Comprehensive comparison of classic Soxhlet extraction with Soxtec extraction, ultrasonication extraction, supercritical fluid extraction, microwave assisted extraction and accelerated solvent extraction for the determination of polychlorinated biphenyls in soil

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Abstract

This paper compares the extraction effectiveness of six different commonly applied extraction techniques for the determination of PCBs in soil. The techniques included are Soxhlet, Soxtec, ultrasonication extraction, supercritical fluid extraction, microwave-assisted extraction and accelerated solvent extraction. For none of the techniques were the extraction conditions optimized, but instead the extraction parameters were based on the experience from previous successful investigation published by a number of research groups worldwide. In general, all extraction techniques were capable of producing accurate data for one native PCB contaminated soil diluted with another soil sample to obtain two concentration levels. It could therefore be concluded that any of the investigated techniques can be used with success if the extraction conditions applied are chosen wisely.
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1. Introduction

Polychlorinated biphenyls (PCB) have been among the most studied environmental contaminants for more than three decades. Large efforts have been made to find major sources and pathways of PCBs in the environment, and to determine the chemical and biological stability of PCBs, as well as their toxicity [1,2]. Soxhlet extraction has been the traditional method used for extraction of PCBs from soils and sediments followed by clean-up over acid silica [3–5]. These methods usually require large amounts of solvent and are often carried out for 20 h or more [3–7]. As the demands for minimizing solvent consumption and time has increased, new extraction techniques have been developed during the last three decades [8–11].

An improved extraction technique, based on the Soxhlet system, is Soxtec, which was invented in the early 1970s [12] and commercialized in 1982 [10]. Soxtec is a two-step procedure, involving a boiling and a rinsing step, which drastically reduces the total time of extraction. It has been used in several applications to extract organochlorine contaminants from solid samples [13–18].

A common conventional alternative to Soxhlet is ultrasound-assisted extraction, which has been applied for the extraction of PCBs from various solid environmental samples [6,15,19–23]. One reason for applying acoustic energy is that it enhances soil washing. The predominant mechanisms for this washing are mechanical, and include abrasion of suspended soil in slurries leading to surface removal of

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the contaminants, and improved solvent leaching of contaminants from the interior of particles [24]. A good example of the effects of ultrasonication is a destruction experiment performed of a tetra-chlorinated PCB, where it was found that desorption from the matrix no longer was a very limiting factor when applying ultrasounds to remove the contaminant from a synthetic sediment [25]. In the present study, a previously developed ultrasonication extraction (USE) method was tested [26].

Apart from the above more conventional extraction methods three more recent techniques were also investigated including supercritical fluid extraction (SFE) [27] microwave-assisted extraction (MAE) [28] and accelerated solvent extraction (ASE) [29]. The main key to shorter extraction times and reduced solvent consumption with these techniques is the possibility of working at elevated temperatures above the boiling point of the solvent. Thereby the extraction process is facilitated due to increased analyte desorption and diffusion from the solid matrix.

Analytical-scale SFE was first introduced by Stahl in 1976 [30] but it was not until 1986 that it was applied to the extraction of persistent organic pollutants (POPs) in environmental samples [31]. The main advantages with SFE are the possibility of obtaining clean extracts with reduced solvent consumption and extraction time, where the extracts often can be analyzed with no further clean-up. In case solid phase traps are used, an additional selectivity step can be achieved prior to the final analysis [32]. Consequently, SFE has been applied in several investigations for the extraction of PCBs from environmental samples [4–6,33–40].

The first attempts of analytical-scale MAE was performed by Ganzler et al. [41] using a domestic microwave oven with solvents normally used in Soxhlet. MAE utilizes the energy of microwaves to cause molecular movement and rotation of liquids with a permanent dipole leading to a very fast heating of the solvent and the sample. Several applications utilizing MAE for the extraction of PCBs from solid samples have been published during the last few years [21,23,42–47]. Since pure alkanes cannot be utilized as extraction solvents for the extraction of POPs from solid samples, solvent mixtures including a polar solvent such as acetone/n-hexane are often used [14,21,23,43,45]. In case alkanes are to be used, heat transformer disks must be utilized inside the extraction cell [44].

One of the latest contribution to the increasing number of extraction techniques is accelerated solvent extraction (ASE), and some of the first publications appeared in 1995 [48,49]. This technique soon gained wide acceptance since it provided quantitative extractions with very short extractions times. The technique is also simple to learn and apply in the laboratory. Consequently, several publications for the extraction of PCBs in solid matrices have been published the last 10 years [6,7,23,44,50–52].

In this work the accuracy of some of the most important classical methods are compared to techniques that are more modern in order to study differences in terms of

exhaustiveness of six commonly applied techniques of today. The extraction conditions have not been optimized individually for the different methods, but have been chosen from the comprehensive reference list, which covers some of the most important articles published on PCB extraction from soils. It is also based on the authors' long experience and knowledge from the field of PCB analysis.

