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Correlating Selective Supercritical Fluid Extraction with Bioremediation Behavior of PAHs in a Field Treatment Plot

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Selective supercritical fluid extraction (SFE) behavior of PAHs from manufactured gas plant (MGP) site soils was determined on untreated soil and on soils collected after 1/2 year and 1 year of bioremediation in a field land treatment plot. Sequentially stronger SFE conditions gave selective extraction of PAHs associated with "fast" (or "rapidly desorbing"), "moderate," "slow," and "very slow" sites on the soil collected before and during bioremediation. While all PAHs from the untreated soil showed "stair-step" extraction curves (with molecules in each of the four "fast" to "very slow" SFE fractions), two- and three-ring PAHs were found mostly in the "fast" fraction, while the five- and six-ring PAHs were found almost completely in the "slower" fractions. SFE comparisons of the untreated and bioremediated soils showed that bioremediation only removed PAH molecules which were found in the "fast" fractions by SFE and that remediation for 1 year did not result in the migration of PAHs from "slower" to "faster" sites. One hour SFE of the untreated sample at the mildest condition (120 bar, 50 °C) gave good quantitative agreement with removals achieved after 1 year of bioremediation, and SFE correctly predicted that two- and three-ring PAHs would show ∼90% removals, four-ring PAHs ∼50% removals, and five- and six-ring PAHs <10% removals. Mild SFE reduced the total PAHs on the untreated soil from 6860 mg/kg to 2360 mg/kg (after SFE), which is in excellent agreement with the reduction to 2420 mg/kg achieved following 1 year of bioremediation. The results show that mild SFE may be a rapid and useful test to predict the bioavailability of PAHs on contaminated soil.

Introduction

Understanding the sequestration or binding of organic chemicals which occurs during environmental aging on soils and sediments is important for a broad range of reasons ranging from determining the effect of such pollutants on plant and animal receptors and human health to evaluating the need for and predicting the effectiveness of various remediation and control approaches. A large number of investigations of biological uptake, treatment, and analytical extraction have demonstrated that, in general, longer exposures of persistent organics to a soil or sediment matrix leads to tighter associations with that matrix and, consequently, less availability for transport (e.g., water desorption) and for uptake by biological systems (*1*−*25*). Multisite models and kinetic approaches to explain the sequestration and release of aged organics from soils and sediments are gaining acceptance, as are ideas that aging causes organics such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) to become increasingly associated with soil polymeric organic matter and/or to diffuse further into soil micropores (*1*−*3, 16, 18, 19, 22, 23, 26*−*33*). Regardless of the mechanism (as concluded by Alexander (*3*)), the outcome is the same, i.e., molecules that are sequestered in the soil/sediment matrix are much less available to organisms.

The need to understand the uptake and release of persistent organic pollutants has led to various laboratory approaches for determining the degree of "availability" (whether to water or to biological systems) of organics on soils and sediments. Tests include long-term (several months) water rate-of-release studies (*34*−*36*), biological availability assays such as earthworm uptake (*37*), to chemical assays including solid-phase extraction (*37, 38*), organic solvent extraction with mild solvents (*37, 39, 40*), dialysis (*41*), and pyrolysis (*42*). For the purpose of assessing the risk associated with a chemical in soil or sediment, it would be useful to have a rapid laboratory test capable of predicting the fraction of chemicals that are "available" for biological uptake, treatment, and water transport.

Supercritical fluid extraction (SFE) with pure carbon dioxide (CO_2) has recently been proposed as a potentially rapid method to determine the "availability" of soil- and sediment-bound organics (*43*−*47*). The potential advantage of SFE is that the solubility of target analytes can be varied continuously over several orders of magnitude by controlling the extraction pressure and temperature (*48, 49*). In addition, the kinetics of desorption processes can be enhanced by simply changing the temperature used for extraction. In contrast to organic solvent extractions (which can extract significant fractions of the soil organic matrix), SFE with pure CO_2 can extract hydrophobic pollutants (e.g., PAHs, PCBs) without significantly altering the soil organic matrix *(47)*. Although developed independently, the models used to explain the desorption kinetics of organic pollutants from sediments into water and those used to explain SFE behavior of organics are of essentially the same form (*50*−*55*). The similarity of these models and the ability to vary solvent strength over a wide range suggests that SFE could be used as a simple test to investigate the "availability" of organic pollutants.

At present, the relationship between SFE behavior and real-world behavior of organic pollutants is mostly conjectural. However, in a recent series of articles, SFE performed under increasingly stronger conditions showed that PCBs were present in several different types of sites on every soil and sediment tested and that PCBs were associated with sites ranging from "fast" (extracted at the mildest SFE conditions) to "slowly desorbing" sites (*45*−*47*). Furthermore, when the same sediments were exposed to PCBs in water for up to 18 days, the exposure time was only sufficient for the PCBs to sorb to only the "fast" sites, demonstrating that very long exposure times would be needed for the PCBs to gain the "slowly desorbing" sites which were occupied in the original environmentally aged sediments (*47*). In the present study, we extend the SFE conditions developed in the earlier PCB studies to investigate the behavior of PAHs during a 1-year, large-scale field bioremediation of a PAH-impacted soil from a manufactured gas plant (MGP) site.

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Materials and Methods

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 and 4 g of the test soil. Extracted PAHs were collected in 22 mL vials containing 15 mL of methylene chloride (CH_2Cl_2) (Fisher Optima grade). Flow rates were controlled at 1 mL/min (measured as compressed CO_2 at the pump) using a variable coaxial restrictor (ISCO) heated to 80 °C. Note that extraction flow rates must be carefully monitored since they may affect the extraction rates of the "fast" PAHs (although changes in flow rate are unlikely to change the extraction rate of the "slow" PAH fractions) as previously described (*56*). In addition, it is important to place the sample at the outlet end of the SFE cell so that cell void volume does not affect the extraction rates.

