Modeling PAH mass transfer in a slurry of contaminated soil or sediment amended with organic sorbents

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ABSTRACT

A three-compartment kinetic partitioning model was employed to assess contaminant mass transfer and intraparticle diffusion in systems comprising dense slurries of polluted soil or aquifer sediment with or without sorbent amendments to sequester polycyclic aromatic hydrocarbons (PAHs). The model was applied to simulate temporal changes in aqueous and particle-bound PAH concentrations comparing different pollution sources (heavy oil or tar sludge) and various sorbent amendments (polyoxymethylene (POM), coke breeze, and activated carbon). For the model evaluation, all the parameters needed were directly measured from a series of experiments, allowing full calibration and verification of model predictions without parameter fitting. The numerical model reproduced two separate laboratory-scale experiments reasonably: PAH uptake in POM beads and PAH uptake by semipermeable membrane devices. PAH mass transfer was then simulated for various scenarios, considering different sorbent doses and mass transfer rates as well as biodegradation. Such model predictions provide a quick assessment tool for identifying mass transfer limitations during washing, stabilization, or bioslurry treatments of polluted soil or sediment in mixed systems. It appears that PAHs would be readily released from materials contaminated by small oil droplets, but not tar decanter sludge. Released PAHs would be sequestered rapidly by activated carbon amendment but to a much lesser extent by coke breeze. If sorbing black carbon is present in the slurries, POM pellets would not be effective as a sequestration amendment. High first-order biodegradation rates in the free aqueous phase, e.g., in the order of $0.001\,s^{-1}$ for phenanthrene, would be required to compete effectively with adsorption and mass transfer for strong sorbents.

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1. Introduction

Sediment treatment by sorbent addition to achieve the sequestration of hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) is a subject of current research. For example, in-situ sediment treatment with activated carbon (AC) has been studied by several researchers at the laboratory scale, and pilot-scale field applications are currently under investi-gation (Alcoa, 2007; Cho et al., 2007; Cornelissen et al., 2006; Werner et al., 2005; Zimmerman et al., 2005). Those studies show the potential benefit of the technique in reducing the aqueous concentration and bioavailability of hydrophobic contaminants. If successfully applied, a substantial reduction in aqueous concentration and contaminant release rates is expected and consequently a significant decrease in the uptake of PAHs and PCBs by sediment-dwelling invertebrates could likely be achieved (McLeod et al., 2004). Alternatively,

one may envision the ex-situ addition of sorbent materials to sediment or soil slurries during dredging, transport, and processing (size separation, washing, dewatering, etc.) to achieve a stabilized product, or addition towards the end of a bioslurry or other bioremediation treatment to sequester contaminant residuals.

Current studies on AC amendment of contaminated sediment show promising results, including a significant reduction in aqueous pollutant concentrations and benefit to benthic organisms (Alcoa, 2007; Cho et al., 2007). However, there remains a lack of mechanistic understanding of processes occurring in sediment at the particle scale in which the contaminant is distributed among sediment particles, the aqueous phase, the applied sorbent, and the biota in the system. Recently, a numerical model based on intraparticle diffusion was developed and applied to the simulation of results from several laboratory studies employing PCB-contaminated sediment mixed with AC (Werner et al., 2006). The model simulation qualitatively reproduced the experimental results and provided an assessment of the various system parameters affecting the reduction in PCB aqueous concentrations. Some of the parameters required to describe the contaminant, the sediment, and the sorbent were measured from experiments and a few were estimated based on literature values.

In this study, the model developed by Werner et al. (2006) was adapted to simulate the mass transfer phenomena in a well-defined system comprising a contaminated soil or sediment amended with organic sorbents such as polyoxymethylene (POM) or AC or coke. For these systems, all the parameters needed for the model simulation were directly measured from experiments, and thus for the first time allows full calibration and evaluation of model predictions without parameter estimation. Experimental measurements also provide range values for the precision of parameter values, as may be obtained from the standard deviations of replicate measurements. The resulting uncertainty in the model output can then be accounted for by Monte Carlo simulations, using corresponding averages and standard deviations (Kalos and Whitlock, 1986). This feature makes the model predictions more practical by providing a statistical variation for the output based on combinations of given parameter values within the range of parameter uncertainty. The mass transfer model was tested and compared to the experimental results, and then the model and some additional literature data were used to assess different remediation scenarios in which slurries of soils or sediment are treated with or without application of sorbent materials.

2.   Materials and methods

2.1.   The numerical model

A numerical model was used to simulate PAH mass transfer during the mixing of contaminated soil or sediment with added sorbents. The core of this model was designed by Werner et al. (2006) and was modified to accommodate the experimental system employed in this study. The numerical model is based on the principles described by Wu and Gschwend (1988) for the modeling of sorption kinetics of organic compounds to soil and sediments having different particle sizes. A schematic diagram of the modeled system is depicted in Fig. 1. In the model, the solid releasing the contaminants comprises two different sorption domains: a light density fraction that contains mostly black carbonaceous particles, and a heavy fraction consisting of minerals with coatings of carbonaceous materials (e.g., natural organic matter). The third domain is the added sorbent that picks up the released pollutants. The model assumes complete mixing and neglects external mass transfer resistance. A linear partitioning equilibrium between the surface of each compartment particle and the external aqueous PAH concentration is assumed in the standard version of the model, whereas a more complex version allows for the description of the sorption equilibrium by the Freundlich isotherm. In the standard model, the uptake and release of PAHs into or out of the different particles are described by intraparticle diffusion:

$$\frac{\partial S_i}{\partial t} = \frac{D_i}{r_i^2} \frac{\partial}{\partial r} \left(r_i^2 \frac{\partial}{\partial r} S_i \right) \tag{1}$$

