Effects of Natural Organic Matter on PCB-Activated Carbon Sorption Kinetics: Implications for Sediment Capping Applications

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In situ capping of polychlorinated biphenyl (PCB)–contaminated sediments with a layer of activated carbon has been proposed, but several questions remain regarding the long-term effectiveness of this remediation strategy. Here, we assess the degree to which kinetic limitations, size exclusion effects, and electrostatic repulsions impaired PCB sorption to activated carbon. Sorption of 11 PCB congeners with activated carbon was studied in fixed bed reactors with organic-free water (OFW) and Suwannee River natural organic matter (SR–NOM), made by reconstituting freeze-dried SR–NOM at a concentration of 10 mg L⁻¹ as carbon. In the OFW test, no PCBs were detected in the column effluent over the 390-d study, indicating that PCB-activated carbon equilibrium sorption capacities may be achieved before breakthrough even at the relatively high hydraulic loading rate (HLR) of 3.1 m h⁻¹. However, in the SR–NOM fixed-bed test, partial PCB breakthrough occurred over the entire 320-d test (HLRs of 3.1, 1.5, and 0.8 m h⁻¹). Simulations from a modified pore and surface diffusion model indicated that external (film diffusion) mass transfer was the dominant rate-limiting step but that internal (pore diffusion) mass transfer limitations were also present. The external mass transfer limitation was likely caused by formation of PCB–NOM complexes that reduced PCB sorption through a combination of (i) increased film diffusion resistance; (ii) size exclusion effects; and (iii) electrostatic repulsive forces between the PCBs and the NOM-coated activated carbon. However, the seepage velocities in the SR–NOM fixed bed test were about 1000 times higher than would be expected in a sediment cap. Therefore, additional studies are needed to assess whether the mass transfer limitations described here would be likely to manifest themselves at the lower seepage velocities observed in practice.

Historically, marine and fresh water sediments in the United States contaminated with polychlorinated biphenyls (PCBs) in excess of 1 mg kg⁻¹ dry weight have been dredged and disposed of in hazardous waste landfills (NRC, 2001). However, dredging has been mired by high monetary costs, poor long-term effectiveness due to incomplete removal of the source contamination zone, and possible release of significant amounts of semivolatile compounds to the atmosphere (Chiarenzelli et al., 1998). In situ sediment capping is being considered as an alternative to dredging because it has the potential to reduce the risks posed by PCBs by creating a long-term barrier between the contaminated sediments and the above biota and water. To increase the effectiveness of sediment caps, engineered sorbents (e.g., activated carbon) are being evaluated due to their proven utility in water treatment (Pirbazari et al., 1992). Three application strategies have been proposed: (i) placing activated carbon amended geotextiles (~1 cm thick) directly on the contaminated sediments (McDonough et al., 2007), (ii) dewatering an area around the sediment and directly blending activated carbon into the sediment by tilling or pressure injection (Cho et al., 2007), and (iii) broadcasting the activated carbon in a slurry onto the contaminated sediment. The goal of these applications is to reduce PCB bioavailability (Werner et al., 2005; Zimmerman et al., 2004, 2005) and/or to eliminate PCB migration into the above biota and water over the long term (several decades or more), thus removing them from the food chain and ultimately reducing human exposure. The work reported herein can be most directly applied to the first application, PCB transport through an activated carbon amended geotextile.