2. Materials and methods

2.1. Chemicals

PCB standards (delivered as neat crystals) IUPAC Nos. 101, 105, 118, 128, 138, 149, 153, 156, 170, 180 and the soil CRM 481 came from Community Bureau of Reference (BCR, Brussels, Belgium). Sodium sulphate powder and granula were purchased from Merck (Darmstadt, Germany) and BHD Laboratory Supplies (Poole, England), respectively. Rathburn Chemicals Ltd. (Waterburn, Scotland), delivered n-hexane, n-heptane, acetone and diethyl ether (HPLC-grade/glass distilled grade).

2.2. Preparation of materials for the comparison

The two samples used for the comparison study originated from the same polluted soil collected by an enterprise handling contaminated soil. Before use, the soil was dried moderately, ground using an ATOX 3.5 mill (F.L. Smidth, Copenhagen, Denmark) so that more than 99% of the sample had a particle size less than 90 μm, and homogenized, all in one procedure. The sample was treated with γ-radiation to reduce the number of viable microorganisms that might degrade the contaminants. This together with the low content of water, less than 5%, ensured that the sample was stable [40]. The number of heterotrophic plate counts (HPC) was originally $(2–3) \times 10^5 \, g^{-1}$ soil and after treatment less than the detection limit (50–100 HPC/g soil). From this sample two sub samples of 15.0 kg were taken and mixed with approximately 2.2 and 22 g of an industrial soil CRM 481 (Community Bureau of References, Brussels, Belgium), respectively, a sample which is heavily contaminated with PCBs [37]. Samples were mechanically mixed for more than 1 h. Finally, the samples were transferred into cans, each containing 100 g. The two samples were labeled low level (LL) and high level (HL). All extractions were carried out in six replicates using either 1 g HL soil or 2 g LL soil.

2.3. Soxhlet

The soil was mixed with 5–7 g of anhydrous Na_2SO_4 powder, placed in a 22 mm × 80 mm extraction thimble (Scheider & Schuell GmbH, Dassel, Germany), and extracted with 100 ml n-hexane/acetone (1:1, v/v) for 18 h in a 30 ml Soxhlet apparatus (4–5 cycles/h). After the extraction, internal standards (PCB 35 and PCB 169) were added and the sample went through the clean-up procedure.

2.4. Soxtec

A FOSS Soxtec Avanti 2055 Manuel System (Tecator, Höganäs, Sweden) was used. The soil was mixed with 5–7 g of anhydrous Na_2SO_4 powder, placed in a 33 mm × 80 mm extraction thimble (supplied by the manufacture), and extracted with 50 ml n-hexane/acetone (1:1, v/v) in boiling solvent for 60 min. Thereafter the thimble was raised to the rinse position for another 60 min. After the extraction, internal standards (PCB 35 and PCB 169) were added and the sample went through the clean-up procedure.

2.5. Ultrasonication extraction method

The soil was wetted with ca. 1 ml water before 3–5 ml acetone/g of soil was added. The samples were sonicated for 5 min and shaken vigorously for 1 h (HS 501 Digital Orbital Shaker, IKA, Staufen, Germany). After centrifugation (10 min at 3000 rpm) the organic phase was transferred to a separator funnel containing 50 ml of 0.2 M NaCl/0.1 M H_3PO_4. Thereafter 3–5 ml n-hexane/acetone (3:1, v/v) g^{-1} of soil was added to the samples, sonicated for 5 min, and shaken vigorously for 1 h. The organic phase was added to the previous phase in the separator funnel and shaken. The water phase was removed to another separator funnel. The organic phase was put into a round bottom flask. The water phase was washed twice with 10 ml n-hexane/diethyl ether (9:1, v/v) and the organic phases were added to the round bottom flask. Internal standards (PCB 35 and 169) were added and the sample went through the clean-up procedure.

2.6. Supercritical fluid extraction

A HP 7680A Supercritical Fluid Extraction Unit (Hewlett Packard, Wilmington, DE, USA) was used. The soil was mixed with 5–7 g of anhydrous Na_2SO_4 granular and 1 g copper powder. A glass-microfiber filter (GF/B, Whatman, Kent, England) was placed at each end of the 7 ml standard stainless steel extraction thimble to prevent clogging of the system. Samples were extracted with CO_2 at either 80 °C and 305 bar (SFE A, density of 0.75 g/ml) or at 100 °C and 355 bar (SFE B, density of 0.72 g/ml), both with a 5 min static extraction and 30 min dynamic extraction. The flow rate was set to 1 ml/min (liquid) and the extracted PCBs were collected on a solid phase trap containing 1 ml Florisil. The temperature of the nozzle and the trap during the extractions were 45 and 20 °C, respectively. The trap was eluted with 2 ml × 1.4 ml n-heptane, 4 ml acetone and 3 ml n-heptane. Only the first 1.4 ml was analyzed. Internal standards (PCB 35 and PCB 169) were added and the volume was adjusted to 1.8 ml. Extracts were ready for analysis without any further clean-up.

