

# Microwave-assisted extraction versus Soxhlet extraction for the analysis of short-chain chlorinated alkanes in sediments<sup>☆</sup>

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## Abstract

Microwave-assisted extraction (MAE) was evaluated as a possible alternative to Soxhlet extraction for analysing short-chain chlorinated alkanes (commonly called short-chain chlorinated paraffins, SCCPs) in river sediment samples, using gas chromatography coupled to negative chemical ionisation mass spectrometry. For MAE optimisation, several extraction parameters such as solvent extraction mixture, extraction time and extraction temperature were studied. Maximum extraction efficiencies for SCCPs (90%) and for 12 polychlorinated biphenyl (PCB) congeners (91–95%) were achieved using 5 g of sediment sample, 30 ml of *n*-hexane–acetone (1:1, v/v) as solvent extraction, and 15 min and 115 °C of extraction time and temperature, respectively. Activated Florisil was used to clean-up the extracts, allowing highly selective separation of SCCPs from other organic contaminants such as PCBs. MAE was compared with a conventional extraction technique such as Soxhlet and good agreement in the results was obtained. Quality parameters of the optimised MAE method such as run-to-run (R.S.D. 7%) and day-to-day precision (R.S.D. 9%) were determined using spiked river sediment samples, with LODs of 1.5 ng g<sup>-1</sup>. This method was successfully applied to the analysis of SCCPs in river sediment samples at concentrations below the ng g<sup>-1</sup> level.

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## 1. Introduction

Chlorinated alkanes (also called chlorinated paraffins, CPs) are complex industrial mixtures formed by direct chlorination of *n*-alkane feedstocks under forcing conditions of temperature and UV–vis irradiation [1–4]. These formulations contain a high number of isomers and homologues of polychlorinated *n*-alkanes (PCAs), with carbon chain lengths between 10 and 30 and a chlorination degree between 30 and 70% (w/w) [5]. Depending on the carbon chain length, CPs can be classified into three group of compounds: short-chain (C<sub>10–13</sub>, SCCPs), medium-chain (C<sub>14–17</sub>, MCCPs) and

long-chain (C<sub>18–30</sub>, LCCPs) chlorinated alkanes (CPs). Due to their physical and chemical properties, CPs are used as additives in plastics, paints and cutting oils and as flame retardants [6–7]. Of the different CP formulations, short-chain (C<sub>10–13</sub>) CPs are the most extensively used mixture in the industry [8]. In the 1970s, the United States Environmental Protection Agency (EPA) and the Chlorinated Paraffins Industry Association (CPIA) undertook a comprehensive study of the health and environmental impact of CPs and in 1990 the International Agency for Research of Cancer (IARC) classified short-chain CPs (C<sub>12</sub>) with an average chlorine content of 60% as possibly carcinogenic to humans (group 2B) [9]. However, no evidence of carcinogenicity was found in the other commercial mixtures of CPs (MCCPs and LCCPs). The result was that several organisations (Oslo and Paris Commission for the Protection of the Marine Environment for the North-East Atlantic: OSPAR, Canadian Environmental Protection Act: CEPA) and environmental protection agencies

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listed SCCPs as substances requiring special action and regulations [10,11]. The European Union [12] has recently included SCCPs [13] on its list of priority hazardous substances in the field of water policy, amending Directive 2000/60/EC [14].

The presence of CPs in various environmental matrices such as biota [8,15,16], sediments [3,15,17,22], air [18] and water [19–23] has been reported, but information about environmental levels is still limited. CPs have been detected in river and marine sediments from industrial zones at concentration levels between 0.2 and 65  $\mu\text{g g}^{-1}$ , while in lake and river sediments of remote or agricultural areas CPs are found at concentrations from 10 to 250  $\text{ng g}^{-1}$ . Generally, the analysis of CPs is difficult due to the large number of congeners (a minimum of several thousands) present in technical products. Furthermore, single-capillary GC column is by far insufficient to separate all the compounds, as individual peaks and the chromatograms obtained are characterised by a broad profile corresponding to a large number of co-eluting peaks [4]. Most of the methods used for the determination of CPs are based on gas chromatography with electron-capture detection [23–25] (GC–ECD) or coupled to high- or low-resolution mass spectrometry. Detection of CPs using mass spectrometry frequently involves electron-capture negative ionisation (ECNI), due to its high selectivity and sensitivity [3,8,26,27].

