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 $0.001\,\mathrm{s}^{-1}$ 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:

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

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.
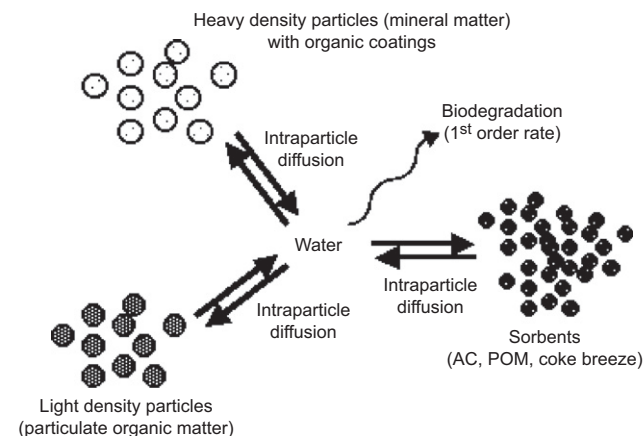

Fig. 1 – Schematic domains of the mass transfer model in a slurry of contaminated soil or sediment and added sorbent.