Report for 2004OH10B: Rapid Characterization of PCB Contaminated Sediments toward Effective Enhanced Remediation

There are no reported publications resulting from this project.

Report Follows

Completion Report

Project Title: Rapid Characterization of PCB Contaminated Sediments toward Effective Enhanced Remediation

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Summary. Point and non-point source discharges from industrial facilities, municipalities, and dumpsites combined with urban and agricultural runoff to the Great Lakes have resulted in major contamination issues. Many of the toxic substances (e.g., polychlorinated biphenyls (PCBs), heavy metals) identified accumulate in sediments. The Maumee River area of concern (AOC) located in Northwest Ohio is defined as the area from River Mile 22.8 in the city of Bowling Green downstream to the Maumee Bay and Lake Erie. Sediment cores collected from the Ottawa River located in the Maumee AOC contain PCBs concentrations up to 1,000 ppm. These levels are harmful for humans, aquatic species and wild life. PCBs are known to be carcinogenic to animals and might be carcinogenic to humans. PCBs cause damage to the immune, endocrine and reproductive systems.

It has been observed that PCBs can be degraded by indigenous microorganisms resulting in lower chlorinated and thus less toxic compounds. However, this is typically an extremely slow process that requires up to one year for the removal of one chlorine. Microorganisms need carbon as a nutrient source and electron donors as a source of energy. Sediment microbial communities compete for available resources. In an environment that has a limited source of electron donors, these microorganisms may out compete indigenous dechlorinating bacteria, in turn, adversely affecting PCB degradation. The addition of excess electron donors can dramatically increase the number and activity of dechlorinating bacteria, resulting in an increased PCB dechlorination rate. Significant interest exists in the development of techniques to accelerate the dechlorination process in the field to provide a viable sediment remediation alternative to dredging.

The purpose of this research was to determine the potential for accelerated PCB dechlorination in freshwater sediments by providing excess electron donors, delivered in the form of Hydrogen Release Compound (HRC^{TM}, Regenesis, San Clemente, CA). This experiment involved the incubation of sediment samples collected along the Ottawa River from four different locations (at depths ranging from 2" to 24" below the surface). Triplicate samples with HRC added in proportion 1% V/V were incubated along with unamended control samples under anaerobic conditions for up to 6 months. Periodically (1, 3, and 6 months), microbial numbers, percent activity, biogas production, and PCB levels were be recorded. During the first month of incubation, a significant increase in the percent of active bacteria was observed in all HRC-amended samples (14-32%) as compared to the unamended control samples (5-14%). Gas production was observed in amended samples within one week of incubation, suggesting anaerobic biological activity. Biogas produced in amended samples (90mL/month) was significantly higher

than that observed in unamended samples (10mL/month) during the first 3 months of incubation. Results following 6 months of incubation, suggest that hydrogen donor amendment increases anaerobic microbial activity which may lead to increasing dechlorination rates in contaminated sediments.

INTRODUCTION. Point and non-point source discharges from industrial facilities, municipalities, and dump sites combined with urban and agricultural runoff to the Great Lakes have resulted in major contamination issues. Many of the toxic substances (e.g., polychlorinated biphenyls (PCBs), heavy metals accumulate in sediments. The Maumee River Area of Concern (AOC) located in Northwest Ohio is defined as the area from River Mile 22.8 in the city of Bowling Green downstream to the Maumee Bay and Lake Erie. PCBs have been identified as a problematic toxic substance in the Maumee AOC, particularly in the Ottawa River which has been impacted by industrial activities and leaky landfills (Figure 1).

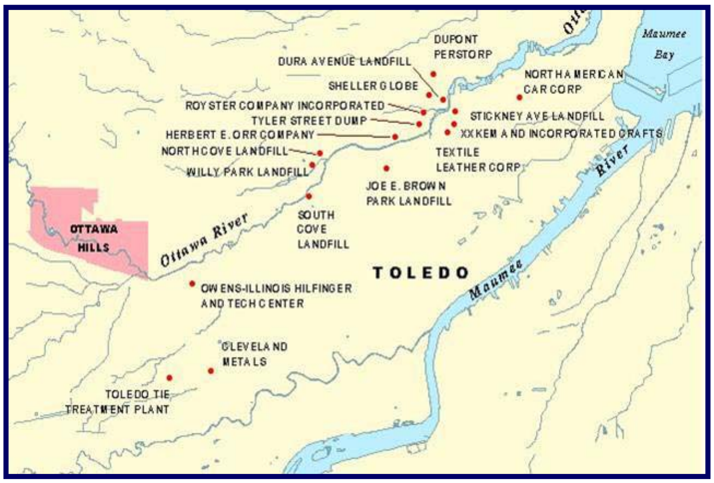


FIGURE 1: Map of Ottawa River in the Maumee AOC

Sediment management strategies pose some of the most challenging issues facing the Great Lakes region. Chlorinated contaminants (e.g., PCBs) are strongly sorbing and bioaccumulative, thus impacting ecosystem degradation, public health, and economic development. Volumes of contaminated sediments tend to be large and contaminant concentrations low such that application of expensive conventional control technologies such as incineration or disposal in a secure landfill may be cost-prohibitive. Under such conditions, enhanced recovery processes that involve manipulation strategies designed to stimulate natural fate pathways may be investigated.

