Environ. Sci. Technol. **2000**, *34,* 2542−2548

Relationship between PCB Desorption Equilibrium, Kinetics, and Availability during Land Biotreatment

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The purpose of this research was to study the changes in polychlorinated biphenyl (PCB) availability as measured by desorption equilibrium and kinetics from industrial lagoon sediments collected at different times during a 24-month period of pilot-scale land biotreatment. During biotreatment, reductions of the lower chlorinated PCB congeners in the industrial lagoon sediments were observed. On the basis of past work on soils and sediments, it was originally hypothesized that these reductions in PCB concentration would result in reduced PCB availability. To evaluate this hypothesis, equilibrium partitioning studies and desorption kinetic studies were conducted with the industrial lagoon sediments (containing 0.91% oil and grease) as a function of biotreatment duration. Contrary to initial expectations, equilibrium aqueous total PCB concentrations increased with PCB loss during land biotreatment. This behavior was attributed to the association of PCBs with a waste oil phase in the lagoon sediment and an oil phase loss rate greater than the PCB loss rate during the biodegradation study. Maximum PCB desorption rates for the lagoon sediments also changed with biotreatment. A two-phase desorption behavior characterized by fast and slow desorbing fractions were observed. The estimated fast pool fraction for each PCB homologue decreased with biotreatment time, suggesting preferential removal of the PCBs from the fast pool during the bioremediation process. Although PCB availability based on estimated fast pool fraction decreased with biotreatment, availability based on aqueous equilibrium measurements increased with biotreatment over the 24 months of study.

Introduction

The primary objective of bioremediation is contaminant reduction leading to reductions in contaminant availability for toxicity and migration. Historically, predictions of contaminant leaching from sediment have assumed equilibrium partitioning between dissolved and sorbed contaminants. The simplest equilibrium model is based on a linear partitioning of contaminant between the sediment organic matter and the aqueous environment (*1*). In some situations, nonlinearity is observed in the equilibrium behavior and is described by a limited-surface Langmuir isotherm or the empirical Freundlich isotherm (*2*). Heterogeneity in soil/sediment sorption properties can lead to more complicated formulations of sorption equilibrium behavior (*3*).

While an equilibrium approach has been used historically to establish cleanup guidelines, this approach may not be valid for hydrophobic organic compounds (HOCs) such as PCBs where desorption kinetics may limit the contaminant flux to the dissolved phase (*4*). Desorption of HOCs from soils and sediments have often been observed to take place in two stages: a rapid stage followed by a stage of much slower release (*5*−*7*). The fraction that is rapidly released has often been considered available for biodegradation and toxic response (*4, 8*−*12*). Previous work suggests that biotreatment reduces this available fraction and thereby reduces the availability and toxicity of the contaminant sequestered in soil or sediment (*4, 11*−*15*). Contaminants such as PCBs sorbed on degradable organic matter (OM) may behave differently if the amount and nature of the OM is altered during biotreatment. Thus, an understanding of the changes in amount and nature of OM in sediment is necessary for predicting changes in availability with biotreatment.

In sediments where the organic carbon is comprised primarily of stable ossified remains of biological origin, little change in organic carbon content of the sediment is expected during typical time frames of bioremediation. However, fresh natural material from plant or animal origin or oils originating from industrial sources may be present in the sediment as biodegradable organic matter. For example, Avnimelech et al. (*16*) studied decomposition rates of organic matter in (> 6 in. deep) sediments from 64 lakes, reservoirs, and estuaries in the United States and estimated average first-order degradation rates of 0.024 yr^{-1} (half-life of 30 yr). In contrast, degradation rates for fresh organic matter in surface sediments derived from algal blooms have been reported at 0.6 yr^{-1} (half-life of 1 yr) (*16*). Reductions of an oily OM or nonaqueous-phase liquid have been reported in several studies during bioremediation (*17, 18*) and with water flushing (*19*). Salanitro et al. (*17*) observed that for soils contaminated with crude oil hydrocarbons, 3−4 months of bioremediation resulted in 70−90% removal of carbon number species in the range of C_{11}−C_{22}, 40−60% for C_{23}−C_{34}, and 35−60% for C_{35}−C_{44}. In comparison to oil degradation, biodegradation of certain HOCs like higher chlorinated PCBs may be much slower (*20*).

Although several studies to date have investigated bioremediation of PCB-contaminated soils and sediments, none have examined the resulting changes in OM and the influence on PCB equilibrium and kinetics during bioremediation. Therefore, the purpose of this study was to investigate how availability of PCB congeners as determined by desorption equilibrium and kinetics was altered as a function of land biotreatment for an industrial lagoon sediment containing an appreciable amount of oily OM. Batch equilibrium and desorption rate tests were conducted to measure PCB equilibrium partitioning and desorption kinetics, respectively, from field contaminated sediments during a pilot-scale land biotreatment. Changes in oily OM were monitored during the biotreatment process.

