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Journal of Chromatography A, 774 (1997) 229–242

JOURNAL OF
CHROMATOGRAPHY A

Supercritical fluid extraction with solid-phase trapping of chlorinated and brominated pollutants from sediment samples

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Abstract

Trapping efficiencies for selected polychlorinated benzenes, polybrominated biphenyls and polybrominated diphenyl ethers were studied to determine the trapping capability of these and similar compounds in real samples. A study was made of the effect on recovery of supercritical fluid extraction (SFE) temperature, pressure, flow-rate, addition of modifier, types of solid phase trapping material and elution parameters. Florisil and ODS, used as trapping materials, both produced satisfactory recoveries (>95%) for most compounds under optimised conditions, but the performance of Florisil was less dependent on SFE flow-rate. At higher flow-rates, ODS gave lower recoveries of the chlorinated benzenes and it generally could not trap the dichlorobenzenes, which Florisil recovered up to 95%. When pure CO₂ was used at constant flow-rate, change in the SFE conditions did not significantly affect the trapping efficiency. Experiments with modifiers showed good recoveries with a trap temperature close to or above the boiling point of the modifier. Sequential SFE was applied to extract chlorinated and brominated organic pollutants from nine sediments. 80%–95% of the total SFE recovery was obtained with CO₂ alone, and further recovery with addition of modifier. The recovery varied with the sediment, indicating that the usefulness of the modifier depends on the sample matrix. Altogether, 46 analytes were quantified in the sediment extracts in one run at levels down to 10 pg/g using two-channel GC with electron-capture detection. Polychlorinated biphenyls and common pesticides such as *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT were found to be the most abundant pollutants in all sediment samples. Polybrominated aromatic compounds also were found in all samples, with the highest levels for dibromodiphenyl ether, polybrominated biphenyl 52, pentabromodiphenyl ether, 2,3,7,8-tetrabromodibenzo-*p*-dioxin and 2,3,4,7,8-pentabromodibenzofuran. Levels in Baltic Sea area sediments were in the low ppb (ng/g) range. The use of two capillary columns of different polarity greatly decreased the number of errors arising from coeluting compounds. © 1997 Elsevier Science B.V.

Keywords: Extraction methods; Sediments; Super critical fluid extraction; Environmental analysis; Polybrominated biphenyls; Polychlorinated benzenes; Polybrominated diphenyl ethers

1. Introduction

Most of the extraction techniques applied for trace analysis of solid sample matrices are nonselective, which creates a problem because concentrations of

the target analytes usually are much lower than concentrations of the coextracted compounds. Although selective detection methods like electron-capture detection (ECD) and MS (selected ion monitoring, SIM) can be used to suppress the background, chromatographic behaviour may be poor, or the lifetime and quality of the chromato-

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graphic columns may suffer, creating problems in the quantitation. With normal chromatographic procedures, moreover, these selective detectors sometimes do not offer sufficiently high resolution and peak capacity and more selectivity must be added to achieve good quality analysis.

Supercritical fluid extraction (SFE) has great potential for replacing traditional solvent extractions in a wide range of applications. Reviews on environmental SFE have recently been published [1,2]. SFE offers some selectivity through adjustment of the extraction power via extraction temperature, pressure and polarity of the extraction fluid. Unfortunately, great selectivity can not be achieved in this way where compounds are many and of different type. Selectivity can easily be achieved, however, by using solid-phase trapping, which adds on-line fractionation and clean-up capability. Additionally, powerful methods for very complex samples can be obtained through linking of SFE and solid-phase trapping with multidimensional systems such as GC–GC and SFC–GC or with multichannel chromatographic systems.

SFE with solid-phase trapping can be considered as two separate extraction processes: SFE and solid-phase extraction (SPE). The success of SFE is determined by parameters affecting solubility and mass transfer from a solid sample matrix to the supercritical fluid: i.e., extraction temperature, pressure, extraction time, flow-rate and composition of fluid. After depressurising in SFE the extracted compounds are deposited onto a small packed LC column containing a suitable adsorbent and are chromatographically retained. In SFE the trapping efficiency is affected by the SFE parameters, the nature of the trap material and the trap temperature. For recoveries to be quantitative, analytes must be effectively eluted from the trap, and this requires optimisation of the elution parameters (rinse solvent, rinse flow-rate, and the amount of solvent used).

Polychlorinated biphenyls (PCBs), organochlorine pesticides, chlorinated dibenzo-*p*-dioxins and dibenzofurans have been widely studied in a variety of environmental samples. Concern about the environment and active research into their effect on human health has, unfortunately, also revealed not only their extreme toxicity but how widespread they are in nature. Use of these hazardous compounds has been

curtailed as a result. Even where production has ceased, as in the case of PCBs, the input to the environment will nevertheless continue for quite some time, making monitoring of these highly stable compounds a necessity.

Much less attention has been paid to the analogous brominated compounds, although their chemical similarity suggests a like toxicity. Polybrominated biphenyls (PBBs) have been widely used as flame retardants for plastics, textiles and other materials. PBBs were evidently first recognised as an environmental risk after the accident in Michigan in 1973 [3,4]. Surprisingly, very little attention is paid to these compounds today. A wide survey of the occurrence of bromobiphenyls in fish, sediments, soils and vegetation was carried out in 1979, and hexabromobiphenyl, the most prevalent species, [5] was detected in 84% of the 144 samples analyzed, in concentrations ranging from 0.2 to 50 000 ppb (ng/g). Other compounds (already found in various environmental matrices) that may threaten the environment are polychlorinated naphthalenes (PCNs), [6–8] polychlorinated diphenyl ethers (PCDPEs), [9] polybrominated diphenyl ethers (PBDPEs), [7,10] polychlorinated camphenes (toxaphene) [11–13] and many other chlorinated and brominated organic compounds [14–17] PBDPEs, as well as hexabromobenzene [18], are widely used as flame retardants and are widely disseminated in the environment. In Japan the annual consumption of brominated organic compounds increased from 2500 tonnes in 1975 to 22100 tonnes in 1987 [19]. A similar trend probably prevails in other countries and the environment is now more heavily loaded with these compounds. PBDPEs appear to accumulate in animals preying on fish, such as grey seal and guillemot; and the highest level found in fish samples (collected from Sweden) was 24000 ppb. [10] Levels of PBDPEs in sediments have increased as much as 20-fold during the last few decades. [7] Incomplete combustion of PBDPEs may also lead to formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) [20]. Some degradation of PBDDs and polybromochloro dibenzo-*p*-dioxins (PBCDDs) has been observed under laboratory and environmental conditions [21].

