Appendix I. PCB extraction and analysis.

PCB Extraction. PCBs in the lagoon sediment were extracted following EPA method 3550B using three volumes of 40 mL each of acetone-hexane mixture (1:1) and sonicating the slurry for 6 minutes (pulsing for half minute on and half minute off). The XAD was extracted by adding three volumes of 10 mL of acetone-hexane mixture (1:1) to the XAD in a 12 mL glass vial and shaking horizontally in a rotary shaker for 24 hours. The aqueous phase from the equilibrium test vials was extracted by shaking with three aliquots of fresh hexane (3 mL each). Pesticide grade hexane and acetone was used for all extractions.

Silica gel sample cleanup. EPA method 3630C was followed for sample cleanup where, the dried and concentrated extracts were passed through a deactivated silica gel column for the removal of oil and grease and other possible interferences.

GC-ECD analysis. PCB congener specific analysis was performed using a modified version of EPA Method 8082. A Hewlett Packard gas chromatograph (model 5890) with a fused silica capillary column (DB-5, J & W Scientific, 60 m x 0.25 mm inner diameter) and an electron capture detector was used for analysis. PCB standards for calibration were purchased as hexane solutions from Ultra Scientific (North Kingstown, RI). A multi-level calibration table was prepared using a PCB mixture containing 250 µg/L of Aroclor 1232, 180 µg/L of Aroclor 1248 and 180 µg/L of Aroclor 1262 yielding a total PCB concentration of 610 µg/L. Concentrations of individual PCB congeners in the mixture were obtained from Swackhamer (1), and Mullins *et al.* (2). Hexachlorocyclohexane was used as an internal standard, and 22'344'566' octachloro biphenyl, which is not present in commercial Aroclor mixtures, was used as a reference standard. Using this protocol, 89 PCB congeners could be identified and quantified. With the analytical method used, there were some coeluting peaks in the analysis. Where this occurred, coeluting

peaks were plotted together.

Appendix II. Mass balance of total PCB during batch desorption experiments.

To check for any losses of PCBs during the batch desorption kinetic tests, the mass of PCBs

extracted from the lagoon sediment and XAD phases at each time sample were added. Aqueous

PCB concentrations were below detection limits at all times. The results shown in Figure 1 do

not indicate any significant losses during the desorption tests for the untreated lagoon sediment.

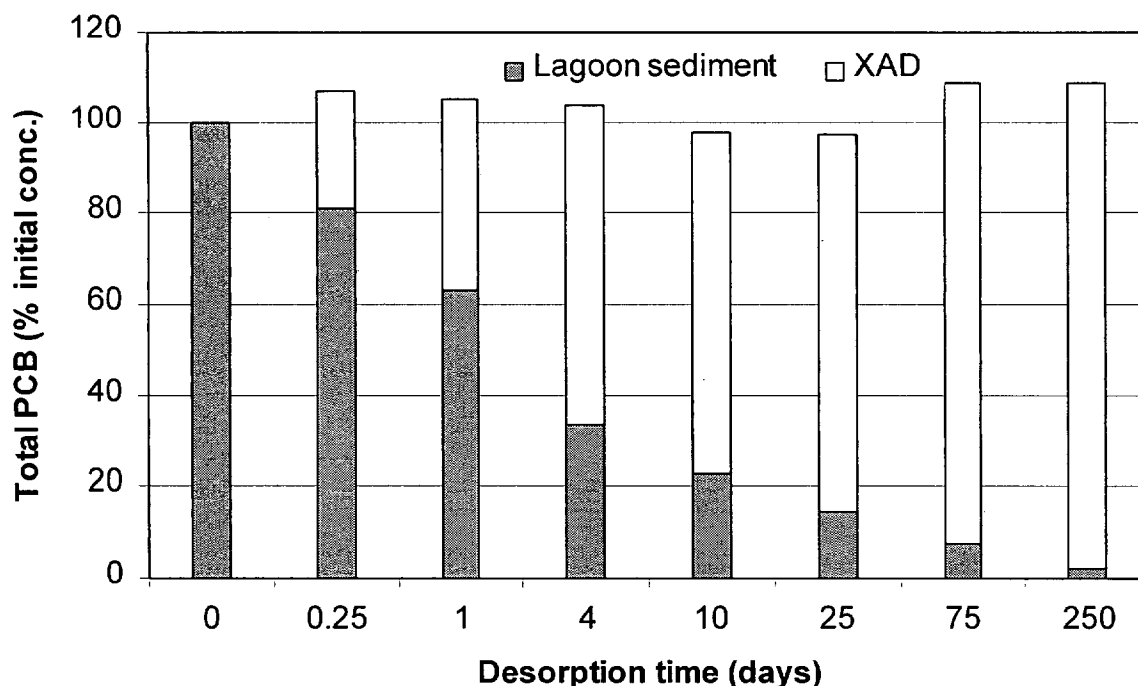Material balance for the treated lagoon sediment studies also indicated no losses.