A recent study published by this research group (McDonough et al., 2008) demonstrated that PCB equilibrium adsorption capacities to activated carbon were sufficiently large to be affective in sediment applications even when the activated carbon was preloaded with natural organic matter (NOM). However, it is not...
known if equilibrium sorption capacities can be attained in sediment capping scenarios in the presence of groundwater seepage. These concerns stem from drinking water treatment research that showed NOM decreased PCB sorption to activated carbon by blocking access to pores and forming complexes with the PCBs that were too large to sorb within the activated carbon pores (Pirbazar et al., 1992). Others studies have documented extensive PCB binding with dissolved and particulate organic phases, although estimates vary widely. For example, Totten et al. (2001) showed 6 to 93% of PCBs were bound to NOM, depending on the degree of chlorination. In contrast, Burgess et al. (1996) showed the ratio of PCBs bound to organics to PCBs freely dissolved varied from approximately 3000 to 300,000, indicating a maximum of 0.03% was freely dissolved. Similarly, Vilanova et al. (2001) showed that PCBs in lakes were predominantly bound to particulates, and Marvin et al. (2004) determined that PCBs were primarily associated with humic particulates <2 μm in diameter. The type TOG activated carbon used in this research was previously reported by McDonough et al. (2008) to have a total specific surface area of 990 m² g⁻¹ with >80% contained in micropores (generally less than 2 nm in width). For Suwannee River natural organic matter (SR–NOM; which was used in this work), one study reported diameters between 1.5 and 2.1 nm (Lead et al., 2000), while another reported diameters between 30 and 110 nm (Wagoner et al., 1997). Despite this disparity, size exclusion effects could impair PCB sorption to Type TOG activated carbon. Additionally, NOM can impart a negative surface charge to activated carbon (Fairey et al., 2006), which could further impair sorption of NOM-bound PCBs through electrostatic repulsion.

To be adsorbed by activated carbon, aqueous phase PCBs flowing through a fixed-bed must (i) transport via mixing from the bulk liquid to the stagnant boundary layer surrounding the activated carbon particles, (ii) diffuse through the external boundary layer (by film diffusion), (iii) diffuse into a pore of the activated carbon (by pore and/or surface diffusion), and (iv) adsorb to the activated carbon. Generally, the first and last steps are relatively fast and thus likely not the rate-limiting step (Badruzzaman et al., 2004). External mass transfer (film diffusion) is proportional to the film mass transfer coefficient, $D_f$, and the concentration gradient between the bulk liquid and the external surface of the activated carbon particle. Intraparticle diffusion may occur within the pore space (pore diffusion) or along the pore wall (surface diffusion). To aid in the interpretation of the fixed-bed data and make mechanistic inferences as to the rate-limiting mechanisms, the pore and surface diffusion model (PSDM) (Crittenden et al., 1987a) was applied to the fixed-bed data. Rapid small-scale column test (RSSCT) scaling equations, developed by Crittenden et al. (1986), were used to design the fixed-bed tests because they can be completed in a fraction of the time and consume less water than full-scale experiments. One fixed-bed test was run exclusively with OFW, and a second fixed-bed test was run with background water containing 10 mg L⁻¹ as carbon SR–NOM. The goal of this paper was to assess the degree to which kinetic limitations, size exclusion effects, and electrostatic repulsions impaired PCB sorption to activated carbon in fixed-bed reactors under low flow conditions. Implications of these limitations for application of activated carbon in sediment caps are discussed.

## Materials and Methods

### Chemicals

Eleven PCBs were used in the fixed-bed tests: 22′-, and 34-dichlorobiphenyl, 22′-, and 33′,34′-trichlorobiphenyl, 22′,25′-, 22′,26′-, 22′,26′, 23′,25′, and 33′,34′,35′,36′-tetrachlorobiphenyl, and 22′,33′-, and 33′,34′-,35,36′-pentachlorobiphenyl. Polychlorinated biphenyls were obtained from AccuStandard, Inc. (New Haven, CT) as a solution of 11 PCBs in hexane (100 mg L⁻¹ for each except for 22′-dichlorobiphenyl, which had a concentration of 1000 mg L⁻¹). These congeners were chosen for analysis as the experiments reported herein are an extension of batch isotherm studies (McDonough et al., 2008).

### Source Water

Nanopure water (Barnstead, Dubuque, IA) was used for all aqueous preparations. For the OFW test, nanopure water was amended with 10 mM CaCl₂, as was done in the previously reported batch isotherms (McDonough et al., 2008). For the SR–NOM test, nanopure water was amended with either 10 mM CaCl₂, or 20 mM NaCl and reconstituted freeze-dried SR–NOM (International Humic Substances Society, Atlanta GA, Cat. No. 1R101N) at a concentration of 10 mg L⁻¹ as C. The source waters were buffered at pH 7 using Na₂CO₃.

