Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps

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Abstract: In situ capping manages contaminated sediment on-site without creating additional exposure pathways associated with dredging, e.g., sediment resuspension, and potential human exposure during transport, treatment, or disposal of dredged material. Contaminant mass is not immediately removed in sediment capping, which creates concerns over its long-term effectiveness. Groundwater seepage can also decrease the effectiveness of in situ capping. This study compares the effectiveness of commercially available sorbents that can be used to amend sand caps to improve their ability to prevent contaminant migration from the sediments into the bioactive zone. Amendments evaluated include coke, activated carbon, and organic-rich soil. The properties relevant to advective-dispersive transport through porous media (sorption, porosity, dispersivity, and bulk density) are measured for each material, and then used as inputs to a numerical model to predict the flux of 2,4,5-polychlorinated biphenyl (PCB) through a sand cap amended with a thin (1.25-cm) sorbent layer. Systems with and without groundwater seepage are considered. Isolation times provided by the sorbent layers increased with increasing sorption strength and capacity (activated carbon $\gg$ coke $\approx$ soil $\gg$ sand). The effective porosity, dispersivity, and bulk density of the sorbent layer had little effect on cap performance compared to sorption strength (K_f). In the absence of seepage, all sorbents could isolate PCBs in the underlying sediment for times greater than 100 years and would be effective for most cap applications. With groundwater seepage (Darcy velocity $= 1$ cm/day), activated carbon was the only sorbent that provided contaminant isolation times greater than 60 years. Long isolation times afforded by sorbent-amended caps allow time for inherently slow natural attenuation processes to further mitigate PCB flux.

CE Database subject headings: Sediment; Activated carbon; Adsorption; Ecology; Remedial action; PCB; Biodegradation.

Introduction

Polychlorinated biphenyls (PCBs) have been associated with a variety of risks to humans and ecosystems [National Research Council (NRC) 2001], and the proper management of PCB contaminated sediment has proven to be a widespread, complex, and costly issue. A NRC committee on the remediation of PCB contaminated sediment recently proposed a risk management framework designed to minimize short-term and long-term risk to human and ecological endpoints (NRC 2001). Within this framework, Reible et al. (2003) consider the surface-area weighted average concentration (SWAC) as a useful surrogate risk metric. SWAC is the average contaminant concentration in the biologi-

cally active portion of sediment, estimated as the top 10 ± 5 cm (Thibodeaux 1996). SWAC assumes that PCBs that are not in or likely to enter the biologically active zone do not pose significant risk. Within this framework, treatments that mitigate PCB flux from the underlying sediment into the bioactive zone can effectively manage risk.

Monitored natural attenuation (MNA), dredging, and in situ capping (ISC) are commonly employed techniques to minimize SWAC. In many cases, an insufficient rate of sediment deposition or contaminant biodegradation makes MNA alone an insufficient management technique for PCB contaminated sediment (USEPA 1998). Dredging is a frequently prescribed management technology that provides rapid PCB mass removal from the local environment (USEPA 2002; USEPA and WDNR 2003), but has many potential disadvantages, such as the need to treat the wastewater generated and the residual contamination left behind (Palermo et al. 1990; Reible et al. 2003). ISC can potentially overcome some of the problems associated with dredging and MNA. ISC eliminates contact between the benthic community and the underlying contaminated sediment with a physical barrier of clean material, usually sand. The objectives of ISC are to isolate and stabilize contaminants in the underlying sediment, reduce contaminant flux into the biologically active portion of the sediment, and create new habitats for aquatic organisms (Reible et al. 2003). Layered sediment cap designs have been proposed (Palermo et al. 1998) (Fig. 1). PCBs from the underlying sediment can be transported through a sorbent layer placed between the sediment and the bioactive zone by diffusion and by porewater advection if groundwater infiltration is occurring. Increasing the (PCB-solid) partitioning coefficient in this layer will lengthen

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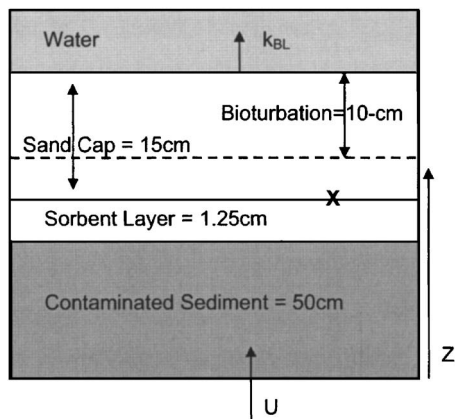
Fig. 1. Proposed design for thin active layer in sand cap. X denotes location where flux was calculated.

the time before PCBs break through the layer, and will decrease the maximum contaminant flux into the bioactive zone (Thoma et al. 1993).