Kinetic profiles from the different soils were obtained using four sequentially stronger SFE conditions, each applied for either 30 min or for 1 h. The sequential SFE conditions were 120 bar, 50 °C ("rapidly desorbing" or "fast" fraction); 400 bar, 50 °C ("moderate" fraction); 400 bar, 100 °C ("slow" fraction"); and 400 bar, 150 °C ("very slow" fraction). Collection vials were changed at set time intervals during each extraction period (e.g., at 5, 10, 20, and 30 min at each SFE condition) so that the shape of the extraction curve could be determined at each condition. Since adding the PAH concentrations from the multiple fractions collected for the kinetic plots could introduce error in the PAH quantitations, the quantity of each PAH extracted at each SFE condition was further verified by repeating each extraction (in triplicate) and collecting and analyzing the entire fraction for each of the SFE extraction conditions. After the four-step SFE procedure was completed, the soil residue was finally extracted overnight with acetone/CH_2Cl_2 (1:1) to recover any PAHs which were not extracted by SFE. Additional minor procedural details are the same as previously reported (*45*).

Gas Chromatographic Analysis. A Hewlett-Packard model 5890 Series II gas chromatograph (GC) equipped with a flame ionization detector (FID), a split/splitless injection port (300 °C), and a model 7673A auto injector were used for analyzing the extracted fractions. Separations were performed on a 50 m DB-5 column (0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Rancho Cordova, CA). Injections were at an oven temperature of 80 °C followed by a temperature ramp of 6 °C/min to 320 °C (hold for 5 min). Each fraction was spiked with *n*-undecane as an internal standard. Quantitations were based on calibration curves (PAH peak area versus the internal standard) using pure PAH standards for all major species (at least one PAH for each molecular weight reported). Total PAH concentrations were based on the total FID peak areas (versus the internal standard) of the PAH calibration standards. PAH identifications were confirmed by GC/MS analysis using the same chromatographic conditions.

Samples. Soil samples were collected from an MGP site in the Midwest during biological land treatment in a several hundred m^3 field unit. The bioremediation process essentially involved placing the contaminated soil in a prepared bed land treatment unit ~30 cm deep, supplying water and nutrients, and tilling frequently to supply oxygen for approximately 1 year beginning in May. Detailed descriptions of the process have been previously reported (*36*). During the treatment, the site was divided into 16 separate subplots, and each sampling event consisted of subsamples collected from each subplot which were composited and sieved. The homogenized soils were air-dried and stored at 4 °C until used. Particle sizes of the untreated soil were (1−6 mm) 40 wt %, (0.5−1 mm) 15 wt %, (0.25−0.5 mm) 16 wt %, (0.125−0.25 mm) 17 wt %, and (<0.125 mm) 12 wt %. Carbon, hydrogen, and nitrogen contents of the untreated soil were 4.6, 0.4, and 0.1 wt %, respectively.

Results and Discussion

Effect of Bioremediation on PAH Selective SFE Behavior. Stepwise SFE extraction profiles of representative PAHs from the untreated soil and soils after 1/2 year and 1 year of bioremediation are shown in Figure 1. Each sequentially stronger SFE condition was applied for 30 min to yield the "stair-step" plots showing the PAHs extracted from "fast" sites (0−30 min), "moderate" (30−60 min), "slow" (60−90 min), and "very slow" (90−120 min) sites. (PAH concentrations shown after 120 min are those extracted from the soil residue after SFE by 18 h of Soxhlet extraction.)

Two trends in these plots are worth noting. First, the low molecular weight PAHs (naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, dibenzothiophene, phenanthrene, and anthracene) all show similar behavior, i.e., the majority (~80 to 90%) of each PAH was found in the "fast" (extracted at the mildest SFE condition) fraction. More importantly, as the bioremediation continued to 1/2 and 1 year, *only the molecules which were located in the "fast" fraction show significant removal by the bioremediation process,* while the molecules in the "slower" three SFE fractions show no significant change. Note that the SFE extraction curves for the treated soils are essentially identical to those of the untreated soils in the SFE fractions after the first 30 min (i.e., the "moderate, slow, and very slow" fractions), clearly demonstrating that only the "fast" molecules as defined by SFE are significantly removed by the field bioremediation process.

As the molecular weights of the PAHs increase (4-, 5-, and 6-ring PAHs including fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[*1,2,3-cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene), the distribution of the PAHs shifts to the "slower" SFE fractions, and the removals achieved by bioremediation also decrease (Figure 1). Similar to the trend for low molecular weight PAHs, only the fractions of PAHs found in the "faster" two SFE fractions (from 0 to 60 min in Figure 1) show any significant reduction by the bioremediation process. Finally, for the five- and six-ring PAHs, there is no significant reduction in the PAH concentrations over the 1-year bioremediation treatment. (Note that the small changes in concentrations shown for the higher molecular weight PAHs such as benzo[*a*]pyrene and benzo[*ghi*]perylene are likely associated with soil heterogeneity at the field site, since the site was sampled over a 1-year period, and related analytical error.)

When the extraction data are viewed as the percent in each SFE fraction (rather than the PAH concentrations used in Figure 1), the extraction behavior for the high molecular weight PAHs is essentially identical for the untreated and bioremediated soils, as shown for benzo[*a*]pyrene in Figure 2. Therefore, it appears that (in addition to not being removed from the soil by the bioremediation process) the high molecular weight PAHs did not migrate between "slower" and "faster" sites during the 1-year bioremediation period. For the lower molecular weight PAHs, the percentage of molecules shifted toward the "slower" SFE sites (as shown by naphthalene in Figure 2), as would be expected since only the PAH molecules found in the "fast" SFE fraction were removed by the 1-year bioremediation (Figure 1).