The two fixed-bed tests were operated at a rate of 1.2 to 2.0 L d⁻¹ for over 300 d. Dissolution of neat PCB congeners was impractical given the long times needed (several weeks to months) to make the required volumes (Luthy et al., 1997). Instead, the generator column technique described by Ghosh et al. (1998) was used. This method was capable of making the necessary volumes of PCB-laden water without using organic solvents that have been reported to alter sorption properties (Coyle et al., 1997). However, this method resulted in time-varying PCB concentrations, which necessitated the use of the PSDM to help make mechanistic inferences.

For each generator column, 125-g batches of 60 × 80 mesh glass beads were washed repeatedly with pesticide-grade hexane. A 5-ml ampoule of the 11 PCBs in hexane was added to the glass beads, mixed thoroughly, covered partially with a glass plate, and left overnight in a fume hood to evaporate the hexane. Next, 2.5-cm i.d. glass columns, 30 cm in length, with Teflon end fittings (Ace Glass, Vineland, NJ) were loaded with the PCB-laden glass beads. Generator columns had an effective bed length between 25- and 75-cm and were operated at the same flow rate as the accompanying fixed-bed test (0.25-, 0.50-, or 1.00-ml min⁻¹). Multiple generator columns were prepared as needed to maintain sufficiently high concentrations (e.g., above the 20 ng L⁻¹ detection limits) of the 11 PCBs throughout these studies. Lastly, source water (either OFW or SR–NOM) was pumped through the generator column(s) in an up-flow mode to a 4-L glass vessel that supplied the fixed-bed reactors.

### Fixed-Bed Column Tests

The RSSCT scaling equations developed by Crittenden et al. (1986) were used to size the column tests. The OFW and SR–NOM fixed-bed tests each consisted of two columns in series, which permitted collection of effluent data for a given empty-
The OFW test was operated for 390 d at a flow rate of 1 mL min–1 (a hydraulic loading rate [HLR] of 3.1 m h–1), which corresponds to a Reynolds number (Re) of 0.12 and EBCTs of 6 (for A1) and 12 (for A2) seconds. The SR–NOM experiment was run for 320 d under five combinations (herein referred to as Phases I, II, III, IV, and V) of flow rate (1.00, 0.50, and 0.25 mL min–1) and source water type (Table 2) to allow independent evaluation of the effects of approach velocity (Re number), NOM, and electrolyte type on PCB sorption with activated carbon. The slowest flow rate was chosen as such to match the EBCT of the OFW test.

Influent and effluent samples were collected in volumetric flasks containing 15 mL of hexane. The sample size collected depended on the flow rate (Table 2)—1000 mL was collected at 1.00 mL min–1, 500 mL was collected at 0.50 mL min–1, and 250 mL was collected at 0.25 mL min–1. Sampling was done in a top-down mode, beginning at B2, for example, followed by B1, and finally B0. This sampling method interrupted flow to the downstream columns; however, the sampling time (∼17 h) was short relative to the length of the experiment (320–390 d), and flow interruptions did not take place within 96 h of sampling at a given port. The sample volume collected, final hexane volume, and gas chromatography (GC) settings resulted in PCB detection limits of 20 ng L–1. Once collected, samples were liquid/liquid extracted with hexane by capping the volumetric flask, inverting, shaking vigorously for 2 min, and decanting the hexane into concentrator tubes. This procedure was done three times, each with fresh hexane. Each hexane extract was reduced to 2 mL under a gentle stream of nitrogen in a water bath maintained at 60°C and stored for up to 1 wk at 4°C until GC analysis.

**Gas Chromatography–Micro-Electron Capture Detector Analysis**

A Hewlett-Packard gas chromatograph (Model 6890) with a 30-m DB-XLB column (diameter 180 μm and film thickness 0.18 μm; Agilent Technologies, Palo Alto, CA) equipped with a micro-electron capture detector and autosampler (Agilent Technologies) was used to quantify the concentrations of the 11 PCB congeners. Details of this method were previously reported by McDonough et al. (2008).