Materials and Methods

Description of Sediment Source and Land Biotreatment. Industrial lagoon sediments containing PCBs employed in these studies were obtained from a pilot-scale biological land treatment unit operated by Alcoa in Massena, NY. The PCB-

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10.1021/es9905389 CCC: $19.00

impacted sediments originated primarily from two industrial lagoons in the site, which had been in operation for several years till the early 1980s and contained a significant oil and grease content. These lagoons received varied waste ranging from waste oils and wastewater from industry operations containing PCBs and were historically used as settling/treatment units. Approximately 1500 kg (dry weight) of sediment from these lagoons were mixed with 1500 kg of clean sand (medium to fine grade) to produce the sediment mixture that was easy to handle and was added to the land treatment unit. The land treatment unit consisted of a lined trench in the ground in which the amended lagoon sediment was placed in a layer 6−24 in. deep. The active biotreatment process entailed periodic tilling to enhance aeration, addition of growth nutrients, and irrigation to regulate moisture content. Lagoon sediment/sand samples (henceforth called lagoon sediments) were collected before bioremediation, after 3 months of active bioremediation, and after 21 months of subsequent passive treatment (total of 24 months) during which no tilling or nutrient addition was performed.

Particle Size Distribution. The mixed lagoon sediment that went into the land treatment units was analyzed for particle size. A total of 15% of the dry sediment consisted of gravel (>2.0 mm), and 66% consisted of medium to coarse sand (2.0−0.15 mm). The remaining fines (19%) that passed through a 100 mesh sieve (nominal diameter = 150 μm) were analyzed for particle size distribution using Malvern Mastersizer/E particle size analyzer. The particle size distribution of the fines based on a mass distribution ranged between 1 and 100 μm with a peak at about 7 μm. Further details of particle analysis are provided in Ghosh et al. (*21*).

PCB Extraction and Analysis. Congener-level PCB analysis was performed in this study. Samples were extracted in an acetone−hexane mixture by sonication (EPA Method 3550B), passed through a silica gel cleanup procedure (EPA Method 3630C), and analyzed using a gas chromatograph equipped with an electron capture detector (EPA Method 8082). The sample preparation, cleanup, and PCB analysis procedures are described in detail in Appendix 1 in the Supporting Information.

Organic Matter Measurements. Four organic matter measurements were performed on the lagoon sediment samples.

Total Extractable Organics (*TEO*). A 6-h Soxhlet extraction using dichloromethane was used to extract the oil phase in the sediment as outlined by Rutherford et al. (*22*). The mass of extractable organic matter was determined gravimetrically after dichloromethane was removed by evaporation.

Total Organic Carbon (*TOC*). TOC measurements were performed by an outside analytical laboratory using EPA Method 9060 based on oxidation of the organic carbon and measurement of the CO_2 evolved. The TOC value of the 24-month treated lagoon sediment was measured on a composite sample. However, the TOC value for the untreated lagoon sediment had to be estimated based on the measured TOC values of the constituents of the sediment mixture.

Oil and Grease. Oil and grease measurements were performed by an outside laboratory based on Freon extraction following EPA Method 9071A.

Volatile Matter. Volatile matter was measured based on ASTM Method D2974C, which involves measurement of loss of weight of the sample by heating at 550 °C. This includes both organic and inorganic volatiles.

Batch Equilibrium Tests. Sediment−water equilibrium tests were conducted in 50-mL glass centrifuge tubes with Teflon-lined caps. To initiate the equilibrium testing, centrifuge tubes were filled with measured quantities of sediment and water in the weight ratio of 1:10. The tubes were then tumbled end-over-end at 3−4 rpm at 25 ± 2 °C in darkness. At each sampling time, replicate tubes were removed from the tumbler, and the solid and aqueous phases were separated.

Because of the high partitioning of PCBs on particulates, special care was taken to ensure proper solid/liquid separation. To remove colloidal particulates from solution without sacrificing aqueous PCB composition integrity, tube contents were centrifuged for 10 min at 2000*g* to settle the coarse particles. This step was followed by the addition of 0.001 M alum solution and adjustment of pH back to neutral with NaOH solution. The supernatant water was mixed carefully using a glass pipet for 2 min to mix and flocculate the alum without disturbing the settled particles. Sweep floc was formed in less than 1 min, which was subjected to centrifugation for 40 min at 2000*g*. A very clear supernatant was formed after centrifugation of the sweep floc. The supernatant then was transferred carefully to an extraction vessel using a glass pipet and extracted with three fresh volumes of hexane. The extracted hexane was collected together, dried using anhydrous sodium sulfate, concentrated to 1 mL, and cleaned by a silica gel cleanup method, and the final clean eluate was concentrated to 1.5 mL for GC analysis.