Potential sorbent amendments include organic rich soils and sediments or thermally altered carbonaceous materials such as coke and activated carbon (AC). The tendency for hydrophobic organic compounds, such as PCBs and polyaromatic hydrocarbons (PAHs) to strongly sorb to these materials is well documented (Grathwohl 1990; Luthy et al. 1997; Accardi-Dey and Gschwend 2002). Coke and AC have demonstrated non-linear sorption isotherms and extremely high equilibrium sorption partition coefficients for PCBs (Kleineidam et al. 2002; Jonker and Koelmans 2002). Further, it has been shown that PAHs and PCBs bound to coke and AC are less bioavailable than when bound to organic carbon (Talley et al. 2002; Ghosh et al. 2003; McCleod et al. 2004). Thus a sediment cap containing these materials should significantly retard PCB transport through it, and decrease the bioavailability of PCBs that are ultimately concentrated in this layer.

Long periods of chemical isolation provided by sorbent-amended sediment caps will allow time for inherently slow PCB dechlorination processes in buried sediment (e.g., anaerobic biodegradation) and will decrease the overall PCB flux into the bioactive zone. Microbial reductive dechlorination of PCBs in buried sediment is well documented (Brown et al. 1987; Quensen III et al. 1990; Abramowicz et al. 1993; Rhee et al. 2001). Preferential dechlorination of para- and metachlorines over ortho chlorines has also been observed (Fennel et al. 2004), so even if anaerobic dechlorination cannot mineralize PCBs in the underlying sediment (Abramowicz et al. 1993; Rhee et al. 2001) it may decrease the overall toxicity of the sediment by selective removal of para- and metachlorines to form less toxic orthosubstituted PCB congeners (Brown et al. 1987; Lowry and Johnson 2004). The sorbents and hydrodynamic conditions that can provide the isolation time required for natural attenuation processes to significantly decrease PCB mass flux into the bioactive zone are not known.

This study compares the ability of sand caps amended with a thin (1.25 cm) sorbent layer of soil, coke, or AC to isolate PCBs and mitigate PCB flux into the biologically active zone. 2,4,5-PCB is used as a model contaminant and provides a conservative estimate for PCB flux as this lower chlorinated congener is less hydrophobic and more mobile than the higher chlorinated congeners that make up the majority of PCBs released into the

environment. Diffusion controlled and advection controlled sediment systems are considered. The objectives were to (1) determine the isolation time provided by each material in the presence and absence of groundwater seepage; (2) compare the effectiveness of low-cost sorbents (coke and soil) with activated carbon; (3) estimate the PCB-attenuation rate needed to achieve significant PCB degradation before breakthrough; and (4) evaluate the effect of PCB degradation in the underlying sediment on PCB mass flux into the bioactive zone of sediment. Physical properties important for estimating cap performance are measured including the Freundlich constant (K_f) and exponent (n), hydrodynamic dispersivity (α), bulk density (ρ_b), and effective porosity (ϵ). The Freundlich sorption parameters (K_f and n) are measured in batch isotherm experiments using 1,2-DCB as a surrogate compound and scaled up to 2,4,5 PCB based on sorbate solubility. The physical properties and the total sorptive capacity of each sorbent were determined in column experiments. The measured physical properties are then used as inputs to a numerical model to predict the PCB breakthrough time and flux through a thin layer (1.25 cm) of the cap material and into the bioactive zone as a function of time. Different assumed PCB chemical half-lives are used to estimate PCB mass loss in each scenario and the impact of degradation on flux.

Materials and Method

1,2-dichlorobenzene (DCB) (99% Aldrich), hexane optima (Fisher), and tetrachloroethene (99% Acros Organics) were used as received. A black carbon surface area reference material (24.1 ± 0.6 m^2/g) was used as received for quality control (Micrometrics, Norcross, Ga). Sorbents evaluated include coke (U.S. Steel Clairton Works, Clairton, Pa.), F-100 and F-200 activated carbon (AC) (Calgon Carbon, Pittsburgh), organic-rich soil (3.2% OM) (Sestili Nursery, Pittsburgh), and silica sand (AGSCO Corporation, Hasbrouck Heights, N.J.).

Sorbent Characterization

The N$_2$-BET specific surface area of soil and coke was measured using a Nova 2100 (Quantachrome). The N$_2$-BET specific surface area for AC was supplied by the manufacturer. For coke, the specific surface area was also determined by Hg porosimitry (Quantachrome Poremaster 60) which includes the surface area contributed by pores up to 960 μm. The total organic carbon of soil and Anacostia River sediment was determined by a commercial analytical laboratory using ASTM D2974-87 (UEC Labs, Monroeville, Pa.). Bulk density (ρ_b) was measured gravimetrically by weighing dried material in a 500 ml container. The effective porosity (ϵ) and dispersivity (α) for a layer of each sorbent was determined from NaC1 tracer studies in sorbent filled columns (10 cm $\times$ 1.25 cm) (van Genuchten and Alves 1982). Sorption capacity (mg sorbate/g sorbent) was measured in identical columns by monitoring the breakthrough of 1,2-DCB. Influent ($\sim$20 ppm) and effluent 1,2 DCB samples (1 mL) were extracted into hexane (1 mL) and analyzed by gas chromatography GC/ECD. The sorption capacity of each sorbent was determined by numerical integration of the area between the influent and effluent 1,2-DCB measurements until complete breakthrough.