Figure 1. Mass balance of total PCB for batch desorption experiment.

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Appendix III. Time course to equilibrium. Aqueous equilibrium PCB concentrations were measured after six different equilibration times ranging from 1 hour to 40 days as shown in Figure 2. Based on data shown in Figure 2, it appears that equilibrium was achieved within a few days. This is not surprising for PCBs where the fractional release from the sediment phase required to reach equilibrium is very small due to the low PCB solubility and the relatively high solid to liquid ratio (1:10).
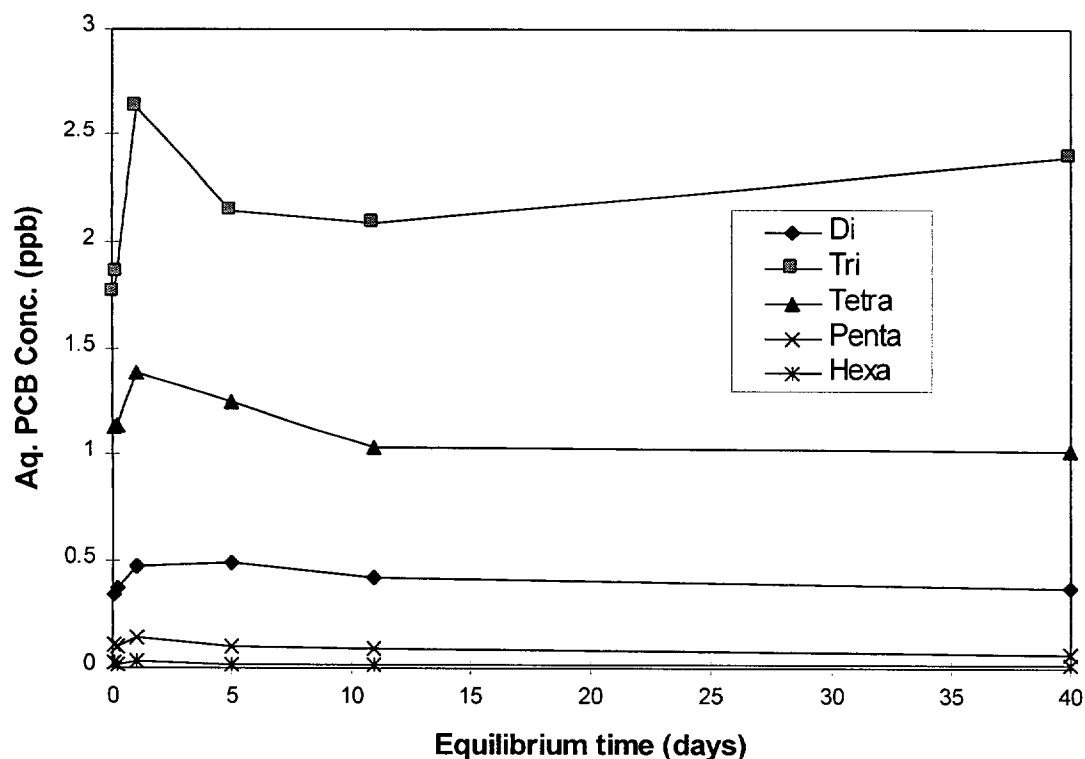

Figure 2. Equilibrium aqueous PCB concentrations measured for different equilibration times.

Appendix IV. Effect of changing PCB composition and oil amount on equilibrium partitioning.

The partitioning of a hydrophobic compound like PCBs or PAHs between an oil phase and the aqueous phase at equilibrium can be modeled based on Raoults Law (3-5). According to Raoult's Law, the solubility of a compound present in an ideal mixture is equal to the solubility of the pure compound multiplied by its mole fraction in the mixture as shown in Equation 1.

$$C_i^{aq} = x_i \, C_i^* \tag{1}$$

where: C_i^{aq} = equilibrium aqueous concentration of component i

x_i = mole fraction of component i in the oil phase

C_i^* = aqueous solubility of pure component i

The mole fraction can be expressed as concentration divided by the molecular weight of the components as shown below.

$$C_i^{aq} = \left[\frac{S_i / M_i}{S_{oil} / M_{oil}} \right] C_i^* \quad \Rightarrow \quad C_i^{aq} = \frac{S_i}{S_{oil}} \left[\frac{C_i^* M_{oil}}{M_i} \right] \tag{2}$$

where: S_i = mass concentration of component i in the sediment

S_{oil} = mass concentration of oil in the sediment

M_i = molecular weight of component i

M_{oil} = average molecular weight of oil mixture

For our study sediments, the contribution of PCBs to the total moles of oil is in the order of 1%, therefore, not significant. So, S_{oil} can be assumed to be independent of S_i. Because the oil is a mixture of various hydrocarbons of unknown molecular weights, a prediction of aqueous PCB

