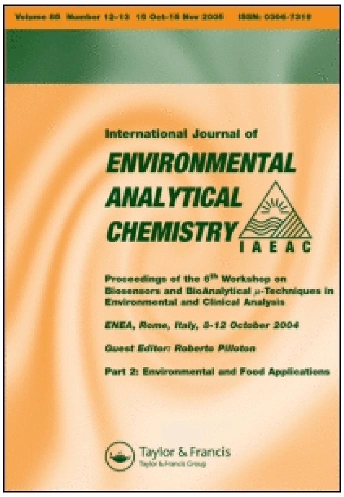

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Determining PCB desorption behaviour on sediments with SFE and investigating the dependency of selective fractions on sediment characteristics

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Determining PCB desorption behaviour on sediments with SFE and investigating the dependency of selective fractions on sediment characteristics

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A method for studying PCB desorption behaviour from sediments using supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) is presented. Four sediments were investigated and extracted with supercritical carbon dioxide employing increasingly harsher extraction conditions ranging from 40°C and 12 MPa to 100°C and 36.5 MPa. To ensure quantitative extractions, the remaining SFE residues were also extracted with PLE. Resulting profiles identified at least three different PCB fractions within the four sediments. Furthermore, a distinct fraction was obtained with extraction for 2 h at 40°C and 36.5 MPa. This fraction has previously been found to correlate well with bioavailable fractions. The dependency of this fraction on sediment total organic carbon (TOC) was investigated, both for sediments examined in this study as well as for previously reported values using the same extraction conditions. It was found that TOC does not correlate to selective SFE, which indicates that the use of TOC to predict bioavailability is questionable.

Keywords: Polychlorinated biphenyls; Supercritical fluid extraction; Sediment; Bioavailability; Total organic carbon

1. Introduction

Synthesizing a new chemical, patenting it, finding areas for its use, and selling it can be economically a very successful formula. Unfortunately, the financial load on society might be devastating if the new chemical possesses properties that are hazardous to health and environment. Polychlorinated biphenyls (PCBs) are one of the best-known examples of what can happen if chemicals are widely used without proper evaluation. In Sweden alone, the cost due to the usage of PCBs is estimated to be some €320–550 million, while the amount spent on PCB and PCB-related research is approximately €60 million. The average remediation cost for a contaminated sediment site is estimated

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to be €5.5–11 million, and there are 40,000–45,000 chemically contaminated sites in Sweden alone [1]. Enormous efforts have been dedicated to understanding the health effects and environmental impact of PCBs and PCB-related compounds, but even 40 years after Jensen's first PCB alarm [2], we still do not fully understand the extremely complex mechanisms and processes occurring when these chemicals enter our global ecosystems.

Within the field of sediment and soil contamination research, many scientists are now stating that persistent organic pollutant (POP) molecules with time can become so sequestered within the matrix that their bioavailability decreases [3–8]. In order to achieve correct risk assessments of POP-contaminated sites, this process, which is often referred to as aging, therefore needs to be considered [3, 5, 6, 8]. An advantage of including this concept in risk assessment would be improved decision making when prioritizing cleanup actions [8], between as well as within polluted sites. Thus, a simple, fast, and reliable analytical tool for estimating contaminant sequestration needs to be developed.

An analytical tool suggested for assessment of PCB association with sediments is selective supercritical fluid extraction (selective SFE) with carbon dioxide [9]. The possibility of fine-tuning subquantitative extractions by controlling the temperature and pressure makes SFE a suitable tool for studying POP–sediment interactions [9–12], and previous studies using selective SFE for desorption studies of PCBs from sediments have been performed [9, 12, 13]. It was reported that selected extraction conditions generated non-quantitative fractions of PCBs, demonstrating the usefulness of SFE to identify discrete PCB fractions within the matrix [9]. It was also shown that discrete fractions generated with conditions of about 40°C and 40 MPa correlated well with fractions available for organism uptake in systems containing sediment and chironomids [14], sediment and eels [13], and soil and earthworms [15]. Thus, selective SFE is a very promising analytical tool for determining PCB bioavailability.

However, in order to understand why a tool predicts biological uptake well, further insights must be sought. A multitude of different processes involved in POP sequestration, release, and uptake have previously been described [8]. Sediment and soil physical and chemical characteristics are often mentioned as key factors when seeking explanations to what controls the aging. For instance, in the equilibrium partitioning theory (EqP) the sediment total organic carbon (TOC) content is fundamental when estimating pollutant porewater concentrations, stating that the pore water content controls bioavailability [16]. It is argued that sediment hydrophobicity increases with TOC content, which leads to a higher degree of POP–sediment association, making molecules less available for biological uptake.

Out of eight sediments previously extracted using selective SFE, discrete fractions were present in all sediments but of a different magnitude in each sediment [9, 12, 13]. In these studies, however, the impact of sediment characteristics on extractability was not completely clear. In this article, possible relations between selective SFE conditions, which extract primarily bioavailable molecules [13–15], and sediment characteristics, primarily different carbon fractions, are investigated.

Four additional sediments have also been studied. They originate from the Hudson River and have been thoroughly characterized in a previous study [17]. Extractions of these sediments were made using increasingly harsher conditions (i.e. increasing temperature and pressure) in order to monitor the desorption behaviour of 10 PCB congeners. The results from these extractions have been added to the previous studies to investigate the effects of some sediment characteristics.

