gel and anhydrous sodium sulfate were heated at 550 °C for 12 h and 660 °C for 6 h, respectively. The preparation of acid silica gel and basic silica gel was described in our previous work [33]. In brief, acid silica gel was prepared from activated silica gel impregnated with 30% (w/w) concentrated H_2SO_4 , and basic silica gel by activated silica gel impregnated with 1.2% (w/w) NaOH (1 mol L⁻¹ solution). PBDEs standard mixture EO5103 was purchased from Cambridge Isotope Laboratories (Andover, MA). ¹³C-labeled surrogate standards of PCBs (EPA 68A-LCS) and PBDEs (BDE-LCS, ¹³C-BDE-47, -99, -153), ¹³C-labeled injection standards of PCBs (EPA 68A-IS) were obtained from Wellington Laboratories (Guelph, Canada).

2.2. Preparation of materials for method comparison

Soil samples were obtained from electronic waste (E-waste) dismantling areas in the southeast of China, where contamination of heavy metals and POPs are very serious. The samples were freeze-dried and homogenized by sieving through a stainless steel 16-mesh sieve. Fish samples were obtained from a lake in the east suburb of Beijing, China, which receives large quantities of effluent wastewater from a municipal sewage treatment plant. The muscle was stripped, then freeze-dried and homogenized. All the samples were stored at -20 °C in a freezer until extraction.

2.3. Extraction

A mixture of *n*-hexane/acetone (1:1, v/v) widely recommended and applied in many previous studies [6,8,11,16,21,23,24,28,31] was employed in this study to extract both PCBs and PBDEs from different matrices. Each extraction was carried out in three replicates for parallel test.

2.3.1. SE

The Soxhlet system was precleaned using *n*-hexane for 24 h. About 3.0 g soil or 2.0 g fish were weighed and mixed with 8–10 g anhydrous sodium sulfate powder, then placed in the Soxhlet extraction thimble and extracted with 150 mL *n*-hexane/acetone (1:1, v/v) for 24 h. After extraction, the extracts were spiked with 10 μL 68A-LCS and 10 μL BDE-LCS, and then went through the clean-up procedure. One blank test (about 10.0 g anhydrous sodium sulfate powder) was processed with each batch of samples.

2.3.2. ASE

ASE was carried out on a Dionex ASE300 Accelerated Solvent Extractor (Dionex, USA). The stainless steel extraction cells were precleaned with *n*-hexane, and a piece of cellulose filter paper was thereafter placed on the bottom. Same amount of weighed samples as in SE procedure were mixed with 8–10 g anhydrous sodium sulfate powder and transferred to the extraction cells. The extraction conditions were based on US EPA method 3545 [29]: the solvent was 100 mL *n*-hexane/acetone (1:1, v/v), the temperature was 150 °C and the pressure was 1500 psi (10.3 MPa) with 7 min for heating, 8 min in the static state and 3 cycles for extraction. In the end, the extraction cell was flushed with solvent (60% of the cell volume) and purged with nitrogen (120 s). The extracts were collected in 250 mL bottles with Teflon septa, then spiked with 10 μL 68A-LCS and BDE-LCS and subjected to the clean-up procedure.

2.3.3. MAE

The MAE extraction was performed on a CEM MARS Xpress Microwave Accelerated Reaction System (CEM Corporation, Matthews, NC, USA). Before usage, the extraction cylinders were rinsed with *n*-hexane and extracted with pure acetone on MAE. As recommended in US EPA method 3546 [31], about 3.0 g soil or 2.0 g fish were weighed and mixed with 3–4 g anhydrous sodium sulfate powder, followed by loading into the extraction cylinders. 30 mL *n*-hexane/acetone (1:1, v/v) was added and the extraction was performed. The condition was as follows: the temperature was ramped to 115 °C in 10 min and held for 15 min, then cooled down in 20 min; microwave power was 1200 W. After extraction, the matrices and solvent were separated by centrifugation (2000 rpm) for 5 min, and then the solvent was decanted into a flat bottom flask. The extracts were spiked with exactly 10 μL 68A-LCS and BDE-LCS and underwent the clean-up procedure.