Sorption Isotherms

Sorption isotherms were measured for coke and soil. Sorbents were pulverized, sieved ($d_p < 0.5$ mm), and dried for 12 h at

105°C to remove H_2O. A measured mass of sorbent was added to glass serum bottles containing 130 mL of an aqueous l,2-DCB solution (2–40 mg/L) and 30 mL of headspace. The bottles were capped and equilibrated for 10 days at 25°C. Headspace samples were analyzed by GC/ECD to determine the concentration of 1,2-DCB. The aqueous phase 1,2-DCB concentration was then calculated using the measured dimensionless Henry's constant (McAuliffe 1971), and the sorbed mass was determined by difference ($M_{sorbed}=M_{initial}-M_{aq}-M_{hs}$). 1,2-DCB was used as a surrogate for PCBs because it is easier to handle in the laboratory and has been used extensively as a probe compound to investigate sorption of chlorinated aromatic semivolatile organic compounds (Culver et al. 2000; Ju and Young 2004). Also, it allowed direct comparison of results with those of Kleineidam et al. (2002) who also used 1,2-DCB. To facilitate the scaleup of the sorption parameters measured for 1,2-DCB to those of 2,4,5-PCB and to other similar sorbates, solubility-normalized sorption isotherms were created (Carmo et al. 2000), where K_f^*=unit-equivalent Freundlich coefficient (mg/kg); S_{aq}=aqueous solubility of the sorbate (mg/L); C_s=sorbed contaminant mass (mg/kg) in equilibrium with an aqueous contaminant concentration C_w (mg/L); and n=Freundlich exponent (dimensionless)

$$C_s = K_f^* \left(\frac{C_w}{S_{aq}} \right)^n \tag{1}$$

The Freundlich parameters for 2,4,5-PCB were then determined using the aqueous solubility of 2,4,5-PCB (Kleineidam et al. 2002). Solubility normalized Freundlich parameters for activated carbon were obtained from the literature (Kleineidam et al. 2002). A PCB-sand partition coefficient was estimated based on the surface area of sand and aqueous activity coefficient of 2,4,5-PCB (Schwarzenbach et al. 2003).

Model Development and Transport Simulations

Migration of 2,4,5-PCB is simulated in an initially uniformly contaminated 50-cm sediment layer which is capped by a thin (1.25-cm) sorbent layer and an overlying 15-cm layer of sand (Fig. 1). The upper 10-cm portion of the sand layer is the bioactive zone and is compromised by benthic activity (Thibodeaux 1996). Benthic activity in this zone reworks the surficial sediments at an effective diffusion coefficient of $D_{bio}=10$ cm²/yr, and a benthic boundary layer mass transfer coefficient (k_{bl}) of 1 cm/h is assumed (Palermo et al. 1998).

For one-dimensional transport with nonlinear sorption and overall first-order contaminant degradation, the governing differential equation for contaminant transported in the sediment porewater is given in Eq.(2)–(4) (Thoma et al. 1993; Fetter 1999)

$$R \frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial z} + D_{eff} \frac{\partial^2 C}{\partial z^2} - R k_r C \tag{2}$$

$$R = \varepsilon + K_f \cdot n \cdot \rho_b \cdot (C^{n-1}) \tag{3}$$

$$D_{eff} = D_w \varepsilon^{4/3} + \frac{U}{\varepsilon} \alpha \tag{4}$$

where C=porewater concentration (kg/m³); R=retardation factor (dimensionless); U=groundwater seepage (Darcy) velocity (m/s); and D_{eff} [Eq. (4)] is the effective hydrodynamic dispersion coefficient (m²/s), which considers molecular diffusion, tortuosity, and dispersivity; k_r (1/s) is the overall first-order decay term for contaminants that includes transformation on the solid and in the

aqueous phases; K_f=Freundlich coefficient (m³/kg *(kg/m³)$^{1-n}$); n=Freundlich exponent (dimensionless); and ρ_b=dry bulk density of the solids (kg/m³). For a linear relationship ($n=1$), K_f represents the commonly used sediment/water equilibrium partition coefficient. The contaminant flux, Γ [kg/(m² *s)], is calculated using

$$\Gamma = U^* C - D_{eff} \frac{\partial C}{\partial z} \tag{5}$$

A no flux condition at the bottom of the contaminated sediment layer (Neumann boundary condition) is applied. Flux at the cap/water interface (Γ), assuming negligible concentrations in the overlying water column, is given by

$$\Gamma = k_{bl}^* c \tag{6}$$

The initial condition assumes a uniformly contaminated sediment layer underneath the cap material, and no contaminants in the cap.

The values of sorption parameters (K_f, n) and porosity (ε) are based on the measured properties for those layers. The values of each of the parameters can be defined separately within each layer (e.g., the reaction terms can be turned off in all layers except the underlying sediment). Linear sorption ($n=1$) is assumed in the contaminated sediment and estimated based on organic carbon content (Karickhoff et al. 1979) (Table 1). This provides a conservative estimate for the calculated flux (i.e., an overestimate), however, the assumed sorption model for the underlying sediment (linear versus nonlinear sorption) does not significantly affect contaminant flux through the cap (Marquette 2005).