The use of organic electron donors such as aliphatic and aromatic acids is a common technique to supply reducing equivalents for enhanced microbial activity and to stimulate dechlorination of aliphatic and aromatic compounds (Bedard and Quensen, 1995; Adriaens et al., 1999). From a thermodynamic perspective, hydrogen has the potential to serve as an electron donor for dehalogenation of aromatic compounds such as PCBs. Generally, freshwater sediments are characterized by a sharp redox-cline from the sediment bed surface downward, resulting in a gradient from aerobic processes near the surface, to denitrifying, iron-reducing and methanogenic conditions within short distances in the vertical direction. Among these processes, the hydrogen concentrations in sediment pore water are controlled by competitive metabolic conditions (Hoehler et al., 1998). Growing evidence indicates that hydrogen is a key electron donor used in the dehalogenation of lesser chlorinated organics (e.g. cis-DCE and VC to ethene), and organic electron donors appear to serve mainly as primary precursors to supply the needed hydrogen via fermentation (DiStefano et al., 1992; Fennell et al., 1997).

METHODOLOGY.

The overarching goal of the proposed work was to assess the efficacy of a hydrogen-based microbial enhancement technology on PCB contaminated sediments from the Maumee AOC. The following specific objectives were addressed:

Objective 1: Collected representative sediment samples from the Ottawa River.
Four samples of Ottawa River sediments were collected from previously characterized locations known to have a range of PCB contamination (up to 1000 ppm). Grab samples (4L) of surface sediments were be decanted, sealed and delivered to the laboratory on ice for homogenization, and split into aliquots for analysis of total organic carbon, physical parameters (percent solids, total/volatile solids), microbial indicators (total number, live/dead/injured cells, and respiratory competence), and PCB screening.

Objective 2: Characterized sediment samples collected in Objective 1. Each sample was subjected to (i) physical characterization (total organic carbon; total/volatile solids); (ii) microbial assessment (total/active number of microorganisms present, amenability to microbial enhancement); and (iii) determination of historical PCB contamination levels.
Task 1: Physical characterization of sediments. Organic content (total/volatile solids) was measured for each sample collected (Standard Methods for the Examination of Water and Wastewater, Method 209G). Metals were extracted from sediment samples using USEPA's Method 3050 for acid-digestion of sediments (Edgell 1988). After filtration of digested samples, the supernatants were analyzed for metals concentrations using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer® Plasma II).
Task 2: Microbial assessment of sediments. Microorganisms were eluted from sediments following an established elution protocol of surfactant addition, sonication, centrifugation, and resuspension in river water (Barkovskii and Adriaens, 1996; Gruden et al., 2003). Sediment-eluted microorganisms were collected, amended with CTC, a redox dye which is reduced to a fluorescent red intracellular precipitate by metabolically active (respiring) bacteria, and counter-stained with the DNA intercalator picogreen (PG, Molecular Probes, Oregon). Epifluorescent microscopy was used for enumeration of total and active bacteria.
Task 3: Determination of historical PCB contamination. Sediment PCB levels were determined using EPA SW-846 Method #4020. This antibody-based assay is commonly used by EPA in the field as a screening method applicable to PCB contaminated sediments (0.5 to 500 ug/kg) (Strategic Diagnostics Inc., Newark, DE). This proven method provides a rapid, qualitative assessment of PCB concentration.

Objective 3: Incubation studies targeted at assessing the efficacy of enhanced PCB dechlorination in sediments collected and characterized in Objectives 1 and 2.
The four sediment samples with distinct characteristics (PCB concentration) were selected for the sediment incubation studies. The sediments were collected, divided into six aliquots of 100 g solids each (100 mL serum vials). Ottawa River water was added to a total volume of 90 mL. Half of vials were amended with a hydrogen donor (1% V/V)

(HRC^{TM} Regenesis, San Clemente, CA). Dechlorination activity was monitored for one, three and six months, and the samples were sacrificed for microbiological assessment and chemical (PCBs) characterization. Samples were originally characterized via the colorimetric assay, however, for the incubation study, congener-specific analysis (GC-MS) will be carried out.

RESULTS AND DISCUSSION.

