Progress Report
Submitted to:
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Hazardous Substance Research Center/South and Southwest

Title: **Sediment Management in the Anacostia and Grasse River: Applying Fe(0)-based Reactive Sediment Caps for in situ PCB Destruction Investigators and co-investigators**

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Institutions: Hazardous Substance Research Center/South and Southwest; Carnegie Mellon University, Dept. of Civil and Environmental Engineering

EPA project Officer: Mitch Lasat

Project period:

Jun 1, 2002 - Sept 30, 2004 (Report period: June 1, 2002 to Nov. 1, 2002)

Current Project amount and period:

June 1, 2002 to September 30, 2004 ($179,437)

Research category:

Physical and Chemical Processes, Contaminant Fate and transport

Goal

The goals of this project are to identify, evaluate, and validate the performance of media capable of transforming or sequestering PCBs in "active" sediment caps. The primary objectives of the research are to:

- Identify suitable Fe(0)-based reactive media for reductive transformation of PCBs and suitable carbon-based sorptive media for PCB sequestration in "active" sediment caps.
- Determine the cap design parameters (composition and thickness) required to mitigate PCB flux to an acceptable level.
- Guide cap design and placement, and evaluate the efficacy of the placement technique
- Evaluate the long-term efficiency of Fe(0)- and carbon-based cap amendments for PCB destruction/sequestration in the laboratory and field demonstration project.
- Provide preliminary cost estimates for applying each cap amendment and perform a cost-benefit analysis for each cap amendment based on the reactivity, lifetime, and materials costs.

Rationale

Previous research has shown that zero-valent iron can be used in reactive barriers to dechlorinate solvents such as trichloroethylene and carbon tetrachloride. Palladized iron (Pd/Fe(0)) is also capable of rapidly dechlorinating PCBs. The efficiency of carbon-based media to sequester PCBs and reduce their bioavailability has also been evaluated. Coal-derived particles in sediment more strongly sorb hydrophobic compounds than do particles of sand, silt, or clay. Furthermore, it has been shown that PAHs associated with coal particles are not bioavailable. Therefore coke, an inexpensive material derived from coal, is a good candidate for cap amendment to sequester PCBs.

The primary focus of this project is to measure the PCB destruction rate afforded by different Fe(0)-based reactive media, and the PCB partitioning to different carbon-based reactive media that may potentially be used as a sediment cap amendment. The primary hypotheses are that Fe(0)-based cap amendments will increase the rate and extent of reductive dechlorination of PCBs within the sediment cap and carbon-based amendments will strongly sequester PCBs, substantially reducing PCB flux through the cap and PCB bioavailability within the cap. The best of these reactive and sorptive media will be determined based on feasibility of cap placement in the field, ability to destroy and/or sequester PCBs, and capital cost.

Approach

The PCB dechlorination rate (k_r) in the presence of commercial Fe(0), Pd/Fe(0), and nanoscale Fe(0) media is being measured in batch experiments. Specific individual PCB congeners are being used in these experiments in order to gain insight into the reactivity of PCBs with different chlorine substituents in different positions. PCB degradation rates are being determined from the loss of substrate as well the formation of lesser-chlorinated PCB degradation products. The solid-liquid equilibrium partitioning coefficients (K_d) for coke (an inexpensive carbon-based media) is being measured by sorption isotherms and obtained from reported literature values. Appropriate Fe(0) and carbon-based media selected from the batch screening process are being used in long-term laboratory column experiments simulating PCB transport through the "active" sediment cap. Specific PCB congeners are being used in these experiments, and the column effluent is monitored for breakthrough of the parent PCB compound as well as lesser-chlorinated degradation products. These experiments will evaluate the long-term efficacy of the selected materials and help determine methods to evaluate the in-place performance. Values of k_r and K_d measured in these long-term experiments will be more representative of those expected in the field demonstration than obtained from batch experiments. A one-dimensional advection-dispersion transport model using experimental values for k_r and estimates of K_d is used to determine the cap design parameters (thickness and composition) required to achieve the desired remedial objectives. Preliminary cost analyses are being performed based on the cap performance measured in the laboratory and field.

Results

<u>PCB Dechlorination by Fe(0)-based Media</u>

Initial reactivity screening of commercial Fe(0), Pd/Fe(0), and synthesized nanoscale Fe(0) has been conducted in batch systems. Some PCB dechlorination was

observed using commercially available Peerless 8-50 mesh Fe(0), but reactivity varied with congener structure. A 234-trichlorobiphenyl was transformed to 2,3-dichlorobiphenyl and 2,4-dichlorobiphenyl, but 22'35'-tetrachlorobiphenyl was not dechlorinated over the duration of the testing. Based on formation of 2,3- and 2,4-dichlorobiphenyl approximately 1% of 234-trichlorobiphenyl was transformed after four months. This estimate of PCB conversion is conservative as conversion to other products is possible. Despite this slow rate, the formation of lesser-chlorinated bi-products indicates that commercial iron can dechlorinate PCBs. It appears that congener structure will dictate the extent and rate of PCB dechlorination in the presence of commercially available iron.