Quantitative Comparison of PAH Removals by Bioremediation and SFE. As shown in Figure 1, PAHs found in the first SFE fraction (and possibly the second fraction for higher molecular weight PAHs) appear to best account for the PAH molecules removed during bioremediation, while the "slower" PAHs (those extracted by the strongest two SFE conditions) appeared unaffected by the bioremediation. Therefore,

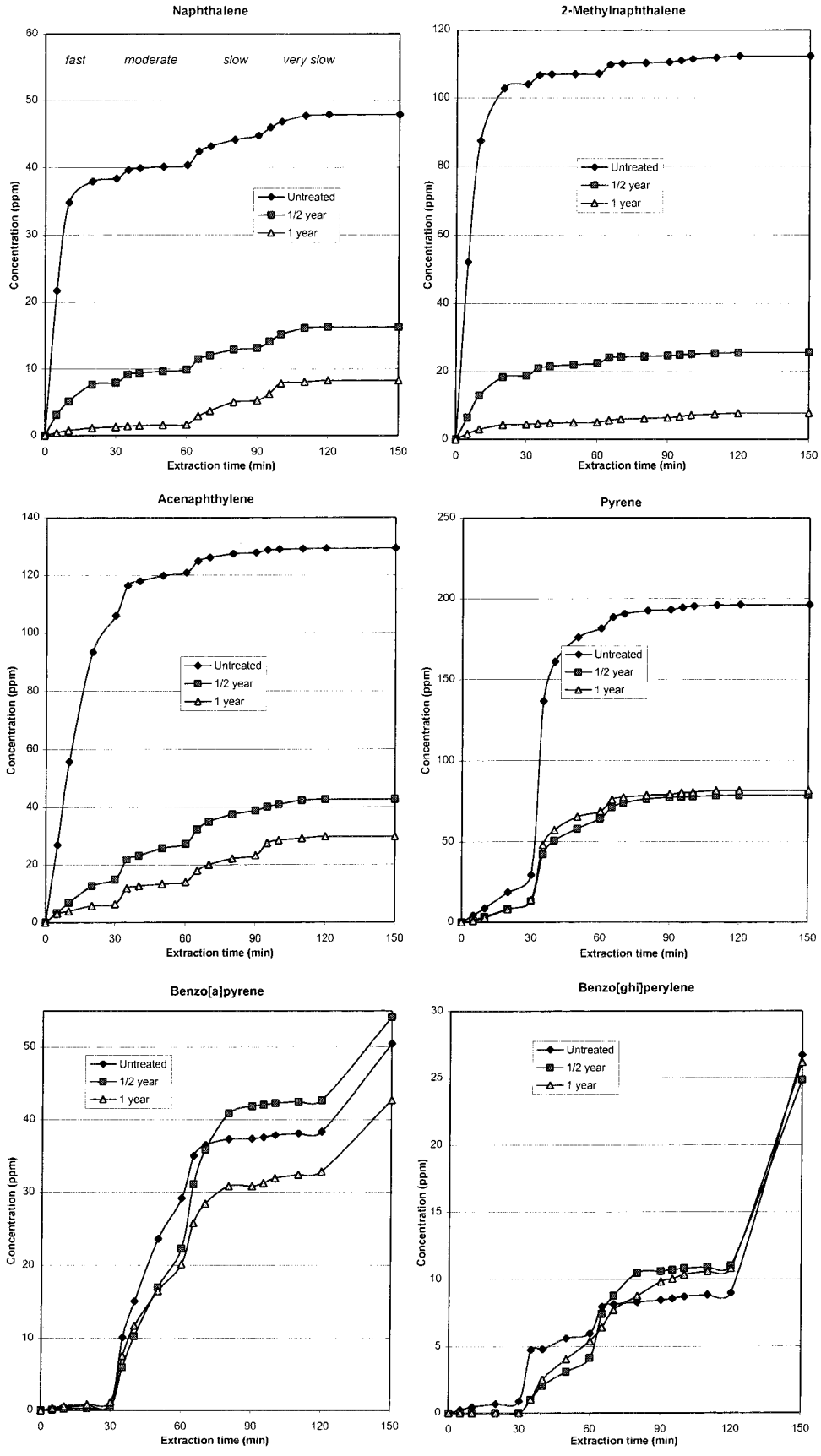

FIGURE 1. Selective SFE removal of representative PAHs from MGP-impacted soil before treatment and after 1/2 year and 1 year of bioremediation in a field site. Sequential SFE was performed with pure CO_2 for 30 min at each condition including 120 bar and 50 °C ("fast" sites), 400 bar and 50 °C ("moderate"), 400 bar and 100 °C ("slow"), and 400 bar and 150 °C ("very slow"). PAHs shown after 120 min are those extracted from the soil residue (after SFE) by 18 h of Soxhlet extraction.