where S_i(g/cm^3) is the volumetric concentration of the compound in the particles, D_i(cm^2/s) is the apparent diffusivity, r(cm) is the radial distance from the particle center, and t (s) is time. The subscript i denotes each solid-phase compartment. For each time step, Δt, the amount of PAH diffusing out of the heavy and light fraction particles and diffusing into the sorbent is calculated from the concentration gradient within the particles. In the standard model, the apparent diffusivity is assumed to be concentration-independent. A first-order biodegradation rate constant for the compound dissolved in the aqueous phase may be incorporated in the simulations. The compound fluxes among the different types of particles and water, and any biodegradation in the aqueous phase, determine the overall change in the aqueous-phase concentration. The model assumes at $t = 0$ that the light and heavy soil particles are in equilibrium with the aqueous phase and that the sorbent is initially free of solute. Details of the numerical, three-compartment, kinetic partitioning model are explained in the supplemental information.
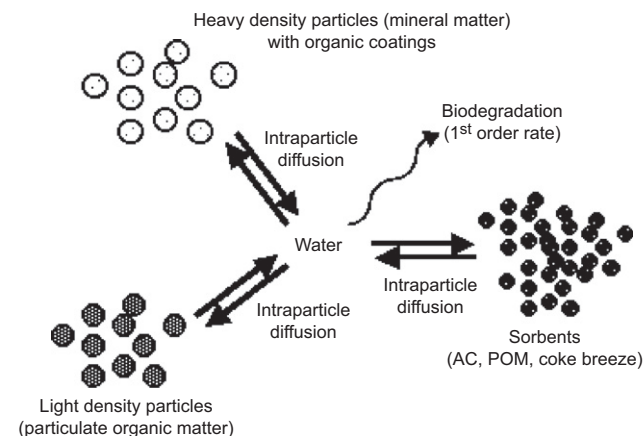

Fig. 1 – Schematic domains of the mass transfer model in a slurry of contaminated soil or sediment and added sorbent.

The mass transfer model requires 17–20 input parameters depending on the linearity of the sorption isotherm of the compartment. For the initial model verification, all the parameter values were measured experimentally and are shown in Table 1. For the most relevant parameters a range of uncertainty is also provided, reflecting the variability of experimental values obtained by replicate samples or different methods. To account for this parameter uncertainty, model runs were performed according to the Monte Carlo method. In the Monte Carlo method, each parameter is given with an average and standard deviation and the model selects a different parameter value according to a Gaussian distribution for each run (Kalos and Whitlock, 1986). Thus, the model simulates a new possible combination of parameters in each run and the simulation was repeated 50 times to obtain the distribution of the output. After 50 runs, the average and standard deviation of the model output were calculated.

2.2. Soil sample and organic sorbents

The soil sample was collected from a contamination hot spot adjacent to the coke oven facility at the Ford Rouge

Table 1 – Input parameters for POM–soil model simulation

Parameter[a]	Value	SD[b]
POM		
Particle radius, r_{POM} (cm)	0.059	
Solid phase density, ρ_{POM} (g/cm^3)	1.43	± 0.2
Porosity, ε_{POM} (dimensionless)	0.00	± 0.01
Dose	Variable	
POM and phenanthrene		
POM–water partitioning coefficient, $\log_{10} K_{POM}$ (cm^3/g)	3.72	± 0.1
Apparent diffusion coefficient, $\log_{10} D_{a,POM}$ (cm^2/s)	-9.70	± 0.3
Ford coke plant site soil		
Mass fraction, light fraction, f (g/g)	0.20	± 0.05
Light particle porosity, ε_l (dimensionless)	0.21	
Light particle density, ρ_l (g/cm^3)	1.50	
Heavy particle porosity, ε_h (dimensionless)	0.14	
Heavy particle density, ρ_h (g/cm^3)	2.50	
Water/soil ratio (cm^3/g)	1	
Ford coke plant site soil and phenanthrene		
Light particle partitioning coefficient, $\log_{10} K_{d,l}$ (cm^3/g)	5.95	± 0.5
Heavy particle partitioning coefficient, $\log_{10} K_{d,h}$ (cm^3/g)	4.53	± 0.5
Light particle apparent release rate, $\log_{10}$ (s^{-1})	-11.02	± 0.3
Heavy particle apparent release rate, $\log_{10}$ (s^{-1})	-9.66	± 0.3
First-order biodegradation rate[c], k_b (s^{-1})	0	

[a] All parameters were derived from experiments (Ahn et al., 2005a, b).
[b] SD, standard deviation.
[c] Sodium azide was added to inhibit biodegradation.

Manufacturing Complex (Dearborn, MI). The characteristics of the soil including characterization of PAH contamination at the particle-scale level, contamination source identification, PAH availability, and kinetics of contaminant release can be found elsewhere (Ahn et al., 2005b). POM was selected as an organic sorbent for laboratory experiments and two additional sorbent materials, coke breeze and AC, were selected for simulation purposes. Information about the model organic sorbents can be found in a previous publication (Ahn et al., 2005a).

2.3. Aqueous equilibrium test

The partitioning coefficient, K_d, between the soil and water is one of the most important parameters in the model simulation, and K_d values for PAHs were measured after equilibration of water with soil. Two approaches to measure the partitioning coefficients were invoked: direct mixing with phase separation by alum flocculation and centrifugation (Hong et al., 2003), and POM solid-phase extraction (SPE) (Jonker and Koelmans, 2001).

2.3.1. Direct mixing

Site soil sample (0.5–5 g) was added to a 4 L glass jar filled with DI water and the jar was rolled at 2 rpm on a bottle roller (Bellco Biotechnology, Vineland, NJ). Three different sets of soil samples were prepared: (1) the whole soil fraction with a size of less than 1 mm (5 g), (2) the heavy fraction (density >1.8 g/cm^3), separated by density with a saturated cesium chloride solution from the 0.25–1 mm sieve fraction of the soil (2.5 g), and (3) the light fraction (density <1.8 g/cm^3) of the 0.25–1 mm sieve (0.5 g). Each sample set was prepared in duplicate and sodium azide (NaN$_3$) was added at the concentration of 1 g/L to prevent biodegradation. The jars were rotated for 9 months to achieve equilibrium. The rollers were shielded from light to avoid possible PAH photodegradation.

After 9 months of contact, the water was pipetted out and dispensed into 780 mL size centrifuge tubes. Aluminum sulfate (alum) was added to flocculate suspended solids and the pH was adjusted to near 7 using sodium hydroxide. The tubes were capped, agitated by hand to facilitate flocculation, and then centrifuged for 15 min at 2000 rpm for floc removal. If needed, the samples were centrifuged further until all the suspended solids were precipitated and clear supernatant was obtained. The supernatant was transferred and combined in a 2 L size separatory funnel and extracted using hexane. A volume of 40 mL of hexane was added to the separatory funnel and then shaken for at least 3 min. Each batch of water was extracted three times to ensure full PAH recovery and the extracts were combined and concentrated using rotary evaporation before clean-up. The clean-up of the concentrated hexane was performed using activated silica gel columns as described in EPA method 3630C. The cleaned up samples were analyzed on an Agilent gas chromatograph 6890N system (Sunnyvale, CA) with a flame ionization detector. The remaining soil sample at the bottom of the jar was collected on filter paper and air-dried for extraction according to EPA standard method 3550B.

