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Trace Enrichment of Polychlorinated Biphenyls in Soil: Efficiency of Sonicated Liquid-solid Extraction with Acetone/n-Hexane Mixture from Different Soil Types

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The efficiency and reproducibility of an analytical procedure for trace determination of polychlorinated biphenyls (PCBs) in soil/ /sediment samples were evaluated by analyses of soils differing in their sorption-controlling properties. PCBs were accumulated from soil by sonicated multiple extraction with a 1:1 acetone/n-hexane mixture. The extracts, purified by treatment with copper powder, mercury, and sulphuric acid were analyzed by gas chromatography. The extraction efficiency from a soil spiked with 4–430 μg kg^{-1} of Aroclor 1242/Aroclor 1260 mixture depended on the initial PCB mass fraction. The matrix effect was evaluated by the analysis of PCBs added to five European reference soils differing in organic matter content, grain size distribution, mineral composition, pH values, and iron and aluminium oxides content. In four of these soils, a linear correlation was found between the slopes of calibration lines for the determination of PCBs and soil organic matter content. An exception was the most acidic soil with the highest, but poorly humified, organic matter. The linear regression of calibration line slopes and the content of soil fine silt particles indicated a positive, but not statistically significant, correlation.

Keywords: Aroclor 1242, Aroclor 1260, soil/sediment analysis, soil sorption controlling properties, Euro-Soils, extraction efficiency, gas chromatographic analysis.

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INTRODUCTION

Due to high chemical and thermal stability, inertness, and excellent dielectric properties, complex mixtures of polychlorinated biphenyls (PCBs) have been used extensively over the past half century as dielectric fluids in transformers and capacitors, as components of hydraulic fluids, and as plasticizers. The wide-spread use of PCBs, coupled with uncontrolled waste discharge, spills, dumps, and accidents has led to significant environmental contamination by their persistent commercial formulations.[1]

Being highly hydrophobic, PCBs tend to be rapidly and strongly sorbed by most soils and aquatic sediments.[2–7] Soil and sediment sorption of PCBs is favoured by a high degree of chlorination and absence of substitution in the *ortho*-positions of the biphenyl.[8] The sorption is stronger for co-planar than for non-planar PCBs with the same degree of chlorination.[9] The soil/sediment properties favouring the sorption of PCBs are high organic carbon, high aluminium and iron oxides, and fine particles like silt.[9]

The quantitative and qualitative analyses of PCBs encounter specific problems due to the complex composition of PCB mixtures in different environmental and biological samples. For easier handling of the 209 PCB synthetic congeners, 100–150 being present in commercial mixtures, a systematic congener numbering has been accepted and the numbers are referred to as Ballschmiter, IUPAC or PCB numbers.[10] High resolution gas chromatographic techniques enable efficient separation and quantitation of individual congeners in different samples, selected either as congeners of a typical structure and high toxicity or congeners taken to be typical and representative of the most widely used PCBs.[11–13]

Methods for determination of PCBs in soil/sediment samples are mostly based on a Soxhlet or ultrasonic solvent extraction and a clean-up step followed by gas chromatographic separation and electron capture detection.[3–7,14–17] The use of solvents of medium-polarity (dichloromethane) or solvent mixtures (n-hexane/acetone) containing a wetting agent (typically acetone) is recommended for liquid-solid extraction procedures.[15,16] Critical comparison of six different extraction methods for PCB extraction from sewage sludge was published recently.[18] At mass fractions of individual congeners of about 100 ng g^{-1} and higher, PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180 were extracted almost quantitatively by Soxhlet Dean-Starch extraction of sludge with toluene, Soxhlet extraction with 2:3 n-hexane/acetone mixture, cold digestion/saponification with KOH in methanol, followed by partition with n-hexane, ultrasonic extraction with 1:1 acetone/n-hexane mixture, and treatment with BF_3-methanol, followed by partition with dichloromethane. Though slightly less efficient (78%), cyclic steam distillation was recommended as an interesting alternative because of the low solvent consumption and the possibility of analyzing the extract directly without the clean-up. Column elution with dichloromethane was the least efficient (61%). Supercritical fluid extraction/supercritical fluid chromatography coupled with FT-IR spectrometry can also be applied to the analysis of PCBs in contaminated soils.[16,17,19] By analyzing certified sediment samples containing less than 10 ng g^{-1} of individual PCB congeners, Fuoco *et al.*[17] have demonstrated that extraction of PCBs either with 1:1 acetone/n-hexane mixture in an ultrasonic bath or by supercritical fluids from certified sediment samples generally gives a quantitative recovery and a lower coefficient of variation than the extraction with a Soxhlet system. The ultrasonic extraction procedure worked out by those authors[14,17] was equally efficient but less solvent consuming and, due to the shorter extraction periods, much faster then the similar extraction procedure applied for determination of PCBs in sewage sludge.[18] This method was successfully used for determination of PCBs at pg/g levels in sediment and soil samples from Antarctica[6,7] and it seemed to be the method of choice for trace enrichment of PCBs in soil. However, environmental analysis including soil/sediment analysis deals with great variation in the composition (matrix) of samples. It is therefore problematic to anticipate the efficiency and imprecision of compound analysis in a soil/sediment sample on the basis of recoveries and standard deviations estimated earlier with a sample of different characteristics. To examine the interferences and matrix effects, additional recovery experiments should be performed with each type of analyzed soils and at different concentration levels, expected in real samples.