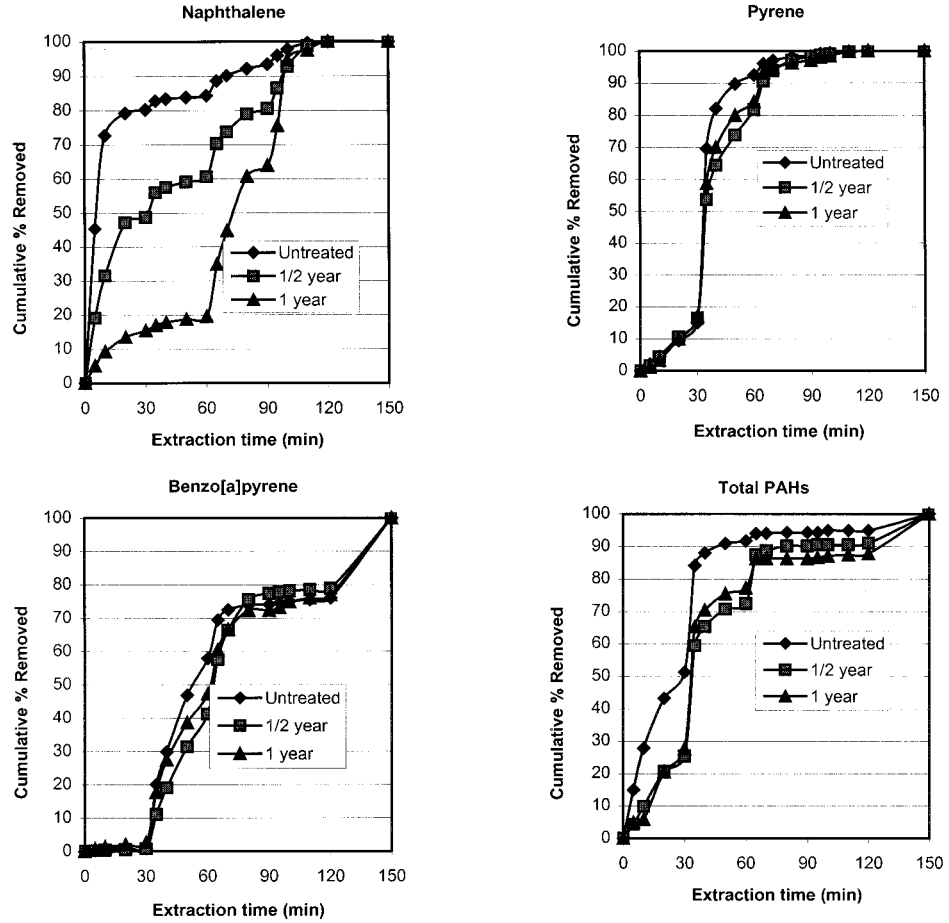

FIGURE 2. Percent removals of representative PAHs from MGP-impacted soil before treatment and after 1/2 year and 1 year of bioremediation in a field site using sequentially stronger SFE conditions. SFE was performed with pure CO_2 for 30 min at each condition including 120 bar and 50 °C ("fast" sites), 400 bar and 50 °C ("moderate"), 400 bar and 100 °C ("slow"), and 400 bar and 150 °C ("very slow"). PAHs shown after 120 min are those extracted from the soil residue (after SFE) by 18 h of Soxhlet extraction.

efforts were made to correlate the quantities of each PAH species removed by the first two SFE conditions (the "fast" and "moderate" molecules) with the quantities of each PAH species removed after 1/2 year and 1 year of bioremediation. Triplicate samples of the untreated soil were extracted sequentially with the mildest (120 bar, 50 °C) and second-mildest (400 bar, 50 °C) SFE conditions to sequentially remove the "fast" and "moderate" PAHs from the untreated soil. Since the 30-min fractions used for Figure 1 were not always sufficient to remove the molecules in a particular fraction (as evidenced by not obtaining a flat extraction curve at the end of each "stair-step" condition), the SFE extraction times were increased to 60 min for each extraction condition. Following extraction at these two SFE conditions, the extracted soil residues were subjected to Soxhlet extraction to determine the unextracted concentrations. The SFE and Soxhlet results were then used to calculate the concentration of each PAH remaining after extraction of the "fast" SFE fractio, and after the extraction of the "fast" and "moderate" SFE fractions, and the results were compared to the concentrations of the same PAHs remaining after 1/2 year and 1 year of bioremediation.

The concentrations of the PAHs found in the field plot after bioremediation and those found after extracting the "fast" and "moderate" PAHs from the untreated soil are shown in Table 1. For the majority of PAHs, the concentrations remaining after the selective SFE removal of both the "fast" and "moderate" PAHs from the untreated soil show good agreement with the concentrations found when the field site was sampled after both 1/2 year and 1 year of bioremediation. The quantitative reproducibility of the selective SFE method was also satisfactory, with the relative standard deviations of replicate SFE experiments (for each fraction) similar to those found for multiple analyses of the bioremediated soils. The generally good agreement obtained between the concentrations predicted by the SFE extraction of the "fast" PAHs and the actual removals achieved by bioremediation are encouraging, especially considering the fact that the predictions were performed with individual PAH concentrations ranging from −10 to over 400 mg/kg, that bioremediation removals of PAHs ranged from − 0% to − 90%, and that PAH molecular weights ranged from 128 to 278 amu (i.e., the entire range of PAHs under regulatory scrutiny).

Figure 3 shows the average percent of PAHs (grouped by ring size) remaining after 1/2 year and 1 year of bioremediation and after the removal of the "fast" and "moderate" PAHs from the untreated soil with SFE. In general, the percent of each group of PAHs removed with the "fast" SFE fraction best agrees with the percent of each group of PAHs removed by bioremediation, regardless of whether high removals were achieved by bioremediation (2- and 3-ring PAHs) or little removal was achieved by bioremediation (5- and 6- ring PAHs). The percent removal for the total PAHs achieved by bioremediation was essentially identical to that removed by the mildest SFE condition (Figure 3). Linear correlation coefficients (r^2) for the percent of each individual PAH (those listed in Table 1) removed by bioremediation and extracted by the mildest SFE condition were 0.93 and 0.92 for 1/2 year and 1 year of bioremediation, respectively.