2.3.2. Polyoxymethylene solid-phase extraction (POM-SPE)

Aqueous equilibrium concentration was measured also with an alternative method for comparison. A POM strip was added to the sample equilibration jars as a third partitioning phase and PAH aqueous concentration was derived indirectly from measuring the PAH concentration in POM. A brief description of the estimation method is given in the supplemental information. Although it requires knowledge of the partitioning coefficients of PAHs between POM and water, this approach is very useful for measuring trace level aqueous-phase concentrations of hydrophobic compounds. By design, the POM added to the jars should not disturb the equilibrium between water and soil. Therefore the total PAH mass in the POM should be less than 5% of the total mass of the chemical present in the system. Further description of this method is found in the article by Jonker and Koelmans (2001).

A 1 g POM strip was added to 40 mL size vials filled with DI water and soil. Two sets were prepared at different soil-to-POM ratios (0.2 and 2 g soil/g POM). Preliminary calculations indicated that the amount of POM added to the system should not absorb more than 5% of the total PAH mass in both scenarios. All samples were prepared in triplicate. After 1 month of rotation on the bottle roller, the POM strips were harvested and extracted using Soxhlet extraction with hexane/acetone (1:1 [v/v]), and the soil was also extracted using ultrasonic extraction.

2.4. Mixing of POM beads and contaminated soil

An experimental setup was prepared to verify the model simulation. In 40 mL size glass vials, 1 g of POM beads were added to the known amount of the contaminated soil at two different soil-to-POM ratios as described above. The void space in the vial was filled with DI water and NaN_3 was added to inhibit biodegradation. The samples were rotated on a horizontal roller and taken out for the analysis after 2 and 4 weeks, respectively. All samples were prepared in triplicate.

3. Results and discussion

3.1. Aqueous equilibrium test

The aqueous-phase concentrations of PAHs in equilibrium with the soil were measured either by the direct-mixing method or indirectly as obtained from the POM-SPE method. The aqueous equilibrium concentrations of PAHs are compared with groundwater risk-based screening levels (RBSLs) in Fig. S1 (California Regional Water Quality Control Board, 2005). Most of the 16 PAHs regulated by the EPA have concentrations ranging from 10^{-4} to 10^{-6} mg/L by either measurement method. These measured concentrations are less than the groundwater RBSLs, implying limited PAH leaching risks despite the high solid-phase concentrations. In fact, low aqueous concentrations were anticipated because previously performed desorption and semipermeable membrane device (SPMD) tests showed very limited availability of PAHs bound to the soil sample due to the predominant PAH source being solid, coal tar decanter sludge (Ahn et al., 2005b). Partitioning coefficients, K_d, defined as the ratio of the solid-
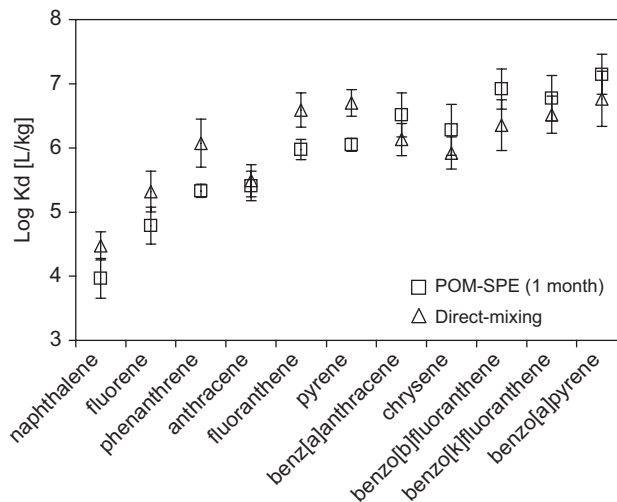

Fig. 2 – Measured partitioning coefficients for PAHs between coke plant site soil and water using the direct-mixing method and the POM-SPE method.

phase concentration over the aqueous-phase concentration of a compound, are shown in Fig. 2. The graph shows K_d values of PAHs for the whole soil fraction and water measured by two different methods: by long-term direct mixing and by POM-SPE equilibrated for 1 month. Measured $\log K_d$ values range from 4 to 7 and the two measurement methods show similar tendencies. Some discrepancies between the two measurement methods are noted. For PAHs smaller than benz[a]anthracene, K_d values calculated from the POM-SPE method are less than the K_d values measured by the direct-mixing method. On the other hand, the POM-SPE method gives larger K_d values than the direct-mixing method for the higher molecular weight PAHs as shown to the right of benz[a]anthracene on the x-axis. For the POM-SPE method, artifacts could result from incomplete equilibration between POM and the surrounding water. Jonker and Koelmans state that when the molecular size of a chemical exceeds a certain threshold, the adsorption rate into POM is significantly reduced. In their sorption experiments, they observed that first-order rate constants for adsorption of PAHs to POM increase with log octanol/water partitioning coefficients ($\log K_{OW}$) towards a maximum and then decrease. For PAHs, this was located at $\log K_{OW} = 5.9$ (Jonker and Koelmans, 2001). Benz[a]anthracene has a $\log K_{OW}$ value of 5.9, so it may be possible that PAHs having larger K_{OW} values would show slower uptake by retarded diffusion from steric hindrance. Yet the possibility of experimental error in the direct-mixing method cannot be ruled out. The most likely artifact for this method is a residual of suspended colloids in the water sample caused by the insufficient flocculation and precipitation and/or PAH partitioning into dissolved organic carbon matter that would lead to an overestimation of the aqueous concentrations, especially for the high molecular weight PAHs having high affinity for the solids. Overestimated aqueous-phase concentrations would yield underestimated K_d values. However, neither retarded diffusion nor suspended solids unambiguously explain the spread in K_d values at the left-hand side of benz[a]anthracene in Fig. 2, and there is a need

for further study for more definite explanation. In this study, this uncertainty in the measurements was reflected in the model simulation by considering +/− one log unit of variability in the K_d parameter value. Partitioning coefficients between water and density-separated fractions (heavy and light fractions) were also measured by the direct-mixing methods. The light fraction solids give K_d values larger than those from the heavy fraction by about two orders of magnitude, which suggests stronger sorption of PAHs in the light fraction because of its higher content of black carbonaceous material. The K_d values measured with the light fraction are thought to be representative of those of coke plant tar decanter sludge associated with a mixture of coal and coke debris. This material was identified as the major source of PAH contamination in this site soil (Ahn et al., 2005b). In Table 2, log K_d values for PAHs in the light fraction are shown ranging from 5.9 to 7.4, and are compared to reported K_d values of other black carbon materials such as lampblack, coal, and charcoal (Hong et al., 2003; Jonker and Koelmans, 2002). As is apparent in the table, measured K_d values from coal tar decanter sludge in the light fraction are indeed comparable to those of other black carbon materials that may be found in environmental samples (Kleineidam et al., 1999).