2. Experimental

2.1 *Chemicals*

Acetone, *n*-heptane (both pestanal-grade) and treated granulated copper used throughout the study were manufactured by Riedel-de Haën (Seelze, Germany). Florisil (60–100 mesh), silica gel 60 (63–200 mesh), sodium sulfate (puriss. p.a., ACS; ≥99.0%), and sulfuric acid (puriss. p.a., 95–97%) used for SFE trap packing and cleanup of extracts were made by Fluka (Buchs, Switzerland). Nitric acid was manufactured by Merck (Suprapur, 65%, Darmstad, Germany). Glass-fibre filters (GF/A, Whatman, Maidstone, UK) were utilized in cell-packing procedures in SFE and PLE. SFE gas was carbon dioxide functioning as both extraction medium (quality 4.8) and cryo gas (quality 2.7). Nitrogen gas was used for PLE purging (quality 4.6), evaporation of extracts (quality 4.6), and as electron capture detector (ECD) make-up gas (quality Detektor OTC-50). Hydrogen (quality Laboratorium OTC-50) was used as carrier gas in the chromatographic setup. All gases were purchased from AGA Gas AB, Sundbyberg, Sweden. Calibration PCB mixtures originated from NIST 2262 (US National Institute of Standards and Technology, Gaithersburg, MD) and PCB 35 (time reference) and 169 (quantification reference) were internal standards (IS) acquired from Larodan (Malmö, Sweden). The 50 µL of IS added to samples contained 27 ng of PCB 35 and 20 ng of PCB 169. Glassware, sodium sulfate, silica, glass wool (Supelco, Bellafonte, PA), and Florisil used throughout the study were baked at 450°C for 12 h prior to utilization. All glass was solvent-rinsed after oven treatment.

2.2 *Sediment samples and characterization*

The four sediments were collected on 2 September 2004 from sites located along the Hudson River (Hudson and Troy, NY). Immediately upon arrival at the laboratory, the cool sediments were air-dried in solvent-rinsed alumina boxes for 24 h in a fume hood under occasional stirring to avoid major aggregation. This was followed by gentle grinding in a mortar before transferring the sediments to dark glass jars. Dry weights of the sediments were determined gravimetrically (105°C, 20 h) according to Swedish Standard SS 02 81 13 [18] and as described in US EPA Method 3545A [19]. Carbon and nitrogen contents were determined on a Vario MAX CN Elementar analyser. The sediments used have, together with another four Hudson River sediments, been studied and characterized in a previous publication [17]; hence the somewhat confusing sediment labelling (Sediment A, B, E, and F).

2.3 *Supercritical fluid extractions*

The extractions were done on a Hewlett-Packard 7680T Supercritical Fluid Extraction unit (Hewlett-Packard, Wilmington, DE). The HP 7-mL stainless steel extraction thimbles were packed from the top: one glass microfibre filter (to prevent clogging of the metal frit and facilitate cleaning), followed by approximately 1 cm of sodium sulfate, another filter, sediment (~2 g), a filter, more sodium sulfate, and finally another filter, leaving 0.5–1 cm of free space. The flow direction was from bottom to top, and the extraction mode was dynamic with a supercritical fluid flow of 1.5 mL min^{-1}. Extracted PCBs were collected on a solid-phase trap packed with Florisil.

The extractions started with a step of 60 min at a pressure of 12 MPa and a chamber temperature of 40°C. The trap was then eluted with 2×1.5 mL of *n*-heptane to two vials, and cleaned with 4 mL of acetone/*n*-heptane (1 : 1, v/v) and 4 mL of *n*-heptane to waste. Fifty microlitres of the internal standard solution containing PCBs 35 and 169 was added to the vials. During extraction, the temperatures of nozzle and trap were maintained at 45 and 20°C, respectively. During the elution and rinse steps, the temperature of the trap was raised to 40°C. Instrument settings and procedures were based on US EPA Method 3562 [20]. The same thimble was then extracted using the same procedure for another 60 min, followed by extraction at 40°C and 36.5 MPa for 2×60 min and 100°C and 36.5 MPa for 2×60 min. All other extraction and elution parameters were maintained. Activated copper was added to the extract, prior to GC analysis, to remove sulfur that interferes with analyte signals in the ECD.

2.4 *Pressurized liquid extractions*

After SFE, the content of each thimble was transferred to a pressurized liquid extraction (PLE) cell. The packing order was: two glass microfibre filters, sodium sulfate, content of SFE thimble, more sodium sulfate, and two more filters on the top, leaving a free space of about 0.5–1 cm. Extraction of the 34 mL stainless steel cell was performed with a Dionex ASE 300 Accelerated Solvent Extraction unit (Sunnyvale, CA). The solvent used for the extractions was acetone/*n*-heptane (1 : 1, v/v), the pressure was 10 MPa, and the temperature was 100°C. The equilibration time was 5 min, and the static extractions were performed for 5 min. The cell was flushed with more solvent, corresponding to 60% of the cell volume, and purged for 90 s with nitrogen gas to expel the remaining solvent. These are conditions recommended by the US EPA in method 3545A [19] with the exception that hexane has been replaced by the less toxic solvent *n*-heptane. The cell was put through four cycles, although a previous investigation has proven quantitative recoveries using only two cycles [17]. Fifty microlitres of IS was added to the bottles, and the samples were evaporated to approximately 1 mL on a rotary evaporator (Rotavapor RE, Büchi Labortechnik AG, Flawil, Switzerland) prior to cleanup.

2.5 *Cleanup*

Cleanup of PLE extracts was performed on columns with an inner diameter of 20 mm and a total length of about 32 cm. They had been packed with a glass-wool plug, 2 cm of sodium sulfate, 6 cm of silica impregnated with sulfuric acid (1 : 1 w/w), and 2 cm of sodium sulfate. Fifty millilitres of *n*-heptane was used to rinse the column before the sample was applied. This was then eluted with 60 mL of *n*-heptane, and the eluate was evaporated on a rotary evaporator to less than 1 mL and transferred quantitatively to a

GC vial, giving a final volume of approximately 1.5 mL. Before GC analysis, copper activated with nitric acid was added to the extract for sulfur removal.