A possible concern in the use of alum was the extent of adsorption of PCBs on the alum floc during particle separation. Control runs were performed to test for adsorption of PCBs on alum floc using aqueous PCB solutions. The total PCB loss during alum treatment was measured at 1.3% and was therefore considered negligible for the rest of the study. There was no observable bias in the loss across PCB homologue groups. A possible reason for the low adsorption of PCBs on alum floc is that aluminum hydroxide solid at neutral pH is hydrophilic and, therefore, not amenable to the adsorption of highly hydrophobic PCB molecules.

Desorption Rate Experiments. Batch desorption experiments were conducted in 12-mL glass vials with Teflon-lined caps as described in detail in ref *21*. Multiple tubes were filled with 1 g of lagoon sediment (wet weight), 1 g of XAD-4 resin, and 10 mL of water and placed in a tumbler. XAD-4 resin is a strong adsorbent of PCBs and provided a maximum driving force for PCB desorption from sediment by reducing the aqueous concentration to near zero. At each sampling time, four vials were removed and sacrificially sampled. PCB analysis was performed on each of the three phases present in the batch desorption vials which were the sediment, the XAD resin, and the aqueous phase. Average sediment PCB concentration for each sample was calculated by averaging the four replicates. There were no losses of PCBs by biodegradation during these tests as indicated by mass balance shown in Appendix II in the Supporting Information. A phenomenological two-compartment model as presented in eq 1 that describes both fast and slow desorbing PCB compartments in sediment was used to describe the observed desorption kinetics. A similar two-compartment model has been used previously to model the desorption of HOCs from sediment (*21*, *23*, *24*):

$$\frac{C_t}{C_0} = f\, e^{-k_f t} + (1 - f)\, e^{-k_s t} \tag{1}$$

where C_t is the PCB homologue concentration in sediment after desorption time t, C_0 is the initial PCB homologue concentration in sediment, f is the fraction of fast desorbing pool in sediment, k_f is the first-order rate constant for the fast component, and k_s is the first-order rate constant for the slow component.

Results and Discussion

PCB Concentration in Land Treatment Units. Total PCB concentration in the lagoon sediment decreased during land

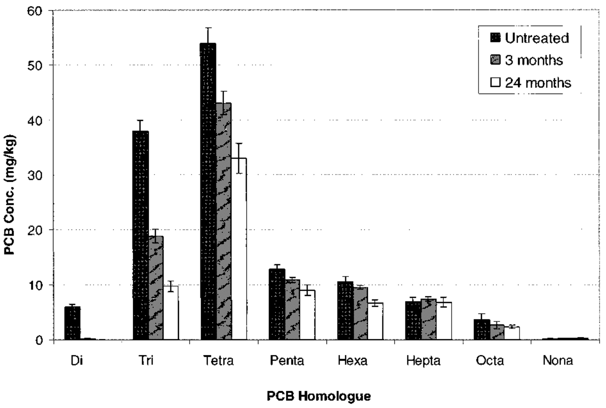

FIGURE 1. Changing distribution of PCBs in industrial lagoon sediment during land biotreatment. Bars show 95% confidence intervals.

biotreatment. PCB concentrations in the lagoon sediment before biotreatment, after 3 months of active biotreatment, and after 21 months of subsequent passive biotreatment are shown along with the 95% confidence intervals in Figure 1. Dichlorobiphenyls were completely removed in the first 3 months. Significant reductions in tri- and tetrachlorobiphenyls were observed in the first 3 months of active biotreatment and also in the following passive phase till 24 months. Small but significant reductions were observed in the concentrations of penta- and hexachlorobiphenyls during the 24-month biotreatment period. Changes in the concentrations of hepta-, octa-, and nonachlorobiphenyls were not significant at the 95% confidence level. The greater removal of the lower chlorinated PCB homologues is attributed to their higher biodegradability, faster desorption rates, higher solubility in the aqueous phase, and/or higher volatility. Several researchers have reported faster rates of biodegradation with decreasing level of chlorination of PCB congeners (*25*, *26*).

