Environ. Sci. Technol. **1999**, *33,* 2193−2203

Determining PCB Sorption/Desorption Behavior on Sediments Using Selective Supercritical Fluid Extraction. 1. Desorption from Historically Contaminated Samples

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Supercritical fluid extraction (SFE) conditions using pure CO_2 from 40 to 150 °C were developed that allow sequential extraction of PCBs associated with “rapidly desorbing, moderately, slowly, and very slowly desorbing” sites on historically contaminated sediments and soil. Five samples with individual PCB concentrations ranging from a few to ∼100 000 ng/g all showed PCBs associated with each type of site, but the fraction of PCBs associated with rapidly desorbing or slowly desorbing sites varied greatly from sample to sample. Although some small differences in the desorption behavior of individual PCBs was observed from a particular sample, the differences among samples were much greater demonstrating that the sample matrix and not the PCB identity was most important in controlling desorption behavior. When all five samples were compared, simple considerations concerning sample particle size, water content, organic content, and PCB concentration could not predict desorption behavior, demonstrating that PCB desorption processes depend on multiple sample characteristics. Comparison of the quantity vs distribution of PCBs on the fast to very slow sites indicates that association with slowly desorbing sites is not limited by the number of sites, but rather that PCBs on historically contaminated samples tend to distribute among the various sites available.

Introduction

Determining processes that govern the slow sorption and desorption of organic chemicals to and from natural matrixes such as sediments and soils is important to understanding the potential biological effects and ultimate fate of organic pollutants in the environment (*1*−*3*). Pignatello and Xing (*1*) concluded that sorption/desorption behavior of organic pollutants is often not explained by their distribution coefficients (K_d values) between the solid matrix and the water phase, since many contaminants sorb very slowly to natural particles. Ball and Roberts (*4*) demonstrated that sorption of halogenated organic chemicals to aquifer material required tens to hundreds of days to reach equilibrium. With an intraparticle diffusion model, they estimated the pore water diffusion coefficients to be 100−1000 times lower than the bulk water diffusion, and the rate of uptake was slowest for higher molecular contaminants (*5*). It was also concluded that the results implied slow desorption of sorbed molecules. Pavlostathis and Mathavan (*6*) showed that volatile organic compounds (VOCs) from field-contaminated soils and clays were desorbed in a biphasic way with a rapid initial release during the first 24 h followed by a slow-releasing phase. Between 48 and 94% of the contaminants could not be desorbed by water during the 7-day experiment. They also demonstrated that the longer a spiked organic chemical was allowed to interact with the matrix, the higher the fraction which was nondesorbable became. Similar experiments for aged polycyclic aromatic hydrocarbons (PAHs) in sediment showed that only a small portion of the total PAHs present were available for equilibrium partitioning and, consequently, pore water concentrations were lower than predicted by the equilibrium model (*7, 8*). The use of equilibrium sorption and spiked solutes to explain PAH sediment trapping and bioavailability has been shown to be invalid (*9, 10*). In conformance with these data, Hatzinger and Alexander (*11*) showed that aging makes contaminants (phenanthrene, 4-nitrophenol) less available, thus decreasing their biodegradability and extractability. Column experiments have demonstrated that the mobility of fresh pesticides in soil is greater than for aged pesticides and that intraparticular diffusion mechanisms are responsible for the slow sorption/desorption behavior (*12*).

SFE has recently become accepted as a replacement for classical extraction methods (e.g., Soxhlet extraction) for the extraction of PCBs from soil and sediment (*13*−*15*). As SFE matured, it was discovered that results obtained from recently spiked samples could not be used to predict the behavior of aged samples, especially not for heterogeneous environmental matrixes (*16*). Freshly added pollutants can often be extracted with supercritical carbon dioxide in a few minutes using relatively mild conditions, whereas quantitative extraction of aged pollutants often requires high temperatures (*17, 18*), addition of a modifier to the supercritical fluid (*19*), or a combination of both (*20*). Increased SFE temperature and modifiers have been shown to act in different ways. While recoveries increase with temperature independent of the matrix investigated, the choice of modifier is highly matrix dependent (*20, 21*). It is believed that temperature increases the rate of sorption/desorption kinetics in general, whereas modifiers break analyte/matrix interactions more specifically. This leads to the conclusion that a single pollutant can be bound in many different ways within a single matrix (“rapidly desorbing” or “fast” sites and “slowly desorbing” or “slow” sites), which is further supported by the kinetic profiles published for PAHs extracted from different environmental solids (*16*).

Two major diffusion models are used to explain the mechanisms of slow sorption of organic chemicals (*1*): diffusion through natural organic matter and diffusion in pore water with pore wall sorption. Interestingly, the kinetic models proposed to explain sorption/desorption processes of organic pollutants closely resemble models that have been developed to describe SFE extraction rates during the past few years (*22*−*27*). More recently, such models were used in

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10.1021/es981071p CCC: $18.00

TABLE 1. Sediment and Soil Characteristics

sample	source	particle size	water content (wt %)[a]	organic matter content (wt %)[a]	typical PCB concn[b] (ng/g)
NIST 1939	river sediment	<45 μm[c]	2.5 (2.7)	12	100−4000
NIST 1944	marine sediment	75−250 μm[d]	1.4	9.2	25−80
CRM 536	harbor sediment	75−1000[e]	2.6 (1.3)	15	13−50
CRM 481	industrial soil	<90 μm[c]	2.3 (1.2−3.0)	12.5	3000−137 000
Lake Järnsjön	freshwater sediment	75−500 μm[f]	0.6	3.3	2−50

[a] Determined using thermal gravimetric analysis and includes volatile organic content lost under argon from 110 to 650 °C and fixed or combustible organic matter determined upon introducing air at 650 °C. Water content values in parentheses are those determined by the certifying agency. [b] Approximate concentration range of individual major PCB congeners determined in this study. [c] Particle size reported by supplier. [d] 90 wt % was in this size range as determined by sieving. 10 wt % was <75 μm. [e] 80 wt % was in this size range as determined by sieving. 10 wt % was >1000 μm, and 10 wt % was <75 μm. [f] 95 wt % was in this size range as determined by sieving. 4 wt % was >1000 μm, and 1 wt % was <75 μm.

an attempt to explain differences in extraction kinetics between spiked and aged contaminants such as PAHs and polychlorinated biphenyls (PCBs) in soils and sediments (*28*). Similar to the models being developed to explain aging processes of organic pollutants in soils and sediments (*1*), models explaining the slow desorption of analytes during SFE include diffusion through organic layers and porous structures of the matrix investigated. This has led to the idea that SFE behavior using selective extraction conditions might be used to describe transport and bioavailability of organic pollutants in real world matrixes (*29−31*). Two of these initial SFE studies (*29, 30*) investigated the desorption behavior of phenanthrene to sediments using supercritical CO_2 and methanol-modified CO_2 and were part of an extensive series of papers (*32−39*) which concluded that "the slow rates of sorption of hydrophobic organic contaminants often observed for soils and sediments is likely attributable to processes other than solute diffusion to 'sorption sites' on internal mineral surfaces" (*36*). A "distributed reactivity model" was postulated that relates overall sorption/desorption behavior by heterogeneous solids to different mechanisms experienced by individual molecules (*36*).

Previous reports have demonstrated that pure CO_2 at elevated temperatures can quantitatively extract PCBs from soils and sediments (*14, 40*). Such extracts are much cleaner than those generated using organic solvents or CO_2-containing organic modifiers. Accordingly, the use of pure CO_2 does not appear to affect the soil/sediment bulk organic content. The present studies report the use of sequentially stronger (higher pressure and temperature) SFE conditions with pure CO_2 to determine the relative "tightness" of PCB binding to real-world soil and sediment samples. In Part 1, the sequential extraction of rapidly desorbing and slowly desorbing PCBs is investigated on historically aged soils and sediments. In Part 2, SFE kinetic models are extended to describe the effects of the temperature rise during the extraction process. Note that for simplicity the word "site" has been used in its general sense throughout this paper and is not meant to imply specific absorption or adsorption processes.