In the present work, we have focused on variations in the extraction efficiency of PCBs from different types of soils by multiple sonication of soil with acetone/n-hexane mixture and following in general the procedure recommended by Fuoco *et al.*[14,17] The matrix effect on PCB extraction efficiency was evaluated by gas chromatographic analysis of PCBs, added as an Aroclor 1242/Aroclor 1260 mixture, in a surface soil collected from a strip land excavation and in four surface and one subsurface European reference soils (Euro-Soils)[20,21] differing in their sorption controlling properties, such as the organic matter content, grain size distribution and mineral composition, pH values, and iron and aluminium oxides content. The extraction recoveries are discussed with respect to the pedological characteristics possibly affecting the efficiency of the procedure.

EXPERIMENTAL

Chemicals

The PCB mixtures Aroclor 1242 and Aroclor 1260 were obtained as standard reference compounds from the U.S. Environmental Protection Agency Repository, Research Triangle Park, NC, USA.

n-Hexane for organic trace analysis (SupraSolv®), mercury (Suprapur®), copper (Kupfer fein gepulvert) and sulphuric acid, 95–97%, *pro analysi,* were purchased from Merck, Darmstadt, Germany. Mercury was washed with 5% HNO_3, rinsed with water up to neutral reaction, then with acetone and 2–3 times with n-hexane. Copper powder was washed twice with diluted HCl (1:1), and rinsed with water, acetone, and n-hexane as described for mercury. Both metals were stored till use in n-hexane.

All other chemicals were the products of *pro analysi* purity of Kemika, Zagreb, Croatia.

Soils

The samples of reference Euro-Soils[20]: Euro-Soil 2 (Rendzina, A-horizon, Peloponnesos, Greece), Euro-Soil 3 (Dystric Cambisol, A-horizon, Wales, Great Britain), Euro-Soil 4 (Orthic Luvisol, A-horizon, Normandy, France), Euro-Soil 5 (Orthic Podzol, A-horizon, Schleswig-Holstein, Germany), and Euro-Soil 6 (Orthic Luvisol, BC-horizon, Normandy, France) were obtained by courtesy of Dr. H. Muntau from the European Commission Joint Research Centre, Environment Institute, Ispra, Italy.

Soil DP was collected from a strip land excavation in Dalmatia, Croatia, and characterized by courtesy of Dr. M. Juračić in the Center for Marine Research, Ruđer Bošković Institute, Zagreb, Croatia.

Equipment

Gas Chromatographs. – Pye Unicam 204 (column 1) and Varian 3400 (column 2) equipped with ^{63}Ni electron capture detector.

Columns. – Column 1: glass, 2.5 m x 2 mm i.d., packed with 5% OV-101 on 0.16–0.20 mm Chromosorb W/DMCS/AW. Column 2: RSL-200 bonded phase fused-silica capillary column, 30 m x 0.25 mm i.d., with a 0.2 μm film thickness, supplied by Alltech-RSL, Applied Science Labs.

Operating Conditions. – Column 1: column, injector and detector temperatures 205, 250 and 300 °C; nitrogen (carrier gas) flow rate 30 mL min^{-1}. Column 2: temperature programmed from 40 to 145 °C at 50 °C min^{-1}, from 145 to 155 °C at 1 °C min^{-1}, from 155 to 225 °C at 2 °C min^{-1}, from 225 to 280 °C at 40 °C min^{-1} and finally kept at 280 °C for 15 min; injector and detector temperatures 270 and 375 °C; helium (carrier gas) linear velocity 0.5 m s^{-1}; splitless injection.

Procedures

Extraction of PCBs from Soil

Soil samples were spiked with Aroclor 1242/Aroclor 1260 standard solutions in acetone using a similar procedure as described by Fuoco and Griffiths.[19] The air-dried and sieved (<1 mm) DP soil samples (10 g) were first moistened with acetone and then mixed with 5.0 mL of Aroclor 1242/Aroclor 1260 acetone solutions containing 8 to 860 ng mL^{-1} of total PCBs (6–615 ng mL^{-1} of Aroclor 1242 and 2–245 ng mL^{-1} of Aroclor 1260). The 10-g portions of Euro-Soils, moistened with acetone, were mixed with 5.0 mL of Aroclor 1242/Aroclor 1260 acetone solutions containing 22 to 178 ng mL^{-1} of total PCBs (16–124 ng mL^{-1} of Aroclor 1242 and 6–54 ng mL^{-1} of Aroclor 1260). The samples were made homogeneous by mechanical shaking at room temperature till the solvent evaporated.

PCBs were extracted from spiked soil samples following a modification of the procedure described by Fuoco *et al*.[14,17] The 10-g soil sample was extracted five times with 15 mL of acetone/n-hexane 1:1 mixture in an ultrasonic bath: four times for 3 min and the last time for 15 min. The combined extracts were evaporated to 10 mL under a stream of nitrogen. To remove the sulphur, 0.5 g of Cu powder and 0.5 g Hg were added and the sample was stirred for two hours. The liquid phase was decanted and evaporated to dryness under a stream of nitrogen. The dry residue was redissolved in 1.0 mL of n-hexane and washed with 1.0 mL of conc. sulphuric acid by mixing the sample for 30 s. A 0.7-mL aliquot of organic layer was separated, evaporated to dryness under a stream of nitrogen and redissolved in 1.0 mL of n-hexane immediately before gas chromatographic analysis. Solvent and reagent blanks were prepared and analyzed with each new set of spiked and non-spiked soil samples.