Following collection, physical, chemical, and microbiological characterization of the samples was completed (Table 1). All of the sediment samples, which were collected in the same river mile along the Ottawa River, had similar physical and chemical characteristics with the exception of sample #53 which had an elevated PCB concentration (~1000 ppm) and volatile solids (VS) (22%). The higher VS will result in more significant partitioning of hydrophobic contaminants (e.g., PCBs) to sediments and is usually associated with higher numbers of bacteria. TOC values, which were between 150 and 250 mg/L, were measured in an effort to determine if ample organic matter was present to support microbial activity and to delineate any differences between samples. It should be noted that metals analysis (Al, As, Cd, Fe, Cu, Ni, Pb, and Zn) indicated that none were above recommended levels. Microbial assessment of samples was also completed as outlined in Objective 2. The percent of active bacteria in initial samples ranged from 22 to 36%, while the total ($\sim 1x10^7$/mL) and active numbers ($\sim 5x10^6$/mL) were similar for all four samples.

For the incubation study, it was necessary to select an appropriate hydrogen release compound. For short term impact, a technology that has been used in the field and is relatively easy to implement was needed. For this work, we chose Hydrogen Release

TABLE 1: Selected Characteristics of Sediment Samples

Sample	TOC (mg/L)	Volatile Solids	Total PCBs (mg/L)	% Active	Active Number (#/mL)	Total Number (#/mL)
#32	164	10%	<1	36	$7.08x10^6$	$1.97x10^7$
#37	151	6%	10-100	28	$1.32x10^7$	$4.53x10^7$
#441	255	9%	10-100	32	$6.24x10^6$	$1.97x10^7$
#53	154	22%	100-1000	22	$5.89x10^6$	$2.66x10^7$

Compound or HRC (Regenesis; San Clemente, CA). HRC is a viscous fluid at room temperature that breaks down to lactic acid, which can be biologically degraded to produce low concentrations of hydrogen in sediments. This technology has previously been applied to contaminated groundwater sites with success.

Following initial characterization, triplicate samples from each of the four locations were incubated both with and without HRC amendment. HRC addition resulted in a short term (up to 7 days) increase in total and active numbers of sediment microorganisms in all samples (Figures 2A and 2B). Although the total numbers were the same, the active number of bacteria in all four HRC amended samples was statistically higher than in unamended control samples after 1 month of incubation. After 3 months of incubation the increase in active numbers had diminished in most samples (except #53) (data not shown). HRC resulted in an order of magnitude increase in TOC in amended samples. However, there was no statistically significant difference in TOC concentrations of amended samples as compared to unamended samples after 3 months of incubation.

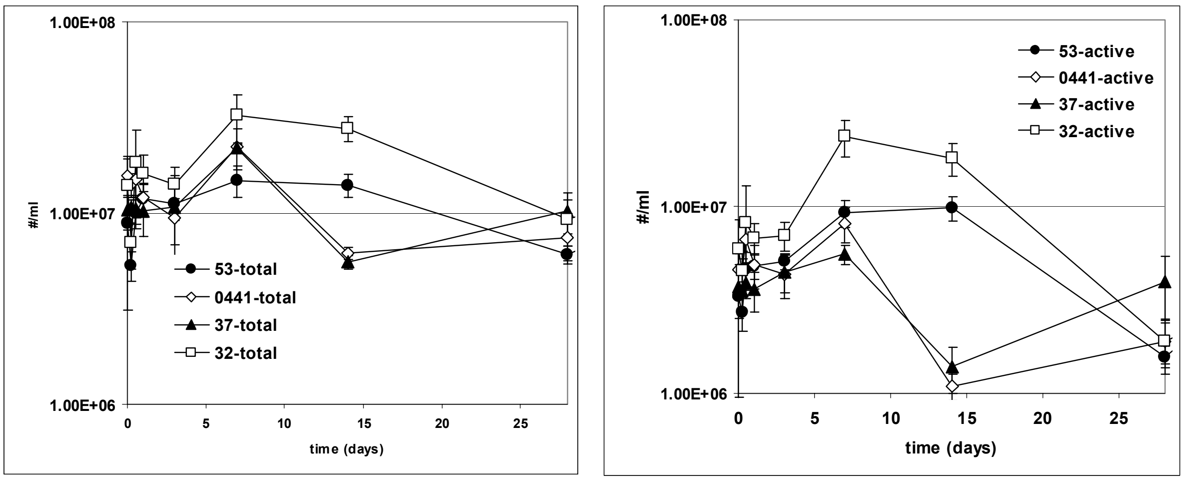


FIGURE 2: Total (A) and active (B) number of bacteria in sediment samples amended with HRC as a function of incubation time.