To solve the system of governing partial differential equations (PDE), the PDE coefficients are determined by MATLAB v6.5 then transferred to FEMLAB 3.0a, finite element solver. The spatial dimension is discretized on a FEMLAB generated mesh consisting of 865 nodes that increase in density near boundaries. Time stepping is optimized by FEMLAB with iterations subject to a relative tolerance of 10^{-4}. Built-in integration functions return flux and concentration point data for specified temporal and spatial coordinates. The model was verified by comparison with the steady-state flux solution for a semi-infinite, constant concentration boundary layer cap model (Reible et al. 2004) for advection and diffusion dominated transport subject to contaminant decay. Boundary conditions of the numerical model were changed to a constant concentration at the sediment/cap interface to be consistent with the analytical counterpart. The numerical model produces a maximum advective flux equivalent to the analytical steady-state value, independent of cap geometry. For the diffusion only case, the flux predicted by the numerical models agree within 2% of the flux predicted by the analytical model. Furthermore, the numerical model satisfies the expectation that a depleting contaminant layer would yield an equal or lower flux as compared to a layer of constant concentration (Reible et al. 2004).

Results and Discussion

Sorbent Properties

The solubility normalized sorption isotherms for coke, soil, AC, and sand are shown in Fig. 2. The measured Freundlich parameters and other physical properties of each sorbent are summarized in Table 1. The measured Freundlich partition coefficient (K_f) for soil [1.6% organic carbon (OC)] and coke were similar. Both were 2–3 orders of magnitude lower than for AC, and ~4 orders of magnitude higher than for sand. One objective of this

Table 1. Measured or Estimated Sorbent Properties used in Model Simulations

Property	AC	Coke	Soil	Sand	Sediment[a]
$\log K_f^*$ (mg/kg)	6.06[b]	3.95	4.13	0.1	3.67
$\log K_f$ (2,4,5-PCB)[d] (mg/kg)$((mg/L)^{-n})$	6.18[b]	4.66	4.9	1.35	3.92
Freundlich exponent (n)	0.28[b]	0.84	0.94	1	1
Sorption capacity					
(mg 1,2-DCB/g sorbent)	260.7	0.39	0.38	0.0016	NM
Fraction organic carbon f_{oc}	NM	NM	0.016	0	0.024
Specific surface area (m²/g)[e]	919	1.9/12.9[f]	6.6	<1	NM
Porosity (ε)	0.53	0.48	0.47	0.29	0.25[c]
Bulk density (ρ_b) (g/cm³)	0.66	0.72	0.99	1.65	1.95
Dispersivity (α) (cm)	0.4	0.5	0.7	0.15	2

Note: NM=Not measured.

[a]"Typical" sediment assumed with K_{Fr}^* estimated based from Anacostia River sediment sample f_{oc} measurement using Karickhoff et al. (1979).

[b]Published F-100 Calgon carbon activated carbon properties (Kleineidam et al. 2002).

[c]Assumed.

[d]Properties of 2,4,5-PCB from Schwarzenbach et al. (2003): $\log K_{om}$:5.74 $L_{water}/L_{octanol}$ C_w^{Sat}: 0.14 mg/L $K_f = K_f^* S^{1/n}$. A conversion factor of $[1 \times 10^6]$ 1000^{-n} is needed to convert K_f from units of $[kg/kg^*(kg/m^3)^{-n}]$ to $[mg/kg^*(mg/L)^{-n})]$.

[e]N₂-BET.

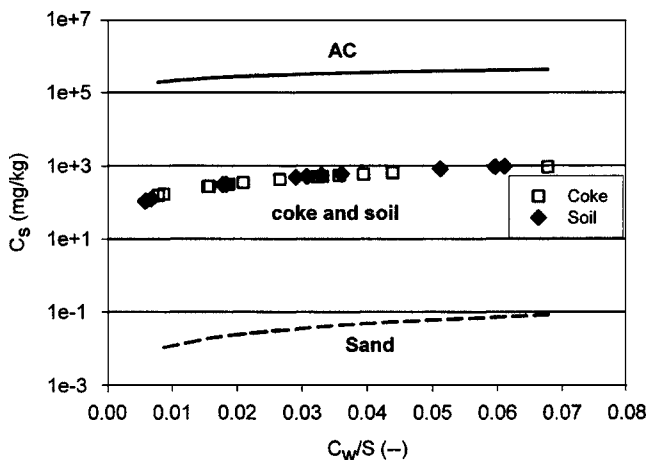[f]Determined using Hg porosimitry.

study was to determine the effectiveness of coke as an inexpensive sorbent, and the similar values of K_f of coke and soil is a surprising result given that previous work (Kleineidam et al. 2002) showed that coal, charcoal, and lignite coke had ~2–3 orders of magnitude higher Freundlich constants than soils. One possible explanation is that the specific surface area of the coke used in this study (2–13 m²/g) is significantly lower than for the charcoal and lignite coke used by Kleineidam et al. (2002) and the soots used by Jonker and Koelmans (2002). The $\log K_f^*$ measured here is consistent with that measured for coal soot by Jonker and Koelmans (2002), which has a specific surface area of 8.2 m²/g, which is similar to that of the coke used in this study. The Freundlich exponent (n) shows that the degree of sorption nonlinearity increased in the order soil (0.94) < coke (0.84) < AC (0.28). This agrees with expectations that contaminant sorption onto soil OC is dominated by partitioning or absorption into the soil OC phase (linear isotherm), while contaminant sorp-