Gas Chromatographic Analysis

PCBs were quantitated against a standard mixture consisting of Aroclor 1242 (49.30 ng mL^{-1}) and Aroclor 1260 (21.74 ng mL^{-1}) at a total concentration of 71.04 ng mL^{-1}. Calibration standard solutions were tested in an interlaboratory comparison. The individual peak method proposed by Sawyer[22] was used for quantification on the packed 5% OV-101 column. Each PCB peak was identified according to the relative retention time to 4,4'-DDE multiplied by 100 ($\mathrm{RRT_{DDE}}$). The 26 major peaks in the gas chromatogram of the standard mixture were calibrated by multiplying the Aroclor 1242 and Aroclor 1260 concentration by the mass percentage of individual peaks in the respective Aroclor, determined under standard operating conditions.[22] The total PCB concentration in a sample was calculated by summing up concentrations corresponding to individual peaks detected in that sample.

The PCB congeners in the chromatogram of the Aroclor 1242/1260 standard mixture on the capillary RSL–200 column were identified by comparison with the Aroclor chromatograms published by Ballschmiter and Zell.[10] The concentration of individual congeners in the standard was calculated by multiplying the mass fraction (%) of a given congener in Aroclor 1242 and 1260[23] by the concentration of that Aroclor and then by summing up the contributions from both Aroclors. The total PCBs in the analyzed samples were calculated by summing up the individual congener mass fractions (µg kg^{-1}) measured in that sample. Calibration lines for determination of total PCBs and selected congeners: 2,4,4'- and 2,4',5-trichlorobiphenyl (PCB 28 and 31), 2,2',3,4,4',5'- and 2,3,3',4',5,6-hexachlorobiphenyl (PCB 138 and 163), and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180) in different Euro-Soils were constructed by analysis of soils spiked with different amounts of Aroclor 1242/1260 mixture.

All results were corrected for blanks prepared by extraction of non-spiked soil samples.

RESULTS AND DISCUSSION

Table I shows the characteristics of DP and Euro-Soil samples. The concept of reference Euro-Soils was developed with the aim to harmonize the testing procedures for adsorption/desorption behaviour of new chemicals to

TABLE I

Characteristics of soil DP and Euro-Soils (ES) 2–6[a]

	DP loam	ES 2 silt loam	ES 3 loam	ES 4 silt loam	ES 5 loamy sand	ES 6 silt loam
Sand / %	49.4	13.4	46.4	4.1	81.6	1.7
Silt / % total	37.5	64.1	36.8	75.7	12.6	82.4
fine	–[b]	19.7	5.8	4.1	1.0	2.6
Clay / %	13.2	22.6	17.0	20.3	6.0	16.0
pH (in water)	7.8	8.0	5.8	7.0	4.6	8.3
SSA[b] / m^2 g^{-1}	27.6	–	–	–	–	–
Organic matter / %	5.89	6.40	6.45	2.85	15.90	0.80
C/N ratio	–	18.50	13.27	9.69	30.77	12.50
Al_2O_3 / %	–	8.66	11.92	12.07	3.85	12.64
Fe_2O_3 / %	–	1.66	4.14	2.71	< 0.05	2.83
PCB / μg kg^{-1} (d.w.)[b]		4.5	5.5	3.0	3.5	1.7
	< 1.0[c]	5.5[c]	2.9[c]	2.9[c]	3.1[c]	2.6[c]

[a] Data for Euro-Soils referring to granulometric composition, pH, organic matter, C/N ratio, Al_2O_3 and Fe_2O_3 content, and PCB mass fractions are taken from Ref. 20.

[b] SSA, specific surface area; d.w., dry weight; –, not determined.

[c] PCB mass fractions determined in this work.

be distributed on the market of the European Union.[20,21] In the first round of soil collection five surface soils (Euro-Soils 1–5) were selected. In addition, one subsoil sample (Euro-Soil 6) was collected to represent material that is very poor in organic carbon content. Euro-Soils cover a wide range of sorption-controlling properties, such as grain size distribution, pH values, organic matter content, and iron and aluminium oxides content. The reported mass fractions of total PCBs in Euro-Soils were calculated on the basis of mass fractions estimated for eight individual PCB congeners (PCB 20, PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180), assuming that these congeners accounted for 40% of all occurring congeners.[20] The highest content of total PCBs (6.5 μg kg^{-1}) was calculated for Euro-Soil 1, which appeared to experience higher PCB exposure than other soils. For our experiments, we have chosen five soils (Euro-Soils 2–6) with a lower calculated content of total PCBs (1.7–5.5 μg kg^{-1}) in order to minimize interferences of the originally present PCBs with the estimation of total PCBs added to investigated soils. Mass fractions of total PCBs in Euro-Soils 2–6 determined in this study were in good agreement with the calculated values (Table I).

The slightly alkaline DP soil consisted mainly of sand and silt and contained an average percent of organic matter. As it was collected from a regularly exploited strip land excavation, located at a considerable distance from any local pollution source, the level of contamination with persistent organochlorine compounds was expected to be very low. This was confirmed by rather low mass fractions of total PCBs determined in this soil. DP soil was also low in sulphur content, which enabled the analysis of PCBs in soil extract with and without previous extract purification for sulphur removal and to test the potential influence of extract treatment with Cu powder and Hg on the PCB extraction recoveries.