Materials and Methods

Samples. Five PCB-containing samples with different origins and levels of contamination were used in this study (Table 1). All samples were collected from areas historically contaminated with PCBs. Four samples were certified for PCB concentrations and included industrial soil CRM 481 (Community Bureau of References [BCR], Brussels, Belgium), river sediment SRM 1939 (National Institute of Standards and Technology [NIST], Gaithersburg, MD), marine sediment SRM 1944 (NIST), and harbor sediment CRM 536 (BCR). CRM 536 is normally available as particles <105 μm prepared by jet milling. In this study, samples of the original sediment (80 wt % between 75 and 1000 μm, 10 wt % >1000 μm, and 10 wt % <75 μm), 1000−3000 μm particles (collected by sieving), and sediment jet milled to <63 μm were obtained. One additional freshwater sediment was collected from Lake Järnsjön, Sweden. All pollutants present in these samples were environmentally aged (not spiked). All materials were used as received. Typical preparation by the certifying agency was air-drying followed by sieving. A summary of the sample characteristics is given in Table 1. Additional pollutants reported by NIST include PAHs (∼0.3−9 μg/g) for SRM 1944 and PAHs (∼0.05−0.2 μg/g) and chlorinated pesticides (∼0.1−0.5 μg/g) for SRM 1939.

Supercritical Fluid Extraction. All extractions were performed with an ISCO model 260D syringe pump (ISCO, Lincoln, NE) filled with SFC-grade CO_2 (Scott Specialty Gases, Plumsteadville, PA) and an ISCO model SFX 2-10 extractor with 10-mL extraction cells. For SRM 1939 and CRM 481 ∼0.5-g samples were mixed 1:1 (v:v) with anhydrous Na_2SO_4, the sample placed at the outlet (bottom) end of the cell, and the cell dead volume filled with Na_2SO_4. For Lake Järnsjön, SRM 1944, and CRM 536, 5 g of the sample was mixed with ∼2 g of copper to reduce the amount of elemental sulfur extracted, and the dead volume was filled with Na_2SO_4. Glass filter papers were placed at each end inside the extraction cell to prevent small particles from reaching the restrictor. After the extraction cell was placed in the extractor, the cell was immediately pressurized (requiring ∼10 s), the outlet valve was opened, and the analytes were collected in 22-mL vials containing 10 mL of acetone (Fisher Optima grade) (*40*). Flow rates were controlled using a variable coaxial restrictor (ISCO) heated to 80 °C.

Kinetic profiles from the different soils and sediments were obtained using four sequentially stronger SFE conditions, each for 1 h for a total of 4 h. SFE conditions were (first hour) 120 bar, 40 °C; (second hour) 400 bar, 40 °C; (third hour) 400 bar, 100 °C; and (fourth hour) 400 bar, 150 °C. The flow rates during the four different time intervals were ∼0.8 mL/min during the first hour and 2.0 mL/min for the other three extraction times. Eight collection vials were used every hour and changed after 5, 10, 15, 20, 30, 40, 50, and 60 min.

The pressure change from 120 to 400 bar (between hour 1 and 2) required only a few seconds with the ISCO pump and, therefore, did not affect the results. However, the changes in temperature between the other extraction times required more time (∼7 min to raise the temperature from 40 to 100 °C and ∼8 min to raise the temperature from 100 to 150 °C). During the heat-up times required, the CO_2 inlet was closed so that no new CO_2 entered the system extractor, resulting in a drop in pressure from the fluid exiting the restrictor and a reduction in extraction rate during the heat-up period. To determine the effect of the heat-up time on the extraction rates, a separate fraction was collected during each heat-up period. In every case, the total amount of PCBs collected during the heat-up periods was less than 2%, which thus could be ignored.

After the extractions were complete, all fractions collected were treated with copper overnight in order to eliminate sulfur interferences in the final GC analysis (*41*), and internal standard hexachlorobenzene (HCB) was added to the samples. If necessary for reliable quantitation in the GC analysis step, samples were concentrated under a gentle stream of clean nitrogen down to a minimum of 200 μL.

Since the collection and analysis of 32 individual fractions for each sample's kinetic profile might introduce error into the quantitative results, the PCB extraction efficiencies for the SFE procedures were verified using several approaches. First, the total amounts of each PCB congener extracted for the kinetic profile experiments were added and compared to the certified concentrations (for the NIST and BCR reference soils and sediments). Second, fresh samples (in quadruplicate for each soil or sediment) were extracted using the strongest SFE condition (400 bar, 150 °C for 1 h) while collecting only one fraction for each sample. These values were also compared to the certified values.

Finally, the ability of the sequential SFE procedure to extract PCBs from each soil and sediment was verified by taking each residue after SFE, extracting for 20 h in a Soxhlet apparatus with 1:1 acetone/*n*-hexane, cleaning over acid silica, concentrating, and analyzing as before.

The above procedures verified the ability at the chosen SFE conditions with pure CO_2 to quantitatively extract the PCBs from each sample. One additional study was performed to verify the shape of the extraction profiles. Because of the potential error in adding the eight fractions for each time period, samples were also extracted under identical conditions except that only one fraction was collected for a 60-min time period. For the 1939 sample, this procedure was repeated for each of the four time periods. For the remaining samples, this procedure was repeated for the first time period. In all cases, the results from summing the eight fractions from a particular 1-h extraction compared well with the result of collecting only one fraction from a duplicate extraction. This demonstrates that no significant error was introduced by collecting and analyzing several fractions for each extraction condition.

Gas Chromatographic Analysis. An HP model 5890 series II GC equipped with a model 7673A auto-injector (Hewlett-Packard, Palto Alto, CA) was used for analyzing the extracted fractions. Detection was with a ^{63}Ni electron capture detector (ECD) with pure and dry nitrogen as the makeup gas (60 mL/min). Because of the large number of fractions to analyze, a rapid separation method was developed that used a split injection (injector held at 300 °C, split ratio ~1:30) with a 25 m × 0.22 mm, 0.10 μm 1,7-dicarba-*closo*-dodecarborane dimethylsiloxane HT-5 column (Scientific Glass Engineering) with hydrogen as the carrier gas at a constant head pressure of 1.52 bar (*42, 43*). A 1-μL sample was injected at an oven temperature of 100 °C (held for 1 min), followed by temperature programming to 280 °C with a rate of 15 °C/min and a hold for 2 min. Total run time was 15 min. Quantitations were based on an eight-point calibration curve utilizing the power fit calibration routine (HP Chem 3365 software). Calibration of individual congeners was made in the concentration range of 1.7−1700 pg/μL.

Because of the potential for coeluting PCB congeners and other interfering species, selected extracts from each sample were also analyzed using a dual-column high-resolution method (*13*). Samples were injected on-column on two parallel columns: a 60 m × 0.25 mm, 0.25 μm 50% diphenyldimethylsiloxane DB-17 column (J&W Scientific) and a 25m × 0.25 mm, 0.25 μm 5% diphenyldimethylsiloxane SIL-8 (Chrompack) in series with 25 m × 0.22 mm, 0.10 μm 1,7-dicarba-*closo*-dodecarborane dimethylsiloxane HT-5 column (Scientific Glass Engineering). The two columns were connected in parallel by means of a quick-seal glass "T" connected to a deactivated retention gap (2 m × 0.53 mm fused silica). Temperature programming was as follows: 90 °C for 2 min, then increased to 170 °C at a rate of 20 °C/min, isothermal at 170 °C for 7.5 min, then increased at a rate of 3 °C/min to 275 °C, and held for 10 min (total time 58.5 min). Quantitation was based on a seven-point multi-level calibration curve in the concentration interval 1.7−573 pg/μL for the individual PCB congeners and with PCB-35 and PCB-169 as internal standards. Comparison of the dual-column results with the single-column method confirmed that the single-column method could be used to determine the concentrations of 10 different congeners (28, 52, 101, 105, 118, 138, 149, 153, 170, and 180) without significant interference from other PCB congeners. However, not all of these congeners could be determined for every sample because of other interfering peaks or because of low concentrations in the kinetic profile extracts. Therefore, only PCB congeners that were demonstrated by the dual-column technique to be free from significant interferences using the single-column method are discussed.

Results and Discussion

Verification of SFE Recoveries. SFE with high temperatures using pure CO_2 has previously been demonstrated to give good recoveries of PCBs and related compounds (e.g., PAHs) from soils and sediments as compared to conventional extraction methods (*13, 40*). In the present study, several approaches were used to verify the ability of SFE to yield complete removal of the PCBs. First, quadruplicate extractions with the most rigorous condition (1 h at 150 °C and 400 bar) typically yielded 75−110% of the certified values for individual PCB congeners for the SRMs 1944 and 1939 and the CRMs 536 and 481 (Table 2). Since some differences between the certified values and our quadruplicate 1-h extractions would be expected based on differing GC conditions and calibration procedures, the agreement among the certified values and those determined by the quadruplicate SFE extractions is quite good.