Effect of Ortho-Chlorination on Extent of Removal by Land Biotreatment. To investigate the effect of ortho-chlorination on removal during land biotreatment, congener-level PCB data were analyzed. As discussed earlier, all the dichlorobiphenyl congeners were removed after 3 months of active biotreatment. Among the tri- and tetrachlorobiphenyls, which were partially removed, there appears to be varying degrees of removal for different ortho-chlorinations as shown in Figure 2. The trichlorobiphenyl congeners were grouped into two categories: coplanar (i.e., congeners with a single chlorine substituent in the ortho position—23′5, 23′4, 24′5, 244′, 233′, 2′34, 22′56′, and 234′) and noncoplanar (i.e., congeners with two or three ortho chlorines—22′6, 22′5, 22′4, 236, 23′6, 22′3, and 24′6). Congener 22′56′ was included in the coplanar group because it coeluted with 233′ and 2′34 and was a minor component of the peak. After 24-month biotreatment, the percentage remaining of coplanar trichlorobiphenyl congeners was 19% as compared to 53% for the noncoplanar congeners. Therefore, greater removal of the coplanar trichlorobiphenyl congeners was achieved as compared to the noncoplanar congeners. Tetrachlorobiphenyls showed a similar trend of greater removal of coplanar PCBs as compared to the noncoplanar PCBs. Two coplanar congeners (23′4′5 and 2′345) showed equally slow removal as the other noncoplanar congeners within the homologue group. For the rest of the coplanar tetrachlorobiphenyls (234′5, 244′5, 2344′, and 233′4), the fraction of total congeners remaining after 24-month biotreatment was 40% as compared to 73% of the other noncoplanar tetrachlorobiohenyl congeners. The extent of removal of the penta and higher chlorinated congeners was small, and relative differences between chlorine positions were not clear.

These observations agree with refs *27* and *28*, who reported that PCB congeners containing two chlorines in ortho positions either on one or each ring were more resistant to biodegradation. In an earlier study (*21*), it was reported that the more hydrophobic coplanar trichlorobiphenyls desorbed more slowly than the less hydrophobic noncoplanar trichlorobiphenyls in batch desorption tests with the same sediment. Had the overall process been mass transfer rate limited, we would have seen slower removal of the coplanar congeners. The faster biodegradation rate of the coplanar congeners appears to dominate the overall rate shift. For a mass transfer limited process, a higher biodegradation rate should not significantly change the overall rate. This indicates that desorption rate is not the limiting process for the slow degradation of the noncoplanar PCBs. It also is evident from the observation of greater removal of coplanar PCBs that biodegradation might have played a more significant role than leaching and/or volatilization in the removal of PCBs in the land treatment units.

An important implication to the fate and transport of PCBs is evident from the above observation. The noncoplanar PCB congeners, which are more leachable due to their lower hydrophobicity, are less degraded during biotreatment. Therefore, these noncoplanar PCB congeners are expected to be more labile during biotreatment. This is supported by aqueous equilibrium measurements later.

Aqueous Equilibrium Concentration as a Function of Land Biotreatment. Lagoon sediment−water equilibrium tests were conducted to evaluate the aqueous availability of PCBs before and after biotreatment. PCB congeners contributing to di through hexachlorobiphenyl homologue groups were measured in the aqueous solution almost immediately, signifying fast approach to batch equilibrium. There was very little change in aqueous phase concentrations of each homologue beyond 5 days of equilibrium up to 40 days (Appendix III in the Supporting Information). Tri- and tetrachlorobiphenyls were the most abundant homologue groups present in the aqueous solution. To compare the change in PCB equilibrium concentration with treatment, the aqueous PCB concentrations during the steady-state period (between 5 and 40 days) were averaged for each treatment time and plotted in Figure 3. With biotreatment, equilibrium aqueous phase concentrations of dichlorobiphenyls decreased from approximately 0.5 μg/L with no treatment to near zero with treatment for 24 months. Trichlorobiphenyls increased from 2.2 to 2.5 μg/L during the first 3 months, followed by little change up to 24 months. Tetrachlorobiphenyls increased with treatment from about 1.2 μg/L for the untreated sediment to 2.6 μg/L for the 24-month treated sediment. The penta- and hexachlorobiphenyls present in small concentrations also showed increased aqueous equilibrium concentration with treatment. The observed increase in equilibrium aqueous PCB concentration with biotreatment was contrary to expectations based on reductions in sediment PCB concentrations.

Organic Matter Changes with Land Biotreatment. To explain the observed increase in aqueous PCB concentrations with biotreatment, it was hypothesized that PCBs were associated with an OM phase that was degraded during biotreatment. Four methods used to measure organic matter in the lagoon sediments were TEO, TOC, oil and grease, and volatile matter. Results of these analyses for the sediment samples are shown in Table 1. All four measures of organic matter showed reductions during biotreatment. Nearly half of the TOC at any time appears to be contributed by a waste oil phase as measured by TEO and oil and grease. It has been shown by Rutherford et al, (*22*) and Sun and Boyd (*29*) that, in the presence of equivalent mass fractions of oil versus other organic matter, the oil compartment dominates the sorption process of a hydrophobic organic compound.