**Modeling**

The PSDM (Crittenden et al., 1987a) was used to help make mechanistic interpretations of the data from the fixed-bed column studies. The PSDM incorporates kinetic and equilibrium parameters and accommodates variable influent concentrations. The model kinetic parameters include external film diffusion and intraparticle pore and/or surface diffusion. The free liquid diffusion coefficient ($D_L$; in cm$^2$ s$^{-1}$) of the PCBs was calculated using the correlation reported by (Hayduk and Laudie, 1974):

$$D_L = \frac{13.26 \times 10^{-5}}{\mu^{1.14} V_b^{0.589}}$$

where $\mu$ is the water viscosity (1 centipoise) and $V_b$ is the molar volume, which was calculated by dividing the PCB

**Table 1. Parameters of the fixed-bed tests.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>OFW test†</th>
<th>SR–NOM test‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC§ mesh size</td>
<td>–</td>
<td>200 × 325</td>
<td>200 × 325</td>
</tr>
<tr>
<td>AC mean diameter</td>
<td>cm</td>
<td>0.0058</td>
<td>0.0058</td>
</tr>
<tr>
<td>Column diameter</td>
<td>cm</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flow rate</td>
<td>mL min$^{-1}$</td>
<td>1.0</td>
<td>1.0, 0.5, and 0.25</td>
</tr>
<tr>
<td>AC bed length</td>
<td>cm</td>
<td>0.5 and 1.0</td>
<td>0.12 and 0.25</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>–</td>
<td>0.12</td>
<td>0.03, 0.06, and 0.12</td>
</tr>
</tbody>
</table>

† OFW, organic-free water.
‡ SR–NOM, Suwannee River natural organic matter.
§ AC, activated carbon.

**Table 2. Conditions in the Suwannee River water fixed-bed test.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Duration</th>
<th>Water type</th>
<th>Electrolyte</th>
<th>EBCT†</th>
<th>HLR‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0–30</td>
<td>SR–NOM§</td>
<td>10 mM CaCl$_2$</td>
<td>1.5, 3</td>
<td>3.1</td>
</tr>
<tr>
<td>II</td>
<td>31–64</td>
<td>SR–NOM</td>
<td>10 mM CaCl$_2$</td>
<td>3, 6</td>
<td>1.5</td>
</tr>
<tr>
<td>III</td>
<td>65–111</td>
<td>SR–NOM</td>
<td>10 mM CaCl$_2$</td>
<td>6, 12</td>
<td>0.8</td>
</tr>
<tr>
<td>IV</td>
<td>112–224</td>
<td>OFW¶</td>
<td>10 mM CaCl$_2$</td>
<td>6, 12</td>
<td>0.8</td>
</tr>
<tr>
<td>V</td>
<td>225–320</td>
<td>SR–NOM</td>
<td>20 mM NaCl</td>
<td>6, 12</td>
<td>0.8</td>
</tr>
</tbody>
</table>

† EBCT, empty bed contact time.
‡ HLR, hydraulic loading rate.
¶ Organic-free water.
molecular weight (MW, g mol⁻¹) by the PCB liquid density (Schwarzenbach et al., 2003). For SR–NOM, Eq. [1] cannot be used because the MW exceeds 1000 g mol⁻¹. In this case, Eq. [2] (Crittenden et al., 1987a) was used:

\[
D_L = 2.74 \times 10^{-5} (\text{MW})^{1/3}
\]  

[2]

The liquid film transfer coefficient, \(D_L\) (in cm s⁻¹), was calculated in the PSDM with the Gnielinski correlation (Sontheimer et al., 1988) and can be thought of as the sorbate velocity through the boundary film layer surrounding the exterior of the activated carbon particles. This velocity is equal to \(D_L\) divided by the boundary layer thickness, \(L_{BL}\), as shown in Eq. [3]:

\[
D_L = \frac{D_L}{L_{BL}}
\]  

[3]

The \(L_{BL}\) increases with decreasing hydraulic loading rate until it reaches its maximum thickness, \(L_{BL\_MAX}\), controlled by the activated carbon particle size (Fig. 1). Hence, the minimum liquid film transfer coefficient is

\[
D_{L\_MIN} = \frac{D_L}{L_{BL\_MAX}}
\]  

[4]

Under the hydraulic loading rates considered herein (and in sediment capping applications), the Gnielinski correlation used in the PSDM breaks down because it does not consider the physical constraint of the boundary layer. In Eq. [4], \(L_{BL\_MAX}\) is calculated based on the geometry of hexagonally closed packed monodisperse spheres of diameter \(D_p\) and is equal to the following:

\[
L_{BL\_MAX} = \frac{D_p}{\sqrt{3}} - \frac{1}{2} D_p \approx 0.077 D_p
\]  