tion is an adsorption-dominated process for AC and coke yielding nonlinear isotherms (Schwarzenbach et al. 2003). The sorption capacity of soil and coke were also similar and significantly lower than for AC, but higher than for sand. The superior sorption capacity of AC relative to coke and soil is not surprising given that AC is an engineered sorbent. The low sorption capacity of coke is consistent with its low internal porosity and N₂-BET specific surface area.
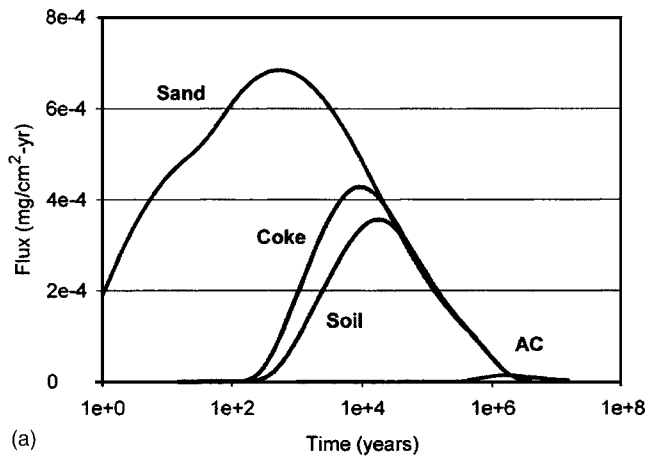
The sorbent physical properties that can affect contaminant transport through a cap include porosity (ε), bulk density (ρ_b), and hydrodynamic dispersivity (α). These properties did not change by more than a factor of 2 to 3 between the different sorbents, which is far less than sorption strength (K_f) which varied by 2 to 5 orders of magnitude between the sorbent types. Based on K_f, AC should provide significantly more contaminant transport retardation and sorption capacity compared to coke or soil. Soil and coke demonstrated similar K_f values and sorption capacity (Table 1), suggesting similar performance as a capping media.
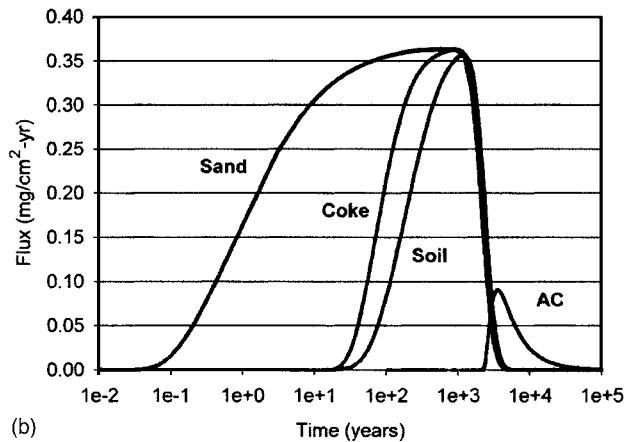
Simulated Cap Performance

The flux of 2,4,5-PCB at the top of a 1.25-cm sorbent layer (marked by an X on Fig. 1) was simulated using the measured properties for each sorbent for two scenarios. The first considers diffusion only, i.e., no groundwater seepage, and the second assumes a groundwater seepage (Darcy velocity of 1 cm/day) from the underlying sediment into the water column. This Darcy velocity was measured at the Anacostia River demonstration site where a sorbent-amended sediment cap was recently placed (Matrix Environmental and Geotechnical Services 2003), and represents moderate to high groundwater infiltration. The flux of 2,4,5-PCB through a cap layer (mg cm⁻² yr⁻¹) under these conditions is shown in Fig. 3. For each scenario, there is a period of time before any PCB has transported through the cap layer (isolation time), followed by a period of increasing flux through the cap and into the bioactive zone until a maximum is reached, then a decrease in flux over time until the underlying sediment layer is depleted. The isolation time provided by each cap material is

Fig. 2. Solubility normalized sorption isotherms for AC, coke, soil and sand, data for AC isotherm adapted from Kleineidam et al. (2002), sand isotherm is estimated on the basis of data from Schwarzenbach et al. (2003).

Fig. 3. Flux of 2,4,5-PCB versus time at top of cap (h_{cap}=1.25 cm) for (a) diffusion only and (b) assuming a groundwater velocity of 1 cm/day

Table 2. Estimated Sediment Deposition Rates Necessary for Infinite Isolation (i.e., Never Reaching 10% Breakthrough) in a Diffusion-Controlled System and in the Presence of Groundwater Seepage (1 cm/day)

	Sediment deposition rate necessary for infinite isolation time (mm/yr)			
	AC	Soil	Coke	Sand
Diffusion dominated	~0	0.01	0.03	30
With groundwater seepage	0.005	0.2	0.4	60

magnitude compared to the diffusion only case. In both the advection and diffusion dominated systems, AC should provide 2–3 orders of magnitude longer isolation times compared to coke and soil and 5–6 orders of magnitude longer isolation times than sand. The duration of chemical isolation is the same as the ordering of Freundlich constants (Table 1), confirming that other physical parameters (porosity, dispersivity, and bulk density) are relatively unimportant.