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concentrations based on equation 2 is not possible. However, if we assume that the average molecular weight of the oil phase does not change during biotreatment, we can predict relative changes in PCB concentrations before and after biotreatment as shown in Equation 3. Where, the variables with prime indicates values after biotreatment.

$$\frac{C_i^{aq'}}{C_i^{aq}} = \left[\frac{S_i'/S_{oil}'}{S_i/S_{oil}} \right] \qquad (3)$$

We can try two scenarios:

1. We can assume that during biodegradation the only changes taking place in the lagoon sediments is the biotransformation of some of the PCB congeners leading to a change in residual PCB composition. Total oil amount in the sediment does not change. Based on Raoult's Law partitioning as shown in Equation 2, we can see that a reduction in S_i would result in a reduction in the corresponding aqueous equilibrium concentration. This is illustrated in Figure 3.

2. If the oil amount in the sediment (S_{oil}) decreases during biotreatment, we can see from Equation 3 that the aqueous equilibrium concentration of PCB components will increase. The difference between scenario 1 and 2 is illustrated in Figure 3. Only when total oil amount in the sediment is reduced, there is a resultant increase in the PCB mole fractions in the sediment leading to increases in the aqueous concentrations. Change in PCB equilibrium aqueous concentration due to change in sediment oil amount as measured by TEO and as O&G for the study lagoon sediments are shown in Figure 3. The increase in aqueous concentration is higher when oil is measured as O&G because the reduction in oil as

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measured by O&G was slightly higher than when measured as TEO. However, these predicted values are lower than those measured in equilibrium studies using the 24 month biotreated lagoon sediment. A possible cause of this discrepancy is an increase in average molecular weight of the redidual oil after biotreatment as explained in the main text.
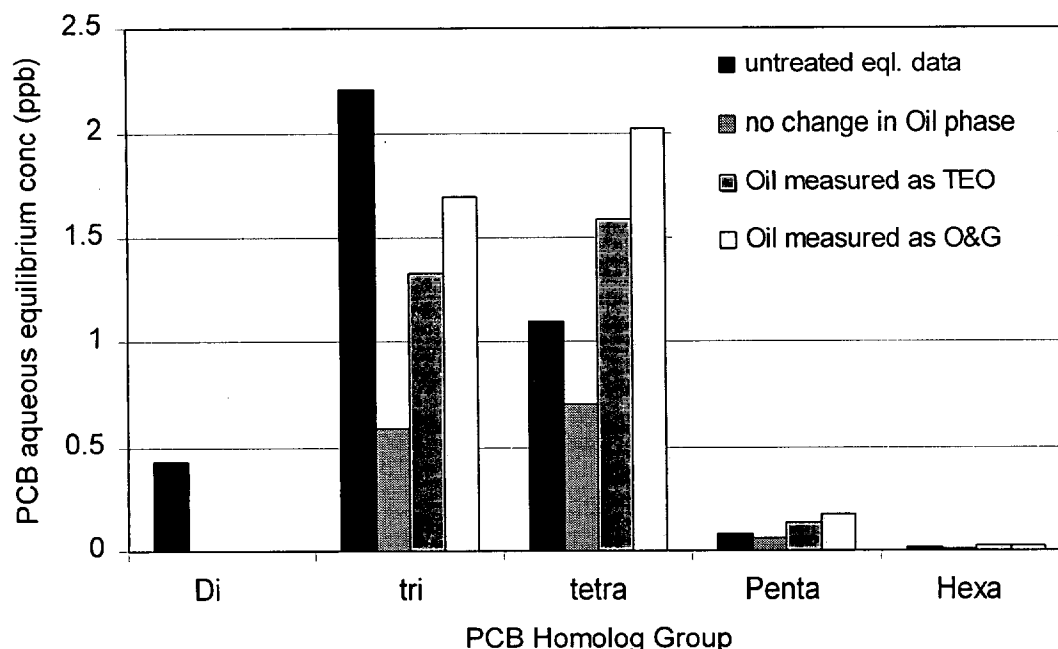

Figure 3. PCB aqueous equilibrium concentration data before treatment and simulated values after 24 month biotreatment for 3 scenarios: 1. Oil amount in sediment does not change, 2. Oil amount in sediment decreases as measured by total extractable organics, 3. Oil amount in sediment decreases as measured by Oil & Grease measurement.

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