Title: Phytoremediation in wetlands and CDFs

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Goal

The primary goal of the study is the development of a scientific basis for a plant-based remedial approach for subaqueous and wetland sediments contaminated with chlorinated organic compounds.

Rationale

Hydrophobic chlorinated organics are common sediment contaminants that pose a threat to sensitive receptors. These compounds are often recalcitrant in sediments and bioaccumulate through the food chain. By contrast, rapid contaminant attenuation for certain chlorinated organics is observed in *vegetated* sediments (i.e., wetlands). In these sediments, enhanced biological processes (aerobic and anaerobic biodegradation and plant uptake) have been observed in the root zone that drives rapid natural recovery. Previous research has indicated that herbaceous wetland vegetation stimulates degradation of chlorinated organics primarily via rhizospheric reductive dechlorination biodegradation processes. The primary hypothesis of the research is that by vegetating sediments contaminated with chlorinated compounds, root matter and exudates will serve as a source of hydrogen for halorespiring organisms that can biodegrade the target compounds. Plant uptake and aerobic biodegradation of lower chlorinated daughter products may also be important mechanisms for certain contaminants.

An objective of the proposed study is to: identify the types of sediments where a plant-based remedial approach would be applicable. It is hypothesized that vegetating sediments will yield the best results in sediments where highly reducing conditions are not yet present due to insufficient organic carbon content or other barriers to achieving low redox potential. Our previous research on plant uptake of desorption resistant contaminants has demonstrated the importance of root sorption as an uptake mechanism. Understanding the fate of chlorinated organics on or near the root, itself, is an important goal of the study.

Approach:

Methodology

Two groups of studies are being conducted in this year of the project. The first group of studies is the completion of an extensive set of experiments on reductive dechlorination of chlorinated ethenes and ethanes in vegetated wetland peat beds. The research, initiated by Ph.D. student, Gabriel Kassenga, and previously supported by a Fulbright fellowship, examined factors controlling the reductive dechlorination of chlorinated ethenes and ethanes in the rhizosphere. These studies were conducted in upflow core mesocosms and in serum bottle microcosms. Natural wetland peats from a freshwater marsh and a constructed wetland mixture were utilized in the experiments. Chlorinated ethenes and ethanes were measured using GC-MS. H_2 was measured using GC with a reduction gas detector. Specific components of the microbial consortia were identified using PCR-based detection using primers for *Dehalococcoides* sp and certain methanogens. In microcosm studies, measured reactant and products concentrations were used to determine actual potential *in situ* energy yields which, in turn, were used to predict the potential for a given hydrogen oxidizing process occurring in the sediment.

The second groups of studies are experiments designed to establish the effects of vegetating sediments contaminated with more hydrophobic chlorinated organics. 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) was chosen as a test contaminant because of its chlorination pattern and because it has been shown to be the most hydrophobic chlorobenzene that is directly dechlorinated by halorespiring organisms. Initial mechanistic studies were conducted in serum bottle and core mesocosms using 2 bayou sediments (Bayou Duplantier and Baton Rouge Bayou adjacent to the Petro Processor, Inc. site) and 2 highly organic peat soils for contrast. Serum bottle studies were conducted under anaerobic conditions to establish dechlorination kinetics, the effects of the methanogenic inhibitor, BES, and the effects of root material on dechlorination. Core studies were also conducted with herbaceous wetland vegetation with known differences in detrital pathways (*Phragmites* and *Typha*). Chlorinated benzenes were measured using GC-MS. H_2 was measured using GC with a reduction gas detector. Changes in the microbial consortia were identified using denaturing gradient gel electrophoresis (DGGE).

Findings

Experiments on the reductive dechlorination of chlorinated ethenes and ethanes were completed in the first year. Because of the rapid rate of treatment in the peat beds, these studies provide a guide to the type of conditions that would be targets for establishing in subaqueous sediments held in a confined disposal facility, for example. Major findings of the completed wetland peat studies germane to this project are the following:

- ✓ High rates of complete reductive dechlorination of chlorinated ethenes and ethanes were established in the rhizosphere of wetland cores. These rates have been maintained for 2 years without supplemental sources of nutrients or carbon.
- ✓ Energetics calculations for reductive dechlorination of chlorinated ethenes and ethanes were useful in predicting which terminal electron accepting processes would occur temporally and under which conditions.
- ✓ Hydrogen thresholds and the effects of sulfate and sulfite have also been examined in detail leading to better understanding of the interaction of various terminal electron-accepting processes in the rhizosphere.

Studies in subaqueous sediments have begun to establish the types of sediments where a plant-based approach would yield results. Laboratory microcosm studies conducted in the initial year of the study have established the kinetics of 1,2,3,4-TeCB dechlorination in sediments with a range of organic matter content. In addition, the studies have identified the role of H_2 as an electron donor, the expected daughter products of dechlorination and the relative role of methanogens in dechlorination. Results indicate that the ability to dechlorinate tetrachlorobenzene is widespread in sediments. 1,2- and 1,3-dichlorobenzene readily forms and subsequently these are dechlorinated at slower rates to chlorobenzene and benzene. Rapid decreases in H_2 as dechlorination commences suggest that H_2 is the electron donor. BES, an inhibitor of methanogenesis, decreased rates, in some cases, and patterns of dechlorination but did not completely inhibit the process.

Additional microcosm studies were conducted with root material from *Phragmites communis* (common reed) and *Typha latifolia* (cat tail). These plants differ in their observed detrital pathways. In sediments amended with fresh *Phragmites* roots, dechlorination rates increased in direct proportion to the amount of root matter added. Ambient H_2 and methane also increased. As observed in previous studies, the low molecular weight organic acid, propionate, accumulated as the primary intermediate. DGGE indicated changes in the microbial community after addition of roots. A more extensive study utilizing a wider range of inhibitors of various anaerobic metabolic processes was conducted in anaerobic media without sediments or chlorobenzenes to better understand anaerobic metabolism of root matter from these 2 types of plants. These results indicated that *Phragmites* root stimulated an order of magnitude higher rate of methane production than *Typha* roots.

A large factorial core study experiment was also performed to examine dechlorination and microbial interactions in a more realistic setting. Sediment from the PPI site was spiked with 1,2,3,4-TeCB and *Typha latifolia* and *Phragmites communis* were grown in the cores. Cores were sacrificed over time and the temporal and spatial location of 1,2,3,4-TeCB, lower chlorinated degradation products, H_2 and methane were established. Although some differences in observed dechlorination patterns and rates were detected, dechlorination occurred rapidly throughout the core. Microbial community structure analysis of these core samples is ongoing.

Future Work

Work during the first year of the project has identified factors in vegetated peat sediments that are desirable for creation in subaqueous sediments. Experiments in serum bottles and core mesocosms in several types of subaqueous sediments demonstrated that reductive dechlorination of the tetrachlorobenzene readily occurred. Root material stimulated the dechlorination process, however, work needs to proceed with sediments that are not so easily reduced to better demonstrate the stimulatory effect of planting. In addition, experiments will be conducted using the techniques developed in previous projects .for establishing known amounts of chlorobenzene in the labile and desorption-resistant fraction, which are expected to be more representative of “aged” field sediments.

Supplemental Keywords: marshes, natural attenuation, wetlands

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Publications and Presentations

Kassenga, G., J.H. Pardue, S. Blair and T. Ferraro. 2002. Treatment of chlorinated VOCs using treatment wetlands. *Ecological Engineering. In Press.*