Several groups have described the use of SFE to extract PCBs and chlorinated pesticides from soils,

sediments and animal tissues. [22–28] Comparisons have been made between SFE and traditional solvent extraction methods for these compounds. [25,29,30] So far, most of the papers have dealt with spiked samples or real samples at levels down only to 5 ppb (in the best cases). SFE publications on chlorinated dioxins and furans are fewer [31–33] and no SFE applications for polybrominated compounds have yet been published.

In this study, trapping efficiency for selected organic pollutants was determined under different SFE conditions. Factors affecting the solid-phase collection were studied, and a SPE method for selected brominated and chlorinated pollutants was optimised for real environmental samples. Nine sediment samples were then extracted with SFE, and the concentrations of 46 compounds were determined by two-channel GC–ECD. Sequential SFE with increasingly stronger extraction conditions was performed to exhaustively extract the analytes from the sediments. The goal in sensitivity was to be able to determine chlorinated and brominated pollutants at ppt level.

2. Experimental

2.1. Standards and chemicals for SFE study

Dibromodiphenyl ether, 4,4'-dibromo-octafluorobiphenyl (internal standard, ISTD), 1,3-di-, 1,4-di-, 1,3,5-tri-, 1,2,4-tri-, 1,2,3-tri-, 1,2,4,5-tetra-, 1,2,3,4-tetra-, penta- and hexachlorobenzenes were purchased from Aldrich. Purities were 98% or higher. Brominated biphenyls (PBB 7, PBB 31, PBB 52, PBB 103 and PBB 153) were purchased from Accu Standard (New Haven, CT, USA) and purities (GC–MS) were 99% or higher except for PBB 7 (97%) and PBB 153 (91.5%). A standard mixture was prepared from neat compounds by dissolving them in isooctane (Fisher Scientific, pesticide grade). The solution was diluted with isooctane appropriate for use with ECD. Concentrations of the analytes in the final spiking solution for the trapping study were in the range 0.7 ng/μl–10.7 ng/μl.

Fiberglass filter (Whatman GF/B), sodium sulphate (certified A.C.S., 10–60 mesh) and Florisil (60–100 mesh) were obtained from Fisher Scientific,

as were methanol and acetone, both of Optima grade. *n*-Heptane (HPLC grade) was from Fisher Scientific, diethylamine (98%) from Aldrich and ethyl acetate ('Baker resi-analyzed') from J. T. Baker. All SFE extractions were performed with SFC-grade CO₂ (Scott Specialty Gases), which was supplied with dip-tube and without helium head pressure.

2.2. Standards and chemicals for sediment samples

n-Pentane (HPLC-grade), *n*-hexane (Optima-grade), water (HPLC-grade), petroleum ether (pesticide-grade), methylene chloride (Optima-grade) and 2-propanol (HPLC-grade) were obtained from Fisher Scientific. Also, electrolytic-grade purified copper, anhydrous sodium sulphite and silica gel (Chromatographic, 100–200 mesh) were from Fisher Scientific. Fuming sulphuric acid and tetrabutylammonium (TBA) hydrogen sulphate (>97%) were obtained from Aldrich. Pesticide-grade glass wool from Supelco was used to retain silica packing inside the cleanup columns (Pyrex glass columns, 20×400 mm with Teflon stopcocks, Fisher Scientific).

PCB standards (neat crystals) were obtained from the Community Bureau of Reference (BCR), Brussels, Belgium. The PCBs were 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180 (IUPAC numbers). Internal standards were PCB 35 and 169. A mixture in methanol containing 16 pesticides with given concentrations [US Environmental Protection Agency (EPA) method 508/608] was purchased from Absolute Standards. 2,3,7,8-Tetrabromodibenzo-*p*-dioxin, 2,3,4,7,8-pentabromodibenzofuran (both 5 ng/μl, prepared in 1991 from Cambridge Isotope Laboratories original) and pentabromodiphenyl oxide (viscous solid, from Ethyl Corporation, Bromine Chemicals Division) were generous gifts from Dr. Rich Kamens (University of North Carolina, USA). All dilutions were prepared gravimetrically in isooctane.

2.3. Preparation of reagents

Acid silica was prepared by drying the silica gel overnight at 200°C and mixing (shaking) it with fuming sulphuric acid in silica–H₂SO₄ ratio 6:4. The TBA-sulphite reagent for sulphur removal was prepared as described by Jensen et al. [34]

Table 1
Abbreviations and descriptions of the sediment samples

EB-1	Baltic Sea (60° 59.35' N/ 19° 43.98' E) 1977/1978, 0–10 cm, freeze-dried.
XV-1 _{0–6}	Baltic Sea (60° 15.01' N/ 27° 14.875' E) 17.5.1994, 0–6 cm, air-dried.
XV-1 _{15–25}	Baltic Sea (60° 15.01' N/ 27° 14.875' E) 17.5.1994, 15–25 cm, air-dried.
1529:1	Vistula River, site Kiezmarm near Gdansk, 6.6. 1992, surface sediment (0–10 cm)
1529:4	Baltic Sea (54° 43' N/19° 14' E), surface sediment (0–10 cm) taken from a depth of 97 m, 27.9. 1992.
Vättern	Lake Vättern, Sweden.
QA	Surface sediment (0–1 cm) from Bothnian Sea, spring 1988, air dried, [42].
SRM 1941	NIST marine sediment, certified for PAHs, uncertified values for PCBs and pesticides were provided. Harbour near the Francis Scott Key Bridge, Baltimore, USA (39° 12.85' N/76° 31.70' W), air-dried.
235c	Positive control sediment from Saginaw Bay, MI. Total amount of PCB about 3 µg/g, air-dried.

2.4. Sediment samples

The sediment samples are listed and described in Table 1. Sediments EB-1, XV-1_{0–6} and XV-1_{15–25} were provided by H. Kankaanpää (Finnish Institute of Marine Research, Helsinki, Finland), sediments Vättern, QA, 1529:1 and 1529:4 by Dr. B. van Bavel (Institute of Environmental Chemistry, University of Umeå, Sweden) and sediment 235c by Dr. C. Orazio (Midwest Science Center, Columbia, MO, USA). Sample size in the sediment extractions was 4 g, except for the Vättern and QA sediments where it was 2 g and for the SRM 1941 and 235c samples where it was 1 g.