2.4. Clean-up procedure

Sample clean-up procedure followed our previously established method with some modifications [33].

2.4.1. Soil sample

The extracts were evaporated on a vacuum rotary evaporator (Hedolph Co. model W. 2000, Germany). After solvent exchange with DCM and concentrated to 5 mL, the extracts were fractionated using auto-gel permeation chromatography (GPC, AccuPrepTM, J2-Scientific; Bio-Beads S-X3 with DCM as the mobile phase) to remove humic substance and sulfur. Subsequently, the collected fractions were solvent exchanged with *n*-hexane and eluted with 100 mL *n*-hexane through a multilayer silica gel column packed from the bottom up with 1 g silica gel, 4 g basic silica gel, 1 g silica gel, 8 g

acid silica gel, 2 g silica gel and 2 cm anhydrous sodium sulfate. The column was pre-rinsed with 80 mL *n*-hexane before the sample was loaded. After concentration, the eluate was transferred to a Kuderna-Danish (K-D) concentrator and evaporated to 0.2–0.3 mL under a stream of nitrogen flow. Finally, it was concentrated into 20 μ L nonane in GC vial with a liner (Agilent technologies, USA). Prior to instrumental analysis, the concentrate was spiked with 10 μ L 68A-IS to determine the recoveries of the ^{13}C -labeled PCBs and PBDEs.

2.4.2. Fish sample

Different from the clean-up procedure for soil sample, the extracts of fish samples were firstly evaporated to dryness for determination of the lipid contents and then dissolved in 50 mL *n*-hexane. About 10 g acidic silica gel was added to remove the lipids. After being shaken for several minutes, the solution was filtered by a column packed with anhydrous sodium sulfate. The filtrate was concentrated and loaded to the multilayer silica gel column as described in the soil clean-up procedure. Then the eluate went through basic alumina column (6 g basic alumina, 1 cm anhydrous sodium sulfate from the bottom up) and eluted with 40 mL *n*-hexane/DCM (1:1, v/v). Thereafter, the eluate was concentrated, evaporated by nitrogen gas, and finally concentrated into 20 μ L nonane. As mentioned previously, 10 μ L 68A-IS was spiked into the solution before the instrumental analysis.

2.5. Instrumental analysis

Both PCBs and PBDEs were analyzed using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS). The HRGC is an Agilent 6890N (Wilmington, USA) with a CTC PAL autosampler, and the HRMS is an AutoSpec Ultima (Waters Micromass, UK) with an electron impact (EI) ion source. The injection was operated in splitless mode with exactly 1 μ L solution and the GC columns were 60 m DB-5 fused silica capillary column (J&W, Scientific, 0.25 μ m film thickness, 0.25 mm i.d.) for PCBs and 30 m DB-5 column (0.10 μ m film thickness, 0.25 mm i.d.) for PBDEs, respectively. Helium was the carrier gas with a constant flow of 1.0 mL min⁻¹. The temperature conditions of chromatographic analysis were described as follows: for PCBs: the initial column temperature was held at 80 °C for 3 min, then increased to 150 °C at a rate of 15 °C min⁻¹ and maintained for 2 min, after increased to 270 °C at 2.5 °C min⁻¹ and held for 3 min, it was heated to 330 °C at 15 °C min⁻¹ and then maintained for 13 min; for PBDEs:

the initial temperature was 90 °C for 2 min, then it was increased to 210 °C at a rate of 25 °C min⁻¹ and maintained for 1 min, after that, it was elevated to 275 °C at 10 °C min⁻¹ and held for 10 min, finally increased to 330 °C at 25 °C min⁻¹ and maintained for 10 min. The HRMS was operated in VSIR mode at $R \geq 10,000$, the electron emission energy was set as 35 eV and the source temperature was 270 °C for PCBs and 280 °C for PBDEs, respectively.