3.2. Model simulation

Two experimental settings with different soil-to-POM ratios were tested for phenanthrene and pyrene mass transfer, respectively, and the results are compared in Fig. 3 with model simulation results. The graphs show as a function of contact time the fraction of the PAH compound transferred to POM from the total PAH compound mass present in the system. In general, the experimentally measured values fall within the range of the simulation results, yet the experimental trend does not unambiguously confirm continued uptake with time due to substantial experimental variability.

It is noticed in the case of a soil-to-POM ratio of 0.2 that one time point in Fig. 3b and d falls outside of the predicted range of uncertainty. In the experiments with a soil-to-POM ratio of

0.2 a rather small amount of soil was used because of limited sample availability. This might have resulted in greater than expected variability since the pollutant distribution in this soil is heterogeneous (Ahn et al., 2005b).

The model was tested additionally by simulating previously reported PAH uptake experiments using SPMDs (Ahn et al., 2005b). The SPMD is a small polyethylene pouch containing triolein, which is often used in aquatic studies to assess the amount of contaminants passively transferred into fatty tissue in biota. SPMDs were contacted with the contaminated soil sample for 14 days for PAH uptake. The details of the experiment are described in the previous publication (Ahn et al., 2005b). In the model simulation, the SPMD was considered as the third solid domain. SPMD parameters for the model simulation were obtained from the literature (Booij et al., 2003). Comparisons between the experiment and the model simulation are shown in Table S1. Expressed as percent uptake relative to the initial PAH mass in batch, SPMD uptake in both the experiment and the model simulation shows agreement within a factor of two, except for fluorene. The model reproduced the previously reported experiments reasonably.

3.3. Assessment of the mass transfer limiting compartment

The simulation of 1 month of mixing of the soil with different doses of POM was modeled and the results are shown in Fig. 4. A typical model prediction shows two distinctive domains. At low dosage, the mass of phenanthrene in POM increases proportionally to the dose, but after a certain dose, it attains a plateau. It was found these two distinctive domains reflect two different restrictions to mass transfer represented by the mass transfer rates from/to each compartment, defined as D_a/r^2 (s^{-1}). At the lower POM doses, the amount of PAH sorbed onto POM is controlled by the POM-side mass transfer rate up to a certain dose. On the contrary, above a certain POM dose of about 100 g POM/g soil, PAH uptake by the sorbent is controlled by the PAH releasing domain, not by the

	Soil light fraction[a]	Lampblack[b]	Charcoal[c]	Coal[c]
Acenaphthylene	5.98 ± 0.23	6.26	–	–
Fluorene	5.80 ± 0.22	4.39	–	–
Phenanthrene	6.60 ± 0.24	6.30	6.19	6.57
Anthracene	5.91 ± 0.24	5.81	7.10	6.10
Fluoranthene	6.93 ± 0.23	7.10	6.34	6.72
Pyrene	6.98 ± 0.25	7.25	6.40	6.95
Benzo[a]anthracene	6.66 ± 0.13	–	7.54	7.95
Chrysene	6.58 ± 0.09	–	7.20	8.53
Benzo[b]fluoranthene	6.60 ± 0.26	–	7.87	8.34
Benzo[k]fluoranthene	6.64 ± 0.30	–	8.07	8.11

Table 2 – Comparison of log K_d values of different black carbonaceous materials

[a] Site soil containing coal tar decanter sludge.
[b] From Hong et al. (2003).
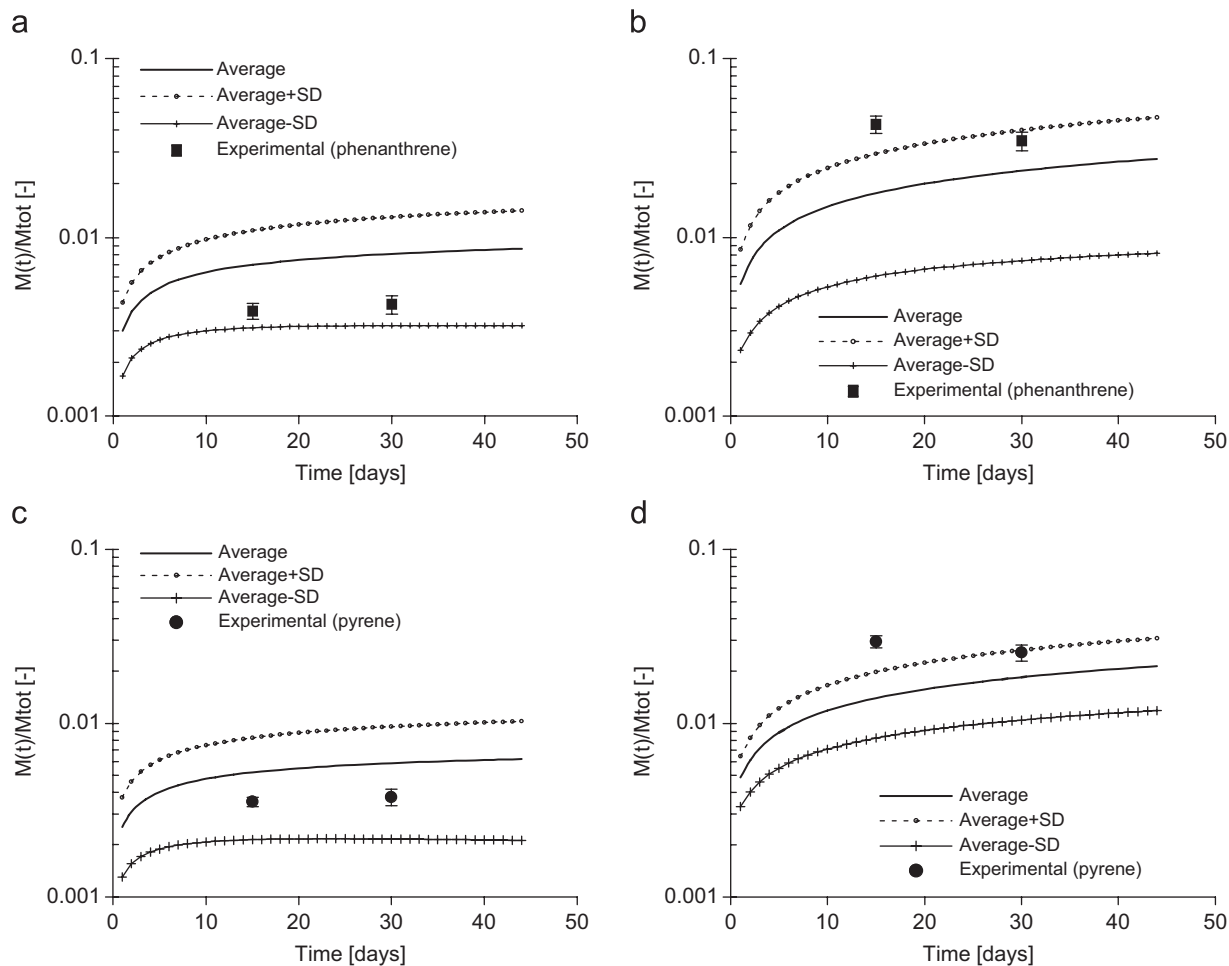[c] From Jonker and Koelmans (2002).