2.5. Supercritical fluid extraction of spiked samples

All SFE extractions were performed with the HP SFE 7680 T automated instrument controlled by computer. Extraction cells (7 ml) were half filled with sodium sulphate, and 50 µl of the standard mixture containing 15 compounds was spiked to each; extraction cells were then filled completely with sodium sulphate. Fiberglass filter was placed at both ends of the extraction cell to keep the sealing surfaces clean. Triplicate SFE extractions under each set of conditions were done in the dynamic mode for 40 min, with pure CO₂ used as supercritical fluid. When methanol, acetone or diethylamine (0.5 ml) was added to the extraction cell as modifier, a 10-min static period was added before the dynamic

period. To see how different parameters affected the trapping efficiency, four sets of SFE extraction conditions were tested: (a) 60°C and 218 bar, density 0.75 g/ml; (b) 60°C and 380 bar, density 0.88 g/ml; (c) 120°C and 221 bar, density 0.45 g/ml; and (d) 120°C and 374 bar, density 0.67 g/ml. In addition, CO₂ flow-rates of 1 ml/min, 2 ml/min and 4 ml/min were tested. Trapping materials were ODS (packed trap supplied by HP) and Florisil. Nozzle (restrictor) temperature was 45°C in all experiments. Compounds extracted with CO₂ were eluted from the solid-phase trap at 40°C directly into the GC auto-sampler vials placed in the SFE collection carousel. Four rinsing steps were applied. Steps 1, 2 and 4 were performed with the same eluent, while step 3 was done with a more polar eluent (methanol). Effluents from steps 1 and 2 were normally led to vials, and those from steps 3 and 4 were sent to waste. 50 µl internal standard solution (0.85 ng/µl) was spiked into collection vials before the SFE sequence was started and the vials were closed. Vials were recapped after SFE to prevent losses due to evaporation.

2.6. Supercritical fluid extraction of sediments

Triplicate extraction of each sediment was performed at 120°C and 374 bar using 20 min static and 40 min dynamic extraction. The CO₂ flow-rate was 1 ml/min (measured as liquid CO₂). Sediment samples were mixed with 3 g of copper powder, which had

been precleaned by rinsing it twice with acetone and twice with petroleum ether and then extracting it with CO₂ at 265 bar and 80°C for 35 min. The sample and copper were placed between layers of sodium sulphate, which was used to fill the extraction cell, and pieces of fiberglass filter were inserted at both ends of the cell. Depending on the available cell volume, some sodium sulphate was mixed with the sample. Temperature of the Florisil trap was kept at 20°C for CO₂ extractions, at 65°C with methanol, at 56°C with acetone and at 55°C with diethylamine. Modifiers (0.5 ml) were added to the sample, before the extraction began, except for diethylamine, which was added dynamically via a modifier pump (HP 1050 HPLC pump). Nozzle temperature was kept at 45°C. Before extractions were begun, 50 µl of the internal standard solution was added to each collection vial and vials were capped.

A three-step method was used for the diethylamine extractions of samples: (1) 40 min dynamic extraction with 2% diethylamine, and rinsing of the trap (first rinsing step), (2) 5 min dynamic extraction (and system cleaning) with 5% methanol and (3) 5 min dynamic extraction with pure CO₂ and rinsing of the trap three times (last three rinsing steps). In all diethylamine extractions, temperature was 60°C and pressure 380 bar; rinsing steps were as described below.

The diethylamine-modified extracts were cleaned over acid silica placed into a Pasteur-type glass pipettes (ca. 1 cm Na₂SO₄+2–3 cm acid silica (40%, w/w, H₂SO₄)+1 cm Na₂SO₄). The extracts were concentrated with nitrogen flow to ca. 200 µl and eluted through the pipettes with 3 ml *n*-heptane. After the cleanup, extracts were reconcentrated to 200 µl. All other SFE extracts were concentrated to 200 µl with nitrogen, without cleanup, before the GC analysis.

The trap temperature during the elution was 40°C. A four-step rinsing program was applied. The 1st and 2nd rinses were with 1.6 ml of 2% ethyl acetate in *n*-heptane (1 ml/min), the 3rd rinse was with 2 ml acetone-methylene chloride (1:1, v/v) (2 ml/min) and the 4th rinse with 2.0 ml 2% ethyl acetate (2 ml/min). Effluents from steps 1 and 2 were collected (but only from step 1 in modifier extractions) and those from steps 3 and 4 were directed to waste.

2.7. Soxhlet extraction of sediments

For comparison, six sediments (EB-1, XV-1₀₋₆, XV-1₁₅₋₂₅, 1529:1, 1529:4 and 235c) and a blank were Soxhlet extracted in triplicate for 20 h with 150 ml acetone-*n*-hexane (1:1, v/v). Each sample was mixed with 3 g of copper powder. After the extraction, 50 µl of internal standard solution was added to the distillation flask and the extract was concentrated with a rotavapor to 2–3 ml and eluted through the acid silica column (2 cm Na₂SO₄+8 cm of acid silica +2 cm Na₂SO₄) with 80–100 ml *n*-pentane (60 ml minimum). *n*-Heptane (2 ml) was added to *n*-pentane as a keeper for the following evaporation step. Cleaned extracts were again concentrated with the rotavapor to 2 ml and further to 1 ml with nitrogen flow.

Sulphur was removed from the Soxhlet extracts by the TBA-sulphite method. [34] Extracts (1 ml) in *n*-heptane were shaken with 0.5 ml of 2-propanol and 1 ml of the TBA reagent until a strong sodium sulphite precipitate appeared. If no precipitation appeared, or if it disappeared, sodium sulphite was added in small portions and the sample was shaken until a solid residue remained. For some samples, precipitation was obtained only after the sample vials were placed in an ice/water bath. After phase separation the *n*-heptane phase was transferred to a GC vial and concentrated with nitrogen to ca. 200 µl.