[5]

For each PSDM run, the \(D_L\) calculated using the Gnielinski correlation (Sontheimer et al., 1988) was compared to \(D_{L\_MIN}\) (Eq. [4]), with the larger of these two values used in each simulation. Following the fitting procedure developed by Crittenden et al. (1987a), the intraparticle tortuosity, \(\tau\), was arbitrarily set to one, making the pore diffusion coefficient, \(D_s\), equal to \(D_L\). The surface diffusion coefficient, \(D_s\), was calculated using the Sontheimer correlation with the surface diffusion flux to pore diffusion flux ratio (SPDFR) equal to 6.58. The liquid film transfer coefficient, \(D_L\), was calculated using the Gnielinski correlation unless the correlation produced a value of \(D_L\) that was physically impossible given the maximum thickness of a film layer surrounding packed spheres of mean diameter 0.0058 cm. For spheres of this size, \(D_L\) was calculated using Eq. [4] and the maximum boundary layer thickness (\(L_{BL\_MAX} = 4.5 \times 10^{-4}\) cm) from Eq. [5]. Given the assumptions for \(\tau\) and SPDFR, specific values of \(D_L\), \(D_s\), \(D_p\), and \(D_s\) were in a sense arbitrary; however, the PSDM response to perturbations of these parameters (e.g., sensitivity) is not arbitrary and provides evidence of the relative importance of each parameter and system level evidence of the nature of the mass transfer limitations. The equilibrium capacities of the PCBs on the activated carbon was handled within the PSDM by the Freundlich isotherm parameters (\(K_F\) and \(1/n\)) that have been previously reported by McDonough et al. (2008). As with the kinetic parameters, equilibrium sorption capacities were perturbed in the PSDM to determine their relative importance.

Results and Discussion

Organic-Free Water Fixed-Bed Test

Influent PCB concentrations (A0) ranged from 20 to 30,000 ng L⁻¹; however, none of the 11 PCB congeners were detected in the column effluent (A1) at any point of these fixed-bed tests (data not shown). This result indicated that kinetic limitations did not manifest themselves even at this relatively high HLR (3.1 m h⁻¹). As such, the assumption of equilibrium sorption at lower loading rates typical in sediment systems (i.e., <0.002 m h⁻¹ [Himmelheber et al., 2007]) is likely valid for PCBs in OFW. For sorption processes controlled by equilibrium sorption capacities, breakthrough times for PCBs in OFW through activated carbon can be estimated using the Equilibrium Column Model (Crittenden et al., 1987b). Given the high equilibrium sorption capacities for PCBs with type TOG activated carbon can be estimated using the Equilibrium Column Model (Crittenden et al., 1987b). Given the high equilibrium sorption capacities for PCBs with type TOG activated carbon (McDonough et al., 2008), isolation times could be on the order of several decades or centuries (Murphy et al., 2006). However, such modeling efforts are not representative given that sediment pore water contains NOM, which has been shown to reduce equilibrium sorption capacities (McDonough et al., 2008) and impair PCB-activated sorption kinetics (Pirbazari et al., 1992).

SR–NOM Fixed-Bed Test

The SR–NOM fixed-bed test was operated for 320 d. Concentration profiles plotted on a bed volumes fed (BVF) basis are shown in Fig. 2 for 9 of the 11 selected PCBs. Profiles for the two most hydrophobic PCBs selected (33′44′ and 33′44′5) were not shown because the influent concentrations were below detection (20 ng L⁻¹) throughout the majority of the study. Each panel in Fig. 2 shows the PCB concentrations in the influent (B0) and effluents (B1 and B2) over the five phases (Table 2). As expected based on previous work (Ghosh et al., 1998), B0 concentrations varied temporally because of the generator column technique used to make the aqueous phase PCB solution.