Few papers on the analysis of CPs in solid matrices, e.g. soils, sediments and sludges, have been published. Most of the methods used in these studies are based on classical Soxhlet extraction. Nevertheless, this traditional sample extraction technique often uses large quantities of organic solvents and is usually time-consuming. In the last few years, established methods, such as supercritical fluid extraction (SFE), pressurized liquid extraction (PLE) and microwave-assisted extraction (MAE), were used to reduce the volume of solvents required, to improve the precision of analyte recoveries and to reduce extraction time. Of these techniques, SFE is the most selective extraction method, but its use has been limited by the strong matrix dependence of the extraction process. Most of the time, extraction conditions need to be optimised for each new matrix [28]. PLE and MAE techniques offer advantages over the SFE method, but to date accelerated solvent extraction is the only technique used for the isolation of CPs from soil and sediment samples [15,17,24]. Nevertheless, microwave-assisted extraction can be an excellent alternative sample preparation technique for the extraction of CPs. In fact, this technique has been successfully applied to the analysis of environmental pollutants such as hydrocarbons [29], organochlorine pesticides [29–35], polychlorinated biphenyls [35–40], polychlorinated aromatic hydrocarbons [31,41–45], phenols [41,46], from soil and sediment matrices.

This paper focuses on the development of a new method for the analysis of SCCPs in sediment, using microwave-assisted extraction and gas chromatography–electron-capture negative ion-mass spectrometry (GC–ECNI-MS). For this

purpose, MAE parameters, such as extraction temperature, extraction time and the composition of the extraction solvent, were optimised in order to maximize the extraction efficiency of SCCPs and other environmental contaminants such as polychlorinated biphenyls present in sediment samples. The optimised method was evaluated by comparing the results with those obtained with Soxhlet extraction. Quality parameters for both methods were established, and the proposed method was used for the determination of SCCPs and polychlorinated biphenyls (PCBs) in river sediment samples.

## 2. Experimental

### 2.1. Standards and reagents

Two stock standard solutions of a short-chain chlorinated paraffin (SCCP, C<sub>10</sub>–C<sub>13</sub>, 63% Cl) in acetone and in cyclohexane of 100  $\text{ng } \mu\text{l}^{-1}$  were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Individual analytical-reagent grade PCB congeners, 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180, at purity higher than 99%, were supplied by Promochem GmbH (Wesel, Germany). A stock standard solution mixture of the 12 PCB congeners at 300  $\mu\text{g g}^{-1}$  was prepared by weight in isooctane. Five calibration standard solutions of SCCPs (between 1 and 80  $\mu\text{g g}^{-1}$ ) and PCBs (from 0.5 to 200  $\text{ng g}^{-1}$ ) containing the internal standards were prepared by dilution of the primary standard solutions in isooctane for quantification purposes. Standard solutions at concentration levels of 10  $\mu\text{g g}^{-1}$  for the SCCPs and 1  $\mu\text{g g}^{-1}$  for each PCB congener were prepared for spiking experiments. PCB-30 (1  $\mu\text{g g}^{-1}$  in isooctane) and [<sup>13</sup>C<sub>6</sub>]-hexachlorobenzene (1  $\mu\text{g g}^{-1}$  in isooctane) (Dr. Ehrenstorfer GmbH) were used as internal standards for quantification of PCB congeners using GC–ECD and of SCCPs using GC–ECNI-MS, respectively.

*n*-Hexane, dichloromethane (DCM), acetone and *tert*-butyl methyl ether, of pesticide residue analysis grade, were purchased from Merck (Darmstadt, Germany). Florisil (0.150–0.250 mm) for residue analysis, alumina (aluminium oxide 90 active neutral) and silica gel (0.063–0.2 mm) for column chromatography were obtained from Merck. Fine copper powder was purchased from Merck. Copper powder was activated by nitric acid (1:1, v/v). Anhydrous sodium sulphate was supplied by Panreac (Barcelona, Spain). Before use, alumina and silica gel were cleaned with DCM in an ultrasonic bath for 15 min and were dried in a heater at 120 °C until elimination of solvent. All adsorbents were activated at 650 °C overnight and stored at 120 °C before use.

### 2.2. GC–ECD and GC–MS conditions

Preliminary MAE optimisation procedures were performed with a Trace GC 2000 gas chromatograph (ThermoFinnigan, Milan, Italy), equipped with a <sup>63</sup>Ni electron-capture detector and the AS2000 autosampler. For

the chromatographic separation of SCCPs and PCB congeners, a DB-5 ms (5% phenyl, 95% methylpolysiloxane), 30 m × 0.25 mm i.d., fused-silica capillary column (J&W Scientific, Folsom, CA, USA) of 0.25 µm film thickness was used. In addition, to confirm PCB congeners, a DB-17 (50% phenyl-, 50% methylpolysiloxane), 30 m × 0.25 mm i.d., fused-silica capillary column (J&W Scientific) of 0.25 µm film thickness was used. Helium was used as carrier gas (38 cm/s at 90 °C), and N<sub>2</sub> as ECD make-up gas (40 ml min<sup>-1</sup>). Injector and ECD temperature were set at 250 and 330 °C, respectively, and the splitless injection mode (1 min) was used. The oven temperature program for the analysis of SCCPs using DB-5 ms column was 90 °C (held for 1 min) to 180 °C at 15 °C/min and to 300 °C at 8 °C/min (held for 10 min). For the analysis of PCBs, the oven programme for DB-5 ms and DB-17 capillary columns was: 90 °C (held for 1 min) to 180 °C at 15 °C/min and to 300 °C at 2.5 °C/min. For quantification purposes, the integration of the total area below the SCCP elution profile was used.