To test the dependence of extraction efficiency on the initial mass fraction of PCBs in soil, DP soil samples were spiked with increasing amounts of Aroclor 1242/Aroclor 1260 mixture. The mass fractions of total PCBs in spiked DP soil samples ranged from 4 to 430 μg kg^{-1} (3–308 μg kg^{-1} for Aroclor 1242 and 1–123 μg kg^{-1} for Aroclor 1260). Table II shows the PCB extraction recoveries, determined without treatment of soil extracts with Cu powder and Hg. In total, 75 mL of acetone/n-hexane mixture was used for multiple soil extraction. No significant improvements in extraction recoveries were found because of a larger volume of extracting solvent or because of longer sonication periods. The recoveries of total PCB congeners in Aroclor 1242, and consequently also in Aroclor 1242/1260 mixture, increased with increasing the initial mass fraction in soil. They were significantly different ($P < 0.05$) in the three listed mass fraction ranges. On the other hand, the recovery of Aroclor 1260 was not dependent on the initial content in soil with mass fractions ranging from 1 to >100 μg kg^{-1}. Aroclor 1260 (a mixture of penta- to nonachlorobiphenyls) consists of more lipophilic PCB congeners than Aroclor 1242 (a mixture of mono- to pentachlorobiphenyls) which are efficiently extracted into the organic solvent even at Aroclor 1260 levels lower than 10 μg kg^{-1}. The extraction efficiency achieved with mass fractions of total PCBs higher than 86 μg kg^{-1} was comparable to the average recovery (88±12%) of seven PCB congeners extracted by sonication with n-hexane/acetone mixture from certified sewage sludge.[18] The lowest recovery from sewage sludge, containing 79 to 313 ng g^{-1} of individual congeners, was reported for the least lipophilic trichlorobiphenyl PCB 28 (62%) while the recoveries of tetra- to heptachlorobiphenyls were almost quantitative. However, it should be noted that, even at the highest level of total PCBs (430 μg kg^{-1}), individual congener mass fractions in spiked DP soil were much lower than those in certified sewage sludge: about two times lower for PCB 28, about ten times lower for PCB 52, and about thirty times lower for PCB 138, 153, and 180. The PCB recoveries determined in extracts of DP soil treated with Cu powder and Hg were comparable to those obtained in non-

TABLE II

Accumulation efficiency of PCBs from DP soil spiked with Aroclor 1242/Aroclor 1260 mixture

Procedure	PCB mixture	Mass fraction range μg kg^{-1}	Accumulation efficiency ± S.D. %	(*N*)[a]
Extract not treated with Cu powder and Hg	Aroclor 1242	3–6	56 ±10	(10)
		15–31	64 ± 7	(10)
		62–308	83 ± 7	(15)
	Aroclor 1260	1–123	67 ± 9	(35)
	Aroclor 1242/1260	4–9	65 ± 7	(10)
		22–43	71 ± 6	(10)
		86–430	85 ± 6	(15)
Extract treated with Cu powder and Hg	Aroclor 1242	16	58 ±13	(5)
	Aroclor 1260	7	88 ± 6	(5)
	Aroclor 1242/1260	23	68 ± 9	(5)

[a] S.D., standard deviation; *N*, number of samples (in parentheses).

treated extracts (Table II), confirming that the applied procedure for sulphur removal did not affect the accumulation efficiency.

Figure 1 shows the dependence of extraction recovery of PCBs with different numbers of chlorine atoms in the molecule on their mass fraction in DP soil. Concentrations of di- (RRT_{DDE} = 21), di- and tri- (RRT_{DDE} = 28; RRT_{DDE} = 32), tetra- (RRT_{DDE} = 47), penta- (RRT_{DDE} = 78), hexa- (RRT_{DDE} = 174), and hepta- (RRT_{DDE} = 203) chlorobiphenyls in soil extracts were determined by extract analysis on the packed 5% OV-101 column.[22] The highest recoveries were obtained for the most lipophilic hexa- and heptachlorobiphenyls. However, the extraction efficiency of all PCB congener groups decreased with decreasing the mass fraction in soil, especially at levels below 1 μg kg^{-1}. The greatest recovery decrease with decreasing the mass fraction was observed for di- and trichlorobiphenyls (RRT_{DDE} = 28) and the smallest for hexa- (RRT_{DDE} = 174) and hepta- (RRT_{DDE} = 203) chlorobiphenyls.

If mass fractions of total PCBs (expressed as Aroclor 1242/1260 mixture) in DP soil were equal or higher than 10 μg kg^{-1}, the efficiency of the applied procedure was comparable to the efficiency of the complex procedure worked out for determination of total and individual PCB congeners in marine and river sediments.[14] After an ultrasonic sediment extraction by n-hexane/acetone mixture, the treatment of extracts with Cu and Hg, and the clean-up on a Florisil column, the *ortho* and non-*ortho* substituted PCB congeners were preseparated by high performance liquid chromatography (HPLC) and