2.8. Gas chromatography

The extracts (1 µl) were analyzed with a two-channel GC-ECD system: HP 5890 series II plus GC equipped with two ECD systems, pressure programmable on-column injector and HP 7673 autosampler unit. The GC-ECD was controlled via the same computer as the SFE by using the HP 3365 Chem-Station software. An HP 2.5 m deactivated and uncoated retention gap with I.D. of 0.53 mm was used, connected to two 60 m columns (DB-5 and DB-17) with a universal 'Y' Press-Tight connector (Restek Corporation). Both columns were 0.25 mm I.D. and film thickness was 0.17 µm. Hydrogen was used as carrier gas with column head pressure of 1.65 atm at 80°C to provide linear flow of 46.3 cm/s. The GC system was run in constant flow mode and

with the oven track on. Pressure of the ECD makeup gas (nitrogen) was kept at 2.6 atm, with a resulting flow of ca. 50 ml/min (1 atm=101 325 Pa). The oven was programmed from 80°C (2 min) at 10°C/min to 170°C (7.5 min) and from 170°C at 3°C/min to 285°C (20 min), except in the trapping experiments where it was programmed only up to 280°C (12 min). Detectors were kept at 300°C.

Collection efficiencies (%) were calculated (for both columns) by comparing integrated chromatograms with the calibration made with the Chem-Station program. Calibration curves were obtained by analyzing solutions where 100%, 80%, 50% and 30% of the amount of standard mixture (50 µl) added to the extraction cell was added directly to sample vials. Internal standard was added to the vial, which was then filled with *n*-heptane. The origin was included in the power fit calibration. The recovery (%) of the samples was always determined by referring to freshly prepared calibration standards.

For the sediment samples, six to eight point power calibration was performed (origin included) using peak heights for quantitations. Dibromooctafluorobiphenyl was used as an internal standard for chlorinated benzenes and brominated compounds, PCB 35 for pesticides and PCB 169 for PCBs. The internal standards were also used as time reference peaks.

3. Results and discussion

3.1. Solid-phase trapping

The effects of trap temperature and other parameters for solid-phase trapping have been studied by several authors, [35–38] and reliable data for trapping efficiencies for PCBs and chlorinated benzenes can be found in the literature. [37,38] Florisil and ODS were chosen as trapping materials to study how changes in SFE and SPE parameters affect to the trapping efficiency for chlorinated benzenes and brominated aromatic compounds. The end goal was to develop a trapping method for these compounds in sediment samples.

A temperature of 20°C with pure carbon dioxide was considered adequate to achieve good trapping

efficiency [36,38]. In practice, the maximum rinsing volume for 1.8 ml autosampler vials is ~1.6 ml and this was concluded to be a maximum elution volume sufficient to produce 97% or higher recovery with the ODS trap for all compounds except dichlorobenzenes, which could not be recovered with this trapping material. Further method development was conducted using 1.6 ml elution volume with an elution flow-rate of 2 ml/min. Trapping efficiency experiments showed that within the standard deviation there was no difference between the data obtained from the two analytical GC columns.

ODS was much more sensitive than Florisil to changes in SFE flow-rate. When the CO₂ flow-rate was increased from 1 to 4 ml/min, up to 90% of the trichlorobenzenes were lost with ODS, whereas no loss in trapping efficiency occurred with Florisil. High (4 ml/min) CO₂ flow-rate with Florisil (greater cooling immediately after the nozzle) evidently caused large and polar compounds like dibromodiphenyl ether and dibromobiphenyl (PBB 7) to deposit closer to the inlet of the trap, making them slow to elute.

Collection efficiencies were first better with ODS than Florisil, but this was because *n*-heptane eluted the analytes more effectively from ODS than from Florisil. Florisil trapped dichlorobenzenes with the same efficiency as the other compounds. The structure of Florisil [39,40] causes oxygen, chlorine and planar aromatic compounds, especially polychlorinated dibenzodioxins and furans, to interact strongly with localised positive charges and diffused negative charges caused by Mg²⁺ in the silicate matrix. This was seen especially with dibromodiphenyl ether, which was strongly retained on Florisil, and partially eluted in the second rinse. Since dibromodiphenyl ether and many of the brominated biphenyls were partially eluted in the second rinse, when using *n*-heptane as an eluent, 2% ethyl acetate was added to the *n*-heptane. This procedure, including reduction of the elution flow-rate to 1 ml/min, yielded 95–101% recovery of the compounds with RSD less than 2% (Table 2).

The effect of the extraction pressure and temperature on ODS trapping efficiency was tested for four sets of SFE conditions (see Experimental). Within the standard deviation, SFE pressure and temperature had no effect on the trapping efficiency. Since

Table 2

Average collection efficiency with a Florisil trap, using pure CO₂ and CO₂ with different modifiers^a

Compound	Pure CO ₂ Trap 20°C Mean ^b (% RSD)	CO ₂ /Methanol Trap 65°C Mean ^b (% RSD)	CO ₂ /Acetone Trap 56°C Mean ^b (% RSD)	CO ₂ /Diethylamine Trap 55°C Mean ^b (% RSD)
1,3-Dichlorobenzene	95 (1)	1.1 (17)	1.3 (11)	–
1,4-Dichlorobenzene	95 (1)	1.4 (19)	1.5 (7)	–
1,3,5-Trichlorobenzene	96 (1)	29 (13)	65 (2)	1 (14)
1,2,4-Trichlorobenzene	97 (1)	64 (6)	81 (2)	36 (1)
1,2,3-Trichlorobenzene	97 (1)	72 (4)	81 (2)	63 (5)
1,2,4,5-Tetrachlorobenzene	96 (1)	78 (3)	82 (3)	65 (5)
1,2,3,4-Tetrachlorobenzene	96 (1)	80 (4)	84 (3)	80 (6)
Pentachlorobenzene	96 (1)	84 (3)	87 (3)	80 (7)
Hexachlorobenzene	95(1)	87 (2)	90 (2)	90 (4)
Dibromodiphenyl ether	99 (1)	87 (1)	88 (5)	99 (4)
PBB 7	99 (1)	91 (1)	92 (2)	101 (3)
PBB 31	99 (1)	87 (1)	89 (3)	92 (4)
PBB 52	98 (1)	82 (3)	86 (3)	83 (4)
PBB 103	100 (2)	80 (4)	84 (2)	83 (4)
PBB 153	101 (2)	84 (3)	87 (1)	92 (8)

^a Extraction at 120°C and 374 bar with a CO₂ flow-rate of 1 ml/min. Trap rinse flow-rate 1 ml/min with 2% ethyl acetate in *n*-heptane. Sample and modifier spiked onto Na₂SO₄.

^b The range of recoveries with the second rinse was 0–2.3% with the highest values for the brominated compounds and penta- and hexachlorobenzene.