TABLE 1: Comparison of PAHs Removed by Bioremediation with Those Removed by Selective SFE[d]

	PAH concentration ± SD (mg/kg)				
		after bioremediation[a]		after SFE to extract[b]	
PAHs	untreated soil[a]	1/2 year	1 year	fast fraction	fast and moderate fraction
naphthalene	48 ± 2	16 ± 1	8.2 ± 0.4	17 ± 1	15 ± 1
1-methylnaphthalene	118 ± 4	22 ± 2	6.4 ± 0.4	7 ± 1	4 ± 2
2-methylnaphthalene	112 ± 4	26 ± 3	7.7 ± 0.5	6 ± 1	4 ± 3
acenaphthylene	129 ± 1	43 ± 17	30 ± 6	33 ± 2	25 ± 3
acenaphthene	78 ± 3	16 ± 1	5.7 ± 0.7	4 ± 1	2 ± 2
fluorene	136 ± 6	17 ± 1	12 ± 2	9 ± 2	4 ± 3
dibenzothiophene	70 ± 3	15 ± 2	13 ± 2	7 ± 1	2 ± 1
phenanthrene	434 ± 19	56 ± 1	23 ± 4	52 ± 1	24 ± 10
anthracene	110 ± 7	26 ± 4	14 ± 1	20 ± 5	11 ± 2
fluoranthene	130 ± 6	46 ± 1	41 ± 3	39 ± 8	12 ± 5
pyrene	196 ± 8	79 ± 2	82 ± 5	76 ± 9	21 ± 10
benz[*a*]anthracene	74 ± 2	48 ± 4	46 ± 1	54 ± 3	21 ± 2
chrysene	77 ± 3	52 ± 5	51 ± 1	61 ± 3	28 ± 2
benzo[*b*+*k*]fluoranthene	88 ± 12	73 ± 16	58 ± 10	81 ± 1	43 ± 1
benzo[*e*]pyrene	39 ± 5	39 ± 3	30 ± 2	36 ± 1	25 ± 2
benzo[*a*]pyrene	51 ± 5	54 ± 4	43 ± 3	48 ± 1	33 ± 1
perylene	11 ± 2	11 ± 2	8.3 ± 0.5	11 ± 0	8 ± 1
indeno[*1,2,3-cd*]pyrene	9 ± 2	16 ± 2	14 ± 2	17 ± 1	15 ± 1
dibenz[*a,h*]anthracene	12 ± 1	12 ± 1	12 ± 2	12 ± 0	10 ± 1
benzo[*ghi*]perylene	27 ± 3	25 ± 2	26 ± 3	26 ± 1	23 ± 1
total PAHs by FID[c]	6590 ± 260	2460 ± 240	2420 ± 60	2360 ± 310	1580 ± 180

[a] PAH concentrations and standard deviations based on triplicate Soxhlet extractions of each soil sample. [b]Concentrations remaining after extraction of the fast (60 min at 120 bar, 50 °C) and fast + moderate (previous extraction plus 60 min at 400 bar, 50 °C) fractions from the untreated soil. All extractions were performed in quadruplicate. [c]Total PAH concentrations determined by the sum of individual GC/FID peak areas. [d] Sixty min at each condition.

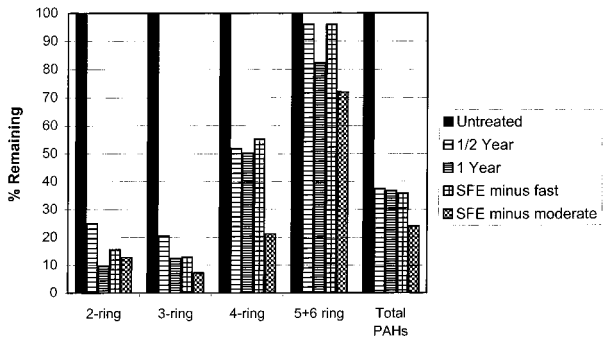

FIGURE 3. Percentage of PAHs (grouped by ring size) remaining on soil after 1/2 year and 1 year of bioremediation, compared to the percentage remaining after 1 h of SFE at 120 bar and 50 °C ("SFE minus fast") and an additional hour of SFE at 400 bar and 50 °C ("SFE minus moderate").

Single Condition SFE Extraction Rates vs Bioremediation Behavior. While the "stepwise" SFE approach described above imitates approaches such as the use of different organic solvents to increase extraction strength (*37, 39, 40*), other approaches to mimic the environmental release of sequestered organics are based on kinetic release curves generated with a single experimental condition. For example, desorption of organics from sediments into water is normally performed for several months, and the desorption rate curves are evaluated to determine "fast" (rapid-desorbing) and "slow" fractions for individual pollutant species (*34, 36*).

In an initial attempt to evaluate the ability of a single SFE condition to mimic field bioremediation behavior of the MGP soil, extractions were conducted using several different pressures and temperatures (ranging from 120 to 400 bar, and 50 to 150 °C) to determine which SFE condition most closely mimicked the actual field bioremediation results. As might be expected based on results of the "stepwise" SFE conditions discussed above, a single SFE condition (200 bar, 50 °C) which was slightly stronger than that used for the "fast" fraction in the stepwise approach (120 bar, 50 °C) appeared to best correlate with the actual bioremediation behavior. This condition was used to extract the untreated MGP soil (in triplicate) for 120 min.

The general shape of the 200 bar (50 °C) SFE curves up to 40 min (right side of Figure 4) show expected trends with the actual removal of PAHs in the field bioremediation treatment (left side of Figure 4), i.e., 1 min of SFE approximates 10 days of bioremediation. Because the bioremediation samples had to be collected over 1 year from a large field site, the jagged nature of the bioremediation curves is most likely a result of soil heterogeneity. However, the agreement between the removal profile by bioremediation over 1 year and the extraction rates by SFE at 200 bar, 50 °C over 40 min are reasonably good for both low and high molecular weight PAHs present in the sample.

Quantitative comparisons of the PAHs removed by bioremediation and the single SFE extraction were also performed by noting that the "fast" fraction of PAHs was generally removed by ~20 min of the SFE process. The quantities of PAHs remaining in the soil after 1/2 and 1 year of bioremediation and after 20 min of SFE at 200 bar, 50 °C (each performed in triplicate) are shown in Figure 5. In general, the concentrations of the PAHs removed by bioremediation and by the single SFE condition agreed well, especially considering that the technique successfully mimics the behavior of PAHs ranging in molecular weight from 128 to 278 amu (two to six rings). Although the selection of 20 min to determine the "fast" fraction in Figure 5 was based only on the soils used in this study, initial extractions of 12 different soils (from different sites) also show similar behavior.