The second approach to verifying extraction efficiencies was to compare the extraction efficiencies using the four-step SFE procedure (discussed above) for each PCB congener by adding the 32 fractions from the extraction of each sample. Although errors in adding so many fractions would be expected to be large, agreement with the certified values is surprisingly good (Table 2).

The final verification of extraction efficiencies was to extract each sample residue (after the four-step SFE extractions) in a Soxhlet apparatus as described above. For every sample studied, the Soxhlet extracts of the SFE residues normally contained <2−4% of the total mass of each PCB congener, thus demonstrating that the pure CO_2 extractions used for the four-step selective extractions effectively removed the PCB molecules present on each sample (Table 2). Since Soxhlet extraction of the SFE residues demonstrated that the SFE procedure efficiently extracted all PCBs, this definition of 100% recovery was used for Figures 1−6.

Selective SFE Determination of PCB Desorption Profiles. Four sequentially stronger extraction conditions were selected based on initial extractions of SRM 1939. Each sequential condition increased the PCB solubilities in the supercritical CO_2. Although little data are in the literature describing PCB solubilities in supercritical CO_2, a recent report shows that the solubility of 2,2′,3,3′,4,4′-hexachlorobiphenyl is ~0.2 mg/g of CO_2 at 120 bar and 40 °C and that it increases to 2.7 mg/g at 400 bar and 40 °C (i.e., similar to the first two conditions used in the present work, respectively). Increasing the temperature at a constant pressure of 400 bar to 140 °C (similar to the 400 bar and 150 °C used for the most rigorous

TABLE 2. SFE Extraction Efficiencies of Individual PCB Congeners

PCB congener	certified concn (ng/g)[a]	% recovery		HRGC concn (ng/g) (%RSD)[d]
		profile[b]	residue[c]	
		CRM 536		
28	44.4 ± 6.3	137	98	46.8 (2.6)
52	38.4 ± 7.1	94	96	34.5 (0.9)
101	43.7[e] ± 6.2	145	98	37.9 (2.4)
118	27.6 ± 4.0	116	98	25.7 (2.6)
138	26.8 ± 3.9	158	98	31.6 (2.5)
149	48.8 ± 5.9	84	97	43.4 (1.2)
153	50.3 ± 5.7	111	98	45.7 (1.9)
170	13.4 ± 1.5	149	98	10.9 (1.5)
180	22.4 ± 3.6	155	97	18.9 (5.3)
		SRM 1944		
28	75.8 ± 2.2	108	99	69.5 (5.5)
52	78.9 ± 1.7	69	99	52.2 (6.0)
101	73.3 ± 1.5	83	100	44.0 (4.5)
105	22.4 ± 0.8	91	99	18.7 (2.8)
118	57.6 ± 1.3	56	99	41.8 (3.7)
138	59.7 ± 1.5	73	99	38.8 (3.2)
149	49.1 ± 1.7	69	99	36.2 (4.4)
153	73.5 ± 1.5	44	99	44.2 (4.9)
		CRM 481		
52	2900 ± 440[e]	98	96	1670 (2.3)
101	37000 ± 4800	92	96	27200 (2.9)
118	9400 ± 1100	125	98	7310 (1.7)
138	92000[e] ± 14000	96	96	71100 (2.3)
149	97000 ± 9700	76	94	72200 (1.7)
153	137000 ± 12000	91	96	107000 (2.6)
180	124000 ± 11000	89	96	99100 (1.5)
		SRM 1939 [f]		
52	4320 ± 130	70	98	2970 (3.3)
101	na		99	448 (2.5)
138	258 ± 7	119	99	216 (1.8)
149	427 ± 17	104	98	349 (2.9)
153	297 ± 19	90	99	228 (3.5)
		Lake Järnsjön[g]		
28		124	98	42 (4)
52		124	93	11 (3)
105		126	92	2.1 (6)
118		103	96	2.8 (12)
138		139	94	1.3 (13)

[a] Concentration reported by the certifying agency. [b] % recovery compared to the certified value based on adding the total amount of each PCB extracted in the 32 fractions from the four-step selective SFE procedure. [c] % recovery determined by Soxhlet extraction of the residue after SFE extraction. [d] Concentration determined based on a 1-h SFE extraction at 150 °C and 400 bar and using the high-resolution GC method described in the Experimental Section. [e] Indicative value only. Not certified by reporting agency. [f] New certified values provided by NIST to be released in 1998. Congeners for which no values are reported by NIST are listed as na. [g] No certified values were available. Concentrations and recoveries were based on a 1-h SFE extraction at 150 °C and 400 bar and using the high-resolution GC method described in the Experimental Section.

extraction) increases the solubility to 64 mg/g (*44*). Since the extraction of even the most highly contaminated sample (CRM 481) yields a maximum mass of <0.1 mg of any PCB and since ~35 g of CO_2 was used for the mildest condition (120 bar and 40 °C), it is clear that all of the extractions were performed below the saturation limit of PCBs in CO_2.

In addition to increasing solubilities, elevating the temperature has been used to dramatically increase recoveries of PCBs from sediments, and it has been demonstrated that higher temperatures accelerate the extraction rate (possibly by helping the analytes overcome the energy barrier of the desorption step) (*14, 17, 40, 44*). Whether the increased recoveries are a result of increased solubilities or faster desorption kinetics (as discussed below), it is clear that increasing the SFE temperature dramatically changes the ability of pure CO_2 to extract PCBs from soils and sediments.

Typical extraction profiles for CRM 536 are plotted as mass extracted (per gram of sample) versus time (Figure 1A) and as the percent of each congener extracted versus time (Figure 1B). Each sequentially stronger extraction condition initially causes a rapid removal of PCBs, followed by a declining rate of extraction toward the end of each 60-min period. At the beginning of the next stronger extraction condition (i.e., at 60, 120, and 180 min), the extraction rates increase rapidly and then again slow toward the end. Thus, the selective SFE steps sequentially extract PCB molecules that are increasingly more strongly bound to the sediment matrix. For the sake of the following discussion, the four fractions will be labeled fast (or rapidly desorbing) (those molecules extracting at the mildest condition, i.e., from 0 to 60 min), moderate (those extracting at 60−120 min), slow (those extracting from 120 to 180 min), and very slow (or very slowly desorbing) (those requiring the strongest extraction conditions, i.e., from 180 to 240 min).

Since the concentrations of individual PCBs on each sample vary substantially (Table 1), the extraction profiles from the remaining samples are plotted as percent removal versus time rather than as mass extracted per time (Figures 1−6). Two of the samples, SRM 1944 and CRM 481, show ~70−85% of the molecules as rapidly desorbing (Figures 2 and 3). However, when the percent extracted scale is expanded (Figures 2B and 3B), the plots clearly show the distinct presence of the three more slowly desorbing fractions. In contrast, the remaining two samples, SRM 1939 and the Lake Järnsjön sediment, show a very high proportion of the more slowly desorbing fractions (Figures 4 and 5).

As shown in Figures 1−5, every congener from every sample shows at least three distinct extraction behaviors when subjected to the last three extraction conditions (i.e., the 400 bar extractions occurring between 60 and 240 min using sequential increases in temperature from 40 to 100 to 150 °C). Although SRM 1939 shows little change in extraction rates between the first two conditions (0−20 min), the other four samples also show distinct breaks in the extraction profiles when the extraction condition is increased from the mildest condition of 40 °C and 120 bar (0−60 min) to 40 °C and 400 bar (60−120 min). On the basis of the results shown in Figures 1−5, each congener on each sample shows a range in extraction behavior from fast (those molecules which extract at the mildest condition, i.e., from 0 to 60 min) to very slow (those molecules that do not extract until the most rigorous conditions are applied, i.e., from 180 to 240 min). These results are consistent with earlier reports showing low recoveries of PAHs, PCBs, chlorinated dioxins, and pesticides from soils and sediments using SFE conditions with pure CO_2 similar to our second most mild condition (400 bar, 40 °C) and high recoveries when the same samples are extracted at conditions similar to our most rigorous condition (400 bar, 150 °C) (*14, 17, 18, 20, 28, 40*).