2.7. Microwave-assisted extraction

A CEM MARS 5 Microwave Accelerated Reaction System (CEM Corporation, Matthews, NC, USA) was used. The soil was loaded into extraction cylinders and 1 ml of water was added together with 25 ml n-hexane/acetone (1:1, v/v). The extraction temperature was 110 °C and programmed as follows: ramp to temperature for 10 min, hold at temperature for 10 min. Microwave power was 1200 W (100%). After completed extraction, soil and solvent were separated in a centrifuge for 10 min and the solvent was decanted into a bottle. Anhydrous Na_2SO_4 powder was added to remove water and the solvent was transferred to a round bottom flask. Thereafter internal standards (PCB 35 and PCB 169) were added and the sample went through the cleanup procedure.

2.8. Accelerated solvent extraction

A Dionex ASE200 Accelerated Solvent Extractor was used. The soil was mixed with Hydromatrix and loaded into Dionex standard 11 ml stainless steel extraction thimbles. A filter paper (GF/B, Ø 20 mm, Whatman, Kent, UK) was placed at each end of the thimble. Extractions were performed with either n-hexane/acetone (1:1, v/v, ASE A) or toluene (ASE B) as extraction solvent, both at 2000 psi and at 100 °C, with a 5 min static extraction (after a 5 min equilibrium time). After the extraction, the thimble was flushed with solvent (60%) and purged with nitrogen. Solvent was collected in 40 ml vials with Teflon septa. Thereafter each extraction cell containing the same sample went through one more identical extraction cycle and the solvent was collected in another 40 ml vial. Internal standards (PCB 35 and PCB 169) were added and the sample went through the cleanup procedure.

2.9. Sample clean-up

The samples that required clean up were evaporated to 1 ml on a rotary evaporator at 45 °C, and loaded on to a 45 cm × 20 mm column. The column contained a glass wool plug, 2 cm of anhydrous Na_2SO_4, 5 cm of activated silica impregnated with 40% (w/w) concentrated H_2SO_4 and another 2 cm of Na_2SO_4. The column had been pre-washed with 50 ml n-hexane prior to use. The sample was eluted with 50 ml of n-hexane, and to the eluate was added 1 ml n-heptane as keeper. The eluate was evaporated to 1 ml, transferred to a GC-vial and the volume was adjusted to 1.8 ml with n-heptane.

2.10. Dual column gas chromatography

A HP 5890 series II with on-column injection and two [63]Ni electron capture detectors (300 °C, purged with N_2 at 40 ml/min) was used. Hydrogen was used as carrier gas with a linear velocity of 43 cm/s (1.7 bar, held constant throughout the analysis by the electronic pressure control). One microliter was injected on-column on two parallel coupled columns, a 60 m × 0.25 mm, 0.25 μm 50% diphenyl-dimethyl-siloxane HP50+ (Hewlett-Packard,

Palo Alto, CA, USA) and a 25 m × 0.25 mm, 0.25 μm 5% diphenyl-dimethyl-siloxane HP-5ms (Hewlett-Packard) in series with a 25 m × 0.22 mm, 0.10 μm 1,7-dicarba-closo-dodecarborane-dimethyl-siloxane HT-5 (Scientific Glass Engineering, Austin, TX, USA). The parallel columns were connected to a deactivated retention gap (2 m × 0.53 mm fused silica) with a glass "T". The temperature program was as follows: initial temperature 90 °C held for 2 min, increased to 170 °C at a rate of 20 °C/min and held for 7.5 min, then increased at a rate of 3.0 °C/min to 285 °C and held for 8.0 min. Quantification was performed with HP Chemstation Rev A.03.02 and a eight point power-fit calibration curve in the concentration interval of 0.5–441 ng/ml in *n*-heptane for the individual PCB congeners. PCB 35 and PCB 169 were used as internal standards.