For the analysis of SCCPs, GC–ECNI–MS experiments were performed on a Trace GC 2000 chromatograph coupled to a GCQ/Polaris ion-trap mass spectrometer (ThermoFinnigan, TX, USA). DB-5 ms fused-silica capillary column was used and the chromatographic conditions were the same as described above for GC–ECD experiments. Xcalibur version 1.2 software was used for control, general operation and acquisition of the mass spectra. The instrument was operated in the ECNI mode and tuned using perfluorotributylamine (FC-43), following manufacturer's directions, in order to achieve the best sensitivity working with automatic gain control. For all experiments, electron energy was 70 eV and emission current 250 µA. Ion source and transfer line temperatures were 200 °C and 275 °C, respectively. Parameters such as automatic gain control (AGC) target and multiplier voltage (1450 V, 10<sup>5</sup> gain) were set by automatic tune. Methane was used as moderating gas and the pressure in the mass analyser region of the vacuum manifold was measured by means of an ion gauge. The MS acquisition method was time programmed in two segments. In the first segment, the internal standard, [<sup>13</sup>C<sub>6</sub>]hexachlorobenzene, was detected by monitoring the *m/z* 286–296 region at 0.64 s/scan (10 µscan/scan), whereas SCCPs were monitored in the second segment by scanning the range *m/z* 70–75 ([HCl<sub>2</sub>]<sup>-</sup> and [Cl<sub>2</sub>]<sup>-•</sup> cluster ions) at 0.63 s/scan (10 µscan/scan). SCCPs were quantified as the sum of total area below the elution profile of SCCPs obtained in the second monitoring segment.

### 2.3. Soxhlet and microwave-assisted extraction procedures

For Soxhlet extraction experiments, an aliquot of 5 g dry mass sediment sample was placed in a glass Soxhlet thimble containing 20 g of anhydrous sodium sulphate and 20 g of activated copper powder for sulphur removal. The sample was extracted with 300 ml of *n*-hexane–DCM (1:1, v/v) for 16 h. The organic extract was then concentrated to ca. 1 ml using

a rotary evaporator without heating. The extract was then purified following the clean-up procedure described below (Section 2.4).

Microwave-assisted solvent extraction used a CEM MARS 5, microwave sample extraction system (CEM, Matthews, NC, USA), equipped with twelve closed vessel-microwave extraction cells. Microwave energy was produced by a 1200 W magnetron. The extraction reactor cells were made by a closed pressure-resisting system that contains an inner vessel of Pyrex (“GreenChem”) with a volume of 85 ml and allows maximum pressure and temperature of 200 psi and 200 °C, respectively (psi = 6894.76 Pa). The inner temperature of the sample vessel was measured and controlled with a microwave-inert optical fibre temperature probe, while the pressure inside the microwave system was measured by a gauge probe. The sediment samples (5 g) were extracted at 115 °C for 15 min at the maximum magnetron power, using 30 ml of solvent mixture *n*-hexane–acetone (1:1, v/v). A PTFE-coated stir bar was used as magnetic stirring of the samples. After extraction, the sample was left for a cooling time of 20 min. The supernatant organic extract was then carefully decanted from the extraction vessel to a 50 ml heart-shaped flask and the sample was rinsed with three portions of 5 ml of *n*-hexane. All extracts were combined and filtered through 10 g of anhydrous sodium sulphate. For sulphur removal, the solvent extract was in contact with 20 g of activated copper for 3 h. Finally, the extract was filtered and concentrated to ca. 1 ml using a rotary evaporator without heating. The final extract was then cleaned as described in the clean-up in the extracts section.

### 2.4. Clean-up of the extracts

The extracts obtained after sample extraction using Soxhlet and MAE were carefully transferred to a glass column (200 mm × 15 mm i.d.) filled with 15 g of activated Florisil. After packing, the column was rinsed with *n*-hexane and the entire extract was placed at the top of the column. Two fractions were collected: (F1) with 60 ml of *n*-hexane, where PCBs were eluted, and (F2) with 200 ml *n*-hexane–dichloromethane (1:1, v/v) which contained the SCCPs. The extracts obtained were dried over sodium sulfate and concentrated to ca. 1 ml using a rotary evaporator. Each extract was then transferred in a 2-ml vial and was concentrated under a gentle stream of nitrogen. The final volume of the extract was adjusted to ca. 150 µl with isoctane after addition of the internal standards ([<sup>13</sup>C<sub>6</sub>]hexachlorobenzene and CB 30). The extracts were analysed by GC–ECD (fraction 1) and GC–ECNI–MS (fraction 2).