Florisil retained the compounds more strongly than ODS, changes in the SFE conditions would not affect the Florisil trapping efficiency either, and the temperature and pressure experiments were not repeated for Florisil. Because it trapped all the analytes efficiently, Florisil was selected for further experiments.

The trapping efficiency of Florisil with pure CO₂ and with CO₂ and three different modifiers is shown in Table 2. Earlier reports have shown that good recoveries with modifiers can be achieved when trap temperature is close to the boiling point of the modifier. [36,38] The trap temperature was kept at 56°C with acetone, at 65°C with methanol and at 55°C with diethylamine. Lower temperature would have caused the analytes to elute together with the condensed modifier present in the trap. Reasonable recoveries (80–90%) were obtained with the modifiers, and only dichlorobenzenes and some trichlorobenzenes were partially lost. If sequential extractions were used, these compounds would normally be recovered with the pure CO₂. Compared with acetone, methanol gave lower recovery of more volatile compounds due to the higher trap temperature.

3.2. Sediment samples

Table 3 gives the limit of determination (LOD), calculated as ng/g, together with the relative retention time (relative to PCB 35), for each compound on the two columns. Determination limits for the analytes were obtained by calculating the average of the noise at two points on seven standard chromatograms used for the calibration. Because of the complexity of the chromatograms for real samples, it was decided that a signal-to-noise ratio of 7 would give the most reliable LODs for all sediment samples, even though SFE produced cleaner chromatograms than Soxhlet and thus lower LODs for SFE would have been possible.

Neat CO₂ normally provides efficient SFE of PCBs from sediment samples when the extraction temperature is raised above 100°C. Such might not be the case for brominated organic pollutants or for PCBs present at very low levels, because of stronger matrix binding. All sediments were first extracted in triplicate with CO₂ alone, at 120°C and 374 bar (instrument maximum temperature, and maximum pressure at that temperature). Elemental sulphur was

Retention time relative to PCB 35 and limit of determination (LOD, $S/N=7$) for all compounds studied in sediment samples. Columns with DB-17 and DB-5 stationary phases

	Compound	Relative RT		LOD (ng/g) ^a 235c, SRM 1941	
		DB-17	DB-5	B-17	DB-5
1	1,3-Dichlorobenzene	0.203	0.213	0.41	0.30
2	1,4-Dichlorobenzene	0.208	0.216	0.84	0.18
3	1,3,5-Trichlorobenzene	0.253	0.280	0.07	0.04
4	1,2,4-Trichlorobenzene	0.285	0.305	0.08	0.05
5	1,2,3-Trichlorobenzene	0.309	0.326	0.05	0.03
6	1,2,4,5-Tetrachlorobenzene	0.350	0.386	0.04	0.03
7	1,2,3,4-Tetrachlorobenzene	0.386	0.412	0.02	0.02
8	Pentachlorobenzene	0.470	0.490	0.03	0.01
9	Dibromooctafluorobiphenyl	0.520	0.616	–	–
10	Hexachlorobenzene	0.669	0.653	0.03	0.01
11	α -HCH	0.717	0.640	0.04	0.02
12	γ -HCH	0.810	0.718	0.04	0.02
13	β -HCH	0.832	0.707	0.06	0.04
14	Heptachlor	0.880	0.900	0.03	0.02
15	PCB 28	0.892	0.867	0.08	0.04
16	PBB 7	0.905	0.841	0.07	0.03
17	δ -HCH	0.913	0.788	0.05	0.03
18	Aldrin	0.950	0.987	0.03	0.02
19	PCB 52	0.962	0.958	0.05	0.05
20	PCB 35	1.000	1.000	–	–
21	Dibromodiphenyl ether	1.062	1.035	0.13	0.06
22	Heptachlor epoxide	1.074	1.093	0.03	0.02
23	PCB 101	1.127	1.179	0.04	0.02
24	Endosulfan I	1.144	1.181	0.04	0.03
25	<i>p,p'</i> -DDE	1.201	1.253	0.04	0.02
26	Dieldrin	1.207	1.240	0.04	0.03
27	PBB 31	1.241	1.246	0.05	0.02
28	PCB 118	1.254	1.330	0.04	0.02
29	PCB 149	1.264	1.326	0.03	0.03
30	Endrin	1.278	1.297	0.05	0.02
31	PCB 153	1.282	1.383	0.03	0.02
32	<i>p,p'</i> -DDD	1.312	1.354	0.06	0.03
33	Endosulfan II	1.315	1.323	0.04	0.02
34	PCB 105	1.336	1.393	0.04	0.03
35	PCB 138	1.365	1.449	0.03	0.02
36	<i>p,p'</i> -DDT	1.368	1.440	0.12	0.04
37	Endrin aldehyde	1.381	1.371	0.04	0.02
38	PBB 52	1.384	1.407	0.04	0.02
39	Endosulfan sulfate	1.404	1.427	0.03	0.02
40	PCB 128	1.446	1.512	0.03	0.02
41	PCB 156	1.452	1.564	0.03	0.02
42	PCB 180	1.466	1.602	0.02	0.02
43	PCB 169	1.497	1.647	–	–
44	PCB 170	1.551	1.668	0.02	0.02
45	PBB 103	1.557	1.608	0.04	0.02
46	Pentabromodiphenyl ether	1.765	1.856	0.06	0.04
47	2,3,7,8-TBDD	1.780	1.912	0.10	0.03
48	PBB 153	1.924	2.004	0.09	0.03
49	2,3,4,7,8-PBDF	2.252	2.193	0.40	0.05

^a Values must be multiplied with 0.5 for Vättern and QA sediments (2 g samples used) and with 0.25 for EB-1₀₋₆, XV-1₁₅₋₂₅ and 1529 sediments (4 g samples).