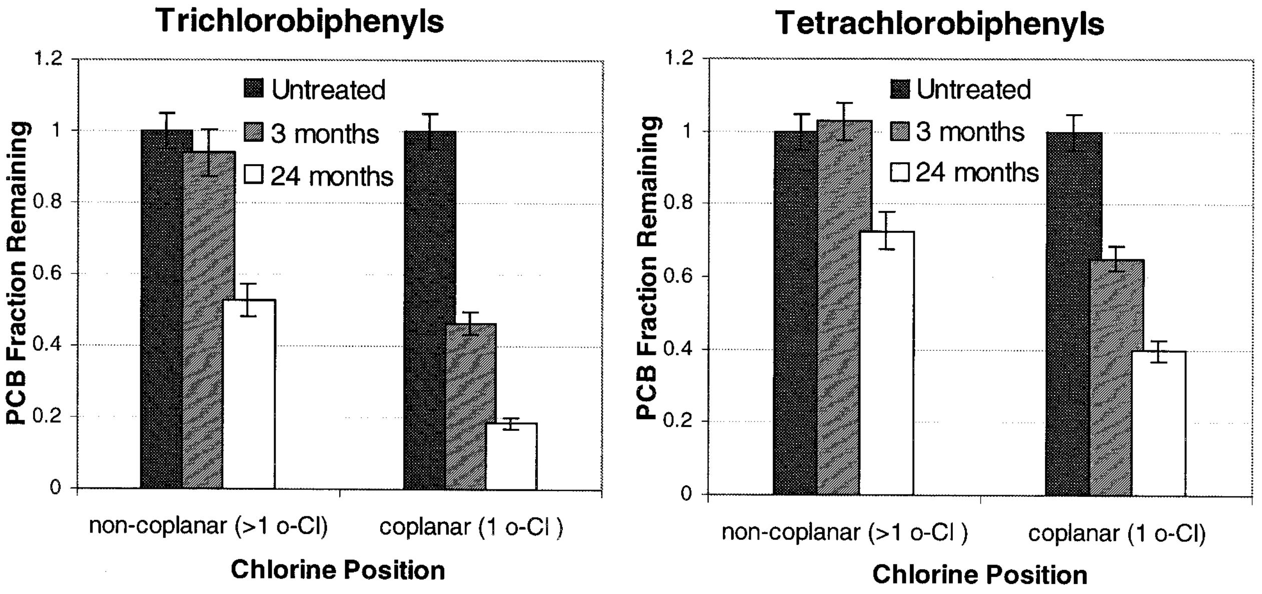

FIGURE 2. Effect of chlorine position on removal during land biotreatment. Bars show 95% confidence intervals.

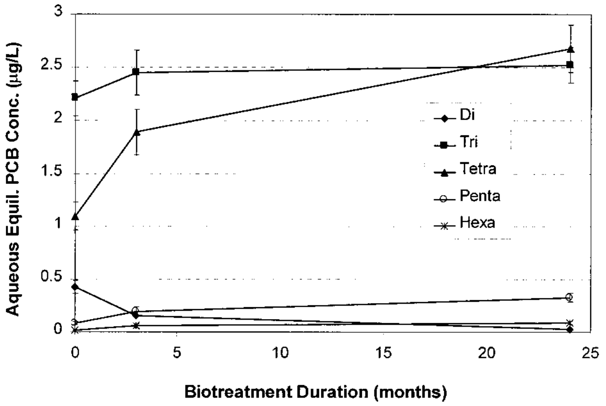

FIGURE 3. Equilibrium aqueous PCB concentration changes with land biotreatment. Bars show 95% confidence intervals.

TABLE 1. Lagoon Sediment Physical/Chemical Characterization

treatment	moisture (%)	pH	volatile matter (%)	total extractable organics (TEO) (%)	oil and grease (O&G) (%)	total organic carbon (TOC) (%)
initial	5.5	6.5	2.4	0.73	0.91	1.8
3 month	12.2	7.2	2.3	0.48	nm[a]	nm
24 month	7.8	6.1	1.8	0.34	0.31	0.67

[a] nm, not measured.