3. Results and discussion

As mentioned in previous studies [23,34], the Soxhlet extraction is generally considered as a reference method and benchmark for evaluation of many other extraction methods, which was also applied in this study.

The recoveries of ^{13}C -labeled PCBs and PBDEs in the clean-up procedure ranged from 65% to 130% and 76% to 128%, respectively, which are deemed acceptable according to US EPA methods 1668A [35] and 1614 (draft) [36]. The limits of detection (LOD) for PCBs and PBDEs were overall lower than 1.52 pg g⁻¹ and 24.8 pg g⁻¹, respectively. Even though they were lower for PCBs than for PBDEs in both of soil and fish samples, no significant difference ($p > 0.05$) was observed among the LOD values from three different extraction methods. Blank tests were also carried out for each method. CB-28 and BDE-47 were the main contributors to laboratory background, CB-118, -138 and -153, BDE-28, -71 and -99 were also detected but at very low level, all of them merely corresponded to <4% and <9% of the concentrations of PCBs and PBDEs in the samples. The presented concentrations were therefore not blank corrected.

3.1. Comparison of the results from the soil sample

The concentrations of PCBs and PBDEs from SE, ASE and MAE are presented in Tables 1 and 2, and the recoveries normalized to the SE results are shown in Figs. 1 and 2, respectively. For PCBs, the ASE and MAE extraction generally yielded higher results compared to the SE extraction, with the normalized recovery ranges of 87–160% and 94–176%, respectively. The highest recoveries were obtained for CB-180 and -153, which have large octanol–water partitioning coefficients (K_{ow}) and present at significant concentrations in the samples. This indicated that the elevated temperature and pressure could significantly increase the yields of compounds with higher K_{ow} values. On the other hand, the results from MAE showed larger relative standard deviations (RSD) than that from ASE. This is different from the report of Sporring et al. [23], who

Table 1

The average concentrations of PCBs and the relative standard deviations (RSD) in the soil and fish samples ($n = 3$).

Compound	Soil						Fish					
	Soxhlet (pg g ⁻¹)	RSD (%)	ASE (pg g ⁻¹)	RSD (%)	MAE (pg g ⁻¹)	RSD (%)	Soxhlet (pg g ⁻¹)	RSD (%)	ASE (pg g ⁻¹)	RSD (%)	MAE (pg g ⁻¹)	RSD (%)
CB-28	8280	3.1	8690	1.6	8060	16	5510	4.8	5610	6.1	5640	11
CB-52	2220	2.1	2900	6.5	2910	20	980	5.5	954	7.4	848	17
CB-77	617	5.0	635	3.4	613	5.9	31.5	2.5	33.0	2.5	29.6	2.7
CB-81	63.2	14	66.3	1.2	60.2	9.5	5.36	7.4	5.97	1.5	4.90	8.0
CB-101	2080	5.8	2540	1.7	2530	21	605	5.4	579	16	588	6.2
CB-105	989	7.0	926	6.8	955	5.7	226	3.8	232	3.7	226	3.9
CB-114	103	19	139	4.3	111	15	21.8	3.2	22.2	4.2	21.0	5.1
CB-118	2120	1.2	2620	1.9	2700	21	503	3.3	514	2.4	492	5.4
CB-123	197	11	243	3.0	231	19	61.9	3.0	62.9	3.4	56.8	5.5
CB-126	28.7	9.1	30.2	4.4	30.5	8.0	5.27	1.2	5.49	0.9	5.25	5.6
CB-138	2310	8.6	2890	2.4	2850	17	613	4.0	529	17	597	5.5
CB-153	2080	11	3150	2.5	3240	11	610	3.0	547	17	582	5.8
CB-156	205	3.2	178	6.8	193	5.2	53.2	3.7	54.8	4.1	52.0	4.5
CB-157	50.2	4.1	48.2	5.6	50.1	4.2	13.1	6.4	14.3	2.7	13.3	3.1
CB-167	75.9	5.6	84.5	2.5	103	17	17.5	3.1	19.4	4.8	17.6	3.7
CB-169	2.77	15	2.90	16	2.60	21	0.61	12	0.67	12	0.68	2.5
CB-180	552	7.2	882	16	971	12	122	2.0	115	15	106	23
CB-189	6.70	16	7.27	13	7.20	20	3.62	8.2	3.90	4.8	3.83	7.3
CB-209	23.8	14	24.7	16	31.3	15	65.5	2.0	67.4	4.5	66.5	9.8