Table 4

Average concentration (ng/g) and %RSD of representative compounds in sediment samples XV-1₀₋₆, Vättern and QA as determined by sequential SFE

	Pure CO ₂ Mean (RSD) ng/g (%)	CO ₂ +MeOH Mean (RSD) ng/g (%)	CO ₂ +Acetone Mean (RSD) ng/g (%)	CO ₂ +DEA ^b Mean (RSD) ng/g (%)
<i>XV-1₀₋₆</i>				
1,2,3-Trichlorobenzene	0.15 (81)	0.22 (16)	0.17 (21)	0.02 (38)
Pentachlorobenzene	0.81 (70)	0.01 (20)	^a	0.02 (36)
Hexachlorobenzene	0.22 (26)	0.03 (23)	0.05 (125)	0.13 (6)
δ-HCH	1.1 (3)	^a	0.14 (140)	^a
Endosulfan I	1.4 (6)	0.04 (36)	0.07 (45)	^a
Dieldrin	1.2 (1)	0.08 (30)	0.05 (55)	^a
<i>p,p'</i> -DDE	3.0 (18)	0.04 (13)	0.01 (18)	^a
<i>p,p'</i> -DDD	4.7 (8)	0.03 (37)	^a	^a
<i>p,p'</i> -DDT	1.9 (9)	^a	^a	^a
PCB 128	1.9 (17)	0.05 (9)	0.01 (46)	^a
PCB 153	0.50 (9)	^a	^a	^a
PBB 52	0.10 (22)	^a	^a	^a
PBB 153	0.08 (22)	^a	^a	^a
Dibromodiphenyl ether	^a	0.18 (13)	^a	^a
Pentabromodiphenyl ether	0.79 (36)	^a	^a	0.05 (50)
2,3,7,8-TBDD	0.53 (19)	^a	^a	^a
2,3,4,7,8-PBDF	2.4 (28)	^a	^a	^a
<i>Vättern</i>				
1,2,4-trichlorobenzene	3.9 (10)	^a	^a	0.13 (27)
1,2,4,5-tetrachlorobenzene	1.5 (51)	^a	^a	^a
Hexachlorobenzene	1.1 (26)	0.07 (21)	^a	0.26 (52)
α-HCH	1.7 (42)	0.13 (63)	0.07 (11)	^a
Endosulfan sulfate	0.54 (25)	0.14 (46)	0.08 (13)	^a
Endrin aldehyde	0.40 (31)	0.11 (29)	0.06 (33)	^a
<i>p,p'</i> -DDE	2.2 (38)	0.19 (50)	^a	^a
<i>p,p'</i> -DDD	2.2 (30)	0.20 (44)	0.02 (31)	^a
<i>p,p'</i> -DDT	0.50 (18)	^a	0.21 (24)	0.12 (3)
PCB 128	1.1 (33)	0.10 (32)	^a	0.04 (1)
PCB 153	0.69 (44)	^a	^a	^a
PBB 52	1.3 (2)	0.21 (25)	0.06 (21)	^a
PBB 153	0.35 (53)	^a	^a	^a
<i>QA</i>				
1,2,4-trichlorobenzene	2.9 (4)	^a	^a	0.13 (16)
1,2,4,5-tetrachlorobenzene	2.1 (7)	^a	^a	^a
Hexachlorobenzene	0.71 (5)	^a	^a	0.37 (47)
α-HCH	0.48 (7)	0.20 (15)	0.03 (41)	^a
Endosulfan sulfate	0.17 (5)	0.05 (19)	0.04 (9)	^a
<i>p,p'</i> -DDE	0.73 (7)	0.04 (49)	^a	0.01 (34)
<i>p,p'</i> -DDD	0.40 (8)	0.04 (57)	^a	^a
PCB 128	0.23 (10)	0.04 (17)	0.01 (92)	^a
PCB 153	0.43 (5)	^a	^a	^a
PBB 103	0.12 (17)	^a	^a	0.08 (84)
PBB 153	0.18 (14)	^a	^a	^a
Pentabromodiphenyl ether	0.32 (23)	0.05 (3)	0.04 (25)	0.23 (71)
2,3,7,8-TBDD	0.44 (23)	0.03 (54)	^a	^a

^aCompounds not detected or detected at levels lower than described in Table 3.^bDEA=diethylamine.

removed by mixing cleaned copper powder with the sample and allowing it to react during a 20-min static period before dynamic (40 min) extraction. This was an effective way to remove sulphur interference from the GC analysis, since only in one of the 27 extractions was the sulphur not properly eliminated. Quantitative results for frequently detected compounds are presented in Table 4 for three sediments. As can be seen, most of the compounds were recovered with CO₂ alone (see also Table 5). Some compounds were also eluted in the second rinse fraction collected from the trap, and thus recovery from the solid-phase trap was not as good as achieved with standards. Naturally, the trapping process and also the elution step will be negatively affected by a more complex extract with large number of components and possibly interfering compounds. In general, the RSDs were quite good, in some cases less than 10, but below ng/g level they began to increase.

To determine whether or not these conditions were adequate for quantitative extraction, the same sediment samples were further extracted with modifier added. After pure CO₂, samples were successively extracted with CO₂ and three modifiers methanol, acetone and diethylamine (in this order). Methanol was selected as an acidic modifier, diethylamine as a basic modifier and acetone because of its high electron density. Because of the solid-phase trapping, all modifiers had to have relatively low boiling points. Sequential SFE extractions under increasingly severe conditions showed that 80 to 95% of the total amount extracted was recovered with CO₂ alone at

120°C (Table 5). Modifiers had only a slight effect on the extraction from sediments EB-1, XV-1₀₋₆, XV-1₁₅₋₂₅ and 235c. Use of diethylamine provided relatively high recovery of hexachlorobenzene from all sediments, as can be seen in Table 4. Two other compounds that were extracted well with diethylamine were DDT and pentabromodiphenyl ether. Additionally, modifiers produced extra recovery especially of 2,3,7,8-TBDD, Endosulfan II, Aldrin (EB-1, QA and SRM 1941), Dieldrin (1529:4), dibromodiphenyl ether (QA, XV-1₀₋₆ and 1529:4), and 1,2,3- and 1,2,4-trichlorobenzene (XV-1₀₋₆, XV-1₁₅₋₂₅, EB-1, 1529:1 and 1529:4). Methanol and acetone worked extremely well for Dieldrin and Endosulfan II. In five sediments of nine, the recovery for all compounds exceeded 95% with the first modifier (methanol), whereas in the remaining four cases (Vättern, XV-1₀₋₆, QA and 1529:4) relatively large amounts of analytes were recovered with the last two modifiers.

Diethylamine was not a good choice for the basic modifier because of its reactivity (strong nucleophile). When the diethylamine was added directly to the extraction cell, the SFE instrument was seriously blocked after the static period, even the steel tubing after the extraction cell. The extraction succeeded only after the extraction conditions were changed viz., diethylamine was added via a modifier pump and extra cleanup steps were added. Even though the diethylamine then produced some extra recovery (Table 5), especially for the sediments Vättern, QA and 1529:4, it also produced more contamination peaks than any of the other modifiers.