The differences in behavior of the five soils and sediments are summarized in Table 3. In general, the marine sediment (SRM 1944) and the industrial soil (CRM 481) had the highest fraction of PCBs that were rapidly desorbed from their parent matrixes. For example, an average of 82 and 71% of each of the congeners were extracted at the mildest condition from SRM 1944 and CRM 481, respectively. The remaining ~20−30% of the molecules were distributed over increasing slow sites as indicated by their approximately equal distribution in the extracts using the three strongest conditions (Table 3).

In contrast, the river sediment (SRM 1939) and Lake Järnsjön sediment showed much higher proportions of slowly desorbing PCBs. For these sediments only ~30−50% of each congener was extracted with the mildest condition, and the remaining ~50−70% of the molecules were more strongly associated with the sample matrix, i.e., they were not extracted until the two most rigorous SFE conditions were used.

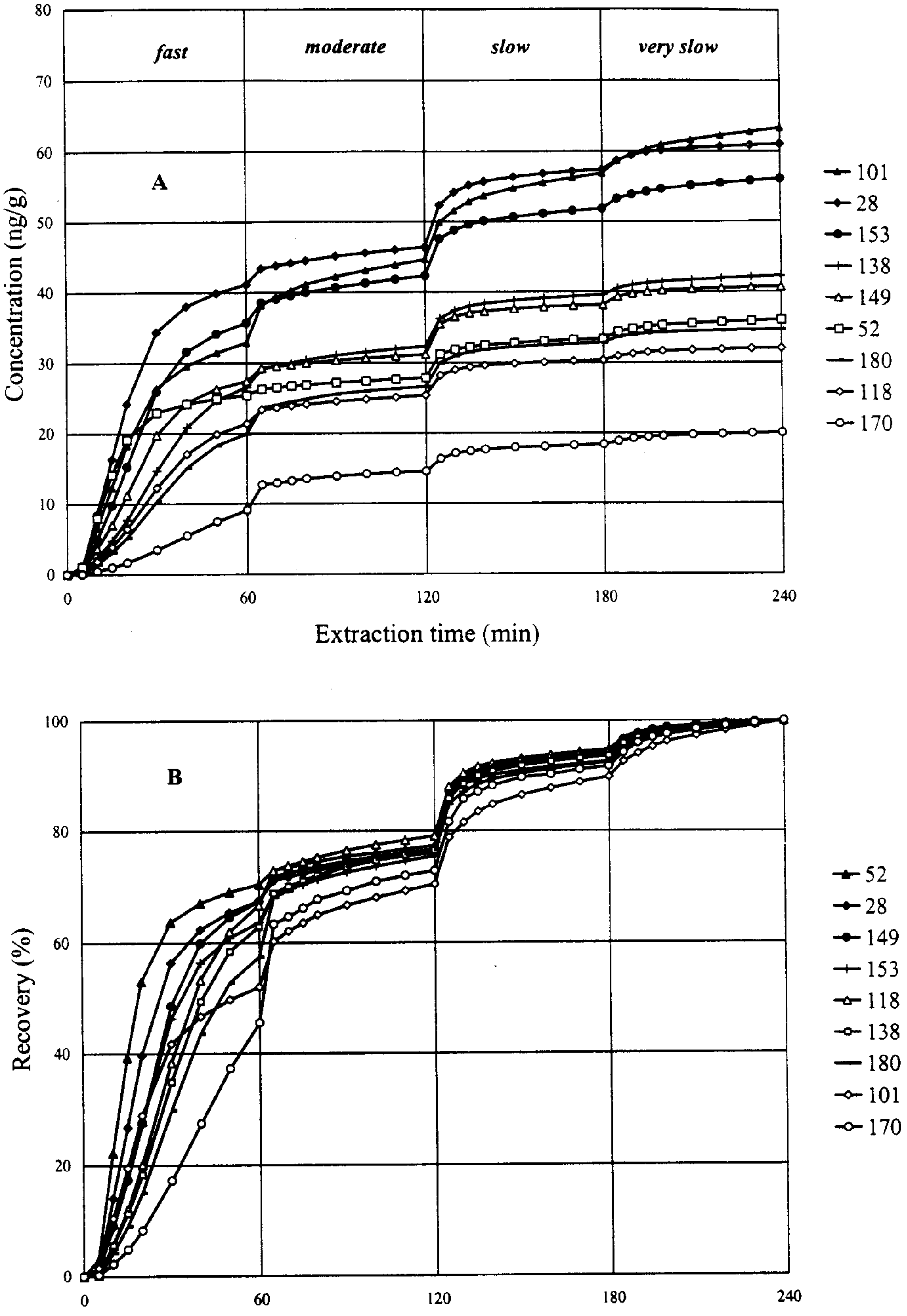

FIGURE 1. Selective SFE desorption behavior for representative PCB congeners from the historically contaminated CRM 536 sediment. Plot A shows the cumulative mass of each PCB congener extracted per gram of sample. Plot B shows the cumulative percent of each congener extracted (vs the total mass of that congener present on the original sample). Desorption behavior is characterized by "fast" (those molecules that are extracted at the mildest SFE condition, i.e., 0−60 min) to "very slow" (those molecules that require the most rigorous SFE condition, i.e., 180−240 min). Extraction conditions: (first hour) 120 bar, 40 °C; (second hour) 400 bar, 40 °C; (third hour) 400 bar, 100 °C; and (fourth hour) 400 bar, 150 °C.

As shown in Figures 1−5, matrixes differ in their ability to release pollutants. This is not surprising considering the great complexity of soil and sediment samples thar can vary in particle size, pore structures, and amount and type of organic matter. It seems very likely that the same type of molecules will find binding sites of varying strength within the same matrix. It also seems reasonable that different matrixes vary in their distribution of adsorptive sites of differing strength, both with respect to where in the matrix the sites are situated and with respect to their energies. The major analyte and sample matrix characteristics that might affect SFE behavior are discussed below.

Effect of PCB Molecular Weight. For at least some of the samples, it was possible to determine the extraction profiles for congeners ranging from trichlorobiphenyls (average mol wt = 258 g/mol, e.g., PCB-28) to heptachlorobiphenyls