2.6 *Gas-chromatographic analysis*

The extracts were analysed on an Agilent 6890N GC system (Agilent, Palo Alto, CA) with dual columns and two ^{63}Ni electron capture detectors (held at 300°C and purged with nitrogen gas at a flow of 60.0 mL min^{-1}). The columns were a DB-17 60 m × 0.25 mm, 0.25 µm 50% phenyl-methyl-polysiloxane (Agilent) and an HP-5 ms 30 m × 0.25 mm, 0.25 µm 5% phenyl-methyl-polysiloxane (Agilent) coupled in series with a HT-5 25 m × 0.22 mm, 0.10 µm 5% phenyl-polycarboran-siloxane (Scientific Glass Engineering Europe, Milton Keynes, UK). The columns were connected in parallel using a quick-seal glass 'T' to a retention gap (2 m × 0.53 mm deactivated fused silica, Agilent). Hydrogen was used as carrier gas at a linear velocity of 43 cm s^{-1}. The temperature was programmed as follows: 90°C for 2 min, followed by an increase with 20°C min^{-1} to 170°C, which was held for 7.5 min, then increased at a rate of 3°C min^{-1} to 285°C, which was held for 8 min. Injection was done on-column with an Agilent 7683 Autosampler and 7683 Injector, injecting 1 µL of the extract.

The following 10 congeners were examined: 28, 52, 101, 105, 118, 128, 138, 153, 170, and 180. Quantification was done using the software HP Chemstation Rev A. 09.01 using peak height measurements and a calibration curve with eight points (power-fit) in the concentration interval 0.4–40 ng mL^{-1}. The lowest signal from the two detectors was selected to minimize possible quantitative errors due to coeluting compounds. The GC method for PCB analysis is based on a method described by Bøwadt *et al.* [21].

3. Results and discussions

3.1 *Method validation*

As has been mentioned, the four sediments in this investigation have been thoroughly evaluated in a previous publication [17]. It was demonstrated that PLE conditions of 100°C and 10 MPa using acetone/*n*-heptane for 2 × 5 min can be used to quantitatively extract the 10 studied individual PCB congeners from the sediments seemingly independent of sediment characteristics such as TOC and soot carbon. In the present study, the total sediment PCB concentration is given as the sum of the seven different fractions generated in order to establish the desorption patterns. The fractions are summarized in table 1. In short, the extraction parameters range from relatively mild extraction conditions to very harsh, ending with a proven quantitative PLE step of the SFE residue remaining in the cell after 6 h of extraction. Observe that the definitions of the SFE extraction strengths (mild, medium, and harsh) are defined in this way to illustrate the increasing harshness of the extractions, not to be confused with other mild SFE settings used for instance when studying PAH desorption from soil [10, 22].

The total PCB content of the four sediments for the studied congeners can be seen in table 2. It is clear from the table that there is a substantial variation in the total PCB concentrations of the four sediments ranging from 123 (sediment F) to 951 ng g^{-1} (sediment A), as well as in the concentration of different congeners. PCB 28 is the

Table 1. Extraction conditions (time, temperature, and pressure) used and definitions of the seven fractions obtained from each sediment extraction.

Fraction no.	Time (min)	Settings	Definition
1	60	40°C, 12.0 MPa	Mild SFE
2	120		
3	180	40°C, 36.5 MPa	Medium SFE
4	240		
5	300	100°C, 36.5 MPa	Harsh SFE
6	360		
7	PLE of residue	See reference [17]	Quantitative PLE

Table 2. Total sediment concentrations ($\mathrm{ng\,g^{-1}}$) determined as the sum of six supercritical fluid extractions (SFE) and a quantitative pressurized liquid extraction fraction of the SFE residue. Relative standard deviations (RSDs) are also included ($n = 3$).

	Sediment A		Sediment B		Sediment E		Sediment F	
PCB	Conc. ($\mathrm{ng\,g^{-1}}$)	RSD (%)	Conc. ($\mathrm{ng\,g^{-1}}$)	RSD (%)	Conc. ($\mathrm{ng\,g^{-1}}$)	RSD (%)	Conc. ($\mathrm{ng\,g^{-1}}$)	RSD (%)
28	637.7	10	316.6	5	83.0	3	68.6	4
52	220.1	10	114.2	6	50.3	4	21.2	9
101	27.5	11	19.7	4	10.3	3	8.5	8
105	6.0	9	8.2	6	3.2	7	4.1	12
118	28.5	9	19.7	6	10.6	2	9.4	11
128	2.5	8	2.0	4	1.2	4	1.1	1
138	8.9	11	6.4	9	3.3	3	4.2	40
153	9.0	8	5.6	3	3.5	5	3.2	19
170	3.6	10	1.4	6	0.9	17	0.8	29
180	6.8	9	3.7	5	2.4	4	1.8	22

dominating congener in all four sediments, but to a lower extent for sediment E. The relative standard deviation (RSD) values indicate satisfying repeatability of the extractions, bearing in mind the small concentrations of some congeners, except for scediment F. The RSDs seem more related to the sediment than to the different congeners and concentrations: sediment E tends to have lower RSDs than sediments A and B, even though the concentrations of PCBs are higher in A and B. Sediment F displays the highest RSDs, higher than sediment E, even though the concentrations of some congeners are higher. This is probably due to the homogeneity or inhomogeneity of each sediment rather than a method-related error, since a similar trend was also observed during quantitative PLE [17].