3. Results and discussion

The PCB concentrations to which all other results were compared were based on Soxhlet extraction for 18 h using *n*-hexane/acetone (1:1, v/v). *n*-Hexane/acetone is one of the most commonly applied extraction solvents with solvent compositions ranging from 20 to 75% acetone (volume basis) and with extraction times from 7 to 48 h [4,5,6,16,17,23,36,37,43,52]. However, 50% acetone in *n*-hexane is by far the most common alternative combined with extraction times between 16 and 24 h. The obtained concentrations for the different extraction methods can be seen in Table 1 (HL-soil) and Table 2 (LL-soil), while the recoveries versus Soxhlet for the individual PCB congeners are presented for the HL-soil and the LL-soil in Figs. 1 and 2, respectively.
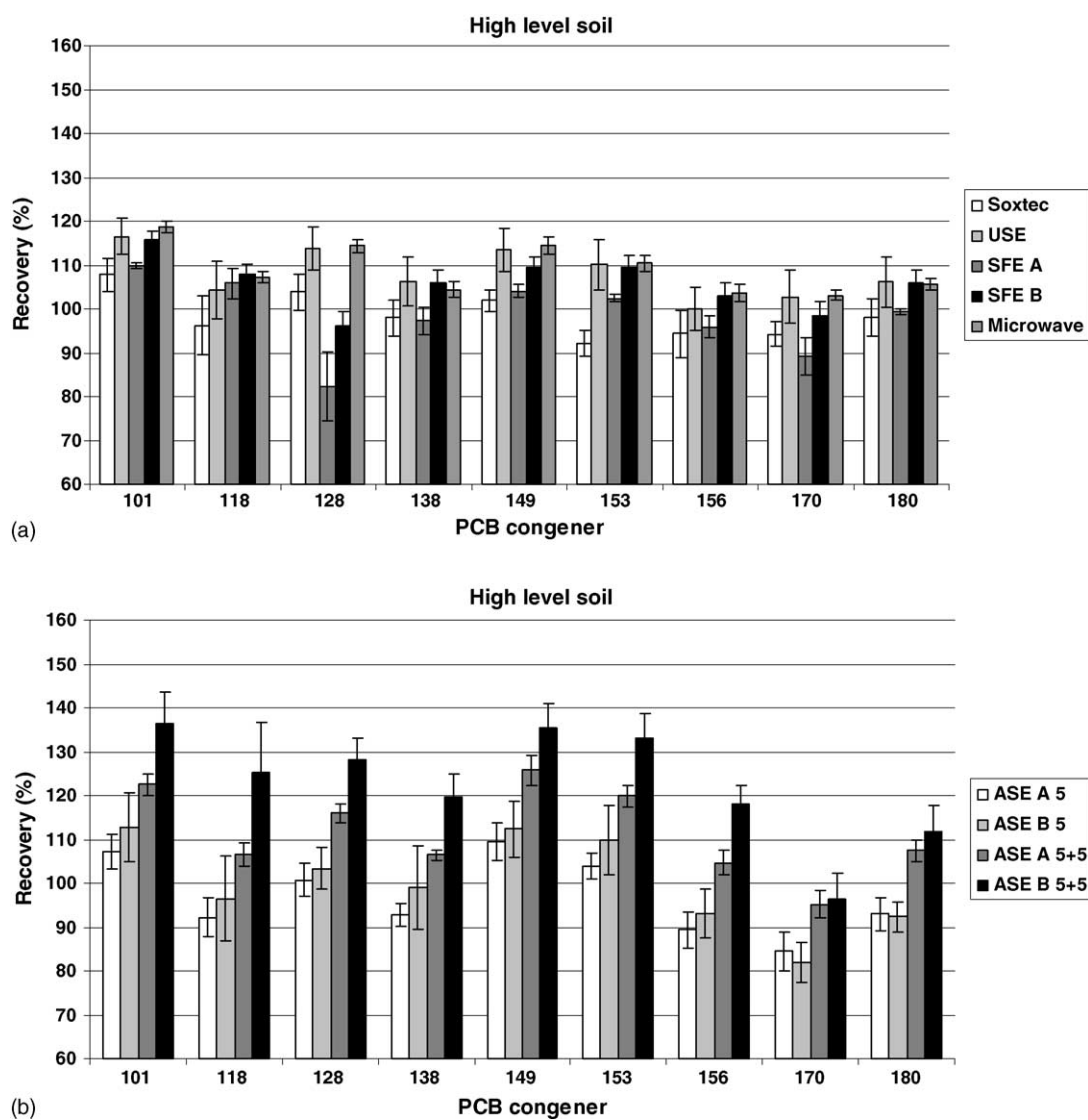