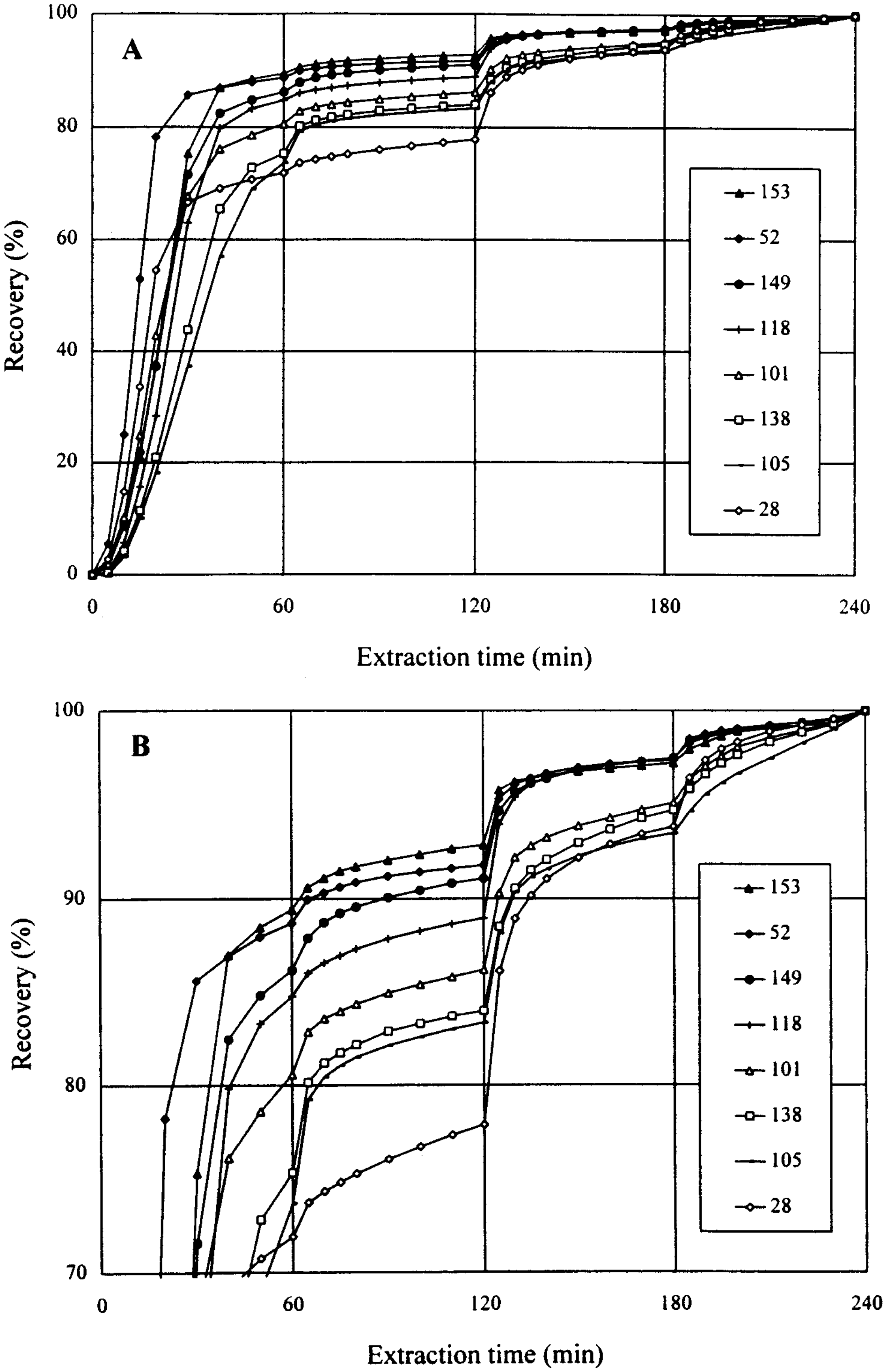

FIGURE 2. Selective SFE desorption behavior for representative PCB congeners from the historically contaminated SRM 1944 sediment. The recovery scale for panel B is expanded to better show the desorption behavior of the PCBs from the "slower" sites. Extraction conditions are identical to those in Figure 1.

(average mol wt = 395 g/mol, e.g., PCB-170 and -180). The molecular weight of a particular congener might influence its extraction profile since solubilities in CO_2 will generally decrease with increasing molecular weight. For example, the solubilities of PCB-70 (2,3′,4′,5-tetrachlorobiphenyl) and PCB-128 (2,2′,3,3′,4,4′-hexachlorobiphenyl) at ~375 bar and 40 °C have been reported as 8.6×10^{-4} and 1.3×10^{-4} mole fraction, respectively (*45*). Therefore, solubility would indicate that higher molecular weight congeners might show slower extraction rates, especially at the milder conditions. This appears to be true for the heptachlorobiphenyls PCB-170 and -180 for CRM 536 during the mildest extraction condition (first 60 min in Figure 1); however, no such trend exists for the other sample with PCB-180, CRM 481 (Figure 3).

In general, the results shown in Figures 1−5 show no clear trend with molecular weight indicating that solubility limitations in the supercritical CO_2 are not the limiting factor in determining the extraction profiles. In fact, the lowest molecular weight congener studied, PCB-28, shows a significantly slower extraction rate than the other congeners from the Lake Järnsjön sediment and SRM 1944, which indicates that this trichloro congener is the most strongly

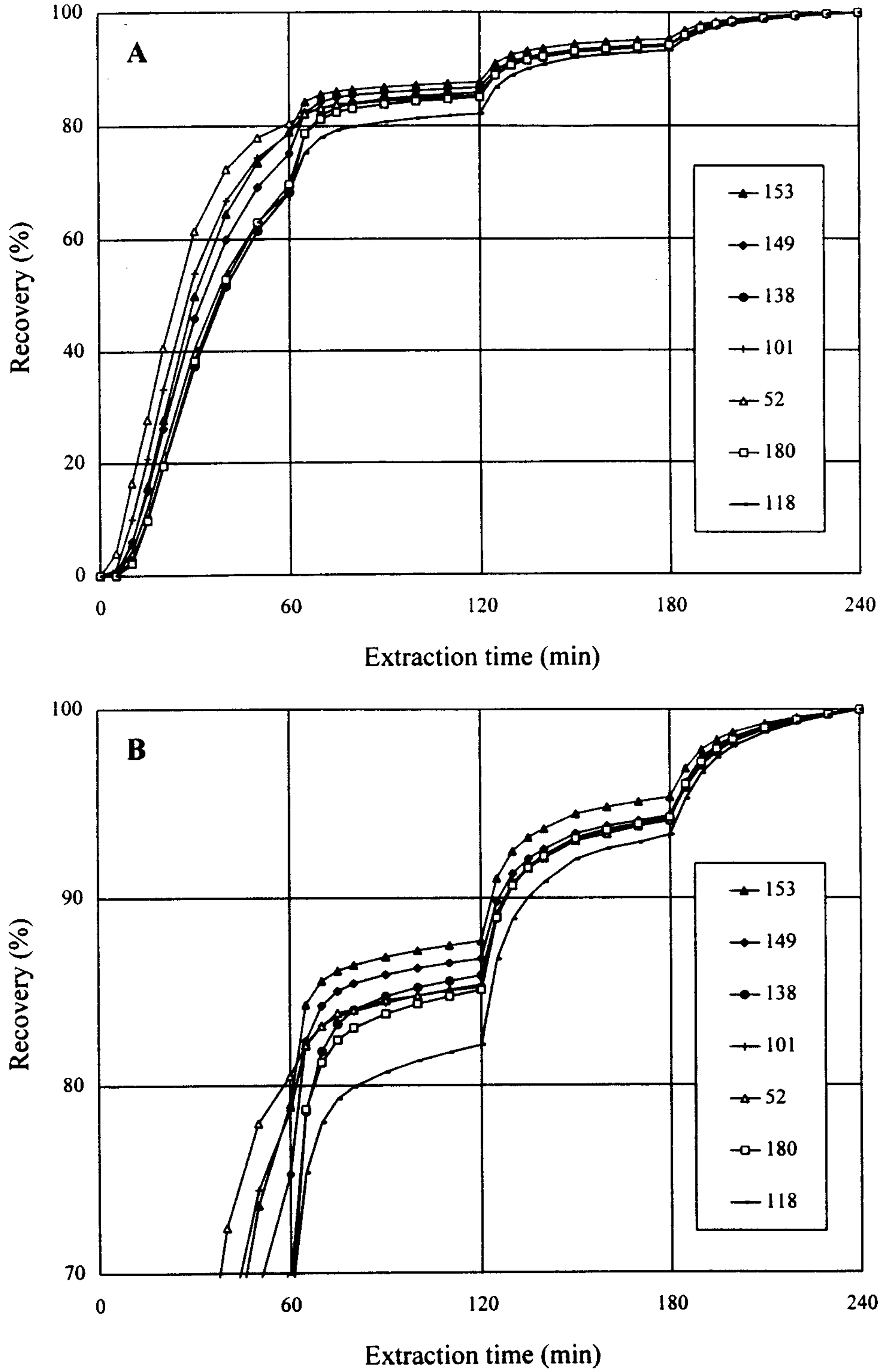

FIGURE 3. Selective SFE desorption behavior for representative PCB congeners from the historically contaminated CRM 481 soil. The recovery scale for panel B is expanded to better show the desorption behavior of the PCBs from the slower sites. Extraction conditions are identical to those in Figure 1.

bound PCB for these two samples. However, this trend does not continue for CRM 536, where PCB-28 shows one of the fastest extraction rates. Overall, the results shown in Figures 1−5 clearly demonstrate that differences in the strengths of association of various PCB congeners with sediments and soils is much more dependent on the matrix than on the nature of the PCB congener.