An important aspect to consider when reporting cumulative values is to ensure that no major errors have been introduced due to the additions. It has previously been shown that no inaccuracy of this kind seems to be present when adding PCB containing SFE fractions in a similar way as in this study [9, 12]. For instance, even when adding as much as 32 fractions of the certified reference material CRM 536 (harbour sediment), on average 128% of the nine individually investigated congeners were recovered *versus* the certified values [9]. The values presented in table 2 were also validated in order to increase the analytical credibility of the applied procedure. This was done by comparing the cumulative sediment concentrations with the total concentrations obtained with the quantitative PLE method described above [17]. The average recoveries of the 10 individually studied congeners, vs. quantitative PLE values [17], were between 83 and

96% for sediments A, E, and F, which is acceptable considering that seven fractions are summed to obtain these values. For sediment B, a lower value of 64% was found. A possible reason for generating a low recovery might be that only the first 1.5 mL eluted from the solid-phase trap in SFE was included in the summed value. Since trap properties might change, additional elutions into separate vials were performed throughout the experiments. This is standard procedure in most SFE methods of this kind as in US EPA method 3562 for instance [20]. Thus, the second 1.5 mL elutions every 60 min might contain small PCB amounts. This scenario was investigated by analysing the second elutions of one replicate from each sediment. The second elutions of all sediments displayed similar percentages, and in no case did the summed concentrations in the second elutions exceed 3% of the total concentration. It was therefore concluded that the PCB content in the second elutions was very low and that lower summed SFE and PLE recoveries vs. quantitative PLE for sediment B apparently do not originate from this source.

From the comparison of the cumulative vs. the quantitative PLE concentrations, it can be concluded that for at least three of the four sediments, the summed value is valid to be used as 100% recovery in the desorption studies. The similarity of the four profiles does, however, suggest that the applied procedure can be valid also for sediment B.

3.2 *Selective SFE and PCB desorption behaviour*

Figure 1 shows that in general, the recovery after mild SFE varies around 75%, after medium SFE the recovery is approximately 80%, and after harsh SFE a recovery of more than 90% is usually achieved. The fraction extracted with quantitative PLE constitutes between 4 and 9% of the cumulative value.

All four profiles show a smooth line from the first mild SFE step (at 60 min) to the end of the medium SFE step (at 240 min). However, the increase in temperature from 40°C to 100°C after 240 min significantly increased the yield from all sediments, which can be seen in figure 2. The harsh SFE settings (100°C, 36.5 MPa for 2 h) are more extreme compared to the US EPA standard method for extraction of persistent organic pollutants from sediments and soil, method 3562 (80°C, 30.5 MPa for 1 h) [20] and should therefore be considered quantitative. Nonetheless, in order to be completely convinced, the residue remaining in the SFE cell after harsh SFE was transferred into a PLE cell and extracted under quantitative conditions for the selected sediments according to Josefsson *et al.* [17]. The PLE fraction was typically well below 10% of the cumulative recovery and thus somewhat confirmed the exhaustiveness of the harsh SFE. This sums to at least three distinguishable discrete PCB fractions within the sediments visible in the profiles. These fractions can be obtained with medium SFE, harsh SFE, and quantitative PLE.

It is also important to observe that within the different fractions, the 10 congeners display similar behaviour; none of them is markedly different from the others in recovery. Sediment B has the lowest congener variation (figure 1b). PCB 28 is the most extreme congener; for instance, it has a higher recovery than the other congeners after medium SFE for sediment A (figure 1a), which would indicate that it is easier to extract than the other congeners. However, it is extracted to a lower extent than the other congeners at medium SFE for sediment E and F (figure 1c–d). The conclusion is that the matrix is more important for the extractions than the nature of the different