### 2.5. Sediment samples

River sediment samples were collected from six different sampling points located in several industrial areas of the Besòs River near Barcelona (NE Spain). All sediment samples were air-dried, pulverized and sieved through a

125-mesh sieve. They were stored in the dark at 4 °C until analysis. A river sediment sample sampled upstream from the industrial zones (agricultural area) was selected as candidate blank sediment sample. Before use, this sediment sample was analysed by GC–ECD to ensure that no compounds of interest were present. The resulting material was spiked with adequate amounts of C<sub>10</sub>–C<sub>13</sub> (63% CI) SCCPs and PCB congener standard solutions. Before use, it was incubated for 24 h at 4 °C. The sample was selected as reference spiked sediment for the optimisation of MAE and clean-up processes.

### 3. Results and discussion

#### 3.1. Optimisation of clean-up procedure

Preliminary studies were carried out in order to develop a suitable clean-up method for the purification of sediment extracts obtained by MAE. For this purpose, sorbents such as Florisil, silica gel and alumina (15 g), fully activated and partially deactivated with water (up to 5%, w/w), were studied. A clean-up procedure based on the elution of two fractions was used to achieve selective separation of the SCCPs from other co-extracted compounds, such as PCBs, present in sediment samples. To elute the less polar compounds (e.g. PCBs) *n*-hexane was selected as solvent, whereas for SCCPs, solvent mixtures of *n*-hexane–dichloromethane and *n*-hexane–methyl *tert*-butyl ether were tested. To determine the recovery of the target compounds, a blank river sediment was spiked at three different concentration levels (200, 300 and 400 ng g<sup>-1</sup> for SCCPs, and 2, 3 and 4 ng g<sup>-1</sup> for individual

PCB congeners). The samples were Soxhlet extracted and the extracts were cleaned and fractionated using the optimum elution conditions for each sorbent (see Table 1). Recoveries were calculated from the slope of the standard addition curve obtained by plotting the ng recovered/g of sediment versus the ng spiked/g of sediments. Table 1 shows the recovery and standard deviation for each sorbent tested. As can be seen, the highest recovery for SCCPs was obtained with fully activated Florisil (95%) and silica gel (87%). Moreover, for PCB congeners, recoveries ranging from 87 to 97% were obtained, whereas recoveries decreased with deactivation of the sorbent. For activated alumina, SCCPs were strongly adsorbed on the sorbent, making it difficult to elute them even using a large volume of pure dichloromethane. For this reason, even though the PCBs were recovered (82–89%) in a first fraction, this sorbent was not considered suitable for the analysis of SCCPs. Since recoveries achieved with Florisil were slightly higher than those obtained with silica gel, and the volume of solvents required for the elution of the analytes were lower, fully activated Florisil was selected as the clean-up sorbent for all subsequent studies.

#### 3.2. Optimisation of the MAE parameters

Preliminary experiments studied the efficiency of various solvent mixtures in extracting SCCPs and PCBs from sediment samples. Solvent mixtures such as *n*-hexane–dichloromethane (1:1, v/v), *n*-hexane–acetone (1:1, 2:1 and 1:2, v/v), commonly used with conventional extraction methods [41], were evaluated. In addition, a more polar solvent mixture *n*-hexane–methanol (1:2, v/v) was also

Table 1  
Recovery (%) and standard deviation of C<sub>10</sub>–C<sub>13</sub>, 63% CI SCCP and PCB congeners obtained in a spiked sediment sample using different clean-up sorbents

Compound	Recovery (%)				
	Florisil <sup>a</sup>		Silica gel <sup>b</sup>		Alumina <sup>c</sup>
	Activated (mean ± S.D. <sup>d</sup> )	1.2% water (mean ± S.D. <sup>d</sup> )	Activated (mean ± S.D. <sup>d</sup> )	5% water (mean ± S.D. <sup>d</sup> )	Activated (mean ± S.D. <sup>d</sup> )
SCCPs	95 ± 3	70 ± 3	87 ± 2	75 ± 3	nd
PCBs					
CB-28	95 ± 4	78 ± 3	91 ± 2	77 ± 2	88 ± 3
CB-52	93 ± 3	81 ± 2	93 ± 2	78 ± 2	83 ± 3
CB-101	95 ± 2	82 ± 3	90 ± 3	82 ± 3	84 ± 3
CB-105	93 ± 5	81 ± 3	93 ± 3	83 ± 4	81 ± 3
CB-118	90 ± 4	83 ± 3	90 ± 3	82 ± 4	89 ± 3
CB-128	91 ± 6	82 ± 3	91 ± 5	78 ± 3	83 ± 3
CB-138	94 ± 3	82 ± 4	89 ± 2	81 ± 4	86 ± 4
CB-149	93 ± 3	81 ± 3	93 ± 4	83 ± 3	88 ± 4
CB-153	97 ± 4	81 ± 3	87 ± 4	82 ± 3	82 ± 4
CB-156	97 ± 3	78 ± 3	92 ± 2	77 ± 4	83 ± 4
CB-170	94 ± 3	79 ± 3	93 ± 2	84 ± 4	84 ± 3
CB-180	95 ± 3	82 ± 3	90 ± 5	80 ± 3	88 ± 4