An additional effect of increasing molecular weight is the negative influence on solute diffusion coefficients. The desorption process during SFE of soils and sediments has best been described by models based on diffusion of the analytes from matrix active sites (e.g., matrix micropores) into the supercritical fluid (*22, 23, 26, 27*). Therefore, higher molecular weight PCBs would be expected to show slower extractions based on lower diffusion coefficients as well as on lower solubilities. However, this would not be true if the original sorption process also included a size exclusion mechanism where smaller molecules were able to enter a larger volume of the interior of a matrix. In such a case, despite higher diffusion constants and larger solubility, the mass transfer rate in the desorption step for smaller molecules might well become lower, depending on either longer

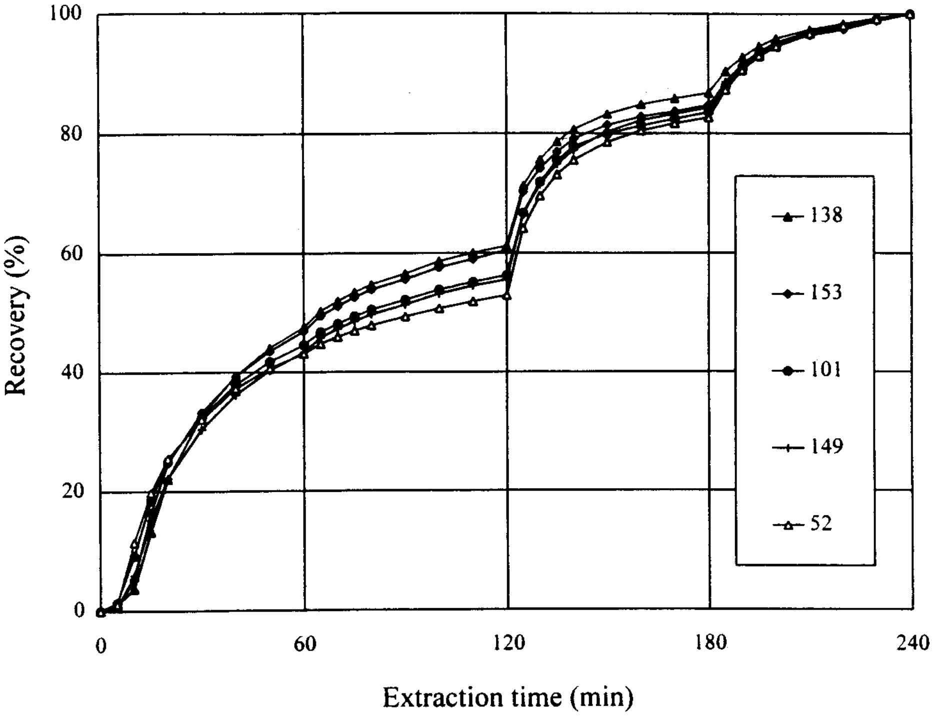

FIGURE 4. Selective SFE desorption behavior for representative PCB congeners from the historically contaminated NIST 1939 sediment. Extraction conditions are identical to those in Figure 1.

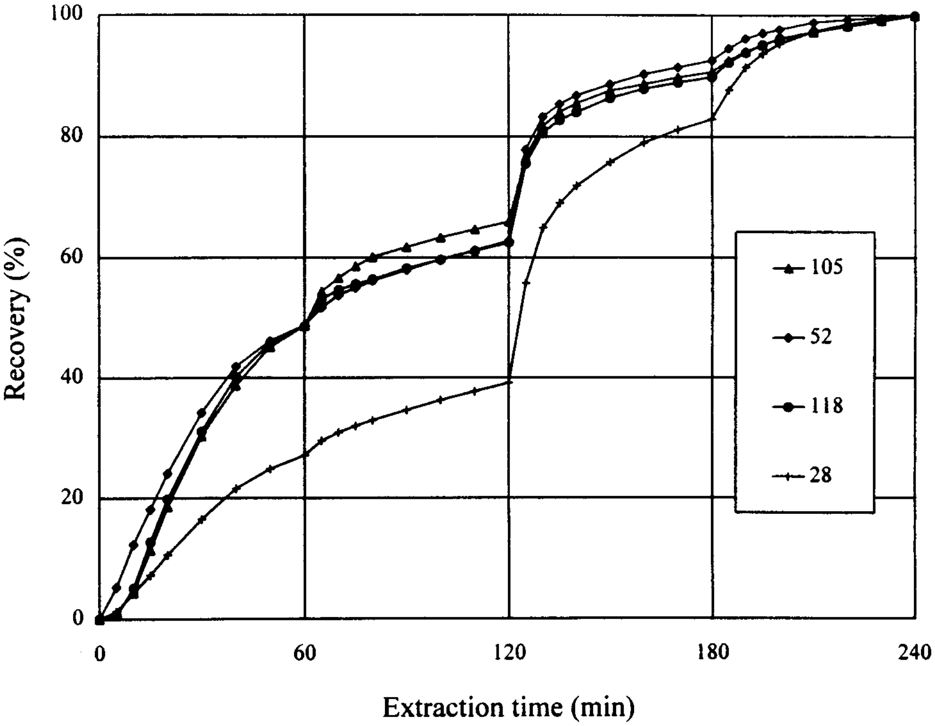

FIGURE 5. Selective SFE desorption behavior for representative PCB congeners from the historically contaminated Lake Järnsjön sediment. Extraction conditions are identical to those in Figure 1.

diffusion distance from the interior to the bulk liquid or adsorption to sites with higher energy accessible only for small molecules (or possibly both).

A close study of the curves in Figures 1–6 indicates that, for very slow, slow, and moderate fractions, the influence on molecular weight of the PCB congeners on the extraction profiles is small. For the first fast fraction, there is an influence that differs depending on the type of sediment. For example, the extraction rate of the two smallest PCB congeners investigated (PCB-28 and -52) are faster than the larger PCBs in the sediment CRM 536 (Figure 1). On the other hand, in the Järnsjön sediment (Figure 5), PCB-28 is substantially slower than the other congeners (including PCB-52). Accordingly, a simple model for PCB extraction (related to PCB desorption in sediments) based on PCB solubility in supercritical CO_2 and analyte diffusion in bulk fluid is, in general, not sufficient to describe interaction between PCB and sediments/soils.

The Distributed Reactivity Model proposed by Weber et al. (*29, 30, 32–39*), which takes into consideration that

TABLE 3. Distribution and Mass of Representative PCB Congeners in the Selective SFE Desorption Fractions

	% in fraction (range)				ng/g in fraction (range)			
time (min) fraction	0−60 fast	60−120 moderate	120−180 slow	180−240 very slow	0−60 fast	60−120 moderate	120−180 slow	180−240 very slow
NIST 1939	43−48	10−14	24−30	13−17	120−1300	36−300	64−900	41−530
NIST 1944	72−89	3−10	4−16	3−7	15−59	1−5	1−13	1−5
CRM 536	46−70	7−26	15−19	5−10	9−41	2−12	4−12	2−16
CRM 481	68−81	5−18	8−11	5−7	2300−99000	140−17000	255−10200	170−6300
Lake Järnsjön	27−49	12−17	25−44	7−17	1−14	0.3−6	0.3−23	0.1−9

individual pollutant molecules can interact with the matrix (e.g., sediment or soil) by many different mechanisms, will most probably be a description closer to the truth. A subsequent paper in this series will extend present SFE kinetic models to describe the effects of the temperature rise during the extraction process discussed above (*46*).

Effect of Sample Characteristics: PCB Concentration and Site Capacity. The most obvious difference among the samples is the large range of PCB concentrations present. As shown in Table 1, the concentrations of the individual congeners measured in this study range from ~2 ppb (ng/g) to >100 000 ppb. If the congener's solubility in supercritical CO_2 controlled the extraction behavior, it would be expected that the most contaminated samples would show the lowest fraction of PCBs extracted at the milder condition (i.e., the condition with the lowest PCB solubilities). In fact, the results are just opposite to this supposition, i.e., the most highly contaminated sample (CRM 481, Figure 3) generally displayed the fastest extraction rates, while the least contaminated sample (Lake Järnsjön, Figure 5) was one of the two slowest samples to extract. Thus, the effect of PCB concentrations clearly demonstrate that solubility limitations in supercritical CO_2 do not control the extraction behavior.

Another potential effect of high PCB concentration is that the slower binding sites on the sediment may be saturated by PCBs. In such cases, the majority of PCB molecules will then simply be layered on the surface of sample particles with no chance for more specific interactions. This scenario appears to be supported by results from the highly contaminated CRM 481 (Figure 3), since the largest fraction of PCBs do extract under the mildest condition. However, the results from the other samples do not support this scenario. The two most difficult samples to extract include the second most highly contaminated sample, SRM 1939 (Figure 4), and the least contaminated sample, Lake Järnsjön (Figure 5), while the easiest samples to extract include one of the least-contaminated samples, NIST 1944 (Figure 2), and the most highly contaminated sample, CRM 481 (Figure 3).