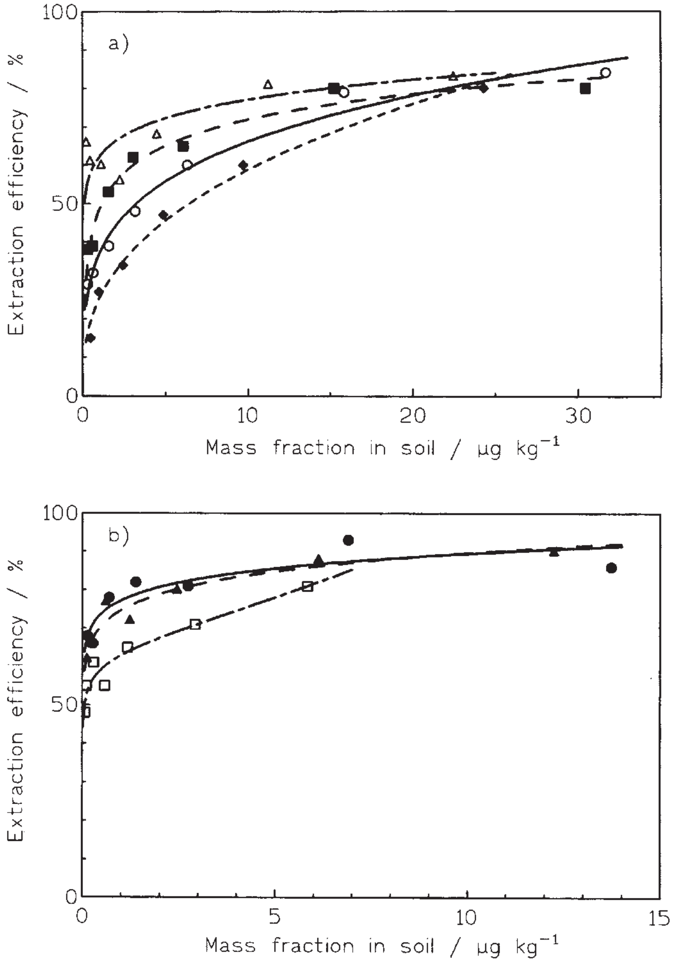

Figure 1. Dependence of extraction efficiency on the initial mass fraction of PCBs in DP soil: a) di – (○ —— RRT$_{DDE}$ = 21), di- and tri- (◆ ---- RRT$_{DDE}$ = 28; Δ – – – RRT$_{DDE}$ = 32), and tetra- (■ - - - RRT$_{DDE}$ = 47) chlorobiphenyls. b) penta- (□ – – – RRT$_{DDE}$ = 78), hexa- (▲ – – RRT$_{DDE}$ = 174), and hepta- (● —— RRT$_{DDE}$ = 203) chlorobiphenyls.

analyzed by capillary gas chromatography/ECD detection. Total PCBs were recovered from certified marine sediment samples containing 1.2 and 112 µg kg^{-1} of Aroclor 1254 in 83 and 90%, respectively. Accumulation efficiencies of individual PCBs from the same sediments, additionally spiked with 10 µg kg^{-1} of each of six non-*ortho* substituted di- to heptachlorobiphenyls, ranged from 83 to 95% with relative standard deviations of 8 to 12%. Slightly lower, but still high accumulation efficiencies of 70 to 90%, with relative standard deviations of 14 to 19%, were also achieved with 100 times lower mass fractions of individual congeners. The same method, save for the HPLC pre-separation step of specific congeners, was evaluated by spiking the real soil and sediment samples from Antarctica with a mixture of Aroclor 1221 (containing mostly mono- and dichlorobiphenyls), 1232 (containing mono-, di-, tri-, and tetrachlorobiphenyls), 1248 (containing tetra- and pentachlorobiphenyls), and 1260 (containing mostly hexa- and heptachlorobiphenyls).[6] The total PCB content was calculated by summing the individual concentrations of identified congeners. At the 0.5 ng g^{-1} PCB level, the recovery was always higher than 70% with a relative standard deviation of 30–32%. Contrary to these results, only more hydrophobic hexa- and heptachlorobiphenyls were recovered 70% from DP soil if mass fractions were lower than 1 μg kg^{-1}, while the recoveries of congeners with two to five chlorine atoms kept below 50% (Figure 1).

Differences in the accumulation efficiency of PCBs from different soils are assumed to be related not only to variations in analytical procedures but also to physical and chemical characteristics of soils and sediments. In order to evaluate the matrix effect on the efficiency of extraction procedure used in this work for trace enrichment of PCBs from soil, five well-characterized Euro-Soils (Table I), including one sub-soil, were spiked with Aroclor 1242/Aroclor 1260 mixture at mass fractions of 22 to 89 μg kg^{-1}. Chromatograms of a) non-spiked Euro-Soil 6 extract, b) extract of the same soil spiked with 89 μg kg^{-1} of Aroclor 1242/1260 mixture (62 μg kg^{-1} of Aroclor 1242 + 27 μg kg^{-1} of Aroclor 1260), and c) of 71.04 ng mL^{-1} Aroclor 1242/1260 standard mixture (49.30 ng mL^{-1} of Aroclor 1242 + 21.74 ng mL^{-1} of Aroclor 1260) are shown as examples in Figure 2. Table III shows the

TABLE III

Accumulation efficiency of PCBs from Euro-Soils (ES) 2–6 spiked with Aroclor1242/Aroclor 1260 mixture

Euro-Soil (*N*)[b]	(Accumulation efficiency ± S.D.[a]) / %		
	Aroclor 1242 15–62 μg kg^{-1}	Aroclor 1260 7–27 μg kg^{-1}	Aroclor 1242/1260 22–89 μg kg^{-1}
ES 2 (6)	50 ± 13	52 ± 16	51 ± 12
ES 3 (6)	64 ± 17	57 ± 18	62 ± 18
ES 4 (6)	41 ± 6	61 ± 11	48 ± 7
ES 5 (9)	81 ± 14	60 ± 14	74 ± 12
ES 6 (9)	75 ± 14	80 ± 8	78 ± 12

[a] S.D., standard deviation;

[b] *N*, number of samples (in parentheses).