During incubation, significant gas production was noted in the amended samples within the first week (Figure 3). Gas production was significantly higher in sample #53 following 8-10 weeks of incubation, sample #37 following 12-15 weeks of incubation, and sample # 32 following 13-15 weeks of incubation. Weekly production ranged from negligible to 100mLs of biogas. During the first 3 months of incubation, biogas production in samples with amendment were significantly higher (approximately 100mL/month) than in unamended samples (<10mL/month). This result is likely attributed to the original TOC of amended samples, which was an order of magnitude higher (~1000 mg/L TOC) than unamended samples. After 3 months of incubation the significant increase in gas production was no longer observed, which concurs with microbiological data which demonstrated no difference between active numbers of bacteria in amended and unamended samples following 3 months of incubation.

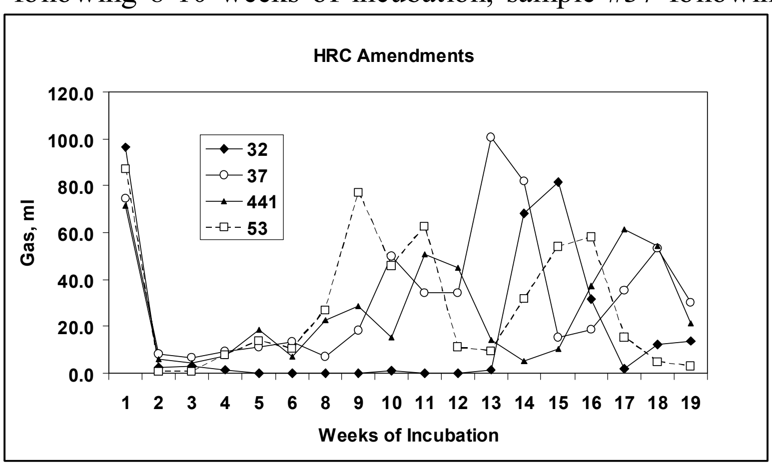
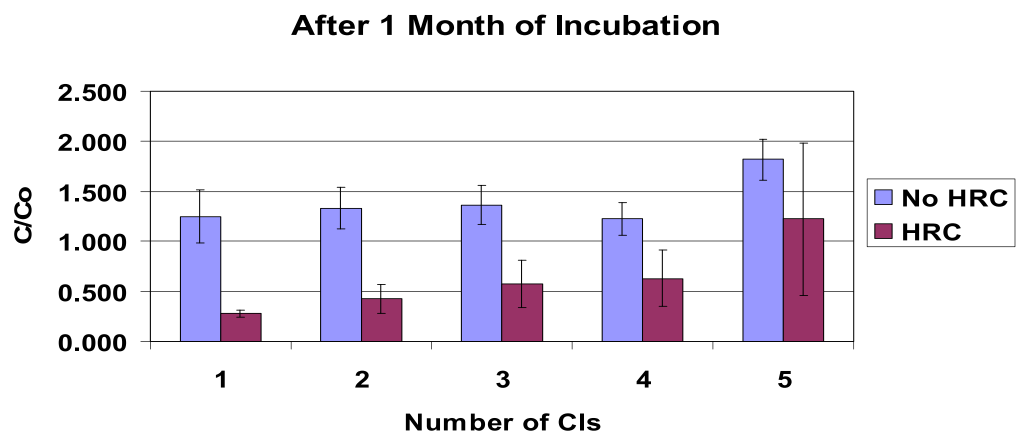


FIGURE 3: Gas production samples with HRC amendment measured weekly during 5 months of incubation.

Since the results of the colorimetric assay for PCB determination were primarily qualitative. Congener specific analyses are currently under way to analyze samples from the incubation study. The results after 1 month of incubation of triplicates of Sample #53 suggest (Figure 4) that only lower chlorinated congeners (up to 5 Cls) are present in the original sample and dechlorination (25-50%) occurs within the first month. After six months of incubation, there is no statistically significant increase in dechlorination of this sample, suggesting that dechlorination activity peaked within the first month of the study.



CONCLUSIONS. Results following 6 months of incubation, suggest that hydrogen donor amendment increases anaerobic microbial activity as evidenced by increased biogas production and active numbers of bacteria in all sediment samples amended with HRC and, subsequently, a reduction in the concentration of lower chlorinated congers in a highly contaminated (>1000 ppm PCB) sample (#53) amended with HRC. For sample #53, it appeared that a positive response in terms of both gas production and enhanced activity suggested the potential for PCB dechlorination. However, this result must be verified with subsequent analysis. Congener-specific PCB analysis of the remaining sediment samples is ongoing as part of a related research project.

This project investigates an enhanced remediation alternative for PCB-contaminated sediments. Results from this study will provide the basis for establishing causal relationships between sediment characterization and efficacy of hydrogen donor amendment strategies toward PCB dechlorination in sediments. Although enhanced natural recovery strategies represent some of the most promising and cost-effective medium-term sediment management approaches, causal relationships have yet to be established. In addition, this proposed technology may provide a viable alternative for contaminated areas where sediment removal technologies are cost prohibitive yet remediation is warranted.

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