Fig. 1. Recoveries for individual PCB congeners in the HL soil for different techniques compared to Soxhlet concentrations: (a) Soxtec, ultrasonication extraction (USE), supercritical fluid extraction (SFE), microwave-assisted extraction (microwave), (b) accelerated solvent extraction (ASE). Experimental details are presented in Section 2. Error bars represent RSD (%, *n* = 6).
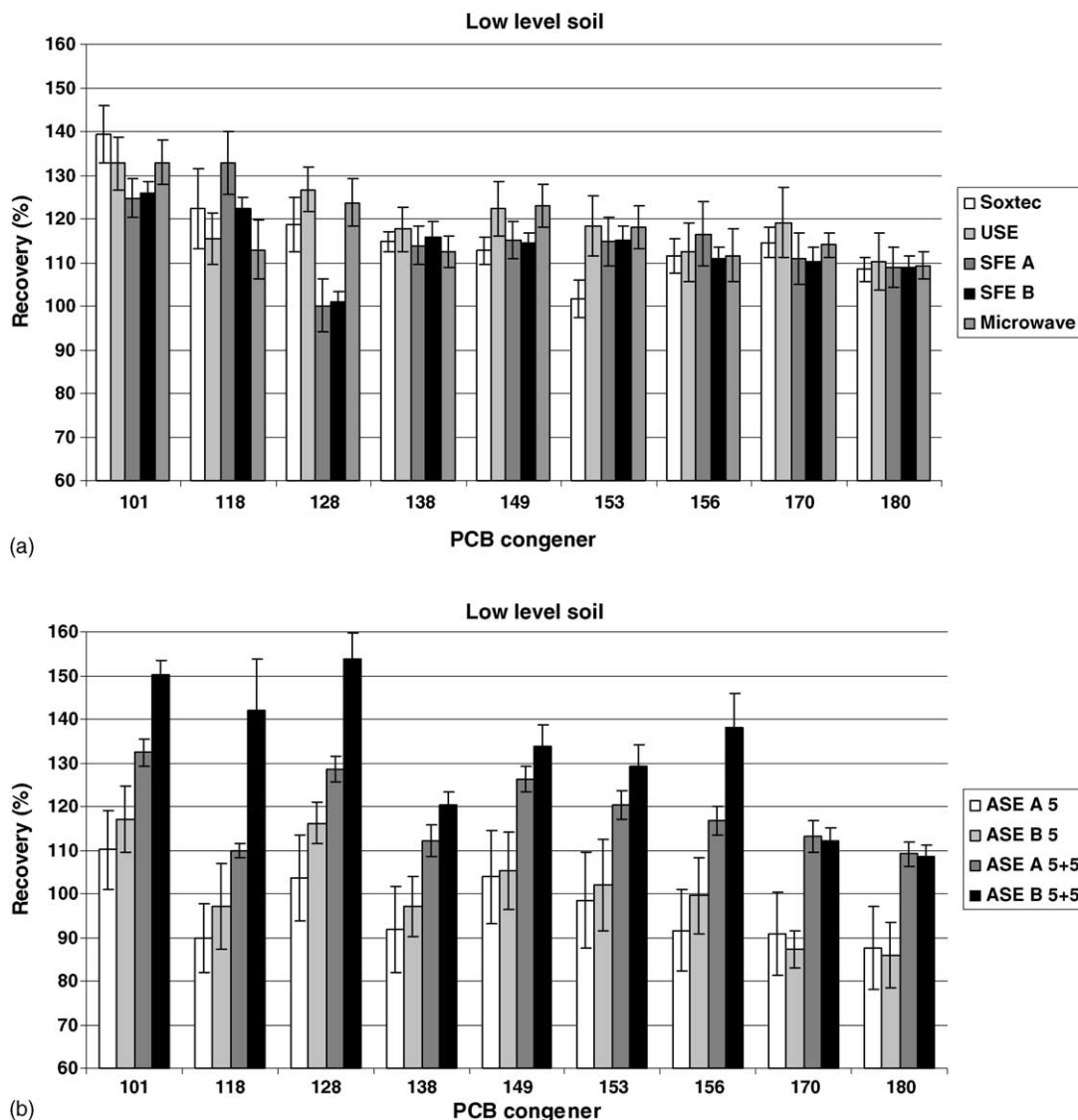
Fig. 2. Recoveries for individual PCB congeners in the HL soil for different techniques compared to Soxhlet concentrations: (a) Soxtec, ultrasonication extraction (USE), supercritical fluid extraction (SFE), microwave-assisted extraction (microwave), (b) accelerated solvent extraction (ASE). Experimental details are presented in Section 2. Error bars represent RSD (%, $n = 6$).

3.1. Soxtec

In general the Soxtec concentrations are very close to Soxhlet data for the HL-soil, while they are somewhat higher for the LL-soil (Tables 1 and 2). This means that the applied Soxtec method using *n*-hexane/acetone (1:1, v/v) with a 60 min boiling step and a 60 min rinsing step is capable of replacing Soxhlet. The chosen methodology is based on the Soxhlet method and has previously been used as an alternative to Soxhlet [15,17]. Armnet and coworkers found that Soxtec lead to somewhat improved recoveries and precision as compared to Soxhlet [17], and from Tables 1 and 2 it can also be seen that the SD values are consistently lower for the Soxtec data.