Table 2The average concentrations of PBDEs and the relative standard deviations (RSD) in the soil and fish samples ($n = 3$).

Compound	Soil						Fish					
	Soxhlet (pg g ⁻¹)	RSD (%)	ASE (pg g ⁻¹)	RSD (%)	MAE (pg g ⁻¹)	RSD (%)	Soxhlet (pg g ⁻¹)	RSD (%)	ASE (pg g ⁻¹)	RSD (%)	MAE (pg g ⁻¹)	RSD (%)
BDE-17	44.1	12	51.8	12	37.4	2.4	95.8	2.8	107	0.8	89.7	5.3
BDE-28	60.3	11	62.8	12	42.3	5.7	1700	1.0	1890	2.1	1590	9.4
BDE-47	215	4.7	209	0.7	206	16	8160	1.5	8190	2.0	6060	7.1
BDE-66	68.3	8.1	66.1	6.4	43.3	10	1180	2.9	988	4.1	1010	17
BDE-71	161	3.1	136	7.1	97.4	7.7	1190	3.2	1080	3.2	979	13
BDE-85	3.55	2.8	3.49	16	3.22	7.1	89.9	3.9	107	8.0	107	8.3
BDE-99	133	5.0	115	3.2	107	10	1720	1.8	1640	1.1	1330	3.5
BDE-100	32.9	4.6	29.7	2.4	26.3	9.0	304	0.6	233	2.3	304	16
BDE-138	n.d. ^a	–	n.d.	–	n.d.	–	49.5	2.1	47.1	4.6	55.8	4.3
BDE-153	55.0	11	58.6	16	38.2	20	530	2.0	520	1.1	397	1.6
BDE-154	48.1	0.4	42.3	6.7	34.5	6.1	424	2.0	463	6.7	290	5.9
BDE-183	18.1	9.1	19.2	11	9.08	10	309	0.6	264	7.5	290	3.9
BDE-190	n.d.	–	n.d.	–	n.d.	–	35.3	10	34.7	17	34.1	9.1

^a n.d., not detected. **Fig. 1.** The recoveries of individual PCB congeners in the soil sample for different techniques normalized to the Soxhlet method ($n = 3$).

indicated that MAE provided the overall lowest standard deviation (SD) values when comparing the extraction efficiencies of six different techniques for the determination of PCBs in soil. For PBDEs, ASE yielded comparable extraction results to SE, with normalized recoveries between 79% and 118%. On the contrary, the results from MAE were generally low, with recovery range from 50% to 96%. This

Fig. 2. The recoveries of individual PBDE congeners in the soil sample for different techniques normalized to the Soxhlet method ($n = 3$). BDE-138 and -190 were not detected in any samples, the recoveries were therefore considered as same as that of the SE extraction.

is very similar to PBDEs extraction from marine biological tissues [13], of which the same temperature (115 °C) was utilized. However, Shin et al. [16] employed a mixture of *n*-hexane/acetone (3:1, v/v) and temperature of 130 °C in the MAE extraction of PBDEs from the sewage sludge, and obtained a comparable result to SE. Furthermore, Vilaplana et al. [37] used isopropanol/*n*-hexane as solvent in MAE at 130 °C to extract brominated flame retardants (BFRs) from styrenic polymeric matrixes, and obtained almost complete recovery of tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD), while deca-BDE was extracted at lower calculated concentration. Therefore, the relatively lower recovery of PBDEs in this study could be attributed to the unoptimized extraction conditions for the matrix.