Fig. 3 – Comparison of experimental results with the modeling results. (a) Soil-to-POM ratio = 2 g/g (POM dose = 0.5 g/g), phenanthrene, (b) soil-to-POM ratio = 0.2 g/g (POM dose = 5 g/g), phenanthrene, (c) soil-to-POM ratio = 2 g/g (POM dose = 0.5 g/g), pyrene, (d) soil-to-POM ratio = 0.2 g/g (POM dose = 5 g/g), pyrene. The graphs show the average of 50 individual simulations (expressed as the solid line) with standard deviation (SD).

sorbent-side mass transfer rate. The same trend was observed for the AC-soil case. However, with AC the transition in mass transfer being controlled by the sorbent-side uptake versus solid-side release occurs at very small AC dose compared to POM, about a factor of 10^{-5}–10^{-6} less as seen in Fig. 4.

A practical application of the results in Fig. 4 is a guide to optimize the amount of the sorbent amendment to be added to the system to minimize the contaminant's aqueous-phase concentration and availability by transferring pollutants from the contamination source to the sorbent. If too small a dose of the sorbent is used, the overall mass transfer would be controlled by the sorbent-side uptake rate, which would unnecessarily delay the mass transfer. On the other hand, adding unnecessarily excessive amounts of the sorbent is also unfavorable for economic reasons. Thus, finding an optimal range of the dose of the sorbent is important in engineering applications to control the contaminant mobility at minimal cost by sorbent amendment.

It would be helpful if one can estimate the sorbent dose above which there is no longer the risk of mass transfer limitations on the sorbent side. The critical dose where the

transition of the mass transfer controlling domains occurs can be found easily by interpreting the graph generated by iterative runs of the model. In a graph like Fig. 4, the critical dose is defined as the dose above which there is no substantial increase in the mass of PAH associated with the added sorbent. The ratio of PAH mass on sorbent to the maximum mass of PAH on sorbent under the given conditions was calculated and the dose for which the ratio approaches unity was defined as the critical dose. The critical doses were calculated from the graphs and the calculated doses for the selected particle sizes were 100 g/g for the POM–soil system and 0.0005 g/g for the AC–soil system, respectively. The calculation shows that adding only 0.05% of AC by weight to this soil should be sufficient in terms of avoiding the problem of uptake limitation as compared to a very large amount of POM. This result reflects more than five orders of magnitude difference in the K_d values of POM versus AC, with phenanthrene having much higher affinity for the latter because of its large surface area and micropore volume. It should be noted that the PAH sorption capacity of AC may be reduced in soil or sediment slurries (McDonough et al., 2007), and that one should use appropriate corrections to the
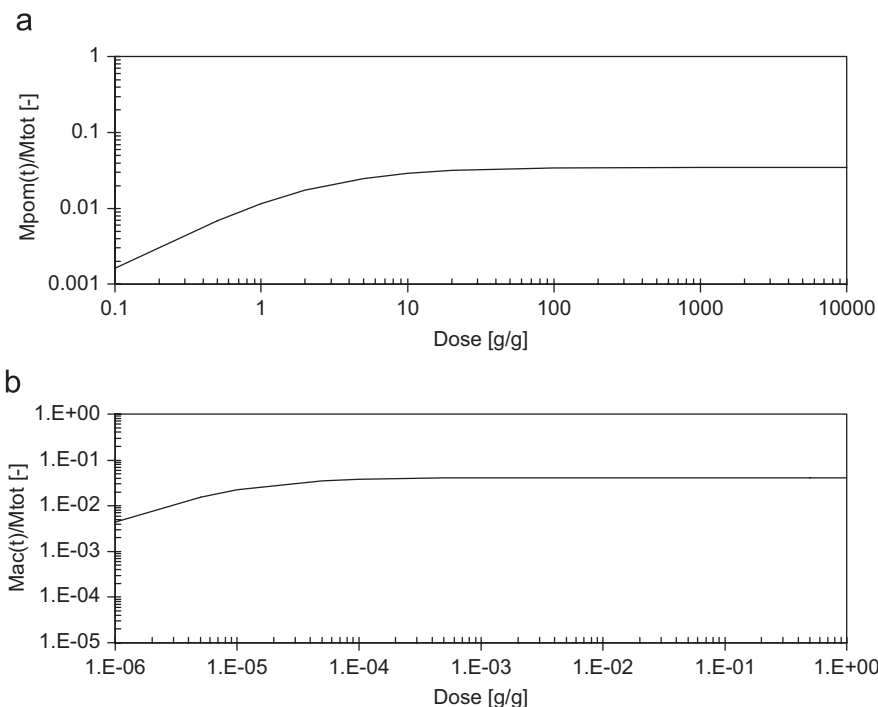
Fig. 4 – Phenanthrene uptake in sorbent added to Ford coke plant site soil showing the transitions of mass transfer controlling domains. (a) POM and (b) AC.