Fig. 1. Schematic of activated carbon in a fixed-bed reactor. The left panel shows particles of diameter, \(D_p\); the middle panel shows the intraparticle pore space with the boundary film layers (dashed lines) surrounding the particles drawn at the maximum film thickness of \(L_{BL\_MAX}\); the right panel shows the intraparticle pore space with polychlorinated biphenyls freely dissolved and bound with natural organic matter.
Figure 2A (22′-PCB) showed the greatest variability in the influent concentration, starting around 25,000 ng L⁻¹, but rapidly dropping off to less than 200 ng L⁻¹ by the middle of Phase I until a new generator column was added in Phase III, where this trend was repeated. Influent profiles for 22′5, 34, 22′66′, and 22′56′ (Fig. 2B–E, respectively) were similar in trend and magnitude (<3000 ng L⁻¹) with a peak in Phase I followed by a steady decrease and subsequent leveling off during Phases IV and V. In contrast, influent profiles for 22′55′, 33′4, 23′55′, and 22′344′ (Fig. 2F–I, respectively) increased throughout Phase I, leveled off during Phases II and III (<600 ng L⁻¹), and then diverged from a uniform trend in Phases IV and V. As expected, the trends observed in the influent concentration profiles followed values of log $K_{OW}$ (a measure of hydrophobicity) as reported by Hawker and Connell (1988). The group of more hydrophobic PCBs had lesser influent concentrations. The log $K_{OW}$s for 22′5, 34, 22′66′, and 22′56′ ranged from 5.21 to 5.62, whereas those for 22′55′, 33′4, 23′55′, and 22′344′ ranged from 5.84 to 6.30.

For a given PCB and BVF (Fig. 2), concentrations of B0 > B1 > B2, indicating that the activated carbon was never exhausted and sorbed PCBs to varying degrees throughout the fixed-bed test. For each PCB congener, we calculated the differences in the influent concentrations ($C_i$) from one sample to the next ($\Delta C_{in,i} = C_{in,i+1} - C_{in,i}$) and took the averages of those differences ($\bar{\Delta}C_{in} = \sum \Delta C_{in} / n$). For 22′-PCB, $\bar{\Delta}C_{in}$ was 3650 ng L⁻¹, whereas it ranged from 140 to 270 ng L⁻¹ for all other congeners. Based on the relatively large value of $\bar{\Delta}C_{in}$ for 22′-PCB, we concluded that reliable inferences regarding its removal could not be made because its influent concentration may have been changing substantially over each 3-d sampling period. Conversely, the relatively small values of $\bar{\Delta}C_{in}$ for the other congeners indicated their influent concentrations were more stable over the 3-d sampling period, which permitted inferences regarding their removal to be made by normalizing the effluent data (B1 and B2) by their influent concentrations (B0).

Insights into the rate-limiting sorption mechanism were made by comparing ($C_i/C_0$)AVG values (Fig. 4) for two hydraulic loading rates at a given EBCT. For the SR–NOM test, ($C_i/C_0$)AVG values were compared for (i) Phases I and II at the 3-s EBCT (values in red boxes in Fig. 4) and (ii) Phases II and III at the 6-s EBCT (values in black boxes in Fig. 4). In 13 of 15 instances (the 6-s EBCT in Fig. 4B was not included because both values were zero), these ($C_i/C_0$)AVG values increased at the 95% confidence level with decreasing HLR (Table 2)—this trend held for the two aberrant instances (Fig. 4H); however, the large 95% confidence levels precluded statistically

Fig. 2. Influent (B0) and effluent (B1 and B2) polychlorinated biphenyl concentrations in the Suwannee River natural organic matter fixed-bed test. Background colors indicate the phase corresponding to the conditions in Table 2: Phase I, gray; Phase II, green; Phase III, tan; Phase IV, blue; Phase V, pink.
significant conclusions in these cases. These data support the assertion that PCB sorption to activated carbon was external film diffusion limited. The thickness of the boundary layer thickness, $L_{BL}$, increases with decreasing HLR until it reaches $L_{BL_{MAX}}$ (Fig. 1). Because we observed an indirect relationship between $(C/C_0)_{AVG}$ and HLR for a given EBCT, we can conclude that sorption was external film diffusion limited.