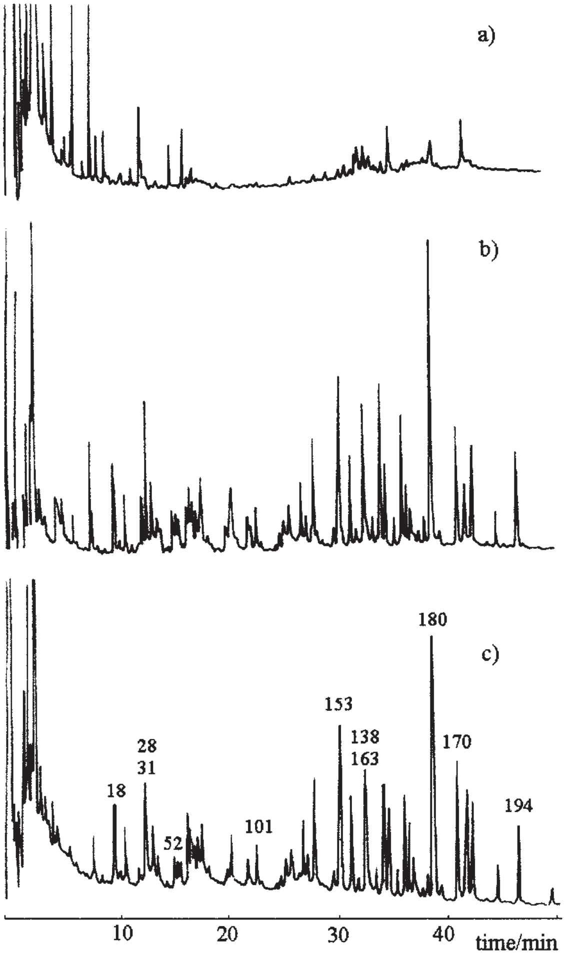

Figure 2. Gas chromatograms of a) extract of non-spiked Euro-Soil 6; b) extract of Euro-Soil 6 spiked with Aroclor 1242/1260 mixture; c) standard mixture of Aroclor 1242/Aroclor 1260. Column: RSL-200.

achieved accumulation efficiencies of total PCBs from different soils. Aroclor 1242 and Aroclor 1260 were extracted with equal efficiency from Euro-Soils 2, 3, and 6. From Euro-Soil 5, however, the extraction efficiency of Aroclor 1242 was about 20% higher and from Euro-Soil 4 lower than that of Aroclor 1260.

Although the extraction results seemed to indicate better recovery of total PCBs from Euro-Soil 3 than from Euro-Soil 2, the accumulation efficiencies from these two soils were not significantly different. Euro-Soils 2 and 3 have a comparable organic matter content and more or less balanced grain size distribution although Euro-Soil 3 reveals a slight dominance of the sand fraction. Euro-Soil 2 has a higher percent of silt and fine silt particles than Euro-Soil 3, which could increase the sorption intensity of PCBs in soil[9] and result in a less efficient accumulation of PCBs. However, when comparing the particle size distribution in Euro-Soil 2 with those of other soils, one has to bear in mind that it consists of more than 60% of calcium carbonate, which reduces the content of minerals to nearly one third of the total, and the percentage of individual grain fractions is given relating to total mineralogical components.[20] Euro-Soils 2 and 3 differ considerably in the pH value, the latter being moderately acid and the former moderately alkaline due to the high amount of free calcium carbonate.

According to its granulometric composition and organic matter content, Euro-Soil 3 was the most similar to DP soil. Accumulation efficiency of PCBs expressed as Aroclor 1242 from these two soils were comparable but the more hydrophobic PCBs in Aroclor 1260 accumulated significantly better from the slightly alkaline DP soil than from the acidic Euro-Soil 3. Compared to the neutral Euro-Soil 4, the extraction efficiency of PCBs from the DP soil was significantly higher, despite twice as high organic matter content that could promote the sorption of PCBs. PCBs in Aroclor 1260 were accumulated with equal efficiency from the acidic and neutral Euro-Soils 3 and 4, while those in Aroclor 1242 were extracted more efficiently from the former soil.

The most acidic Euro-Soil 5, sampled in a coniferous forest, is characterized by the highest organic matter content, which is considered to be one of the most important sorption promoting soil properties. A linear relationship between PCB sorption intensity and soil organic matter has been demonstrated.[8] According to Cortes *et al.*,[9] other soil properties, such as the specific surface area and amorphous iron and aluminium oxides, become decisive only in soils with little organic matter. However, a very high carbon to nitrogen (C/N) ratio, used as a measure of organic matter humification,[24] indicates that Euro-Soil 5 contains high amounts of poorly humified organic matter, probably due to the inhibited microbial activity under acidic conditions.[20,21] Consequently, PCBs in Aroclors 1242 and 1260 were extracted from Euro-Soil 5 more efficiently than from Euro-Soils 2, 3, and 4, and as efficiently as from the subsurface Euro-Soil 6 containing very little organic substance (< 1%). Euro-Soil 5 is also characterized by a high sand fraction and low content of aluminium and iron oxides, which could decrease the PCB sorption intensity. Besides, it should be pointed out that the sorption intensity depends not only on the amount but also on the type of organic matter. Organic matter composition in an explicitly acidic soil is quite likely to be different from that in slightly acidic, neutral, or alkaline soils.

The highest accumulation efficiency was achieved by the extraction of PCBs from Euro-Soil 6, indicating the expected low sorption intensity in a soil poor with organic matter. Subsoil 6 has the highest content of total silt of all the studied Euro-Soils, but it is composed mainly of coarse particles (62.5%) and the fraction of fine silt particles is small (2.6%).