nd: not detected (<LOD).

<sup>a</sup> 60 ml *n*-hexane (fraction 1) and 200 ml *n*-hexane–dichloromethane (1:1, v/v) (fraction 2).

<sup>b</sup> 120 ml *n*-hexane (fraction 1) and 120 ml *n*-hexane–methyl *tert*-butyl ether (9:1, v/v) (fraction 2).

<sup>c</sup> 60 ml *n*-hexane (fraction 1) and 200 ml *n*-hexane–dichloromethane (1:1, v/v) (fraction 2).

<sup>d</sup> *n* = 3.

Table 2  
Recovery of C<sub>10</sub>–C<sub>13</sub>, 63% Cl SCCP in a sediment sample spiked at concentration range between 200 and 400 ng g<sup>-1</sup> using MAE procedure

Solvent extraction mixture	Mean (%) <sup>a</sup>	R.S.D. (%)
<i>n</i> -Hexane–dichloromethane (1:1, v/v)	84	7
<i>n</i> -Hexane–acetone (1:1, v/v)	90	8
<i>n</i> -Hexane–acetone (2:1, v/v)	76	7
<i>n</i> -Hexane–acetone (1:2, v/v)	70	7
<i>n</i> -Hexane–methanol (1:2, v/v)	58	8

<sup>a</sup> *n* = 3.

studied. For this purpose, a blank sediment sample (5 g) spiked with C<sub>10</sub>–C<sub>13</sub> (63% Cl) SCCPs and the PCB congeners at three concentration levels between 200–400 and 2–4 ng g<sup>-1</sup>, respectively, was used. The samples were extracted at 115 °C for 30 min using a volume of 30 ml for each solvent mixture. As *n*-hexane–dichloromethane do not absorb microwave energy because the components are not polar, a microwave absorbing material was added to the extraction cell. The extracts were cleaned using the optimised Florisil method and the two fractions were analysed by GC–ECD (fraction 1: PCBs) and GC–NCI-MS (fraction 2: SCCPs). Under these conditions, the highest extraction efficiency for SCCPs (90%) was obtained using *n*-hexane–acetone (1:1, v/v) (Table 2). In addition, recoveries ranging from 91 to 95% were achieved for the PCB congeners using this solvent mixture. Therefore, *n*-hexane–acetone (1:1, v/v) was chosen as a suitable solvent mixture for subsequent studies.

After selection of the solvent extraction mixture, the extraction time and extraction temperature were optimised. Initially, the extraction temperature was fixed at 115 °C and the effect of the extraction time on MAE efficiency for all analytes was examined from 5 to 20 min in 5-min increments. The recoveries obtained for SCCPs and some PCB congeners are given in Table 3. The highest recovery for all compounds was found at 15 min. The effect of the temperature on the extraction efficiency of the SCCPs and PCB congeners were then studied from 70 to 120 °C (Table 3). The recoveries of the analytes increased with temperature, reaching their maxima at 115 °C. However, the recoveries decreased at temperatures and extraction times higher than 115 °C and 15 min, respectively. This fact has also been reported for other compounds [47] and can be attributed to losses of the analytes

Table 3  
Effect of extraction time and extraction temperature in the recovery of SCCPs and PCB congeners using MAE method

Compounds	Recovery (%)								
	Extraction time (min)					Extraction temperatures (°C)			
	5	10	15	20	25	70	100	115	120
SCPP	60	73	98	86	80	51	76	96	80
CB 52	60	74	94	87	72	70	89	93	78
CB 101	48	75	95	81	78	56	74	94	83
CB 118	43	73	95	84	77	68	83	94	85
CB 138	51	84	96	85	77	72	81	95	80
CB 153	61	78	96	88	70	71	83	96	74
CB 180	52	65	95	84	74	70	87	95	79