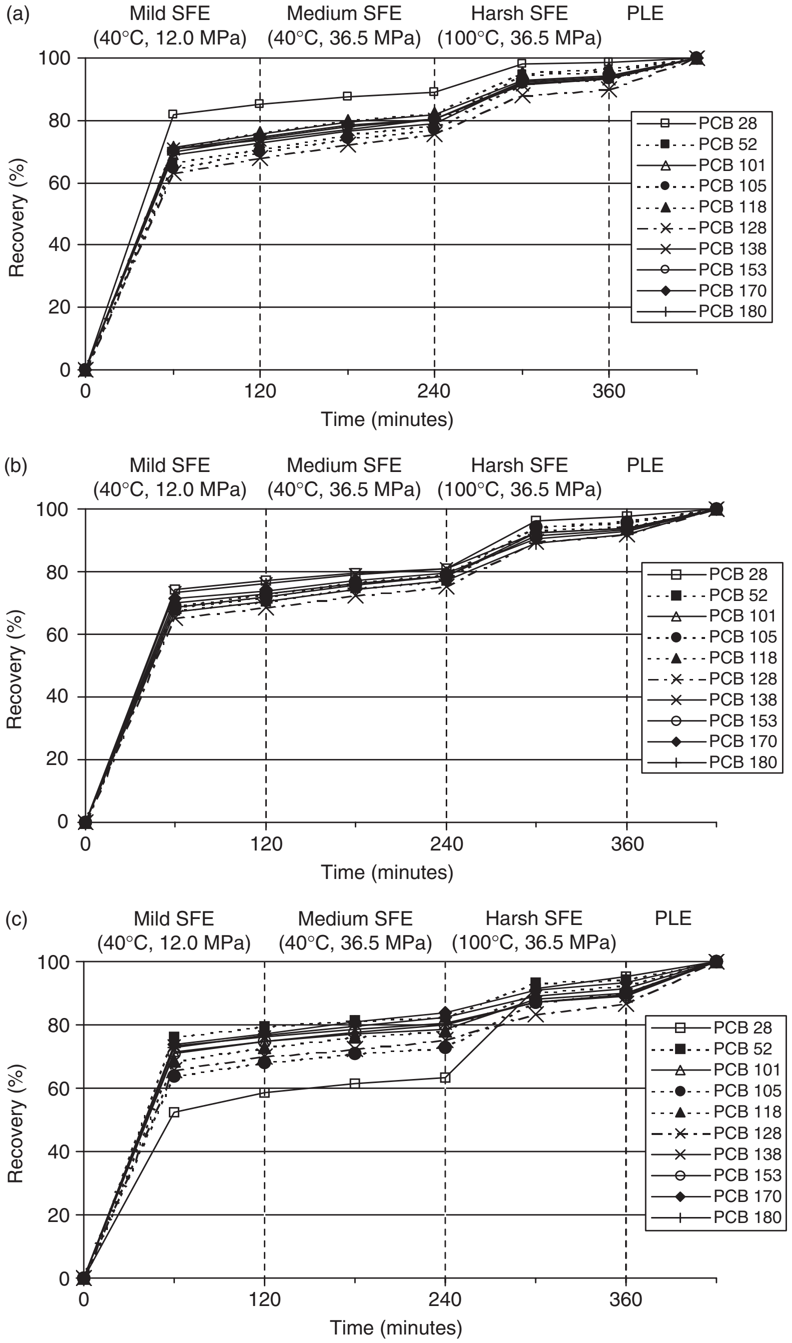


Figure 1. Cumulative desorption behaviour of individual PCB congeners during supercritical fluid extraction (SFE) (and pressurized liquid extraction (PLE)) from sediment A (a), B (b), E (c), and F (d). Extractions of increasing harshness were used, starting with mild conditions for 2 × 60 min at 12.0 MPa and 40°C. This was followed by medium conditions for 2 × 60 min at 36.5 MPa and 40°C, ending with harsh conditions for 2 × 60 min at 36.5 MPa and 100°C. A fraction for GC analysis was recovered every hour. One hundred per cent recovery was defined as the sum of all SFE fractions plus a quantitative PLE fraction of the SFE residue. The values are averages of triplicate measurements.

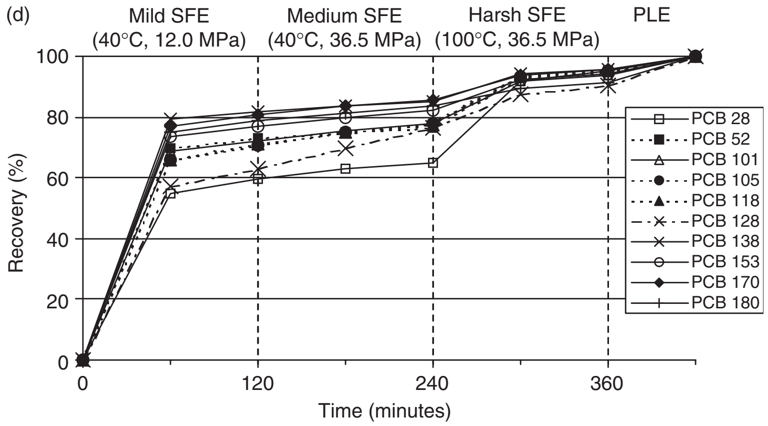


Figure 1. Continued.

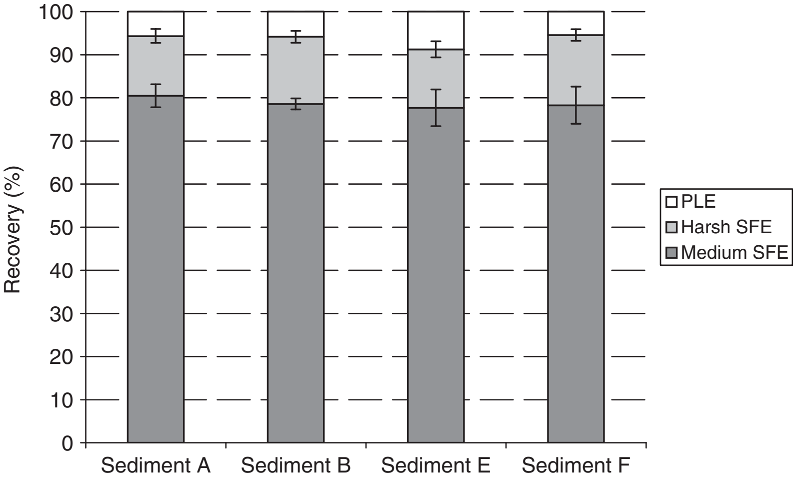


Figure 2. Average recovery for the 10 studied PCB congers for each sediment after medium supercritical fluid extraction (SFE) (36.5 MPa, 40°C, and 240 min) and harsh SFE (36.5 MPa, 100°C, and 360 min). For each sediment 100% recovery was defined as the sum of the average congener value of all SFE fractions plus a quantitative pressurized liquid extraction fraction of the SFE residue. All measurements were conducted in triplicate, and the confidence limits (0.99) can be seen as error bars.

molecules, in accordance with Björklund *et al.* [9]. Therefore, the recoveries of the 10 congeners are summed to give an overall recovery for each sediment at medium SFE and harsh SFE conditions, as can be seen in figure 2. The sediment similarity in this figure is striking, and the significant difference between the medium SFE and harsh SFE fractions is also evident for all the sediments (*t*-test, $p < 0.01$).