Figure 3 shows the calibration lines for determination of total PCBs in Euro-Soils 2–6. Correlation coefficient r was 0.769, 0.929, 0.985, 0.974, and 0.992 in ES2, ES3, ES4, ES5, and ES6, respectively. The extracts of soils spiked with Aroclor 1242/Aroclor 1260 mixture were analyzed by gas chromatography using the capillary column 2. Slopes of the calibration lines for the PCB determination in different soils were different and became steeper in the sequence Euro-Soil $2 < 3 < 4 < 5 < 6$. The highest calibration curve slope coefficients were obtained for determination of Aroclor 1242/Aroclor 1260 mixture ($\alpha = 0.023$) in Euro-Soil 6. Statistically significant differences ($P < 0.05$) in slope coefficients were determined for the calibration lines for determination of total PCBs in Euro-Soils 5 and 6, and 3 and 4. The difference was not statistically significant between the calibration curve slopes for determination of PCBs in soils 4 and 5, and 2 and 3. Similar differences in calibration curve slopes were obtained by determination of selected PCB congeners. Figure 4 shows an example with the calibration curves for determination of PCB congeners with three (PCB 28 + PCB 31), six (PCB 138 + PCB 163), and seven (PCB 180) chlorine atoms in the molecule. PCB conge-

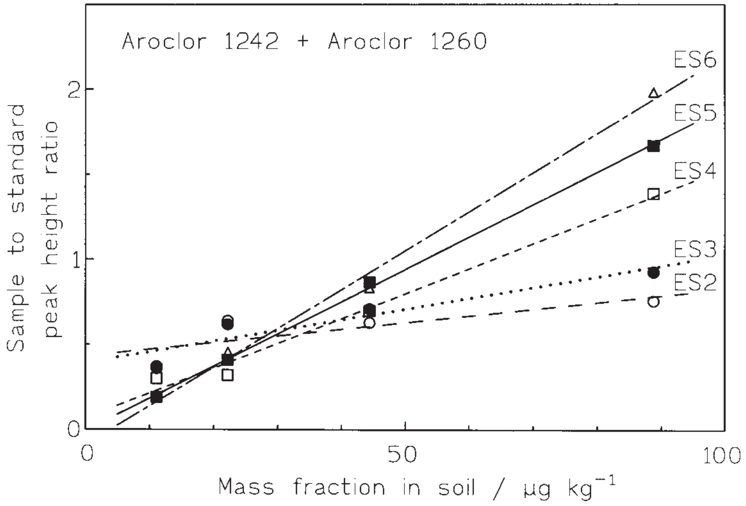

Figure 3. Calibration lines for determination of total PCBs (as Aroclor 1242/Aroclor 1260 mixture) in Euro-Soils (ES) 2–6. Standard: Aroclor 1242 (49.30 ng mL^{-1})/Aroclor 1260 (21.74 ng mL^{-1}) mixture.

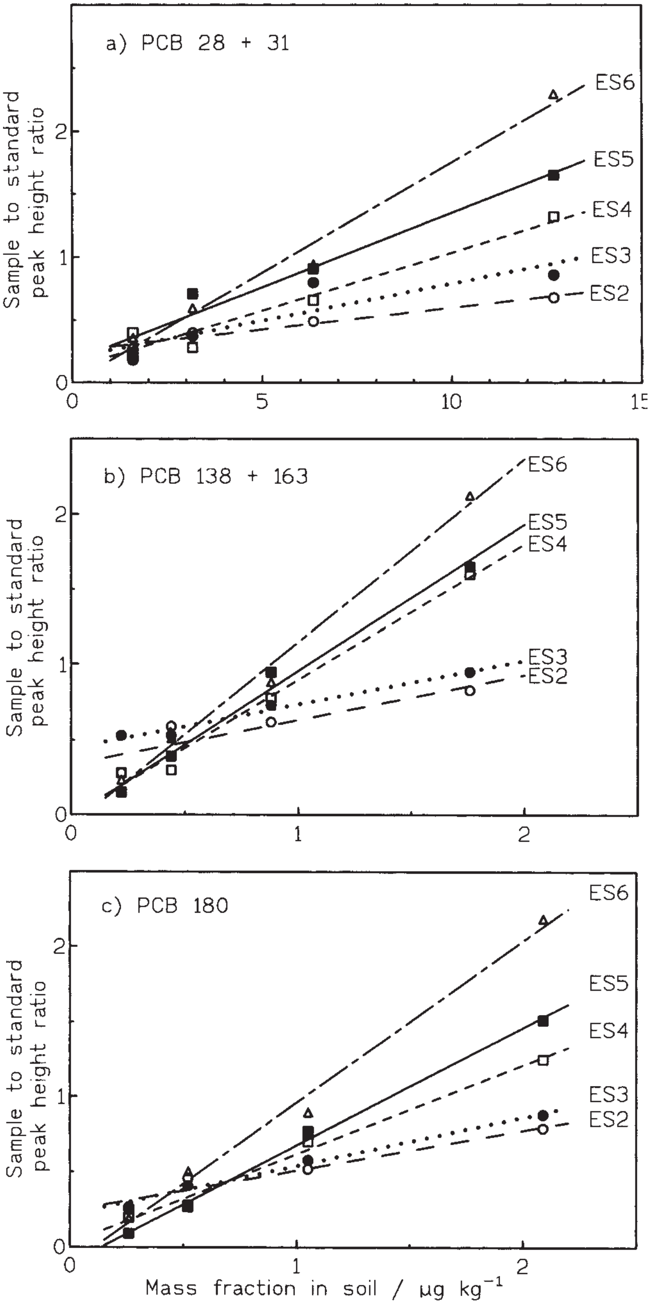

Figure 4. Calibration lines for determination of selected PCB congeners in Euro-Soils (ES) 2–6: a) sum of the PCB 28 and PCB 31; b) sum of PCB 138 and PCB 163; c) PCB 180.

ners 28 and 31 are presented as a sum because of incomplete separation of the corresponding peaks under the applied gas chromatographic conditions. Similarly, PCB congener 138 cannot be separated on the applied gas chro-