The isolation time provided by a thin layer of coke or activated carbon is significantly affected by the presence of moderate groundwater seepage (Table 2) so the presence of groundwater seepage must be considered carefully in cap design. Model simulations indicate that sand caps amended with a thin AC layer could isolate PCBs for ~200 years, even in systems with sustained high (~10 cm/day) groundwater seepage velocity. This implies that AC-amended sediment caps applied at large scale capping projects (e.g., river miles) are likely to ensure chemical isolation for long periods (centuries) even in areas where the spatial and temporal seepage velocity patterns cannot be measured with any certainty. Coke and soil provide minimal chemical isolation (~20 years) as the seepage velocity increases (>~2 cm/day) and is not practical for areas where groundwater seepage exists.
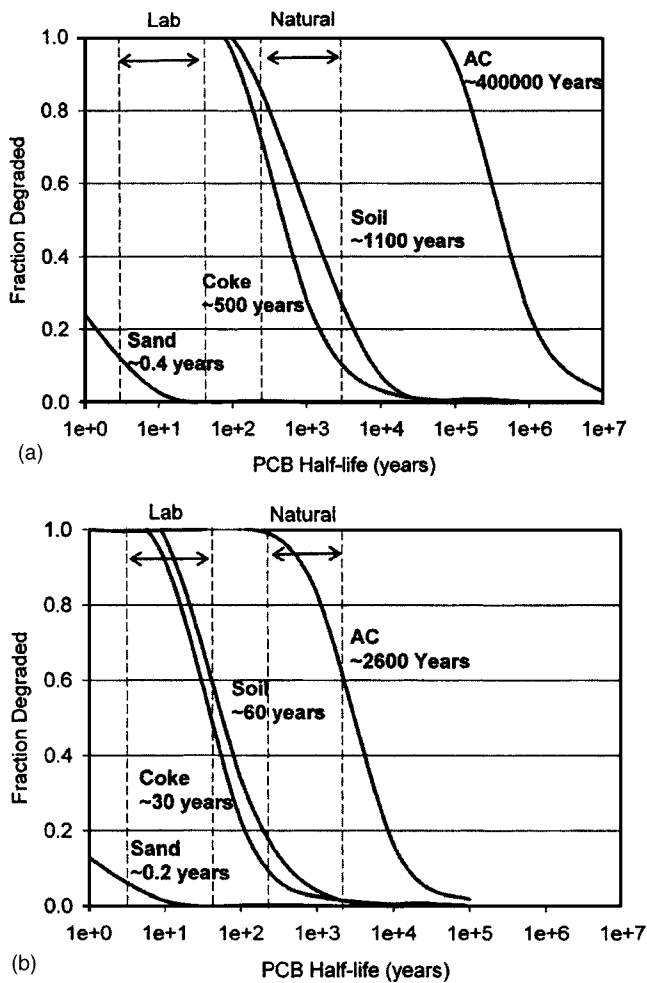
Effects of Attenuation Processes

Burial Processes

Capping isolates contaminants and allows time for inherently slow natural or engineered attenuation processes can occur, such as the deposition of clean sediment over the cap and biodegradation. Assuming that the depositing sediment has a similar capacity to retard PCB transport as the sorbent layer, the isolation time, i.e., the time to reach 10% of the maximum flux, can be considered infinite if the deposition rate is greater than or equal to the sorbent layer thickness (1.25 cm) divided by the isolation time not considering deposition. The estimated sediment deposition rates required for infinite isolation time based on these criteria are given in Table 2. Even with groundwater seepage, deposition rates of only a few tenths of a millimeter per year may be sufficient to provide infinite isolation times for soil-, coke-, and AC-amended caps. These deposition rates are comparable to or lower than that expected in shallow low-energy (depositional) environments (Middelburg et al. 1997). While not explicitly considered in these simulations (Fig. 3), this deposition would further increase the isolation time provided by the cap.

Biodegradation

Capping can provide time for natural or engineered biodegradation of PCBs in the underlying sediment. The rate and extent of natural PCB biodegradation in anaerobic sediment is controversial, and depends on many site specific parameters, such as PCB

operationally defined as the time when the flux of 2,4,5-PCB at the top of the 1.25 cm capping layer reaches 10% of the maximum flux simulated in that scenario. In these cases, it is assumed that no PCB degradation (mass loss) occurs so all PCB initially present in the underlying layer is transported through the cap and into the water column. Performance metrics for each sorbent include the isolation time and the magnitude of the maximum flux.

In the absence of groundwater seepage, a 1.25-cm layer of sorbent provides chemical isolation times on the order of centuries for coke and soil. Consistent with the measured properties, soil does a similar, although slightly better job, than coke at mitigating PCB flux. The high K_f and sorption capacity afforded by AC effectively mitigates PCB flux from the underlying sediment. In all cases, the maximum PCB flux into the bioactive zone is lower than would be achieved with a thin sand cap. It is important to note that these results are for thin caps (1.25 cm) and do not intend to proport that capping with sand is never a viable technique to chemically isolate PCB contaminated sediment from the biologically active portion of sediment for significant periods of time. In a system where diffusion controls the transport of contaminants through a cap, sand caps thicker than ~30 cm provide hundreds of years of chemical isolation (data not shown).