The first plateau in all four sediment profiles ranging from mild SFE (60 min) to medium SFE (240 min) shows that only a small additional amount is extracted when increasing the pressure from 12.0 MPa to 36.5 MPa. Also, the increase caused by second elutions at the different SFE conditions (fractions 2, 4, and 6 in table 1) is very small.

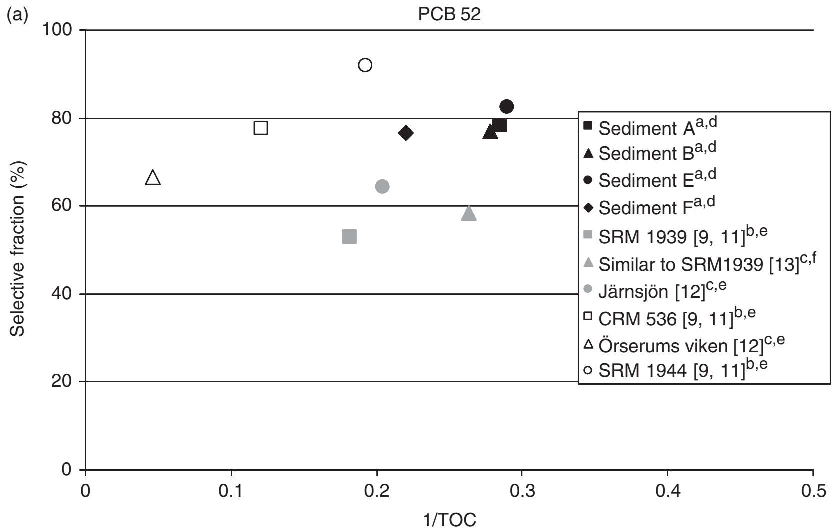
It has previously been shown that second hour fractions at 40°C and 36.8 MPa extracted on average 2.5% of what was extracted during the first hour [13]. The same figures for sediments A, B, E, and F were 1.6, 1.8, 2.7, and 2.0%, respectively. It was also shown that if extractions were continued for four more hours on the set conditions, only an additional 2.7% were extracted [13]. It is not unreasonable to assume that the four sediments studied will behave in a similar way. These are important findings indicating that only a certain absolute amount might be selectively extracted from sediments at certain conditions seemingly independent of greatly prolonged extraction times. Therefore, it is suggested that certain SFE conditions emptied the sediment of specific analyte fractions.

An interesting aspect of selective extractions is the relation between fractions obtained at about 40°C and 40 MPa (medium SFE) and fractions available for biological uptake, a relation which has been found in animal studies [13–15]. The experimental setup of the studies monitored PCB uptake in animals from medium SFE extracted matrix and unextracted matrix. The relative uptake, defined as a quota resembling biota-soil/sediment-accumulation factors (BSAFs), in the two matrix systems was calculated. If all pollutant molecules were equally bioavailable, no difference in uptake quota could be seen when part of the pollutants was removed. However, in systems where the medium SFE fraction was removed, the relative biological uptake proved to be far less than in unextracted systems. A model based on this experimental setup, assuming the presence of a non-bioavailable PCB fraction, has been shown to correlate well with actual biological uptake [13–15]. The harsh SFE and quantitative PLE fractions thus corresponds to what is described as either 'bound contaminants' [8] or 'non-bioaccessible' [23], not immediately available for biological uptake. It has also been revealed that medium SFE settings seem to be in good agreement with PCB desorption from sediment to water in studies lasting up to one year [24].

The findings are very encouraging, suggesting that settings around medium SFE extract almost exclusively PCBs that are available for uptake in the studied organisms. This opens the possibility that selective SFE can become a tool for fast evaluations of immediate PCB risk at different contaminated sites. However, more research to further establish the findings is needed, and this investigation presents characteristic desorption patterns for another four sediments. An extension of the work presented here will be biological uptake studies including the sediments from this study.

3.3 *Dependency of selective fractions on sediment characteristics*

The BSAF model is a suggested tool for predicting bioaccumulation [25]. Here, accumulation is based on partitioning between the carbon compartments in biota lipids and sediment TOC. An increase in sediment carbon content would help bind PCBs, thereby decreasing the availability. Assuming that the selectively removed fractions (40°C, ~40 MPa) are equal to what is available for biological uptake and assuming that the BSAF model is valid, a correlation between the selectively removed concentration and total PCB concentration divided by TOC would thus be expected. To offset the effect of the total concentration in order to observe more clearly if such a correlation exists, the selective fraction is plotted against the inverse of the sediment organic carbon content (wt%), as can be seen in figure 3. Together with the four sediments extracted in this study, all results from previous publications with selective SFE of



[a] TOC determined as described in the experimental section.

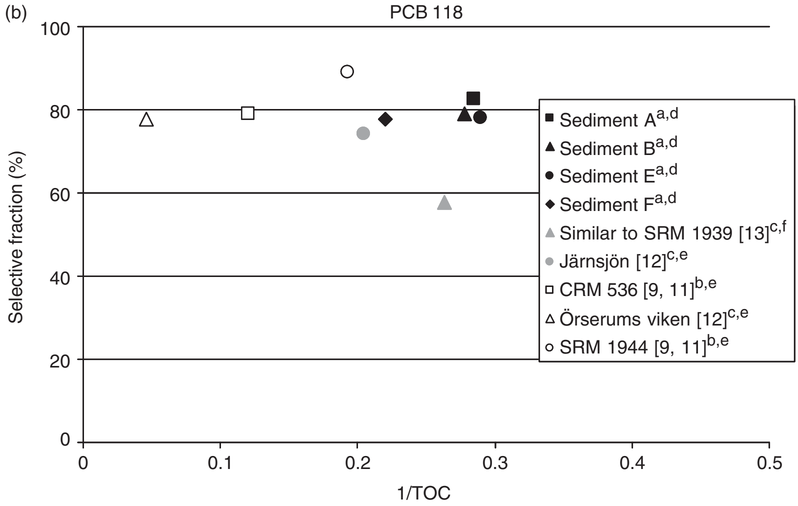
[b] TOC determined as described in the experimental section but with a Leeman Labs model CE 440 elementar analyser.