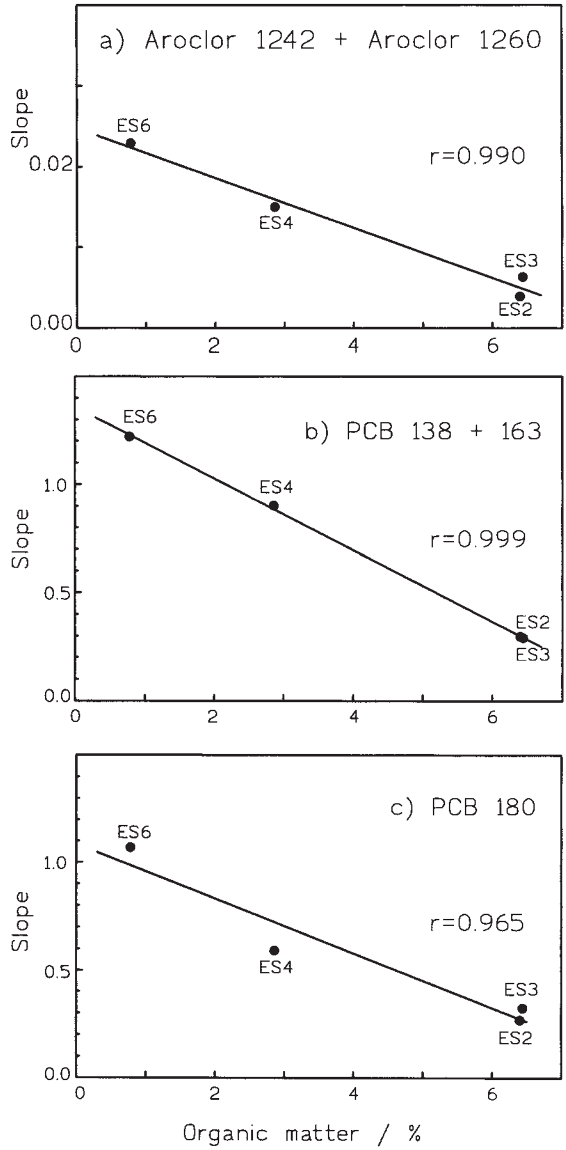

Figure 5. Correlation of calibration line slopes for determination of PCBs in Euro-Soils 2, 3, 4, and 6 *vs.* soil organic matter for: a) total PCBs (as Aroclor 1242/1260 mixture); b) PCB congeners 138 + 163; c) PCB 180.

matographic column from congener 163.[12] Correlation coefficients ranged from 0.879 to 0.982 for PCB 28+31, from 0.818 to 0.990 for PCB 138+163, and from 0.913 to 0.991 for PCB 180.

The calibration line slope coefficients were correlated with different soil properties. Slope coefficients of the calibration curves for determination of either total PCBs as an Aroclor 1242/Aroclor 1260 mixture or selected congeners in Euro-Soils 2, 3, 4, and 6 followed the changes in the soil organic matter content (Figure 5). The slopes increased with the decrease in the percentage of organic matter. An exception were the calibration curves for determination of total or single PCBs in Euro-Soil 5, from which those compounds were efficiently extracted despite the high soil organic matter fraction. Slopes of the calibration curves for determination of PCBs in that soil were similar to those for PCB determination in Euro-Soils 4 and 6 having a low organic matter content.

No correlation was found between the calibration line slope coefficients and pedological characteristics such as the content of total silt, clay, and sand as well as the content of aluminium and iron oxides. However, the linear regression of calibration line slopes and the content of fine silt particles in soil indicated a positive correlation, but it was not statistically significant.

The results presented should be regarded as an indication of matrix characteristics that could possibly influence the efficiency of PCB trace enrichment, and affect the accuracy of PCB determination in different soils by the applied sonicated extraction procedure. The results emphasize the necessity to test the extraction recoveries from each investigated soil type at different PCB levels or to apply a standard-addition method. The results should also stimulate further research into the relationship between the pedological characteristics and the extraction efficiency of PCBs from soils using different extraction techniques and correlating the recoveries with the PCB sorption behaviour in investigated soils.

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SAŽETAK

Akumuliranje malih količina poliklorbifenila iz tla: djelotvornost ultrazvučne ekstrakcije sa smjesom aceton/n-heksan iz različitih tipova tla

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Ispitana je djelotvornost i ponovljivost analitičkog postupka za određivanje tragova poliklorbifenila (PCB) u tlu/sedimentu analizom tala različitih sorpcijskih svojstava. PCB su akumulirani iz tla višekratnom ekstrakcijom smjesom otapala aceton/n-heksan 1:1. Ekstrakti su čišćeni izmućkavanjem bakrenim prahom, živom i sumpornom kiselinom te analizirani plinskom kromatografijom. Djelotvornost ekstrakcije PCB iz tla, u koje je dodano 4–430 μg kg^{-1} smjese Aroclora1242 i Aroclora 1260, ovisila je o masenom udjelu PCB u tlu. Utjecaj svojstava tla na djelotvornost ekstrakcije ispitan je analizom PCB dodanih u pet Europskih referentnih tala različitih sadržaja organske tvari, granulometrijskog i mineralnog sastava, vrijednosti pH i sadržaja željezova i aluminijeva oksida. U četiri tla uočena je linearna korelacija između nagiba baždarnih pravaca za određivanje PCB i sadržaja organske tvari u tlu. Izuzetak je bilo najkiselije tlo s najviše (slabo humificirane) organske tvari. Dobivena je pozitivna, ali ne i statistički značajna korelacija nagiba baždarnih pravaca i sadržaja finih čestica silta u tlu.