As shown in Figure 4, the extraction rate curves begin to flatten out at longer extraction times, especially for the lower molecular weight PAHs. Two explanations may apply. First, if the extraction rate goes to zero at a certain SFE condition, it could be inferred that the individual PAHs extracted at that condition were in one "compartment," while unextracted PAHs were in a more tightly bound "compartments." However, if the PAHs desorb in a continuum of rates, an infinitely long extraction at a mild SFE condition should

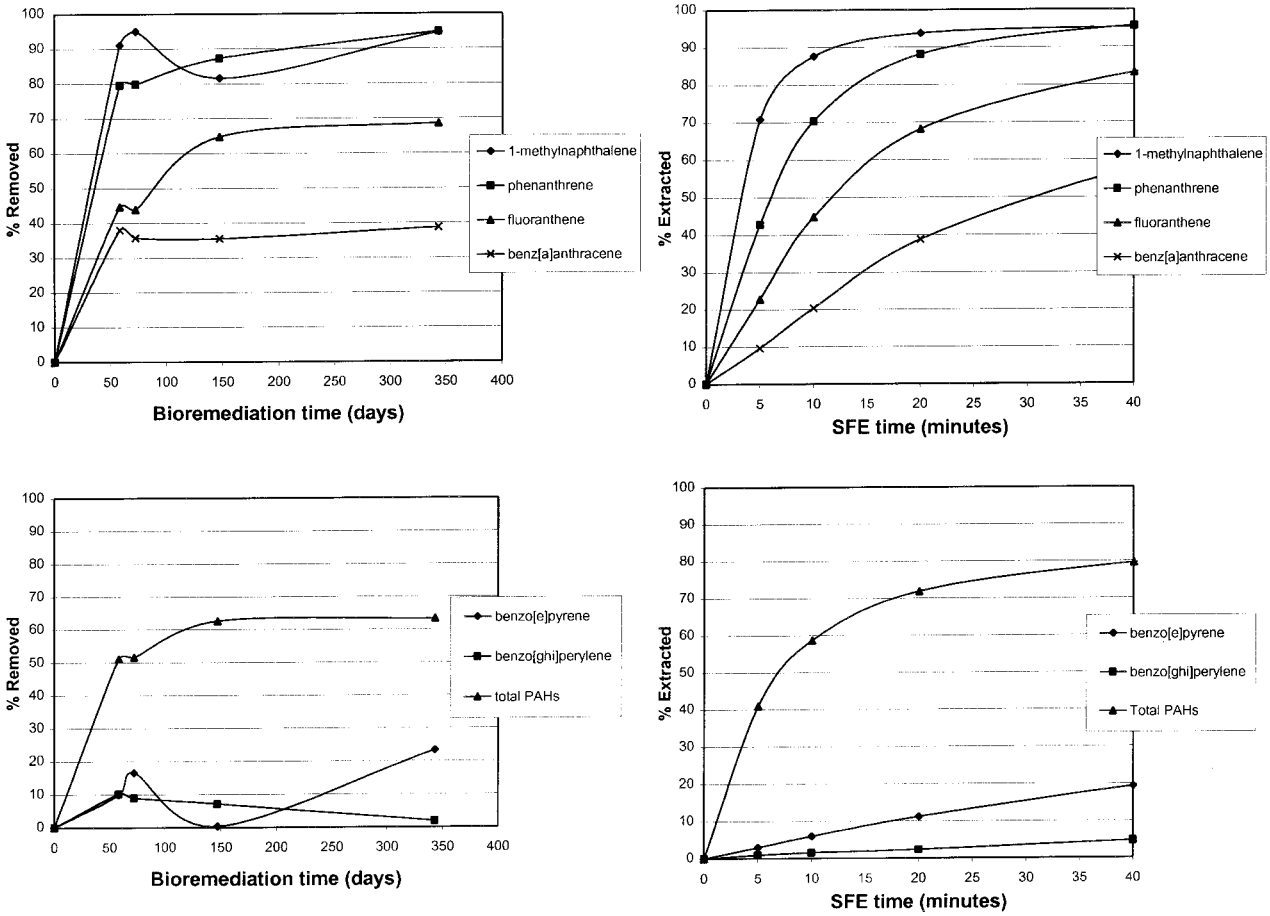

FIGURE 4. Removal of representative PAHs from a historically contaminated soil with bioremediation (left side of figure) and SFE at 200 bar and 50 °C (right side of figure).

remove 100% of the molecules. In an effort to differentiate these mechanisms, additional extractions at 200 bar, 50 °C were conducted on the untreated and the 1-year treated soils for 8 h, with fractions collected every 20 min. For both soils, measurable concentrations of all the PAHs listed in Table 1 were found in all fractions (even the 460−480 min fraction), demonstrating that desorption of the PAHs occurs in a continuum manner, rather than from discrete compartments.

PAH Characteristics, Treatability, and SFE Behavior. The ability to rapidly mimic environmental behavior of PAHs on historically contaminated soils and sediments is complicated by the fact that the physicochemical properties of PAHs vary so greatly. For example, the PAHs commonly associated with MGP sites range from two rings (naphthalene, 128 amu) to six rings (e.g., benzo[*ghi*]perylene, 276 amu), with associated boiling points ranging from 218 to − 500 °C, and water solubilities ranging from 32 to 0.0003 mg/L, respectively (Table 2). Given this wide range of PAH characteristics, the strong correlation between SFE and bioremediation behavior described above may initially seem counterintuitive.