From Phases III to IV, the source water was changed from SR–NOM to OFW while holding the HLR constant. From Fig. 4, $(C/C_0)_{AVG}$ values decreased for all PCBs that had detectable effluent concentrations at the 6- and 12-s EBCTs. Therefore, it can be concluded that PCB sorption sites were available before Phase IV, but their occupation was precluded. Values of $C/C_0$ generally decreased through Phase IV (Fig. 3), suggesting that NOM diffused out of the activated carbon pores due to the driving force for NOM desorption from the activated carbon, freeing additional PCB sorption sites and improving fixed-bed performance. These results support the assertion that in addition to NOM pore blockage, other processes impaired PCB sorption in Phases I, II, and III. Pirbazari et al. (1992) showed that PCBs were bound to NOM in activated carbon effluents. Because of their increased size, PCB–NOM complexes would diffuse slower to sorption sites within the activated carbon or not at all due to size exclusion (e.g., if the PCB–NOM complexes were larger than the activated carbon pores). The rate-limiting sorption processes were evaluated further in the modeling section.

Lastly, electrostatic repulsion between the NOM-coated activated carbon and the PCB–NOM complexes could impede sorption processes (Fairey et al., 2006). This hypothesis was tested in Phase V where SR–NOM was amended with 20 mM NaCl instead of 10 mM CaCl$_2$. Despite the dissimilar ionic strengths and background cations, $C/C_0$ values were comparable to those in Phase III for all the congeners (Fig. 4), indicating that fixed-bed performance was similar with both calcium and sodium background electrolytes. As such, under the conditions of these experiments, electrostatic repulsion appears to not be as important as size exclusion and kinetic limitations induced by PCB–NOM complexation and NOM fouling of the activated carbon.

Pore-Surface Diffusion Model Calibration

The PSDM was used to help make mechanistic inferences into the SR–NOM fixed-bed data. Congener 22’55’-PCB was selected for PSDM calibration purposes because it had a midrange $K_{OW}$ (5.82) of the selected PCBs (range 4.65 to 6.89). Had another congener been selected for calibration, the values of the various fitting parameters may have been different, but the assessment of their relative importance would not change. Only Phases I, II, and III (SR–NOM with calcium amendment) were modeled because the background water was changed in Phases IV (OFW) and V (SR–NOM with sodium amendment).
Figure 5 displays the results from several PSDM model simulations with varied model parameters. Figure 5A–B evaluated the effect of changing equilibrium sorption capacity (i.e., $K_F$ and $1/n$). Under these conditions, the PSDM predicted no breakthrough, indicating sorption capacity was not a limiting factor and supporting the results from the OFW experiment. Model sensitivity to film diffusion was evaluated (Fig. 5C) by arbitrarily decreasing $D_f$ one order of magnitude. While the resultant $D_f$ is not physically possible (i.e., $D_f$ for a PCB with its known MW requires a boundary layer thickness than $L_{BL_{MAX}}$), the resultant PSDM simulation captured the shape of the B1 data, indicating that the actual conditions in the SR–NOM fixed-bed test manifested themselves as an external mass transport limitation that can be modeled as a film diffusion limitation in the PSDM. To evaluate intraparticle mass transfer effects, surface and pore diffusion were effectively disabled in Fig. 5D and E, respectively. Collectively, Fig. 5D and E indicated that pore (and not surface) diffusion appeared to be the important intraparticle mass transfer mechanism but that external mass transfer was the dominant rate-limiting mechanism. This result agrees with previous experimental research that found sorption of synthetic organic chemicals was controlled by pore diffusion because NOM coated the activated carbon internal pores, eliminating chemical mass transport by surface diffusion (Hand et al., 1989). For Fig. 5F, an ad hoc approach was used to fit the B1 data through changing $D_f$. While the resultant PSDM fits captured the B1 data in Phases I, II, and
Fig. 5. Experimental (symbols) and model simulated (lines) results for influent (B0) and effluent (B1) concentrations of 22′55′ polychlorinated biphenyl vs. bed volumes fed in the Suwannee River natural organic matter fixed-bed test. P1 (Phase I), P2 (Phase II), and P3 (Phase III); $K_F$, Freundlich coefficient, in (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$; $D_L$ (free liquid diffusion coefficient), $D_s$ (surface diffusion coefficient), and $D_p$ (pore diffusion coefficient) in cm$^2$ s$^{-1}$; and $D_f$ (liquid film transfer coefficient) in cm s$^{-1}$; $L_{BL_{MAX}}$ maximum boundary layer thickness; PSDM, pore and surface diffusion model.
III, the required values of $D_t$ were smaller than physically possible given the maximum boundary layer thickness ($L_{BL\_MAX}$). As such, other phenomena, not yet considered, must have occurred in the SR–NOM fixed-bed tests. Another phenomenon that was investigated assumed PCB–NOM complexes diffused rather than freely dissolved PCBs (Fig. 5G–H). Because of the existing disparity in the literature regarding the diffusivity of Suwannee River NOM, two diffusivities were used. For Fig. 5G, values reported by Lee et al. (2004) were used ($MW = 2360\ \text{g mol}^{-1}$ and $D_t = 1.4 \times 10^{-6} \ \text{cm}^2 \ \text{s}^{-1}$). For Fig. 5H, the MW of SR–NOM reported in Wagoner et al. (1997) ($MW = 22,000–26,000 \ \text{g mol}^{-1}$) was used with the correlation reported in Crittenden et al. (1987a) to calculate $D_t = 9.5 \times 10^{-7} \ \text{cm}^2 \ \text{s}^{-1}$. The resultant simulations were similar to Fig. 5C without having to violate the physical limits of the boundary layer (i.e., $L_{BL\_MAX}$) and are further evidence that PCBs bound with NOM may have limited PCB sorption to activated carbon. The conditions that produced the PSDM model fit in Fig. 5F (the “best-fit”) were applied to seven of the PCBS. The results from these simulations are presented in the Supplemental Materials (Application of the Calibrated PSDM and Supplementary Fig. S2).