Therefore, waste oil from historical industrial operations as described before was assumed to be the primary constituent responsible for PCB sorption in the lagoon sediments. Waste oil in the sediment was reduced to less than half of the initial amount during the biotreatment process and could have resulted in increased relative amounts of PCBs in the oil phase and thereby in aqueous equilibrium concentrations. In an earlier work using pure PCB mixtures, we observed increased leaching with time of the higher chlorinated PCB homologues from a generator column due to initial removal of more soluble components (*30*). A similar phenomenon of increased leaching of benzo[*a*]pyrene due to compositional changes in a complex mixture during remediation has been predicted by model simulation (*31*).

To further confirm the role of waste oil in determining PCB partitioning behavior, equilibrium studies were conducted using the extracted oil from the untreated lagoon sediment. The dichloromethane-extracted oil from 40 g of sediment was contacted with 400 mL of Nanopure water to test equilibrium partitioning between the oil and aqueous phases. The extracted oil was dried in a 500-mL flask, which resulted in the oil forming a coating inside the flask surface. The flask with the extracted oil and water was shaken very slowly in a shaker table during equilibration to ensure mixing of the water phase without dislodging the oil from the glass surface. The oil was found to be viscous, heavier than water, and adhered to the glass surface. After the equilibration period, the aqueous phase was centrifuged and subjected to alum flocculation to remove any particulate or organic phases and extracted to measure PCBs by congener. The results of

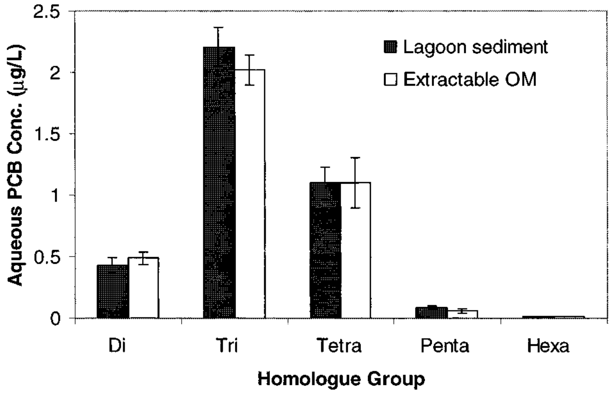

FIGURE 4. Comparison of aqueous equilibrium concentrations of untreated lagoon sediment and extractable organic matter. Bars show 95% confidence intervals.

TABLE 2. Equilibrium Partition Coefficients

		lagoon sediment–water partition (log K_d)			oil phase partition (log K_{oil})		
	log K_{ow} (ref *30*)	0 month	3 month	24 month	0 month	3 month	24 month
di	4.9–5.3	4.1	2.9	2.9	6.3	5.2	5.3
tri	5.5–5.9	4.2	3.9	3.6	6.4	6.3	6.1
tetra	5.6–6.5	4.7	4.4	4.2	6.8	6.7	6.6
penta	6.2–6.5	5.2	4.8	4.5	7.3	7.1	7.0
hexa	6.7–7.3	5.9	5.1	4.7	8.0	7.4	7.2