[c] TOC determined according to Swedish standard SS 13137.

[d] Selective conditions of 40°C and 36.5 MPa.

[e] Selective conditions of 40°C and 40 MPa.

[f] Selective conditions of 40°C and 36.8 MPa.



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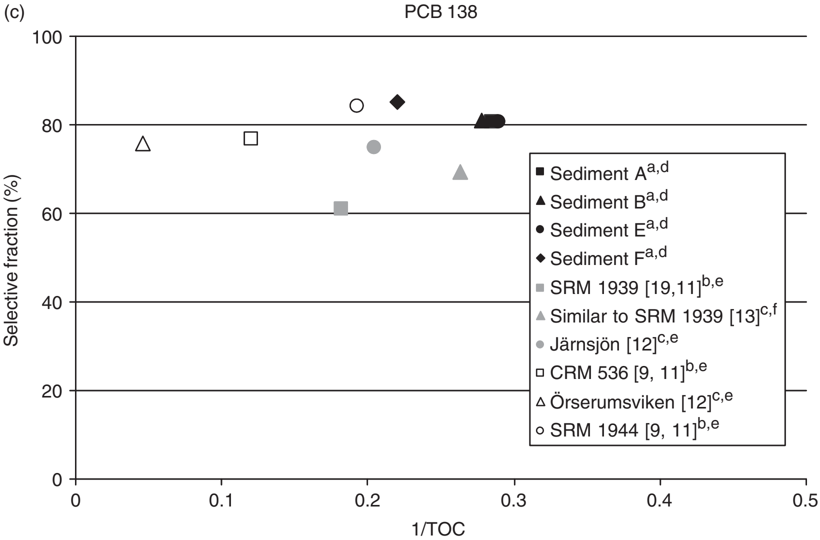
[e] Selective conditions of 40°C and 40 MPa.

[f] Selective conditions of 40°C and 36.8 MPa.

Figure 3. Dependency of the selective PCB fraction (%) obtained using supercritical fluid extraction at 40°C and about 40 MPa on the inverse of the sediment total organic carbon content (wt%). Results presented for PCB 52 (a), 118 (b) and 138 (c).



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[d] Selective conditions of 40°C and 36.5 MPa.

[e] Selective conditions of 40°C and 40 MPa.

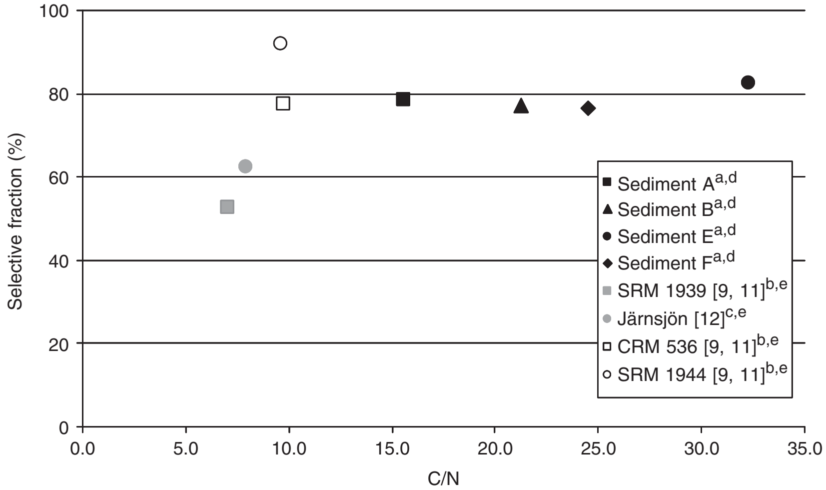
[f] Selective conditions of 40°C and 36.8 MPa.

Figure 3. Continued.

sediments [9, 12, 13] are also included in the figure. The chosen congeners are the ones present in most studies and constitute PCBs with different degrees of chlorination, PCB 52 (tetra chlorinated), PCB 118 (penta chlorinated), and PCB 138 (hexa chlorinated).

The TOC values reported in the figure are determined by distinct, but similar, procedures. For sediments A, B, E, and F, and the sediments from two previous studies [9, 11], the total carbon (TC) content was determined. Since all pH values are below 7.4, no correction for inorganic carbon has been made, and TC has been considered as TOC, according to the procedure recommended by Schumacher [26]. In the other sediments included [12, 13], TOC was determined according to Swedish/European standard SS-EN 13137 [27]. This method includes the addition of acid to remove inorganic carbon that might be present.

The appearance of figure 3(a)–(c) indicates no correlation between the organic carbon content and the selective fraction for the PCB congeners investigated. The lack of correlation can be interpreted in several ways. The first alternative is that a connection exists between the organic carbon content and the bioavailable contaminant fraction, and that the selective SFE fractions do not correctly describe the amount of PCBs available for biological uptake. This alternative is less likely, since several experiments have demonstrated that the fraction extracted using selective SFE under the aforementioned conditions corresponds well to the bioavailable fraction [13–15]. The most likely alternative, in our opinion, is that bioavailability is determined not only by the organic carbon content but by a number of processes not included in the BSAF model, as suggested by others [8]. This interpretation indicates that the model is not



[a] C and N determined as described in the experimental section.