The results of the selective extraction profiles can also be used to investigate the relative capacity of the fast, moderate, slow, and very slow sites. Since all of the samples used in the present study had been contaminated for decades, it seems reasonable to assume that the PCB distribution over the different types of matrix sites would be approaching equilibrium. Two limiting cases that could control the distribution of the PCB molecules between fast and slow sites seem possible. First PCBs may initially sorb to fast sites, and then with sufficient time, the PCBs may migrate to and saturate the slower sites. Any additional PCBs would distribute among faster sites. If the number of slow sites is similar for all five samples above, their total concentration of PCBs associated with the slower sites would be similar provided that sufficient PCBs are available. The second limiting case would be that there are sufficient numbers of all types of sites to accommodate the pollutant PCBs and that (after a long period of aging) the PCBs distribute between slower and faster sites in an equilibrium manner regardless of their concentrations. Under this scenario, the percentage of PCB molecules associated with each type of site would be similar for the various sediments, while the mass concentration associated with each type of site would vary proportionally with the total PCB concentration.

Although the number of samples investigated is not large enough to warrant final conclusions, the distribution results summarized in Table 3 do strongly suggest that the second scenario (i.e., that large numbers of each type of site are available and that PCBs tend to distribute in an equilibrium manner) is most important. Note that the concentrations of the individual PCB congeners associated with the slow and very slow sites for the less contaminated samples range from less than nanogram to a few nanogram per gram. In contrast, the concentrations of individual PCBs associated with slow and very slow sites for CRM 481 range from several hundred to several thousand nanograms per gram (Table 3). In contrast to this very broad range of PCB concentrations associated with the four types of sites, the relative distribution of PCB congeners between the sites (i.e., the percent in each fraction) is similar for all five samples. Consideration of the distributions shown in Table 3 demonstrates that the dominant processes controlling distribution between slow and fast sites are based on partitioning among the sites (whether by adsorption or absorption) rather than saturation of the slowest sites.

Effect of Organic Content. Bulk organic content (e.g., humic and fulvic acids) is frequently implicated as a major factor causing sorption of PCBs to sediments and soils. Recently, diffusion in organic polymers has been used to describe kinetic processes controlling the sorption of organic pollutants in water/sediment systems (*1, 2, 35, 37, 39, 47−49*). Unfortunately, a simple hypothesis that high organic content causes stronger binding of PCBs to sediments has very little predictive value for these real-world samples. This is confirmed by results obtained in our investigation, where samples with relatively high organic contents (see Table 1) include one of the most difficult samples to extract (SRM 1939) as well as the easiest samples to extract (CRM 481 and SRM 1944). Furthermore, the sample with the relatively low organic content of 3% (Lake Järnsjön) was found to be the most difficult to extract. Obviously, other matrix characteristics, e.g., type of organic matter, particle size, mineralogy, and PCB concentration, need to be considered to be able to predict the distribution of PCBs among fast and slow sites.

Effect of Particle Size and Water Content. Since the samples with smaller particle sizes would have higher surface areas (per gram of sample), they may be expected to have stronger associations with the PCB molecules. However, there appears to be no relationship between particle size (Table 1) and the SFE behavior (Figures 1−5 and Table 3). For example, the two samples that showed the highest fractions of slowly desorbing PCBs, SRM 1939 and Lake Järnsjön, had the smallest and one of the largest particle sizes, respectively (Table 1). In addition, the two easiest samples to extract, CRM 481 and SRM 1944, had fairly small (<90 μm) and fairly large (75−250 μm) particle sizes, respectively. Since all of the samples were air-dried prior to use, the water content of the five sediments and soils were all similar (Table 1).

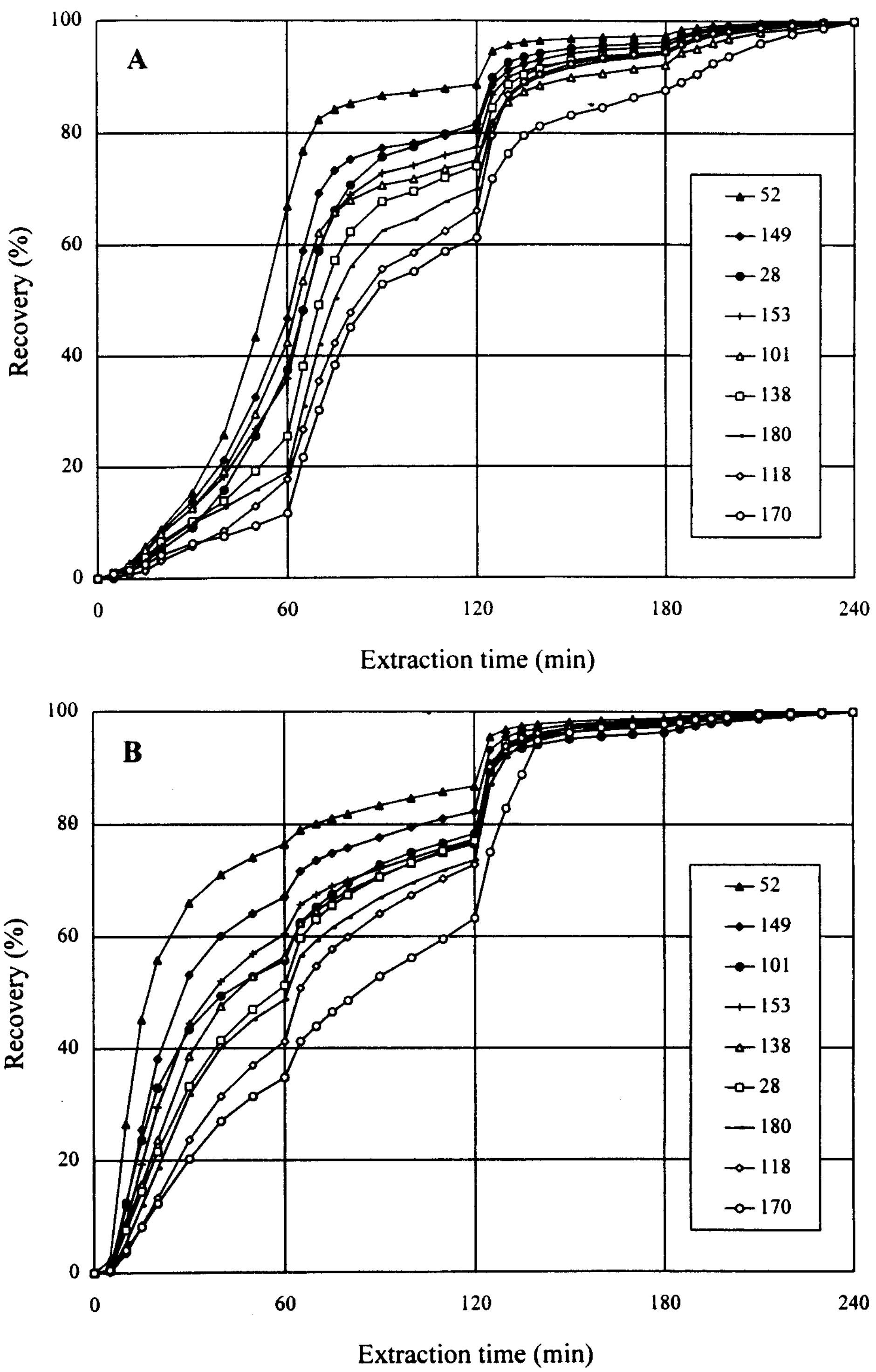

FIGURE 6. Selective SFE desorption behavior of PCBs from CRM 536 sediment particles <63 μm before (A) and after (B) exposure to water for 2 months. Extraction conditions are identical to those in Figure 1.

To further investigate the effect of particle size on the extraction profiles, extractions were performed on different size fractions of CRM 536 including 1000–3000 μm, the original sample (mostly 75–1000 μm), and particles <63 μm (prepared by jet milling and sieving the original sample). On the basis of the sum of quantities of the extraction profile (32 fractions) for each PCB congener, all samples with different particle sizes had concentrations similar to those found for the original sample.

The extraction profiles obtained for the 1000–3000 μm particles were very similar to those obtained for the original 75–1000 μm sample shown in Figure 1, demonstrating that particle surface area had no detectable effect on the distribution of PCBs among the fast to very slow sites. However, the 63 μm sample showed a much lower fraction of PCBs associated with the fast sites, with the largest fraction generally associated with the moderate (between 60 and 120 min) fraction, as shown in Figure 6A. The results shown in Figure 6 were verified by performing quadruplicate extractions at the mildest condition as well as repeating the experiment with a separate bottle of the smaller particles.