K_{AC} when calculating the appropriate dosage. Nevertheless, our analysis shows that plastics are not suitable as a sequestering agent for PAHs in tar-sludge polluted soil, but AC may be a sufficiently strong sorbent to be effective at low dosage.

3.4. Application of the model: contamination scenarios

The model in its current version can simulate up to three solid-phase compartments, e.g., the light density (or black carbon) fraction of soil/sediment, the heavy density (or mineral) fraction of soil/sediment, and an added sorbent. These compartments are linked by the external aqueous phase. Here, the model is applied to simulate several contamination scenarios and possible remediation strategies, including sorbent amendment or biodegradation in slurries.

The contamination scenarios can be set up relatively easily by modifying and re-defining the model and its compartments. In these simulations, one compartment becomes the source matrix of the contamination that releases the contaminants to the aqueous phase. Another compartment is unpolluted sediment receiving the contamination. The third compartment is a sorbent added to the system to adsorb released contaminants. First-order rate biodegradation is assumed to occur in the free aqueous phase. The model thus simulates the pollutant fate in slurries based on the physicochemical properties of the contamination source, sediment, and added sorbent, and first-order rate biodegradation.

Two distinctive contamination scenarios were simulated and compared to each other. Tar decanter sludge and transmission oil were selected as distinct contamination

Table 3 – Properties of transmission oil and coal tar decanter sludge and phenanthrene apparent diffusion coefficients, release rates, and partitioning coefficients

	Transmission oil[a]	Tar decanter sludge[b]
Density, ρ (g/cm^3)	0.8	1.5
Porosity, ε (dimensionless)	0	0.21
Radius, r (cm)	0.005	0.025
Apparent diffusion coefficient, $\log_{10} D_a$ (cm^2/s)	−10.42	−14.22
Release rate, $\log_{10}$ (s^{-1})	−5.8	−11.02
$\text{Log}_{10} K_d$ (cm^3/g)	4.90	5.95
Phenanthrene concentration (µg/cm^3)	30	227

[a] From Ortiz et al. (1999). The oil drop diameter was assumed to be 100 µm.
[b] From Ahn et al. (2005b).

sources. Semisolid tar decanter sludge was identified as a major source of PAHs in the coke oven soil in the previous study with Ford site soil, and it is understood that PAHs from tar decanter sludge are available only slightly despite high concentrations (Ahn et al., 2005b). The other source selected for the simulation is transmission oil (Ortiz et al., 1999). Transmission oil is a nonaqueous-phase liquid and is known to release PAHs much more readily. Thus, these two selected sources, tar decanter sludge and transmission oil, are expected to show very different patterns of PAH release, describing a wide range of PAH source properties one might

Table 4 – Properties of the model sediment and organic sorbents

Particle radius (cm)	Sorbent	ε[a]	K_{fr}[b] [(g/g)(cm^3/g)^N]	N[c]	D_a[d] (cm^2/s)	Tortuosity[e] (dimensionless)
0.018	Sediment, coaly particles[f]	0.008	2.94	0.55	1.4×10^{-14}	2.5
0.059	POM	0	5300	1	2×10^{-10}	–
0.013	Coke	0.31	460,000	1	7.9×10^{-13}	3.2
0.0075	AC[g]	0.55	6983	0.70	7.8×10^{-14}	1.8

[a] ε, intraparticle porosity.
[b] K_{fr}, Freundlich constant.
[c] N, Freundlich exponent.
[d] D_a, apparent diffusion coefficient. D_a values for the sediment and AC are concentration dependent and are reported at an aqueous concentration of 1×10^{-12} g/cm^3.
[e] From Karapanagioti et al. (2001).
[f] Tortuosity is equal to the inverse of the particle porosity.
[g] From data in Cornelissen et al. (2006), using the recommended mean factor of six reduction for K_{fr} to account for competitive sorption in sediment.

expect to find at various contaminated sites. Properties of the two sources are given in Table 3, for which the transmission oil is assumed to exist as 100 μm diameter droplets. As a contaminant for modeling, phenanthrene was selected because it is one of the most soluble and best investigated PAHs. Parameter values characterizing the sediment were obtained from the literature, and its properties are listed in Table 4. This sediment is an aquifer material sampled from a closed landfill site and consists of several types of organic and inorganic materials such as coal, charcoal, phytoclast, quartz aggregates, and amorphous organic matter. Among those particle types, coaly particles are reported as dominating materials (Karapanagioti et al., 2000; Karapanagioti and Sabatini, 2000), making this sediment matrix a relatively strong sorbent for PAHs. POM, coke, and AC were selected as model sorbents. They show very distinct sorption properties as described in a previous study (Ahn et al., 2005a).

Biodegradation in the aqueous phase was considered to assess the potential relationship between biodegradation, PAH availability, and the sorbent amendment. A first-order degradation rate for phenanthrene was reported by Karapanagioti et al. (2001) for the consortium isolated from the sediment described in Table 4 and a value of 1.2×10^{-5} s^{-1} was used. The simulations assume that the biodegradation occurs in the free aqueous phase. As demonstrated by Karapanagioti et al. (2001), this appears to be a valid assumption, at least at the relatively high water-to-solid ratios in those batch studies. The simulations were also run without an added sorbent to investigate the mass transfer of the pollutant from the source to the sediment. Thus, for each contamination scenario, four different situations were modeled: (1) without amendment, (2) with POM, (3) with coke, and (4) with AC. The simulation time spans up to 5 years, and by using a log scale for time emphasis is put on the early stages that are relevant for assessing the initial progress of remediation techniques. Since sediment and AC exhibit strongly nonlinear sorption isotherms, a modified version of the model was applied that describes the local sorption equilibrium as related by the
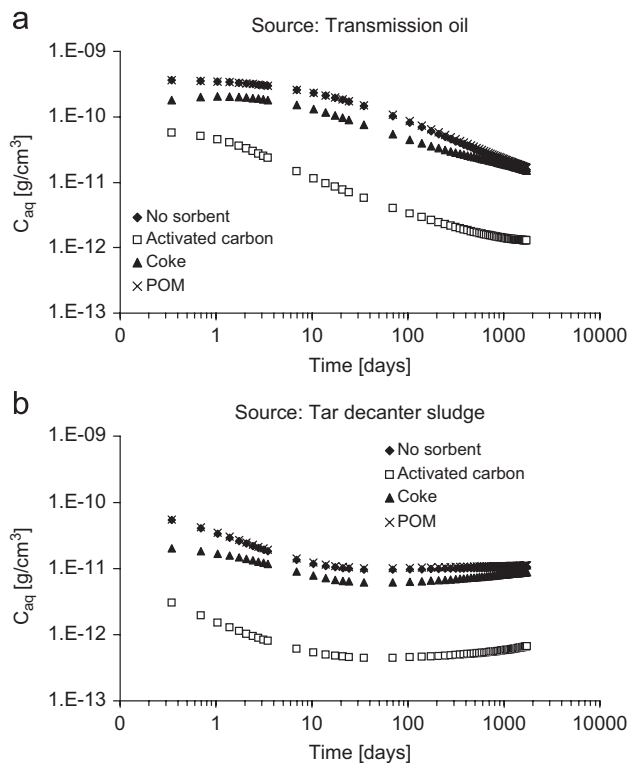