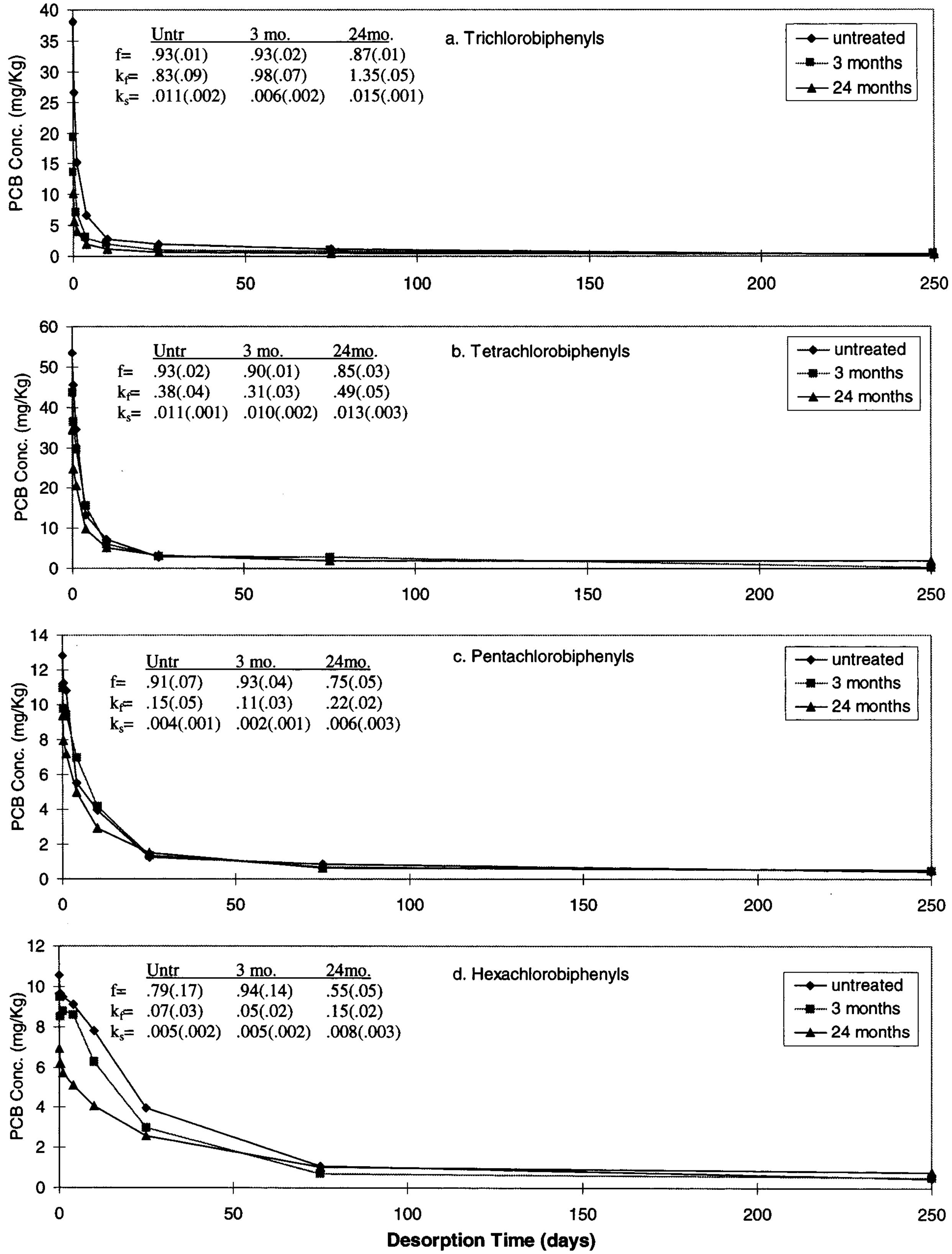

FIGURE 5. Change in PCB desorption during land biotreatment. Standard deviation values shown in parentheses.

11-day equilibrium measurement of the oil phase matched closely to the average equilibrium concentration of the untreated lagoon sediment as shown in Figure 4. This observation supports the hypothesis that partitioning of PCBs between the lagoon sediment and the aqueous phases was controlled by desorption from the waste oil phase present. The effects of changing oil phase amount and PCB composition on equilibrium concentrations are elaborated further in Appendix IV in the Supporting Information.

Partition Coefficient Changes with Land Biotreatment. To quantify the relationship between aqueous and lagoon sediment PCB concentrations at equilibrium, partition coefficients based on total sediment (log K_d) and based on oil (log K_{oil}) were calculated and are reported in Table 2 along with the published range of log K_{ow} values. The values of log K_{oil} for the 24-month treated lagoon sediment were close to the range of reported values of log K_{ow}. However, the values of log K_{oil} for the untreated lagoon sediment were slightly higher. Thus, the aqueous partitioning of PCBs from the sediment oil phase is not very different from that of octanol. Calculated values of log K_d decreased with land biotreatment corresponding to increased aqueous equilibrium concentrations. Values of K_{oil} also decreased with land biotreatment but to a lesser extent. While most of the increase in aqueous phase PCB concentration observed with treatment time may be explained by the reduction in the oil phase, there appear to be other contributing factors as well. One possible explanation for decreasing K_{oil} with biotreatment is that changes in the oil phase composition may lead to changing PCB partitioning. For example, preferential removal of the lower molecular weight fractions of oil with bioremediation has been observed in other studies (*17, 22*). Rutherford et al. (*22*) found an increase in average molecular weight of the total extractable OM from 248 to 338 during soil bioremediation. Increasing average molecular weights of an oil mixture can lead to increased mole fraction of PCBs present leading to increased aqueous concentrations (*30, 31, 33*). Additionally, chemical changes in the oil constituents during biotreatment may alter activity coefficients. Therefore, it is not unreasonable to assume that reduction in oil mass and changes in oil constitution could together lead to increased partitioning of the PCBs into the aqueous phase with biotreatment.