3.2. Ultrasonication extraction method

For the USE method, the concentrations obtained are consistently higher for both the HL-soil and the LL-soil, with the biggest difference for the LL-soil (Tables 1 and 2). This demonstrates that a correctly performed sonication procedure is capable of producing data similar or better than those obtained with Soxhlet. The methodology chosen here involved *n*-hexane/acetone (3:1, v/v) with two extractions steps of 65 min each. This solvent mixture has been applied with success previously with extraction times ranging from 30 min to 12 h, using one to three extraction cycles [6,20,23]. Regarding the SD values there is however no general trend in that precision is improved for the sonication method compared to the Soxhlet method (Tables 1 and 2).

3.3. Supercritical fluid extraction

SFE performed at 80 °C with a 5 min static and a 30 min dynamic extraction (Method A) give concentrations for the HL-soil which are very close to the Soxhlet data (some congeners are even below Soxhlet) while for the LL-soil they are always exceeding Soxhlet concentrations (Tables 1 and 2). This extraction temperature has previously been used on a marine sediment SRM 1944 for which it gave recoveries close to Soxhlet, even though more highly chlorinated congeners such as PCB 192, 206 and 209 showed a decrease of 15% at this relatively modest temperature [5]. Nilsson et al. [39] compared 80–150 °C on two sediments and found that 150 °C gave much higher recoveries for one sediment, while for the other they were very close. This indicated that often reasonable exhaustiveness can be obtained at 80 °C, but for some matrices, harsher conditions are required. Lee et al. [36] showed that already at 40 °C, low chlorinated PCBs could be extracted from sediment, but for more highly chlorinated PCBs, a temperature of 100 °C is required. In Tables 1 and 2, it can be seen that in the extractions performed at 100 °C (Method B) the concentrations obtained for the HL-soil were consequently higher than at 80 °C, while for the LL-soil the concentrations were nearly identical at 100 and 80 °C. In general, the SFE B method also gives recoveries that are similar to the USE method. These SFE data verifies previous results that 100 °C leads to more quantitative extractions than 80 °C for some matrices. However, it should also be stressed that increasing the temperature even further in some cases might give an additional 5–10% increase in concentrations

as showed by Björklund et al. [38]. They extracted a number of soils and sediments at 40, 100 and 150 °C and saw that a small fraction existed which was very tightly attached to the sediment and only could be released at 150 °C. For CRM 481 this fraction was about 5%, meaning that an additional increase of 50 °C in this study might have given rise to a small increase in concentrations in the SFE extracts. However, for most applications, 100 °C still gives acceptable extraction efficiencies. Finally, it is notable that the SD is better for SFE than Soxhlet.

3.4. Microwave assisted extraction

For MAE, the concentrations obtained are consistently higher for both the HL-soil and the LL-soil, with the largest difference for the LL-soil (Tables 1 and 2). The applied MAE method is based on *n*-hexane/acetone (1:1, v/v) at 110 °C with an extraction time of 10 min. This solvent mixture is commonly applied in MAE [14,21,23,42,43,45], even though alternative solvent exists [15,44,46,47]. A number of different temperatures have also been tested ranging from 80 to 155 °C [14,23,42,44,46]. Lopez-Avila and Young evaluated temperatures from 80 to 145 °C for pesticides in soil and sediment and found that 80 °C gave similar recoveries compared to 145 °C [14], while Criado et al. by means of a factorial design concluded that 110 °C was the optimal temperature [46]. Finally, Carro et al. performed their optimized extraction at 155 °C [42]. From the concentrations presented in Tables 1 and 2 it is clear that 110 °C is sufficient to provide recoveries higher than those obtained with Soxhlet, and the
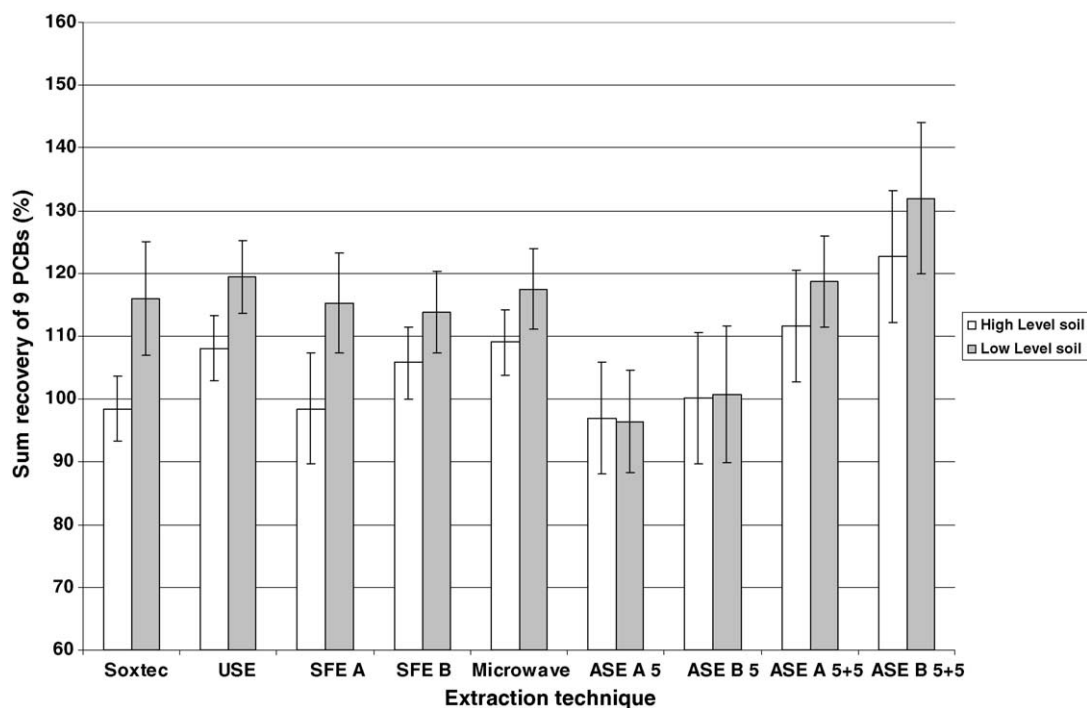