For direct biological uptake (e.g., earthworm ingestion), supercritical CO_2 may appear to be a reasonable solvent, since its polarity is similar to that of biological lipids. However, other biological exposure routes (e.g., microbiological degradation) may require desorption into water prior to biological uptake (*3*, *57*). Even though previous studies with PCBs showed good correlation between SFE and long-term water desorption (*45*, *46*), supercritical CO_2 may initially seem like an unlikely solvent to mimic water-mediated PAH desorption since CO_2 is very nonpolar (similar to hexane), while water is highly polar. Hence, it may seem unlikely that the behavior of PAHs ranging from two to six rings would be similar in water and supercritical CO_2. Surprisingly, when the solubilities of PAHs in ambient water are compared with their solubilities in supercritical CO_2 at the mildest SFE condition (120 bar, 50 °C) previously discussed, the individual PAH solubilities are very similar (Table 2), at least for the PAHs for which data are available. Solubilities are not available for higher molecular weight PAHs at 120 bar and 50 °C, but PAH solubilities at the second strongest SFE condition (400 bar, 50 °C) show excellent correlation with ambient water solubilities (i.e., ~1 order of magnitude higher in CO_2 than water) for PAHs ranging from the two-ring naphthalene to six-ring benzo[*ghi*]perylene. This strong degree of correlation for PAH solubilities between ambient water and supercritical CO_2 is quite striking, especially considering that PAH solubilities vary by five orders-of-magnitude (for naphthalene to benzo[*ghi*]perylene) in both water and CO_2 (Table 2).

TABLE 2: Characteristics of Representative PAHs

PAHs	mol wt (amu)	boiling point (°C)	water solubility (mg/L)[b]	CO_2 solubility (mg/kg)[a] 120 bar, 50 °C	CO_2 solubility (mg/kg)[a] 400 bar, 50 °C
naphthalene	128	218	32	38	116
fluorene	166	297	2	5.7	11
phenanthrene	178	340	1.3	3.2	12
anthracene	178	340	0.073	0.081	0.61
pyrene	202	394	0.14	0.21	1.2
chrysene	228	436	0.002		0.021
perylene	252	498	0.0004		0.005
benzo[*ghi*]perylene	276	500	0.00026		0.002

[a] Adapted from solubilities reported in refs *48* and *49*. [b] Adapted from ref *58*.

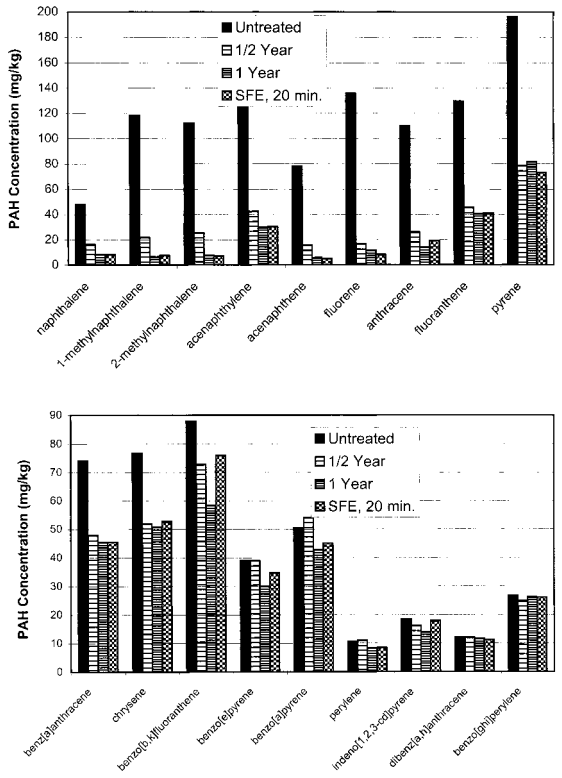

FIGURE 5. Comparison of bioremediation (1/2 and 1 year) and 20 min of SFE at 200 bar (50 °C) on individual PAH concentrations on a historically contaminated soil.

SFE with pure CO_2 also appears to have little or no affect either on the bulk matrix organic material on sediments (in contrast to organic solvents), sediment pH, nor greatly affect their water of hydration (i.e., the 1−2% of water typically left on soils and sediments after air-drying) (*47*). This lack of effect on matrix composition and the correlation between PAH solubilities in water and CO_2 combined with the enhanced mass transfer (faster extraction rates) may contribute to the strong relationship between mild SFE behavior and bioremediation behavior discussed above.

Although the selective SFE approach must be validated by extracting many more soils and sediments and correlating the results with other approaches to determine environmental mobility and bioavailability, the results described above indicate that SFE may be a powerful tool to study the sequestration of PAHs and other persistent organic chemicals and to predict their behavior in the environment. Studies of SFE behavior are planned on several soils and sediments from different MGP processes, and plans include correlating these results with parallel studies on bioremediation behavior, water desorption rates, earthworm toxicity and uptake, and other bioassays.