Table 4  
Quality parameters of the MAE and Soxhlet extraction methods

Compound	Precision (R.S.D., %) <sup>a</sup>				LOD (ng g <sup>-1</sup> )	
	Run-to-run <sup>b</sup>		Day-to-day <sup>c</sup>		MAE	Soxhlet
	MAE	Soxhlet	MAE	Soxhlet		
SCCPs	7	3	9	3	1.5	1.8
PCBs						
CB-28	8	6	10	8	0.012	0.010
CB-52	10	8	13	10	0.016	0.014
CB-101	7	6	9	10	0.010	0.010
CB-105	9	7	12	9	0.010	0.008
CB-118	7	6	9	10	0.014	0.008
CB-128	8	6	10	8	0.012	0.012
CB-138	8	7	11	10	0.010	0.006
CB-149	8	6	11	9	0.008	0.008
CB-153	9	6	12	8	0.016	0.014
CB-156	8	7	12	10	0.014	0.014
CB-170	7	7	11	8	0.010	0.010
CB-180	9	6	10	9	0.014	0.010

<sup>a</sup> Concentration: 200 ng g<sup>-1</sup> for SCCPs and 2 ng g<sup>-1</sup> for PCB congeners.

<sup>b</sup> *n* = 3.

<sup>c</sup> *n* = 3 replicates × 3 days.

from the extraction vessel. Therefore, an extraction temperature of 115 °C and an extraction time of 15 min were chosen as optimum extraction conditions for the analysis of SCCPs and PCBs in sediment samples.

### 3.3. Quality parameters

Quality parameters such as run-to-run and day-to-day precision, limits of detection (LODs) and linearity were established for the proposed MAE method, using GC–ECNI-MS for SCCPs and GC–ECD for PCB congeners (Table 4). For run-to-run and day-to-day precision studies, three replicates of 5 g blank river sediment sample spiked at 200 ng g<sup>-1</sup> for SCCPs and 2 ng g<sup>-1</sup> for PCB congeners were analysed by the proposed MAE method on one day and on three days, respectively. Relative standard deviations (R.S.D.) of 7 and 9% were obtained for run-to-run and day-to-day precision of SCCPs, whereas for individual PCB congeners values ranged from 7 to 10% and between 9 and 13%, respectively. Similar experiments using Soxhlet extraction as a reference method were carried out and the results are given in Table 4. For the

Soxhlet method, run-to-run precision (3% R.S.D. for SCCPs and between 6 and 8% for PCBs) and day-to-day precision (3% R.S.D. for SCCPs and from 8 to 10% for PCBs) were slightly lower than those obtained with the MAE method, although the precision afforded by MAE can be considered good enough, given the complexity of the matrix.

Limits of detection (LODs), based on a signal-to-noise ratio (S/N) of 3:1, were determined experimentally using a river sediment sample without detectable quantities of SCCPs and PCBs, spiked at low concentration levels (0.05 ng g<sup>-1</sup> for each PCB and 10 ng g<sup>-1</sup> for the SCCPs). Under these conditions, the LOD of the MAE method in combination with GC–ECNI-MS for SCCPs was 1.5 ng g<sup>-1</sup>; whereas for PCB congeners, LODs ranged from 0.008 to 0.016 ng g<sup>-1</sup>, using GC–ECD. Similar LODs (1.8 ng g<sup>-1</sup> for SCCPs and between 0.008 and 0.014 ng g<sup>-1</sup> for individual PCB congeners) were obtained with the Soxhlet extraction method. Finally, the calibration range for the C<sub>10</sub>–C<sub>13</sub>, 63% Cl SCCP using GC–ECNI-MS, was studied between 1 and 80 μg g<sup>-1</sup>. Calibration graphs obtained were non-linear and fitted to a second-degree polynomial curve. In the case of individual PCB congeners, good linearity ( $r^2 \geq 0.999$ ) was found in the calibration range between 0.5 and 200 ng g<sup>-1</sup> using GC–ECD.

### 3.4. Analysis of river sediment samples

To examine the applicability of the proposed MAE method, SCCPs and twelve individual PCBs were determined in river sediment samples. Samples were collected from different sites on the Besòs River (Barcelona, Spain) close to industrial effluents. Six river sediment samples were analysed in triplicate, using internal standard method for quantification. As an example, Fig. 1 shows the GC–ECNI-MS chromatogram for a 5 μg g<sup>-1</sup> standard solution of the C<sub>10</sub>–C<sub>13</sub> (63% Cl) SCCPs and that for the S4 sediment sample. As can be observed in the chromatogram, the elution of the SCCPs is characterised by a broad chromatographic profile, due to the co-elution of several thousands of individual polychlorinated *n*-alkanes. The elution patterns of the SCCP standard and the sample were very similar, showing moderate SCCP contamination. In addition, high selectivity in the detection of SCCPs was achieved using GC–MS and electron-capture negative ionisation. SCCP and PCB concentrations and the standard deviations obtained for the samples analysed are summarised in Table 5. In all samples, the presence of SCCPs was detected at concentration levels between 0.25 ± 0.02 and 3.04 ± 0.24 μg g<sup>-1</sup>. For the twelve PCB congeners, concentrations ranging from 0.60 ± 0.07 to 54.8 ± 5.0 ng g<sup>-1</sup> were determined. For all compounds, the precision afforded for the method was less than 11%.