Effect of Ortho-Chlorination on Changes in Equilibrium Concentration. PCB congeners within a homologue group vary in physical/chemical properties and toxicity. Therefore, the influence of chlorine position on partitioning behavior was evaluated. A greater increase in leachability of the noncoplanar congeners as compared to the coplanar congeners of tri- and tetrachlorobiphenyls was observed. The sum of coplanar trichlorobiphenyl congeners decreased by 12% in the aqueous equilibrium concentration in 24 months of treatment as compared to an increase of 52% of the sum of non-coplanar trichlorobiphenyl congeners. For the tetrachlorobiphenyls, both groups of congeners increased in aqueous equilibrium concentration with biotreatment. However, the increase in aqueous equilibrium concentration of the non-coplanar congeners was higher (190%) than that of the coplanar congeners (118%). It should be remembered that concentration of all tri- and tetrachlorobiphenyl congeners in the lagoon sediment decreased during land biotreatment. The non-coplanar tri- and tetrachlorobiphenyls, which are less hydrophobic and more labile, are also less biodegradable. Therefore, a greater partitioning of non-coplanar congeners into the aqueous phase during equilibrium tests is expected as compared to the coplanar congeners.

Thus, during biotreatment, attention must be paid to the less biodegradable non-coplanar PCB congeners that may show increased leachability during biotreatment. Increased leaching of the non-coplanar congeners however may not affect leachate toxicity significantly because non-coplanar congeners are non-dioxin-like and less toxic (*34, 35*).

Comparisons of PCB Desorption Rates and Fast and Slow Pool Speciation. PCB desorption experiments were carried out to investigate how maximum desorption kinetics were affected by land biotreatment. Desorption profiles of tri-, tetra-, penta-, and hexachlorobiphenyl homologue groups for the untreated, 3-month treated, and 24-month treated lagoon sediments are plotted in Figure 5a−d, respectively. Dichlorobiphenyls were completely removed during the first 3 months of treatment and thus are not plotted. For each homologue group, there is a decrease in initial PCB concentration, and the period of fast desorption appears to decrease with increased treatment time.

To estimate desorption rate constants, a dual desorption rate model as presented in eq 1 was fitted to the PCB homologue desorption data for the three sediment treatments. The three parameters fitted to each PCB congener desorption data were the fast and slow desorption rate constants and the fraction of congener in the fast pool and are presented along with the graphs in Figure 5.

A possible mechanistic interpretation of the slow and fast pool speciation of PCBs in the lagoon sediments is the association of PCBs with an oil phase (fast) and a biologically stable sediment OM phase (slow). There is a small increase in the fast pool rate constants after 24 months of biotreatment, which is possibly caused by changes in the nature of the residual oil phase after biotreatment. The estimated fast desorbing fraction for each congener decreased with biotreatment time, which suggests preferential removal of the PCBs from the fast pool during the biotreatment process. Similar decrease in the fast desorbing fraction of PAHs with biotreatment has been reported (*12, 15*). Smaller fast desorbing pool or available fraction of a contaminant has typically been associated with lower toxicity and environmental risk (*4, 11, 12, 15*). In soil/sediment containing little or no oily OM, previous work has demonstrated continued reduction of PCB/PAH availability with biotreatment (*11, 14, 15, 36*). However, in the case of the study lagoon sediments, the equilibrium aqueous PCB concentrations increased with biotreatment. Therefore, in the presence of an oil phase, reductions in total PCBs or fast pool PCBs may not lead to reductions in aqueous PCB availability. Changes in aqueous partitioning behavior caused by alterations in the oil phase during biotreatment may play a more significant role in determining short-term aqueous availability than reductions in total PCBs alone. Therefore, in the short term, PCB availability may increase due to fast reduction in the oil phase. In the long term, PCB availability may be reduced once the oil phase degradation stops or is modified into a different form. It is therefore extremely important to understand the type of contaminant association in soils and sediments and the changes in the nature of organic matter to reasonably anticipate the effect of a treatment process on aqueous availability and leaching. Knowledge gained from this work allows better anticipation of changes in contaminant availability and possible leaching potential during biotreatment of field sediments. Continued monitoring of these study lagoon sediments is ongoing to evaluate very long-term effects (>2 yr) of land biotreatment on PCB and PAH aqueous availability.

Acknowledgments

This study was sponsored by the U.S. Department of Energy, the Office of Biological and Environmental Research (BER) through the Environmental Technology Partnerships (ETP) Program (Contract DE-FG02-96ER62279). The authors would also like to acknowledge Alcoa Inc. (Pittsburgh, PA) for their financial and technical support in this research.

Supporting Information Available

The following additional information are available: 1) PCB extraction and analysis details, 2) PCB mass balance of desorption studies, 3) time to reach equilibrium, 4) Raoult's Law prediction of changes in equilibrium partitioning with treatment. (6 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review May 11, 1999. Revised manuscript received February 29, 2000. Accepted March 3, 2000.

ES9905389