3.2. Comparison of the results from the fish sample

The recoveries normalized to the SE results for PCBs and PBDEs in the fish samples are shown in Figs. 3 and 4, respectively. For PCBs, the ASE and MAE extraction presented the comparable recovery yields with the ranges of 86–111% and 87–112%, respectively. Furthermore, the RSD values were relatively lower than in soil samples, which indicated that the extraction conditions are of great benefit to the analysis of PCBs in fish samples. For PBDEs, the recoveries from ASE and MAE were also in the same level with the ranges of 77–118% and 68–119%, respectively. This is consistent with the report by Tapie et al. [26], who utilized different biological matrices to test the performance of ASE and MAE under different extraction conditions, and found that all the tested protocols were reliable and

Fig. 3. The recoveries of individual PCB congeners in the fish sample for different techniques normalized to the Soxhlet method ($n = 3$).

Fig. 4. The recoveries of individual PBDE congeners in the fish sample for different techniques normalized to the Soxhlet method ($n = 3$).

useful for PCBs and PBDEs analysis. Li et al. [38] also pointed out that MAE coupled with GC–EI–MS is an efficient and quantitative method for analyzing PBDEs in human adipose tissue compared to SE. However, ASE yielded relatively lower RSD values compared to MAE, which indicated that ASE could provide more robust and repeatable results under the specified extraction conditions in this study.

3.3. Overall comparison of PCBs and PBDEs results from different extraction techniques

In general, both ASE and MAE could yield comparable results to SE for the extraction of PCBs in the soil and fish samples, even though high values were obtained for some congeners with higher K_{ow} values in soil. This indicates that elevated temperature and pressure are of great benefit to completely extract non-degradable congeners from the solid matrix compared to the traditional method.

For PBDEs, although commonly applied extraction conditions were employed, it seems that the specified conditions could lead to nonconformity of the extraction performance for different PBDE congeners and different matrices. Especially for MAE, generally low concentrations were obtained in soil samples.

Several factors could explain the variability of the results. Firstly, increasing temperature could increase solubility of analyte in the solvent, weaken the analyte–matrix interaction, and increase the vapor pressure of the analyte [28]. However, higher brominated BDE congeners are sensitive to thermal degradation compared to PCBs, which therefore requires suitable temperature and other related conditions to do the extraction. Secondly, the characteristics of the matrices are different; soil contains high organic carbon and fish has high lipid content, which affects the adsorption behavior of the analytes. As indicated by Abrha and Raghavan [28], PCBs extraction is sensitive to carbon content and matrix structure, as well as the type of compound in the matrix. Besides, reduced particle size of the matrix could enhance the extraction yield, attributable to a higher swelling effect of the solvent and favorable desorption of the analytes from the matrix [37]. On the other hand, comparison of different solvent mixtures applied in lipid extraction from biological organ tissues demonstrated that DCM/acetone and *n*-hexane/acetone systems produced better extraction efficiency than other solvent combinations [39], suggesting that the extraction conditions should be optimized according to the matrix and analyte. With regard to different methodological approaches, it was noteworthy that

different pressures (ASE: 1500 psi; MAE: ≤ 200 psi), extraction times (SE: ≥ 24 h; ASE: ~ 40 min; MAE: ~ 30 min) and different extract–collection steps after extraction (ASE, SE: both are continuous; MAE: discontinuous, requires filtration after extraction) are required, which could also cause the variation of results [18].

4. Conclusion

In summary, ASE and MAE, both temperature/pressure-enhanced extraction techniques, could provide comparable or even better results than the SE extraction for extracting both PCBs and PBDEs from soil and fish samples, and showed a significant advantage of reducing extraction time and solvent consumption. It is noteworthy that, for PBDEs, the extraction conditions with high temperature need careful optimization on different matrices to avoid degradation of higher brominated congeners and obtain optimum extraction efficiency.

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