Implications for Sediment Cap Performance at Field Seepage Rates

Analysis of the data in Fig. 3, 4, and 5 provided evidence that the presence of NOM in the background water fouled the activated carbon surface and formed complexes with the PCBs that may have slowed external (film) and intraparticle (pore) diffusion and/or prevented sorption via size exclusion (PCB–NOM complexes larger than the activated carbon pores). However, these observations were made at approach velocities between 0.8 and 3.1 m h$^{-1}$, whereas values $<0.002 \ \text{m h}^{-1}$ are expected in practice. Thus, contact times in a sediment cap would be larger that those evaluated here, and the apparent kinetic limitations brought about by PCB–NOM binding may be overcome. Operating laboratory-scale columns at approach velocities typical of sediment systems is impractical due to the long time required for breakthrough and to produce sufficient sample volumes required for PCB analyses. However, within a sediment cap, equilibrium sorption of PCBs to activated carbon will indeed be favored given sufficient time for PCB desorption from NOM. The PCB–NOM desorption kinetics should be measured, and this information should be used to further refine models like the PSDM to account for PCB–NOM complexation.

Conclusions

Fixed-bed activated carbon columns were used to evaluate PCB sorption in OFW and synthetic SR–NOM, which contained 10 mg L$^{-1}$ as carbon. In the OFW test, no PCB breakthrough occurred during the 390-d long fixed-bed test, even though the approach velocity was 3.1 m h$^{-1}$, approximately 1000 times higher than would be expected in a sediment capping application. This result suggests that equilibrium PCB sorption capacities could likely be attained for PCBs dissolved in organic-free water. When NOM was present in the background water, however, partial PCB breakthrough occurred throughout the 320-d-long study. Systematic changes in the approach velocity and background water conditions were interpreted using the PSDM modified to prevent physically impossible boundary-layer thicknesses. Simulations showed that PCB sorption was likely inhibited by (i) NOM fouling of the activated carbon surfaces and (ii) PCB–NOM binding which slowed sorption kinetics and/or prevented PCB sorption by size exclusion (e.g., the PCB–NOM complexes were larger than the activated carbon pores). However, these limitations may be overcome at approach velocities more typical in sediment capping (a factor of 1000 less than those evaluated in this research) provided that PCB desorption from NOM is sufficiently rapid. Future work should focus on measurement of PCB desorption kinetics from NOM as a function of NOM characteristics and background solution conditions. This information coupled with the concept of $L_{BL\_MAX}$ introduced in this article, should be incorporated into the PSDM to facilitate realistic PCB capping model simulations. These experimental and modeling efforts are necessary to evaluate the nature of the sorption limitations described in this manuscript and to determine if activated carbon is a suitable amendment for sediment capping applications.

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