Fig. 5 – Simulation of phenanthrene aqueous-phase concentration changes over 5 years: (a) 5% by weight transmission oil alone in sediment, or with 5% activated carbon, coke breeze, or POM, (b) 5% by weight tar decanter sludge alone in sediment or with 5% activated carbon, coke breeze, or POM, and without the sorbent.

Freundlich isotherm for sediment coaly particles and AC (Grathwohl, 1998; Werner et al., 2006). These isotherm parameters are shown in Table 4.

Fig. 5a shows the aqueous-phase concentration changes for sediment with coaly particles contaminated by a transmission

oil source containing phenanthrene. The figure compares three different sorbents added at a dosage of 5% of the sediment weight with that for no sorbent addition. The aqueous concentrations decrease gradually over 5 years in each case during which time the sediment equilibrates with the phenanthrene source. Only the addition of AC results in a significant and sustained reduction of the aqueous concentration compared to the case of no sorbent. The impact of POM addition is almost negligible, whereas coke addition initially achieves greater reduction in aqueous concentration as compared to the unamended sediment, but this effect is predicted to disappear over time. This is explained by the presence of coaly particles in the sediment having equal or even higher sorption strength than coke, but slower sorption kinetics. These predictions are in good agreement with experimental observations of Zimmerman et al. (2004) who found that at equal dosages AC was more efficient than coke in decreasing aqueous PAH concentrations in marine sediments containing charcoal. AC appears to be the only sorbent capable of accumulating PAHs within reasonable time frames and at a reasonably low dosage as represented in Fig. 5b. In the sediment contaminated with transmission oil, natural attenuation is expected to reduce the aqueous phenanthrene concentration significantly because the sediment coaly matter acts as a sink for released phenanthrene. Biodegradation contributes only minimally to the overall reduction if the first-order biodegradation rate reported by Karapanagioti et al. (2001) is applied.

In the case of tar decanter sludge contamination, results in Fig. 5b show quite similar trends to Fig. 5a, with only AC amendment achieving an aqueous concentration reduction substantially less than that of no sorbent addition. Tar decanter sludge has a much larger K_d value and a much slower release rate compared to transmission oil. As a consequence of this, the initial drop in the aqueous phenanthrene concentration is more substantial, indicating that the mass transfer is limited by release from the tar decanter sludge, not uptake by the sediment and sorbents. Aqueous concentrations then increase slightly as more phenanthrene is loaded onto sediment and sorbents.

These results are compared in more detail in terms of the phenanthrene mass fraction associated with each compartment or degraded. Figs. 6a–d show changes of phenanthrene mass fraction in the source, the sediment, and the sorbent, and the fraction of phenanthrene biodegraded for the case of transmission oil as the source of the contamination. Similar graphs are shown in Figs. 6e–h for tar decanter sludge. The two contamination sources show quite different patterns of release. Comparing Figs. 6a and e shows that the transmission oil released more than 96% of its original mass of phenanthrene over 5 years; however, only about 12% of phenanthrene was released from tar decanter sludge over the same period of time. Quite obviously, most of the released phenanthrene is transferred to the sediment when no sorbent was added as seen in Figs. 6a and e for both the cases of transmission oil and tar decanter sludge, with biodegradation playing a very minor role. Because the most important sediment fraction for sorption consists mainly of coaly particulates, which has a very large partitioning coefficient, this compartment plays an important role as a sink for the

released phenanthrene. This is apparent in the graphs, as lines representing the phenanthrene mass fraction source and the sediment are virtually mirror images.

As shown in Figs. 6b and f, AC was the only effective sorbent in this sediment, rendering the fastest and the highest uptake of phenanthrene and the lowest aqueous-phase concentration. Also, it minimizes the phenanthrene mass transfer to the sediment. Coke initially takes up phenanthrene in the transmission oil source case; however, the sediment outcompetes the coke eventually. The larger amount of the sediment compared to the amount of the coke, which was 5% by weight, is responsible for this observation due to slow uptake kinetics of the sediment being responsible for the time trends.

The biodegradation of phenanthrene appears to be negligible in all cases as compared to the mass transfer. Biodegradation is considered to be a first-order reaction in the aqueous phase and the aqueous concentrations are very low in both cases due to the high affinity for the source material, uptake by the sorbents and the sediment, and the slow release from the source in the tar decanter sludge case. For example, within a month a high first-order biodegradation rate in the free aqueous phase of $0.001\,s^{-1}$ would consume 25% of the phenanthrene originating from an oily source without sorbent addition, while 55% would be adsorbed by the sediment and 20% would remain in the source. Sediments having less coaly particulates were simulated for comparison and it was predicted that the fraction biodegraded increases due to the increase in aqueous concentration and faster kinetic exchange (data not shown). Also, the biodegraded fraction is higher in the transmission oil case than in the tar decanter sludge case by about one order of magnitude. This is partly because phenanthrene is more readily available from transmission oil and initially exerts higher aqueous concentration than the tar decanter sludge. In the batch experiments reported by Karapanagioti et al. (2001), the mass fraction of phenanthrene degraded was significant because of the much lower solid-to-aqueous phase ratio of $0.17\,mg/cm^3$ vs. an assumed ratio of 1 g of solid/cm^3 of water in these simulations. It should be noted that earlier studies reported significant biodegradation of rapidly released PAHs (but not of coal-bound PAHs) in Milwaukee Harbor sediment (Talley et al., 2002). Concomitant degradation of the source matrix may contribute additional complexity in the case of model simulations of an oily source. The derivation and parameterization of more complex models of PAH biodegradation in sediments requires further study.