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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) Nam, K.; Alexander, M. *Environ. Sci. Technol.* **1998**, *32*, 71.
(14) Chung, N.; Alexander, M. *Environ. Sci. Technol.* **1998**, *32*, 855.
(15) Kelsey, J. W.; Kottler, B. D.; Alxander, M. *Environ. Sci. Technol.* **1997**, *31*, 214.
(16) Carroll, K. M.; Harkness, M. R.; Bracco, A. A.; Balcarcel, R. R. *Environ. Sci. Technol.* **1994**, *28*, 253.
(17) Kan, A. T.; Fu, G.; Tomson, M. B. *Environ. Sci. Technol.* **1994**, *28*, 859.
(18) Weber, W. J., Jr.; McGinley, P. M.; Katz, L. E. *Environ. Sci. Technol.* **1992**, *26*, 1955.
(19) Weber, W. J., Jr.; Huang, W. *Environ. Sci. Technol.* **1996**, *30*, 881.
(20) Erickson, D. C.; Loehr, R. C.; Neuhauser, E. F. *Wat. Res.* **1993**, *27*, 911.
(21) Kan, A. T.; Fu, G.; Hunter, M.; Chen, W.; Ward, C. H.; Tomson, M. B. *Environ. Sci. Technol.* **1998**, *32*, 892.
(22) Chiou, C. T.; McGroddy, S. E.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 264.
(23) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1998**, *32*, 3549.
(24) Kleineidam, S.; Rügner, H.; Ligouis, B.; Grathwohl, P. *Environ. Sci. Technol.* **1999**, *33*, 1637.
(25) Chung, N.; Alexander, M. *Environ. Sci. Technol.* **1999**, *33*, 3605.
(26) Nieman, J. K. C.; Sims, R. C.; Sims, J. L.; Sorensen, D. L.; McLean, J. E.; Rice, J. A. *Environ. Sci. Technol.* **1999**, *33*, 776.
(27) Cornelissen, G.; Van Noort, P. C. M.; Govers, H. A. J. *Environ. Sci. Technol.* **1998**, *32*, 3124.
(28) Ortiz, E.; Kraatz, M.; Luthy, R. G. *Environ. Sci. Technol.* **1999**, *33*, 235.
(29) Schlebaum, W.; Schraa, G.; Van Riemsdijk, W. H. *Environ. Sci. Technol.* **1999**, *33*, 1413.
(30) Rügner, H.; Kleineidam, S.; Grathwohl, P. *Environ. Sci. Technol.* **1999**, *33*, 1645.
(31) Ten Hulscher, Th. E. M.; Vrind, B. A.; Van Den Heuvel, H.; Van Der Velde, L. E.; Van Noort, P. C. M.; Beurskens, J. E. M.; Govers, H. A. J. *Environ. Sci. Technol.* **1999**, *33*, 126.
(32) Ahn, I.-S.; Lion, L. W.; Schuler, M. L. *Environ. Sci. Technol.* **1999**, *33*, 3241.
(33) LeBoeuf, E. J.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1697.
(34) Opdyke, D. R.; Loehr, R. C. *Environ. Sci. Technol.* **1999**, *33*, 1193.
(35) Cornelissen, G.; Van Noort, P. C. M.; Parsons, J. R.; Govers, H. A. J. *Environ. Sci. Technol.* **1997**, *31*, 454.
(36) Loehr, R. C.; Webster, M. T. *Practice of Hazardous, Toxic and Radioactive Waste Management*, accepted for publication.
(37) Tang, J.; Robertson, B. K.; Alexander, M. *Environ. Sci. Technol.* **1999**, *33*, 4346.
(38) Macrae, J. D.; Hall, K. J. *Environ. Sci. Technol.* **1998**, *32*, 3809.
(39) Kelsey, J. W.; Kottler, B. D.; Alexander, M. *Environ. Sci. Technol.* **1997**, *31*, 214.
(40) Tang, J.; Alexander, M. *Environ. Toxicol. Chem*. **1999**, in press.
(41) Woolgar, P. J.; Jones, K. C. *Environ. Sci. Technol.* **1999**, *33*, 2118.
(42) Guthrie, E. A.; Bortiatynski, J. M.; Van Heemst, J. D. H.; Richman, J. E.; Hardy, K. S.; Kovach, E. M.; Hatcher, P. G. *Environ. Sci. Technol.* **1999**, *33*, 119.
(43) Weber, W. J., Jr.; Young, T. M. *Environ. Sci. Technol.* **1997**, *31*, 1686.
(44) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1692.
(45) Björklund, E.; Bøwadt, S.; Mathiasson, L.; Hawthorne, S. B. *Environ. Sci. Technol.* **1999**, *33*, 2193.

(46) Pilorz, K.; Björklund, E.; Bøwadt, S.; Mathiasson, L.; Hawthorne, S. B. *Environ. Sci. Technol.* **1999**, *33*, 2204.
(47) Hawthorne, S. B.; Björklund, E.; Bøwadt, S.; Mathiasson, L. *Environ. Sci. Technol.* **1999**, *33*, 3152.
(48) Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713.
(49) Miller, D. J.; Hawthorne, S. B.; Clifford, A. A.; Zhu, S. *J. Chem. Eng. Data* **1996**, *41*, 779.
(50) Bartle, K. D.; Clifford, A. A.; Hawthorne, S. B.; Langenfeld, J. J.; Miller, D. J.; Robinson, R. *J. Supercrit. Fluids* **1990**, *3*, 143.
(51) Bartle, K. D.; Boddington, T.; Clifford, A. A.; Hawthorne, S. B. *J. Supercrit. Fluids* **1992**, *5*, 207.
(52) Goto, M.; Sato, M.; Hirose, T. *J. Chem. Eng. Jpn.* **1993**, *26*, 401.
(53) Roy, B. C.; Goto, M.; Hirose, T.; Navaro, O.; Hortacsu, O. *J. Chem. Eng. Jpn.* **1994**, *27*, 768.
(54) Clifford, A. A.; Burford, M. D.; Hawthorne, S. B.; Langenfeld, J. J.; Miller, D. J. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1333.
(55) Pawliszyn, J. *J. Chromatogr. Sci.* **1993**, *31*, 31.
(56) Hawthorne, S. B.; Galy, A. B.; Schmitt, V. O., Miller, D. J. *Anal. Chem.* **1995**, *67*, 2723.
(57) Carmichael, L. M.; Christman, R. F.; Pfaender, F. K. *Environ. Sci. Technol.* **1997**, *31*, 126.
(58) MacKay, D.; Shiu, W. Y. *J. Chem. Eng. Data* **1977**, *22*, 399.

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