When moderate groundwater seepage is considered (U=1 cm/day), the isolation times afforded by soil and coke is shortened to only a few decades, but AC is still able to isolate PCBs in the underlying sediment for long times [Fig. 3(b)]. Groundwater seepage also increases the PCB flux by orders of

Fig. 4. PCB mass removal as a function of PCB biodegradation half-life time: (a) diffusion; and (b) groundwater seepage (1 cm/day). Lines delineate range of PCB half-life times observed under natural and laboratory conditions. Complete PCB dechlorination is assumed.

Table 3. Estimated First-Order Degradation Half-Life Times (Years) Required for 50% and 99% PCB Degradation

| Fraction degraded	Half-life time required (yr)			
	AC	Soil	Coke	Sand
Groundwater seepage (1 cm/day)				
0.5	2,600	30	60	2
0.99	400	3	10	0.3
Diffusion				
0.5	410,000	500	1,100	0.4
0.99	60,000	70	200	0.06

concentration, bioavailability, and the presence of PCB dechlorinating organisms. This uncertainty makes predicting the extent of PCB mass destruction (i.e., complete dechlorination or transformation to a compound other than a PCB) in capped sediment difficult. Despite this, reasonable order-of-magnitude estimates of the biodegradation half-life time needed to achieve significant PCB destruction in situ can be made by assuming first-order PCB destruction. For each sorbent and hydrodynamic condition evaluated, the fraction of PCBs that would be degraded for a given PCB degradation half-life ($t_{1/2}$) are shown in Fig. 4. The half-life times required to achieve 50% and 99% degradation in the underlying sediment are given in Table 3.

Based on reported PCB degradation rates in the field (natural) and the laboratory (enhanced), the potential for significant PCB degradation under the cap can be estimated for each sorbent. Thoma et al. (1993) estimated first-order PCB dechlorination half-life times in field sediment ranging from 30–60 years per chlorine atom (0.01–0.02 Cl atom yr^{-1}). First-order PCB dechlorination half-life times observed in laboratory microcosms ranged from 0.5 to 3.5 years per chlorine atom (0.2–1.5 Cl atom yr^{-1}) (Rhee et al. 2001; Fennel et al. 2004). Using these estimates, the half-life time to remove an average of four chlorines per PCB congener is estimated and shown in Fig. 4. Given the uncertainty

of these estimates, the half-life time assuming a tenfold lower dechlorination rate is also included in Fig. 4. When diffusion is the only contaminant transport mechanisms, AC could provide sufficient isolation time for natural or enhanced biodegradation to dechlorinate a significant fraction of PCBs [Fig. 4(a)]. Soil and coke caps may provide time for significant PCB dechlorination if the PCB dechlorination rate reported in laboratory microcosms could be sustained in the field. With groundwater seepage ($U=1$ cm/day), AC amended caps would be required to realize significant PCB dechlorination.

Even if complete PCB mass loss is not achieved, partial loss of PCB mass in the underlying sediment will substantially lower the maximum and total PCB mass flux entering the bioactive zone. The effect of PCB degradation in buried sediment on the flux of PCBs into the biologically active zone is shown for activated carbon- and coke-amended caps under conditions with groundwater seepage (Fig. 5). A PCB degradation half-life time of 700 years for AC and 7 years for coke can provide greater than 90% total mass reduction in the underlying sediment and will significantly lower the maximum PCB flux into the bioactive zone. A PCB degradation half-life time of 700 years is well within the range observed in field sediments. AC-amended caps therefore have the potential to provide mass reduction without the need to remove contaminated sediments provided that PCB degradation is occurring naturally or through engineered intervention.