Although negligible even without sorbent amendment, phenanthrene biodegradation was the least when AC was added. This fact has implications for the application of in-situ stabilization techniques using sorbent amendment. Once an effective sorbent is added to the contamination, the biodegradation of the pollutants will be significantly reduced as a result of lower free aqueous concentrations, at least for the scenario of a first-order rate biodegradation occurring in the aqueous phase. However, if the contaminated site contains black carbon materials like coaly particulates that may play an important role as a sink for the pollutants, then their presence will also hamper the biodegradation. Thus, if bioremediation or natural attenuation is considered as
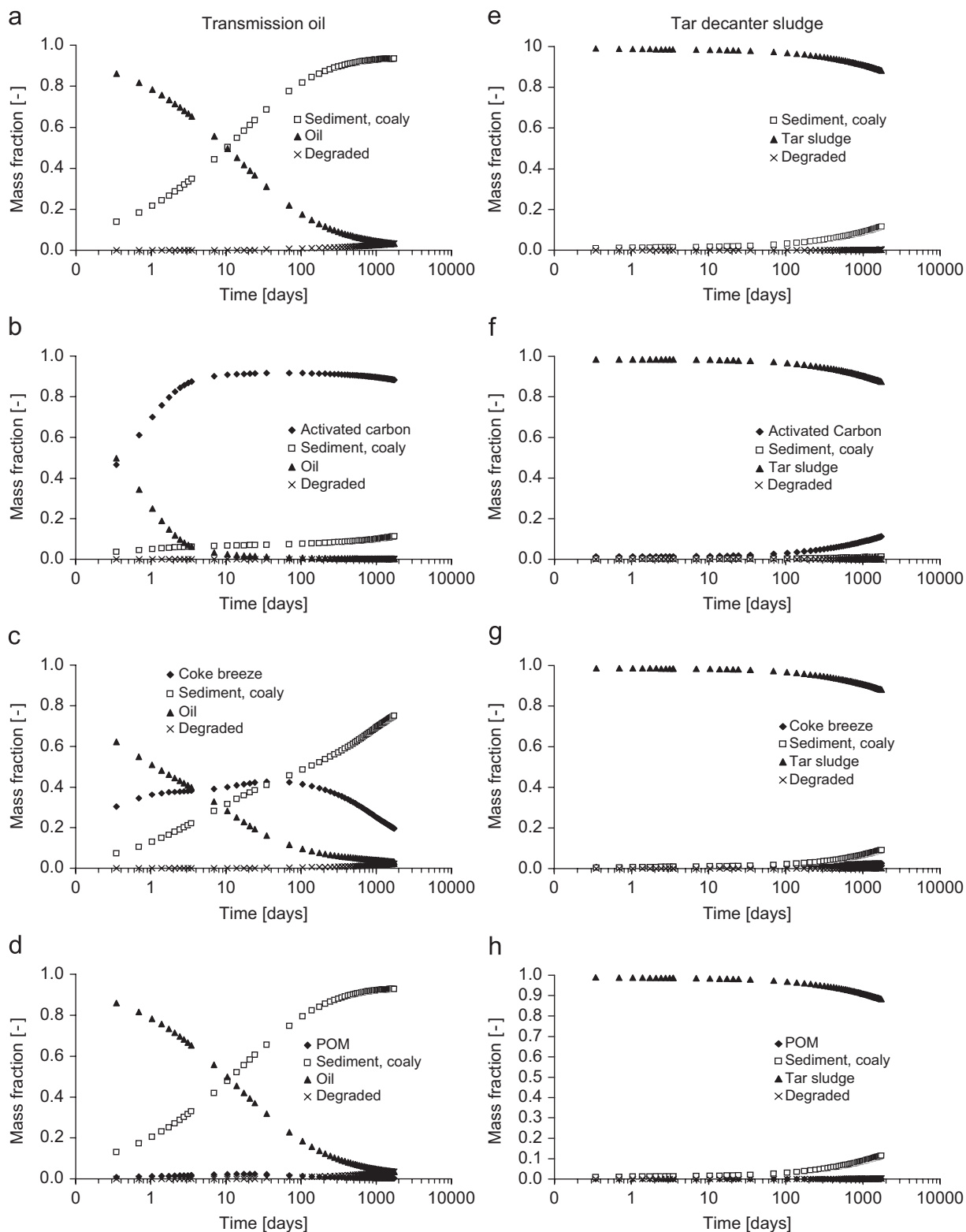
Fig. 6 – Phenanthrene mass fraction in each compartment and the biodegraded fraction for conditions shown in Fig. 5 with or without 5% added sorbent.

a remediation strategy for contaminated sediment, more attention should be paid to the characterization of the site sediment composition, especially the forms of sorbent carbonaceous phases. Still, the biodegradation process can

be an important supplement to the stabilization of pollutants by sorption. As described here, stabilization is based on the idea of re-distributing the pollutants by adding sorbent material that binds the pollutants very strongly. Because the

distribution of contaminants is controlled by partitioning, the sorbents cannot confine all contaminant mass released from the source and a certain amount of the contaminant, even though very low, will remain in the aqueous phase. Biodegradation could minimize the aqueous concentration at this point. Microorganisms may help maintain low aqueous concentrations and, in the long run, may degrade re-released contaminant after the system reaches a steady state or equilibrium. The relationship between the confinement of the pollutant by the added sorbent and the biodegradation under circumstances of in-situ stabilization has not yet been studied systematically and this is a topic for further study. Important in all of the discussion about biodegradation is the assumption that a low aqueous concentration threshold dose not exist below which biodegradation ceases due to lack of enzyme induction or other factors.

4. Conclusions

The three-compartment kinetic partitioning model reproduces the laboratory-scale experiments results reasonably well. It also provides useful predictions regarding the fate and particle-scale movement of the contaminants when applied to remediation scenarios. The application of this model can be quite versatile and can be used to estimate the effectiveness of stabilization or bioremediation techniques prior to actual application. For more accurate and realistic prediction, the model requires thorough particle-scale characterization of the pollutant source, the receiving soil or sediment, and the sorbent introduced to the system for the treatment purposes, as well as an understanding of the local mixing regime and its impact on mass transfer processes in the sediment.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2008.03.011.

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