To evaluate the applicability of MAE to the analysis of SCCPs and PCBs in sediment samples, MAE results were compared with those with Soxhlet-extraction, considered the reference extraction method. The analytical significance of the mean values of the two extraction methods was studied sta-

Table 5  
Concentrations of SCCPs (μg g<sup>-1</sup>) and PCB congeners (ng g<sup>-1</sup>) found in river sediment samples  
Compounds Concentration<sup>a</sup> (μg g<sup>-1</sup>)

Compounds	Sediment S1			Sediment S2			Sediment S3			Sediment S4			Sediment S5			Sediment S6		
	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)	MAE (mean ± S.D.)	Soxhlet (mean ± S.D.)
SCCPs	0.68 ± 0.04	0.71 ± 0.06	0.25 ± 0.02	0.27 ± 0.02	0.41 ± 0.02	0.42 ± 0.02	0.75 ± 0.08	0.81 ± 0.05	1.69 ± 0.11	1.79 ± 0.13	3.04 ± 0.24	3.26 ± 0.13						
Concentration <sup>a</sup> (ng g <sup>-1</sup> )																		
CB-28	0.15 ± 0.01	0.17 ± 0.01	nd	nd	0.13 ± 0.01	0.13 ± 0.01	nd	nd	1.64 ± 0.14	0.17 ± 0.01	0.13 ± 0.01	0.13 ± 0.01						
CB-52	0.70 ± 0.05	0.80 ± 0.04	0.08 ± 0.01	0.10 ± 0.01	0.61 ± 0.05	0.63 ± 0.06	0.07 ± 0.01	0.07 ± 0.01	0.77 ± 0.07	0.78 ± 0.07	0.61 ± 0.04	0.62 ± 0.04						
CB-101	1.32 ± 0.09	1.49 ± 0.10	0.16 ± 0.02	0.18 ± 0.01	1.15 ± 0.11	1.17 ± 0.08	0.13 ± 0.01	0.13 ± 0.01	1.45 ± 0.10	1.47 ± 0.12	1.14 ± 0.08	1.16 ± 0.09						
CB-105	0.37 ± 0.02	0.42 ± 0.03	nd	nd	0.32 ± 0.03	0.33 ± 0.03	nd	nd	0.41 ± 0.03	0.41 ± 0.03	0.31 ± 0.02	0.33 ± 0.02						
CB-118	1.75 ± 0.16	1.99 ± 0.14	0.21 ± 0.02	0.24 ± 0.02	1.53 ± 0.11	1.56 ± 0.13	0.17 ± 0.02	0.18 ± 0.01	1.93 ± 0.20	1.95 ± 0.16	1.51 ± 0.13	1.55 ± 0.12						
CB-128	1.01 ± 0.08	1.15 ± 0.08	0.12 ± 0.01	0.14 ± 0.01	0.88 ± 0.06	0.90 ± 0.06	0.10 ± 0.01	0.10 ± 0.01	1.12 ± 0.10	1.13 ± 0.06	0.87 ± 0.08	0.90 ± 0.06						
CB-138	0.34 ± 0.02	0.39 ± 0.03	nd	nd	0.30 ± 0.02	0.31 ± 0.02	nd	nd	0.37 ± 0.03	0.38 ± 0.02	0.29 ± 0.02	0.30 ± 0.02						
CB-149	3.15 ± 0.18	3.58 ± 0.28	0.38 ± 0.03	0.43 ± 0.04	2.75 ± 0.22	2.81 ± 0.21	0.31 ± 0.03	0.32 ± 0.02	3.48 ± 0.28	3.51 ± 0.27	2.73 ± 0.25	2.79 ± 0.22						
CB-153	4.46 ± 0.32	5.06 ± 0.28	0.54 ± 0.04	0.60 ± 0.05	3.89 ± 0.34	3.98 ± 0.41	0.44 ± 0.04	0.45 ± 0.03	4.92 ± 0.45	4.97 ± 0.29	3.86 ± 0.39	3.95 ± 0.25						
CB-156	0.49 ± 0.05	0.56 ± 0.05	0.06 ± 0.01	0.07 ± 0.01	0.42 ± 0.02	0.44 ± 0.03	nd	nd	0.54 ± 0.03	0.55 ± 0.05	0.42 ± 0.04	0.43 ± 0.03						
CB-170	2.66 ± 0.18	3.02 ± 0.23	0.32 ± 0.03	0.36 ± 0.02	2.32 ± 0.20	2.38 ± 0.20	0.26 ± 0.03	0.27 ± 0.02	2.94 ± 0.18	2.97 ± 0.32	2.30 ± 0.19	2.36 ± 0.18						
CB-180	4.92 ± 0.42	5.58 ± 0.51	0.60 ± 0.06	0.67 ± 0.05	4.29 ± 0.30	4.39 ± 0.27	0.47 ± 0.05	0.50 ± 0.05	5.43 ± 0.48	5.48 ± 0.50	4.25 ± 0.37	4.35 ± 0.32						

nd: not detected (<LOD).