Implications of Simplifying Assumptions in the Model

The simulations in this study employed several simplifying assumptions about the sorbent (no sorption competition or loss of sorbent capacity, equilibrium sorption) the contaminant (properties of a trichloro-PCB and a 1 mg/L porewater concentration are assumed), and the system (absence of colloidal transport of PCBs, and a 1.25-cm thick sorbent layer). The implications of these simplifying assumptions on the model results are briefly addressed. Competitive sorption between PCBs and dissolved OC in sediment porewater may decrease K_f and lower the sorbent effectiveness. Based on a literature review, DOC sorption competition on PCB flux through an AC-amended cap should be less than an order of magnitude (Pirbazari et al. 1992), but ongoing studies are underway to quantify this effect. Slow sorption kinetics of PCBs within the cap sorbent layer or in the underlying sediment may also limit effectiveness. As the groundwater seepage rate increases, the assumption of equilibrium partitioning in the underlying sediment and in the cap becomes less reasonable. A nonequilibrium condition in the underlying sediment would lead to lower PCB flux than predicted because rate-limited PCB desorption would result in a lower sediment porewater PCB concentration. A nonequilibrium condition in the cap layer would lead to higher PCB fluxes than predicted because rate limited sorption in
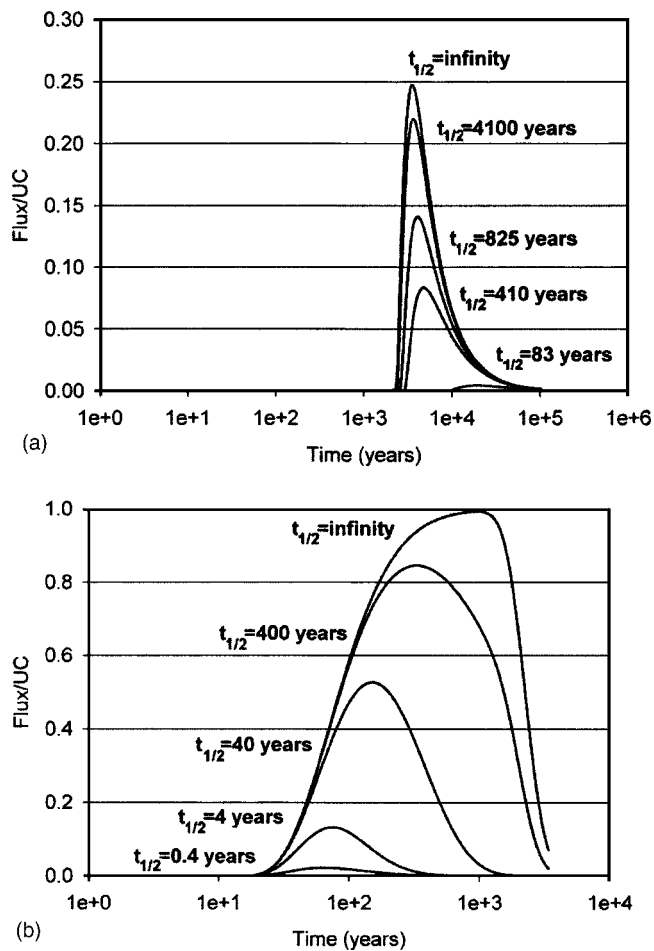
Fig. 5. Effect of PCB mass destruction in the underlying sediment on the flux of 2,4,5-PCB at top of 1.25 cm cap under the influence of groundwater seepage (1 cm/day); (a) AC; and (b) coke. Flux is normalized to the maximum flux expected for an uncapped system without PCB attenuation, Flux=UC [Eq. (5)].

the sorbent layer lead to higher porewater PCB concentration. The magnitude of these effects on the breakthrough times reported here should be minimal at seepage velocities much less than 1 cm/day as time scales for sorption at this flow rate are on the order of days or greater, but further study is needed to determine the range of seepage velocity under which the assumption of equilibrium sorption is valid.

Conducting simulations with a trichloro PCB homolog (2,4,5-PCB) provides a conservative estimate of the breakthrough times. Typical aroclor mixtures released into the environment contain trichloro and higher chlorinated PCB homologs. Higher chlorinated congeners are more hydrophobic and will sorb more strongly, and thus will travel through the cap much more slowly than for a trichloro-PCB. Since the transport velocity scales inversely with the solubility of the PCB congener, the breakthrough times for higher chlorinated congeners will increase by one to two orders of magnitude up heptachloro-PCBs. Assuming an initial porewater concentration of 1 mg/L also provides a conservative estimate for isolation times and for PCB flux as porewater PCB concentrations are typically lower (~0.1 mg/L). For an initial porewater concentration of 0.1 mg/L, the isolation time essentially remains unchanged because it is defined on the basis of

relative flux, but the maximum PCB flux decreased by an order of magnitude as the reported fluxes essentially scale linearly with the chosen initial sediment porewater concentration.

The study considers only a thin (1.25 cm) layer of sorbent. Thicker layers of coke or soil would lengthen isolation times linearly with increased layer thickness. Colloid-facilitated transport of PCBs may also enhance their transport through the cap and decrease the effectiveness by many orders of magnitude depending on the flux rate of colloids from the system. The role of biogenic colloid-facilitated transport of PCBs is currently under investigation.

Conclusions

In the absence of groundwater seepage, a 1.25-cm layer of soil, coke, or AC provided isolation times greater than ~500 years and lowered PCB flux into the bioactive zone compared to sand. With moderate groundwater seepage ($U=1$ cm/day), strongly sorbing high capacity sorbents, such as activated carbon can still provide long isolation times (>1000 years). The sensitivity of coke and soil to seepage velocity make their use less practical in sediments experiencing groundwater seepage. Even with groundwater seepage, slow PCB degradation ($t_{1/2}=700$ yr) in the underlying sediment can lead to significant (>90%) PCB mass removal in the sediment and decreases the maximum PCB mass flux into the bioactive zone by a factor of 3 for an AC-amended sediment cap, provided that complete PCB degradation can be achieved. This rate is within the range of natural PCB degradation rates reported for field sediments and well within the range of PCB degradation rates achieved in laboratory microcosms, suggesting that engineered systems designed to isolate sediment PCBs and to increase the rate of PCB degradation (complete destruction) in underlying sediments could provide a cost-effective means to contain and treat PCB-contaminated sediments in situ.

Acknowledgments

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