Since the <63 μm particles were prepared by jet milling followed by sieving, it is possible that the newly formed surfaces are more active binding sites than the aged material, or alternately, the milling/sieving procedure selects for the smaller sized fractions in the original material. Such smaller particles may have higher clay and organic contents, which could account for the shift to somewhat stronger binding sites for the <63 μm particles. The total organic content of the <63 μm sample was determined to be 18% as compared to the original sample's content of 15% (Table 1), which indicates that the jet milling/sieving process may be selective for higher organic particles. However, the smaller particle sizes could also contain higher amounts of absorptive clays, which may also account for the stronger PCB binding. Interestingly, when the <63 μm sample was soaked in water for 2 months prior to SFE (final water content was 10 wt %), the extraction behavior (Figure 6B) again became very similar to that shown by the original 75−1000 μm sample in Figure 1. Thus, it appears that exposure to water either negates the effects of the jet milling process or (if it is assumed that higher clay content in the < 63 μm sample is responsible for the different extraction profiles) swells the clays so that the adsorbed (or absorbed) PCBs are more accessible for extraction.

Acknowledgments

The authors thank S. A. Wise (NIST) and M. M. Schantz (NIST) for providing the reference materials SRM 1939 and SRM 1944. G. Kramer and K. H. Grobecker from the European Joint Research Center, ERMM in Geel, Belgium, are also thanked for providing the reference materials CRM 536 and CRM 481. S.H. thanks John Harju (Gas Research Institute) for helpful discussions. S.B. gratefully acknowledges financial support from the Danish Research Council. The Swedish Environmental Protection Agency is acknowledged by E.B. and L.M. for financial support.

Literature Cited

(1) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1.

(2) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J., Jr.; Westall, J. C. *Environ. Sci. Technol.* **1997**, *31*, 3341.

(3) Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 2713.

(4) Ball, W. P.; Roberts, P. V. *Environ. Sci. Technol.* **1991**, *25*, 1223.

(5) Ball, W. P.; Roberts, P. V. *Environ. Sci. Technol.* **1991**, *25*, 1237.

(6) Pavlostathis, S. G.; Mathavan, G. N. *Environ. Sci. Technol.* **1992**, *26*, 532.

(7) McGroddy, S. E.; Farrington, J. W. *Environ. Sci. Technol.* **1995**, *29*, 1542.

(8) McGroddy, S. E.; Farrington, J. W.; Gschwend, P. M. *Environ. Sci. Technol.* **1996**, *30*, 172.

(9) Brunk, B. K.; Jirka, G. H.; Lion, L. W. *Environ. Sci. Technol.* **1997**, *31*, 119.

(10) Carmichael, L. M.; Christman, R. F.; Pfaender, F. K. *Environ. Sci. Technol.* **1997**, *31*, 126.

(11) Hatzinger, P. B.; Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 537.

(12) Pignatello, J. J.; Ferrandino, F. J.; Huang, L. Q. *Environ. Sci. Technol.* **1993**, *27*, 1563.

(13) Bøwadt, S.; Johansson, B.; Wunderli, S.; Zennegg, M.; d'Alencastro, L. F.; Grandjean, D. *Anal. Chem.* **1995**, *67*, 2424.

(14) Schantz, M. M.; Bøwadt, S.; Benner, B. A., Jr.; Wise, S. A.; Hawthorne, S. B. *J. Chromatogr. A* **1998**, *816*, 213−220.

(15) Gere, D.; Bøwadt, S.; Lee, H. B.; Bennet, D. Official EPA Method 3562.

(16) Burford, M. D.; Hawthorne, S. B.; Miller, D. J. *Anal. Chem.* **1993**, *65*, 1497.

(17) Langenfeld, J. J.; Hawthorne, S. B.; Miller, D. J.; Pawliszyn, J. *Anal. Chem.* **1993**, *65*, 338.

(18) Hawthorne, S. B.; Miller, D. J. *Anal. Chem.* **1994**, *66*, 4005.

(19) Langenfeld, J. J.; Hawthorne, S. B.; Miller, D. J.; Pawliszyn, J. *Anal. Chem.* **1994**, *66*, 909.

(20) Yang, Y.; Gharaibeh, A.; Hawthorne, S. B.; Miller, D. J. *Anal. Chem.* **1995**, *67*, 641.

(21) Hawthorne, S. B.; Galy, A. B.; Schmitt, V. O.; Miller, D. J. *Anal. Chem.* **1995**, *67*, 2723.

(22) Bartle, K. D.; Clifford, A. A.; Hawthorne, S. B.; Langenfeld, J. J.; Miller, D. J.; Robinson, R. *J. Supercrit. Fluids* **1990**, *3*, 143.

(23) Bartle, K. D.; Boddington, T.; Clifford, A. A.; Hawthorne, S. B. *J. Supercrit. Fluids* **1992**, *5*, 207.

(24) Goto, M.; Sato, M.; Hirose, T. *J. Chem. Eng. Jpn.* **1993**, *26*, 401.

(25) Roy, B. C.; Goto, M.; Hirose, T.; Navaro, O.; Hortacsu, O. *J. Chem. Eng. Jpn.* **1994**, *27*, 768.

(26) Clifford, A. A.; Burford, M. D.; Hawthorne, S. B.; Langenfeld, J. J.; Miller, D. J. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1333.

(27) Pawliszyn, J. *J. Chromatogr. Sci.* **1993**, *31*, 31.

(28) Langenfeld, J. J.; Hawthorne, S. B.; Miller, D. J.; Pawliszyn, J. *Anal. Chem.* **1995**, *67*, 1727.

(29) Weber, W. J., Jr.; Young, T. M. *Environ. Sci. Technol.* **1997**, *31*, 1686.

(30) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1692.

(31) Björklund, E.; Hawthorne, S. B.; Bøwadt, S.; Mathiasson, L. In *Investigation of Polychlorinated Biphenyl Sorption/Desorption Behavior on Sediments and Soils Using Supercritical Fluid Extraction*; Vartiainen, T., Komulainen, H., Eds.; 7th Nordic Symposium on Organic Pollutants, Kuopio University Publications C, Natural and Environmental Sciences 68; Kuopio, Finland, 1997.

(32) Weber, W. J., Jr.; McGinley, P. M.; Katz, L. E. *Environ. Sci. Technol.* **1992**, *26*, 1955.

(33) McGinley, P. M.; Katz, L. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1993**, *27*, 1524.

(34) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1995**, *29*, 92.

(35) Weber, W. J., Jr.; Huang, W. *Environ. Sci. Technol.* **1996**, *30*, 881.

(36) Huang, W.; Schlautman, M. A.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 2993.

(37) Leboeuf, E. J.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1697.

(38) Huang, W.; Young, T. M.; Schlautman, M. A.; Yu, H.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1703.

(39) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 2562.

(40) Bøwadt, S.; Mazeas, L.; Miller, D. J.; Hawthorne, S. B. *J. Chromatogr.* **1997**, *785*, 205.

(41) Bøwadt, S.; Johansson, B. *Anal. Chem.* **1994**, *66*, 667.

(42) Bøwadt, S.; Larsen, B.; Tilio, R. *Intl. J. Environ. Chromatogr.* **1992**, *47*, 47.

(43) Bøwadt, S.; Larsen, B. *J. High Resolut. Chromatogr.* **1992**, *15*, 350.

(44) Miller, D. J.; Hawthorne, S. B.; Clifford, A. A. *J. Supercrit. Fluids* **1997**, *10*, 57.

(45) Yu, E.; Richter, M.; Chen, P.; Wang, X.; Zhang, Z.; Tavarides, L. L. *Ind. Eng. Chem. Res.* **1995**, *34*, 340.

(46) Pilorz, K.; Björklund, E.; Hawthorne, S. B.; Mathiasson, L. *Environ. Sci. Technol.* **1999**, *33*, 2204−2212.

(47) Brusseau, M. C.; Jessup, R. E.; Rao, P. S. C. *Environ. Sci. Technol.* **1991**, *25*, 134.

(48) Carroll, K. M.; Harkness, M. R.; Bracco, A. A.; Balcarcel, R. R. *Environ. Sci. Technol.* **1994**, *28*, 253.

(49) Cornelissen, G.; van Noort, P. C. M.; Parsons, J. R.; Govers, H. A. J. *Environ. Sci. Technol.* **1997**, *31*, 454.

Received for review October 14, 1998. Revised manuscript received March 29, 1999. Accepted April 14, 1999.

ES981071P