Fig. 3. Average PCB recovery for all investigated PCB in the HL soil and LL soil for different techniques compared to Soxhlet concentrations. Error bars represent RSD (%, *n* = 6).

Table 1
Determined PCB concentrations in the HL-soil using different extraction techniques

PCB number	Soxhlet n-hexane/acetone 18 h		Soxtec n-hexane/acetone 2 min × 60 min		USE n-Hexane/Acetone 2 min × 65 min		SFE A CO_2 80 °C 5 min + 30 min		SFE B CO_2 100 °C 5 min + 30 min		MAE n-hexane/acetone 10 min		ASE A n-hexane/acetone 5 min		ASE B toluene 5 min		ASE A n-hexane/acetone 5 + 5 min		ASE B toluene 5 + 5 min	
	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD
101	39.82	2.08	42.91	1.62	46.38	1.75	43.77	0.28	46.07	0.88	47.26	0.62	42.69	1.69	44.91	3.33	48.77	1.05	54.37	3.01
118	10.58	0.94	10.17	0.68	11.02	0.67	11.19	0.35	11.42	0.24	11.34	0.14	9.76	0.45	10.22	0.99	11.28	0.28	13.24	1.19
128	8.99	0.51	9.33	0.37	10.22	0.46	7.39	0.73	8.64	0.31	10.28	0.14	9.06	0.36	9.29	0.44	10.43	0.19	11.51	0.46
138	106.6	6.46	104.5	4.34	113.2	5.86	103.8	3.23	112.8	3.22	111.3	1.93	98.98	2.85	105.5	10.05	113.5	1.22	127.7	5.33
149	96.87	3.62	98.70	2.44	109.8	4.81	100.8	1.43	105.9	2.51	110.7	1.95	106.1	4.23	108.8	6.38	131.1	3.34	131.1	5.52
153	152.0	7.52	140.1	4.12	167.4	8.05	155.8	1.27	166.7	3.43	167.8	2.51	157.9	4.20	167.0	11.04	182.3	3.39	202.6	7.57
156	8.68	0.52	8.18	0.45	8.68	0.40	8.32	0.19	8.94	0.24	8.99	0.17	7.76	0.33	8.09	0.45	9.09	0.23	10.24	0.34
170	68.78	2.29	64.80	1.79	70.66	3.95	61.31	2.69	67.61	2.09	70.92	0.82	58.08	2.82	56.40	2.91	65.50	2.08	66.32	3.72
180	142.7	6.10	140.0	5.94	151.4	8.07	141.8	1.11	151.3	3.87	150.9	1.83	132.7	5.39	131.9	4.79	153.3	3.28	159.5	8.27

Table 2
Determined PCB concentrations in the LL-soil using different extraction techniques