While commercially available iron was not able to induce dechlorination of 22'35'-tetrachlorobiphenyl in 4 months, laboratory-synthesized nanoscale Fe(0) particles did show significant reactivity. Within two months, 45% of 22'35' was dechlorinated to 22'3 (BZ 16). Low levels of other tri- and di-chlorobiphenyls were also measured, but no monochlorobiphenyls were found. Biphenyl was not detected after 2 weeks but has yet to be analyzed in later samples. It is possible that complete dechlorination may occur and biphenyl will be detectable in future samples. The higher reactivity of nanoscale Fe(0) particles is likely attributed to their increased specific surface area. The measured specific surface area of nanoscale Fe(0) is 33.5 m^2/g, compared with 0.2-1.5 m^2/g for Peerless iron. This provides a greater number of reactive sites per unit mass of Fe(0) for PCB dechlorination.

In all of the Pd/Fe(0) experiments, lesser-chlorinated bi-products were detected. The iron media was palladized at two different levels, 0.5% and 0.05% by mass. The later was an attempt to minimize the capital cost of the capping media. Within one week, acid-washed Peerless 0.05% Pd/Fe(0) and Fisher 0.05% Pd/Fe(0) provided 99.5% conversion of 22'35'. Peerless Pd/Fe(0) that had not been acid-washed still retained a significant concentration of 22'35' after two months even though low levels of 22'3, 22'5, and 23 were detected (biphenyl not yet analyzed). This is an expected trend because acid washing the iron removes surface oxides, leading to better deposition of Pd on the surface as well as more active sites.

PCB Partitioning to Coke

An estimate of the solid-water partition coefficient, K_d (L/m^3), for PCBs on coke has been made based on literature values. Isotherm measurements to verify these values are underway. A TCLP test of the coke material under consideration showed no heavy metals of concern in leachate above the detection limits except for Barium, which was present at 0.5 mg/L.

Performance of Selected Cap Amendments

To assist in the design and evaluation of an *in situ* cap, a numerical model was developed based on the one-dimensional diffusive transport of a reactive species. The model serves to minimize cap thickness and material cost while maximizing PCB destruction or sequestration. Model simulations are being conducted to compare the 100-year performance of alternative 10 cm-thick cap media based on reactivity, the ability to sequester PCBs, and cost. Based on initial simulations, coke is the least expensive and most effective cap amendment to mitigates PCB flux, but provides no PCB destruction. Both nanoscale Fe(0) and Pd/Fe(0) provide initial PCB destruction rates rapid enough for use as a sediment cap amendment, but the long term efficacy of this material has not yet

been evaluated. Commercial Fe(0) by itself does not provide rapid enough PCB destruction rates to be a useful cap amendment based solely on abiotic PCB destruction. The ability of Fe(0) to enhance biodegradation of PCBs within the sediment cap is under investigation.

Summary of Results

- Measured the destruction rate of specific PCB congeners in the presence of Fe(0), Pd/Fe(0), and synthesized nanoscale Fe(0) particles
- Identified a useful, inexpensive carbon source (coke) for use as PCB sequestering cap amendment
- Determined the required mass of Fe(0) and coke required to mitigate PCB flux through a sediment cap

Future Work

CMU will continue the study of active capping with the following:

- Measuring the PCB sorption isotherms onto coke material in deionized water and sediment pore water. Estimates of the resulting equilibrium solid-liquid partitioning coefficient will be used in the model to minimize cap thickness.
- PCB-Iron reactivity batch experiments in sediment porewater. The potential increased PCB dechlorination by iron under field conditions will be evaluated.
- Column studies to evaluate long term performance of cap amendment material. These studies will measure the performance of purposed cap designs with PCB-spiked sediment porewater. They will also assess the best methods to evaluate performance of the field-demonstration cap.

Supplemental Keywords: hydrophobic organic contaminants, contaminant flux, remediation

Students Supported
Kathleen M. Johnson (partial), M.S., 2003 (expected)
Paul Murphy (9/1/02-current)

Publications and Presentations

Johnson K. M., Smith, M. L., Lowry G. V., "Sediment Management through Subaqueous Capping: "Active" sediment caps for PCB destruction". Platform presentation at the 34th Annual Mid-Atlantic Industrial & Hazardous Waste Conference, New Brunswick, NJ, September 20-21, 2002.