[b] C and N determined as described in the experimental section but with a Leeman Labs model CE 440 elementar analyser.

[c] C determined according to Swedish standard SS 13137 and N as described in the experimental section.

[d] Selective conditions of 40°C and 36.5 MPa.

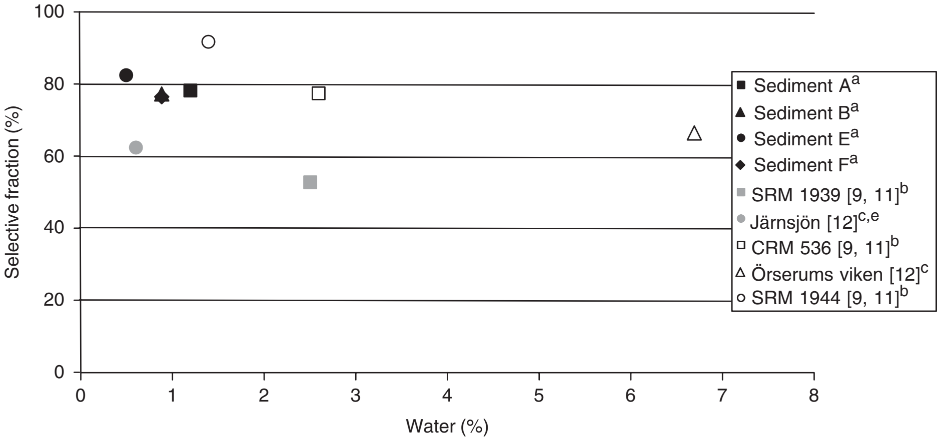
[e] Selective conditions of 40°C and 40 MPa.

[f] Selective conditions of 40°C and 36.8 MPa.

Figure 4. Dependency of the selective PCB 52 fraction (%) obtained using supercritical fluid extraction at 40°C and about 40 MPa on the carbon/nitrogen ratio of the sediment.

valid, at least not in its original form. It should be noted that there are many assumptions in the BSAF model, and if these are not fulfilled, BSAF values can deviate, as mentioned by Wong *et al.* [25]. The interpretation of figure 3 could thus also be that some values are deviating because of incorrectness in any of the assumptions in the BSAF model, hiding a possible trend. By such reasoning, however, the often claimed simplicity of the BSAF model as a tool for estimating biological uptake is lost. Consequently, if a precise and simple tool for bioavailability estimation is requested, BSAF based on correction for TOC is not sufficient. The present work, using selective SFE, shows that bioavailability is not predicted solely from sediment TOC values.

Another carbon-related sediment parameter worth observing is the carbon/nitrogen ratio (C/N) of the sediment. This ratio is, for some researchers, seen as an indication of the age of the sediment: a newly sedimented sediment has a lower C/N ratio than a more mature sediment, due to the predominant loss of the nutrient nitrogen during decomposition [28, 29]. This process could affect the association between POP and sediment due to, for instance, a difference in structure of the organic material causing changed pollutant mobility, and pollutants of the POP type have been shown to become more sequestered within sediments over time. The C/N ratio is also affected by the origin of the organic matter in the sediment [30]. The relationship between the selective fraction and the C/N ratio is shown in figure 4 for PCB 52; other congeners displayed very similar behaviour but with fewer observations and are therefore not presented. As the figure shows, no correlation is present. Thus, there appears to be no strong



[a]Selective conditions of 40°C and 36.5 MPa.

[b]Selective conditions of 40°C and 40 MPa.

[c]Selective conditions of 40°C and 36.8 MPa.

Figure 5. Dependency of the PCB 52 fraction obtained using selective supercritical fluid extraction at 40°C and about 40 MPa on the sediment water content before extraction.

connection between how loose or hard a pollutant is bound to the sediment (the selectively extracted fraction) and the C/N ratio. The C/N ratio is consequently too crude a parameter to be used to predict bioavailable fractions.

Mechanistic understanding of the role of sediment water content during SFE is somewhat unclear. It has been reported that completely dry sediments should be avoided in SFE of PCBs, since this can generate a lower extraction yield [31]. Water contents of about 50 wt% have also been shown to decrease PAH recoveries compared with water contents around 5 wt%, from river suspended particulate matter [32] and a waste sludge [33]. It seems that water contents of around 1 or 2 wt% are desirable [34].

Figure 5 examines, for PCB 52, whether the selective fraction extracted with SFE is dictated by the water content. The figure indicates that there is no apparent connection, which is in agreement with previous investigations showing that the extracted fraction is correlated to the bioavailable fraction. Any effect of the water on the amount of PCBs extracted selectively seems to be of minor importance, for the low water contents of the sediments investigated in this study (up to 6 wt%, but generally below 3 wt%).

4. Conclusions

Selective extraction under increasingly harsher conditions using SFE is a good tool for monitoring PCB desorption behaviour from sediments. The four sediments studied displayed similar trends when extracted, and at least three different discrete PCB fractions were observed in the resulting profiles. The PCB congener distribution within these fractions suggests that the matrix is more important for the extractions than the nature of the different molecules. The presence of a PCB fraction obtained after extraction at 40°C and 36.5 MPa was identified in all four sediments. The PCB content of this fraction does not increase markedly, even after prolonged extraction. This study also indicates that the selective fraction is not primarily dictated by the organic carbon content of the sediments. This is contradictory to the literature stating a total dependency of this parameter and supports studies stating that more complex processes control bioavailability.

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