PCB number	Soxhlet n-hexane/acetone 18 h		Soxtec n-hexane/acetone 2 min × 60 min		USE n-hexane/acetone 2 min × 65 min		SFE A CO_2 80 °C 5 min + 30 min		SFE B CO_2 100 °C 5 min + 30 min		MAE n-hexane/acetone 10 min		ASE A n-hexane/acetone 5 min		ASE B toluene 5 min		ASE A n-hexane/acetone 5 min + 5 min		ASE B toluene 5 min + 5 min	
	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD	Concentration (ng/g)	SD
101	5.14	0.51	7.16	0.47	6.82	0.44	6.41	0.31	6.47	0.19	6.83	0.37	5.66	0.65	6.02	0.54	6.80	0.21	7.71	0.24
118	1.55	0.11	1.89	0.17	1.79	0.11	2.05	0.14	1.89	0.05	1.75	0.13	1.39	0.15	1.50	0.18	1.70	0.03	2.20	0.22
128	1.36	0.10	1.62	0.10	1.73	0.08	1.37	0.10	1.38	0.04	1.69	0.09	1.41	0.16	1.59	0.08	1.75	0.05	2.10	0.10
138	14.81	0.96	17.00	0.40	17.41	0.85	16.86	0.76	17.16	0.61	16.64	0.62	13.60	1.67	14.37	1.20	16.60	0.59	17.84	0.48
149	14.24	1.19	16.05	0.50	17.42	0.99	16.38	0.70	16.29	0.36	17.51	0.80	14.79	1.71	14.97	1.43	17.99	0.48	19.04	0.80
153	21.33	1.53	21.69	0.92	25.27	1.48	24.47	1.22	24.54	0.71	25.16	1.05	21.00	2.39	21.75	2.26	25.67	0.71	27.56	1.04
156	1.26	0.07	1.41	0.05	1.42	0.10	1.47	0.11	1.40	0.04	1.41	0.08	1.16	0.13	1.26	0.12	1.47	0.04	1.74	0.11
170	7.61	0.39	8.71	0.31	9.06	0.69	8.44	0.51	8.37	0.28	8.67	0.24	6.91	0.83	6.64	0.37	8.59	0.31	8.52	0.25
180	20.17	0.98	21.86	0.61	22.20	1.44	21.96	1.01	21.93	0.59	22.03	0.69	17.65	2.06	17.31	1.63	22.01	0.61	21.88	0.57

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MAE concentrations are nearly identical to those obtained with the USE method. The extraction time of 10 min applied also seems sufficient and is close to previous investigations using extraction times of 5–15 min [14,15,42,44–47]. Interestingly MAE is the technique, which provides the overall lowest SD-values, of ten even better than the SFE method, which previously has been shown to give very precise data sets when solid phase traps are, utilized [39].

3.5. Accelerated solvent extraction

ASE was initially performed at 100 °C using *n*-hexane/acetone (1:1, v/v) with a single 5 min extraction step (ASE A). This resulted in concentrations, which were close to Soxhlet, or in some cases even below Soxhlet concentrations for both soil types (Tables 1 and 2). When performing an additional extraction of 5 min with the same solvent, the concentrations increased substantially for both soil types, and were now higher than Soxhlet concentrations for both the HL- and LL-soil, and close to the concentrations obtained with the USE and the MAE method. These types of observations regarding extraction cycles have been made before, where as much as 10% of chlorinated pesticides and PCBs were found in a secondly applied extraction step [16,51]. Consequently, two extraction cycles is preferable, and some applications even make use of a 10 min extraction step in two cycles [18,23]. Another option to improve the ASE method is to use toluene as solvent for difficult matrices [7,16,52]. Toluene has also been suggested for other extraction techniques such as MAE [46]. From Tables 1 and 2 it can be seen that when applying toluene in a single 5 min extraction step the differences are small compared to *n*-hexane/acetone. However, by adding a second 5 min extraction step, the observed concentrations are higher than any of the other techniques using *n*-hexane/acetone. The reason for this is probably that toluene better interacts with various active sites such as organic carbon and soot carbon [52]. This effect would probably have been observed for some of the other techniques as well in case toluene had been utilized, but is here only demonstrated for ASE. However, it should be stressed that the addition of toluene adds to the complexity of the extracts since more coextracted analytes occurs. Therefore, the use of toluene should be restricted to matrices, which are known to cause accuracy problems when extracted with weaker solvents.

3.6. Overall comparison of PCB recoveries applying different extraction techniques

In Fig. 3, an overall comparison between the recoveries obtained for the different extraction techniques are shown using Soxhlet as the definition of 100% recovery. The individual bars are the average of all congeners extracted and gives a compressed overview of the results. Interestingly, all techniques using *n*-hexane/acetone and sound choices of extraction time and temperature gives nearly identical data. These include Soxtec, USE, SFE at 100 °C (SFE B) and ASE

with two extraction cycles (ASE A 5 + 5). The only exception to 100% recovery are Soxtec for the HL-soil, SFE at 80 °C for the HL-soil (SFE A), and ASE with *n*-hexane/acetone when applying a single extraction step of 5 min (ASE A 5). Furthermore the effects of toluene are not very pronounced when a single 5 min step is applied (ASE B 5), while a 10% increase in recoveries can be observed for toluene performed in two steps (ASE B 5 + 5) as compared to any other extraction technique applied. In conclusion, most of the presented techniques are capable of providing accurate results in case the chosen extraction conditions are good enough and based on previous experience form other investigations. In most cases *n*-hexane/acetone is a suitable choice, which should be combined with working temperatures of 100 °C for the more recent extraction techniques such as MAE and ASE.

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