Table 5
Relative SFE recoveries of all quantified compounds from sediments with CO₂ alone and with CO₂ and modifiers

Sediment	Pure CO ₂ (%)	CO ₂ + MeOH (%)	CO ₂ + Acetone (%)	CO ₂ + DEA (%)
SRM 1941	88.9	7.8	2.5	0.8
EB-1	95.1	1.7	1.4	1.7
XV-1 ₁₅₋₂₅	95.3	2.5	1.5	0.9
Vättern	86.6	6.6	2.5	4.1
XV-1 ₀₋₆	90.7	4.1	3.9	1.2
1529:1	91.1	6.5	1.0	1.6
QA	81.2	8.1	3.9	6.6
1529:4	81.8	10.1	4.8	3.4
235c	95.9	3.3	0.6	0.1
Blank	23.3	16.7	7.6	53.8

100% recovery represents the sum of all steps.

Table 6
Comparison of recoveries (ng/g) from Soxhlet and SFE using pure CO₂ for selected sediments

Compound	Sediment EB-1		Sediment XV-1 ₁₅₋₂₅		Sediment 1529-1		Sediment 1529-4		Sediment SRM 1941		Sediment 235c	
	Soxhlet Mean (% RSD)	SFE CO ₂	Soxhlet Mean (% RSD)	SFE CO ₂	Soxhlet Mean (%RSD)	SFE CO ₂	Soxhlet Mean (% RSD)	SFE CO ₂	Soxhlet ^b Mean (%RSD)	SFE CO ₂	Soxhlet Mean (% RSD)	SFE CO ₂
1,3-Dichlorobenzene	a	1.5 (22)	a	a	0.66 (38)	a	a	a	9.4 (54)	a	a	75.2 (9)
1,2,4-Trichlorobenzene	0.84 (28)	2.5 (5)	0.77 (18)	a	0.16 (45)	a	a	a	18.8 (2)	a	a	40.1 (7)
1,2,4,5-Tetrachlorobenzene	20.1 (8)	24.0 (1)	a	0.11 (73)	a	0.11 (73)	2.0 (13)	1.1 (11)	5.8 (5)	4.7 (109)	13.4 (7)	13.4 (7)
Pentachlorobenzene	15.8 (45)	12.2 (1)	a	0.08 (36)	1.0 (32)	0.81 (4)	a	0.37 (23)	12.0 (7)	a	a	3.7 (6)
Hexachlorobenzene	1.3 (29)	1.4 (1)	a	a	2.9 (1)	2.7 (6)	a	0.37 (15)	23.4 (7)	a	a	13.3 (7)
δ-HCH	a	0.13 (64)	a	a	a	0.73 (39)	a	a	0.42 (63)	a	a	0.7 (47)
γ-HCH	a	2.4 (6)	a	3.3 (16)	a	0.71	a	0.78 (3)	0.9 (38)	a	a	0.10 (42)
Dieldrin	0.41 (8)	0.71 (7)	0.32 (13)	1.3 (11)	0.14 (3)	a	0.04 (76)	a	0.63 (5)	19.5 (6)	18.2 (4)	18.2 (4)
Endrin	0.25 (23)	0.45 (10)	a	a	0.10 (41)	0.10 (17)	0.06 (39)	a	3.8 (20)	13.7 (6)	12.3 (5)	12.3 (5)
Heptachlor	a	0.26 (9)	a	0.05 (27)	a	0.14 (70)	a	0.34 (16)	a	a	a	a
Heptachlor epoxide	a	0.25 (9)	a	0.65 (8)	a	0.06 (43)	0.04 (95)	0.03 (13)	0.23 (9)	0.96 (140)	a	6.2 (3)
Endosulfan I	a	0.04 (35)	a	0.51 (19)	a	0.21 (32)	a	0.19 (38)	a	a	a	a
<i>p,p'</i> -DDE	0.90 (4)	1.0 (5)	4.6 (4)	4.4 (8)	1.7 (14)	1.5 (5)	0.33 (6)	0.18 (16)	9.7 (2)	6.7 (13)	8.1 (5)	7.5 (4)
<i>p,p'</i> -DDD	1.3 (5)	1.0 (7)	5.4 (42)	10.1 (5)	4.8 (31)	4.7 (4)	0.48 (73)	0.76 (13)	10.3 (1)	4.0 (28)	3.4 (32)	5.7 (10)
<i>p,p'</i> -DDT	0.33 (46)	0.45 (33)	0.29 (60)	a	0.33 (74)	0.64 (22)	0.30 (50)	0.31 (5)	1.1 (5)	2.2 (21)	a	0.66 (27)
PCB 28	2.5 (72)	4.6 (6)	1.7 (22)	a	a	0.66 (54)	a	a	16.1 (3)	10.2 (10)	139 (63)	313 (9)
PCB 52	1.6 (2)	2.6 (10)	0.52 (13)	1.0 (22)	0.22 (42)	0.24 (67)	a	a	10.4 (4)	15.1 (6)	244 (59)	544 (8)
PCB 101	1.1 (5)	1.4 (9)	1.0 (17)	a	a	0.24 (67)	a	0.14 (39)	22.0 (3)	17.4 (9)	45.9 (59)	82.8 (7)
PCB 105	0.17 (51)	0.02 (27)	0.19 (64)	0.79 (24)	0.05 (25)	0.04 (56)	a	0.06 (16)	5.8 (4)	5.8 (12)	12.4 (168)	33.8 (5)
PCB 118	0.45 (6)	0.73 (28)	0.76 (4)	a	0.11 (42)	0.19 (55)	0.03 (99)	0.08 (5)	15.2 (5)	13.1 (10)	35.8 (56)	70.0 (9)
PCB 128	0.07 (11)	0.22 (10)	0.47 (10)	a	0.15 (40)	a	0.07 (17)	0.08 (70)	—	2.6 (11)	3.9 (60)	6.2 (7)
PCB 153	0.36 (13)	0.48 (9)	1.1 (4)	1.2 (5)	0.21 (13)	0.25 (22)	0.15 (12)	0.05 (1)	22.0 (6)	17.8 (9)	15.0 (61)	27.3 (7)
PCB 180	0.15 (8)	0.07 (18)	0.47 (20)	0.82 (19)	0.13 (32)	0.19 (54)	a	0.04 (39)	14.3 (2)	12.8 (12)	10.7 (59)	16.6 (10)
PBB 7	a	0.16 (21)	a	a	0.19 (115)	0.22 (36)	a	a	0.61 (130)	a	a	a
PBB 52	0.03 (34)	0.09 (10)	0.10 (73)	a	0.02 (7)	0.06 (35)	0.03 (67)	a	—	0.40 (34)	1.3 (73)	1.5 (4)
PBB 153	a	0.04 (11)	a	a	a	a	a	a	—	0.14 (18)	1.7 (17)	6.4 (4)
Dibromodiphenyl ether	a	0.45 (2)	a	1.3 (25)	0.08 (47)	a	a	a	—	2.5 (110)	a	a
2,3,7,8-TBDD	a	0.42 (7)	0.49 (56)	a	0.14 (33)	0.45 (40)	0.26 (53)	1.38 (2)	—	1.0 (48)	0.89 (75)	0.95 (40)