<sup>a</sup> n = 3.

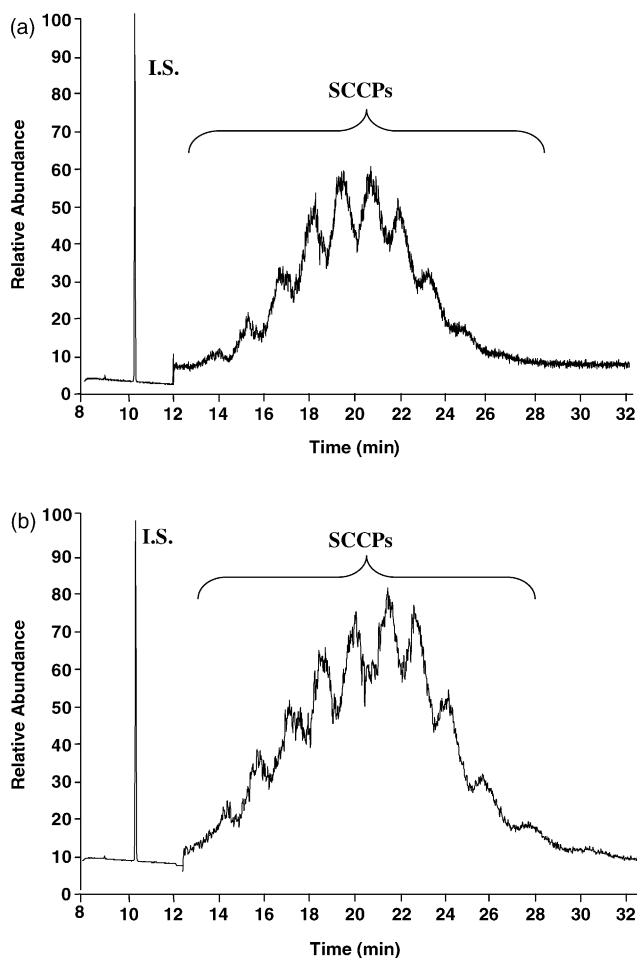


Fig. 1. GC-ECNI-MS chromatogram of (a) a  $5 \mu\text{g g}^{-1}$  standard solution of the C<sub>10</sub>–C<sub>13</sub>, 63% Cl SCCP and (b) S4 river sediment sample. For each chromatogram, detection of the internal standard (IS, [<sup>13</sup>C<sub>6</sub>]hexachlorobenzene, *m/z* 286–286) and the SCCP (*m/z* 70–75) is shown.

tistically using the Student's *t*-test. When unequal variances (*F*-test) were obtained, the Cochran test was applied. For all SCCPs and PCBs, no significant differences were observed between the MAE and Soxhlet methods ( $P > 0.05$ ). Therefore, the proposed MAE method can be successfully applied to the analysis of SSCPs and PCBs in sediment samples. This method showed some advantages over Soxhlet, such as less volume of organic solvents, a reduction in labour-intensive sample handling steps and shorter analysis time.

#### 4. Conclusions

The suitability of microwave-assisted extraction for the analysis of SCCPs in river sediment sample has been demonstrated. For the MAE method, *n*-hexane–acetone (1:1, v/v) was found to be the most effective solvent mixture for the extraction of SCCPs. Maximum recoveries of the target compounds were obtained using 30-ml solvent extraction, extraction time of 15 min and extraction temperature of 115 °C.

Clean-up procedure using fully activated Florisil permitted the complete separation between PCBs and SCCPs in two fractions with recoveries higher than 90%. The MAE method in conjunction with a clean-up step with activated Florisil and GC-ECNI-MS gave good precision values for SCCPs (R.S.D. 7 and 9% for run-to-run and day-to-day precision, respectively) and low detection limits ( $1.5 \mu\text{g g}^{-1}$ ). The MAE method was evaluated by comparison of the results with those obtained with a conventional extraction method such as Soxhlet. Similar results were obtained with both methods, but MAE had the advantages of less organic solvent and shorter extraction time. The developed MAE method can be proposed as a novel and fast alternative to conventional Soxhlet extraction techniques for the analysis of SCCPs in sediment samples at a low  $\mu\text{g g}^{-1}$  concentration level.

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