^aCompounds not detected or detected at levels lower than described in Table 3, or impossible to determine because of interfering compounds (mainly in the Soxhlet extracts).

^bSoxhlet values reported by NIST (not certified).

Some of this contamination was due to the impure solvent, as could be seen in the blank diethylamine chromatogram. The SFE blank showed some additional contamination peaks, probably because of some co-extractant or by-products formed during the extraction. Additionally, the reaction with copper used to remove sulphur produced copper complexes (seen as blue colour in the extracts) and subsequently these were removed by cleaning with acid silica.

Recoveries by Soxhlet and SFE with CO₂ from selected sediments are given in Table 6 (selected to complement the samples in Table 4). In general, the results showed good agreement between SFE and Soxhlet, but SFE produced much cleaner extracts. In SFE only the diethylamine-modified extracts had to be cleaned, and the relative standard deviations were lower. The difference is explained by the more selective nature of SFE and the smaller risk of contamination. For blank SFE, recoveries were in the range 0.01 to 0.35 ng/g (the highest value for pentabromodiphenyl ether), while for Soxhlet they ranged from 0.1 to 1.06 ng/g (except 25.5 ng/g for pentabromodiphenyl ether). Table 6 clearly shows the contamination problem with Soxhlet, as many of the compounds determined by SFE could not be determined by Soxhlet extraction because of interfering matrix compounds. After sulphur cleanup of the Soxhlet extract with TBA-sulphite reagent (copper was not efficient in Soxhlet), recoveries were excel-

lent, as can be seen from Table 7. Unfortunately, the first internal standard (dibromooctafluorobiphenyl) was almost completely lost. All Soxhlet extracts were therefore analyzed using the third internal standard (PCB 169), even for the chlorinated benzenes and brominated compounds. High contamination with PBB 153 also appeared during the sulphur cleanup step.

Recovered by SFE, the total concentration of analytes in sediment samples was 1606.1 ng/g for 235c, 267.9 ng/g for SRM 1941, 74.9 ng/g for EB-1, 41.3 ng/g for XV-1_{15–25}, 28.9 ng/g for XV-1_{0–6}, 28.8 ng/g for Vättern, 18.3 ng/g for 1529:1, 17.0 ng/g for QA and 9.9 ng/g for 1529:4. The SFE blank contained totally 2.1 ng of the analytes. All sediments from the Baltic Sea area were relatively clean (compared to 235c and SRM 1941). Some of the Soxhlet values are missing (see Table 6), not only because of the poor extraction efficiency or recovery losses during the cleanup but because it was not always possible to identify the right peaks in complex chromatograms. The XV-1_{0–6}, XV-1_{15–25}, Vättern and QA sediments contained more brominated compounds than the other sediments (235c and SRM 1941 excluded). Concentrations of dibromodiphenyl ether, PBB 52, pentabromodiphenyl ether, 2,3,7,8-TBDD and 2,3,4,7,8-PBDF were sometimes relatively high, more than 1 ng/g. DDT and its decomposition products DDE and DDD were present

Table 7

The recoveries of spiked chlorinated and brominated pollutants through the Soxhlet extract cleanup steps (includes Soxhlet, all concentration steps, acid silica cleanup and sulphur cleanup with TBA-sulphite) and through the TBA-sulphite step only

Recovery study Compound	All steps Recovery %	TBA-sulphite cleanup Recovery % (% RSD)
1,3-Dichlorobenzene	78	102.2 (1)
1,4-Dichlorobenzene	77.9	103.4 (1)
1,3,5-Trichlorobenzene	86.2	102.5 (2)
1,2,4-Trichlorobenzene	61.2	100.2 (1)
1,2,3-Trichlorobenzene	84.4	95.7 (1)
1,2,4,5-Tetrachlorobenzene	86.8	95.9 (1)
1,2,3,4-Tetrachlorobenzene	86.8	95.6 (1)
Pentachlorobenzene	88.3	94.2 (2)
Hexachlorobenzene	92.3	98.7 (2)
PBB 7	94.2	98.9 (2)
PBB 31	103.2	101.1 (1)
PBB 52	101.7	103.5 (2)
PBB 103	109	112.8 (2)
PBB 153	180.9	152.3 (4)
Dibromodiphenyl ether	99.5	96.7(1)

at high levels in almost all Baltic Sea area sediments, and PCBs were present at about the same or slightly lower levels in all sediments. Levels of DDE, DDD and DDT were highest in the XV-1_{0–6} and XV-1_{15–25} sediments. The sedimentation rate at the XV-1 location is about 1 cm/year and the total extractable halogen (EOX) content is one of the highest in the Gulf of Finland. [41]

4. Conclusions

SFE with solid-phase trapping efficiently extracted chlorinated and brominated organic pollutants from sediments, and a large number of different analytes were determined at ppt levels using two-channel GC with ECD detectors. The use of two capillary columns of different polarity greatly decreased the number of errors arising from the interfering co-eluting compounds. SFE with pure CO₂ gave similar values to Soxhlet extraction but with much cleaner background. Minor improvement of the SFE recovery was obtained by using CO₂ with different modifiers. In addition to some PCB congeners and common pesticides, which were the most abundant species, many polybrominated aromatic compounds were found at ppb or high ppt levels in the sediment samples.

Acknowledgments

The authors would like to thank Hewlett-Packard for making available the SFE 7680 T instrument, Chemstation 3365 and the Bridge software and supplying excellent support. K. Hartonen gratefully acknowledges financial support from the Academy of Finland and S. Bøwadt support from the Danish Research Councils.

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