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Title: Sediment-Based Remediation of Hazardous Substances at a Contaminated Military Base

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Objectives/Hypothesis

The purpose of this research is to advance fundamental understanding of the transformation of hazardous substances in sediment systems exposed to a complex array of chlorinated solvents and petroleum hydrocarbons. This research was conducted to both delineate fundamental pathways of biodegradation and to advance this in-situ technological approach to the field assessment stage.

Approach

The research focus for this project was on the delineation of the fate and transformation of selected contaminants in wetland sediments. The contaminants of concern were TCE, BTEX, chlorobenzene, DCB and related degradation products.

Wetland sediments at various depths and in several areas of high and low influent concentrations, sediment cores and wetland waters were transported to the laboratory under refrigerated and anoxic conditions. The sediment samples were analyzed to obtain the fundamental characteristics, such as organic content, nutrition level, and basic bacterial activity.

Batch slurry reactors of sediments were used to address biodegradation rates under aerobic, anoxic and anaerobic conditions. Results of biodegradation under different environmental and nutritional conditions were analyzed and compared statistically. A soil column with continuous flow was setup to mimic the in-situ biodegradation of contaminants. The soil column was designed based on the results of the batch slurry reactor studies.

Results

Biodegradation of Specific Site Contaminants under Aerobic Conditions

Aerobic respirometry was used to determine sediment-based bioremediation of site contaminants in oxygenated conditions. Exponential oxygen exertion was observed in all sediments with acetone, phenol, benzene, chlorobenzene, and 1,4-dichlorobenzene. Sediments showed exponential increases with acetone at 60-100 hours of experimental run -time in the respirometer reactor . Once initiated, exponential oxygen exertion with acetone occurred at rates of 0.048 hr^{-1} to 0.16 hr^{-1} . Sediments responded with shorter experimental run times before oxygen exertion and with faster rates, as compared to acetone. when phenol was utilized as a substrate. Exponential growth on phenol occurred

at 20 hours and was complete before 40 hours. Utilization rates for phenol ranged from 0.1385 hr⁻¹ to 0.287 hr⁻¹, averaging 0.22 hr⁻¹.

For benzene, exponential-growth, starting times ranged from 50 to 110 hours. Degradation rates of benzene in the sediments ranged from 0.06974 to 0.15 740 hr⁻¹. Chlorobenzene responded with less experimental run time before exponential growth, and the results show initiation of exponential growth ranging from 30 hours to 70 hours. Kinetic rate data for chlorobenzene were also faster than benzene with a range from 0.08373 hr⁻¹ to 0.21140 hr⁻¹.

Sediments from SITE-03 responded to 1,4-dichlorobenzene after shorter incubation times when compared to SED-01 and SED-08. SED-03 and SED-03* responded exponentially at 60-80 hours, while SED-01 and SED-08 responded after 150-170 hours of incubation. Rates for 1,4-dichlorobenzene utilization were lower than other specific contaminant rates. 1,1-dichlorobenzene rates ranged from 0.01194 hr⁻¹ to 0.08612 hr⁻¹.

No net oxygen exertion was observed over a 7-day incubation period with TCE as substrate. Thus, intrinsic bioremediation did not appear to be feasible for TCE under aerobic conditions. Further focused investigation of TCE in aerobic systems indicated that TCE was inhibitory to the degradation of natural organic matter at TCE concentrations of 10-34 mg/L. The presence of TCE did not inhibit degradation of mixtures of easily-degraded compounds or mixtures of specific site contaminants, although subsequent degradation of natural organic matter was inhibited at 34 mg/L of TCE.

Biodegradation of Specific Site Contaminants Under Anaerobic Conditions

Biological conversion of contaminant carbon to carbon dioxide is a standard means to access biodegradability in the laboratory. Carbon dioxide production is a widely used measurement of mineralization or the complete oxidation of parent compounds. Under ideal conditions, mineralization is proportional to the amount of contaminant present and can be used to establish a mass balance for biodegradation. In this study, measurements of [¹⁴C]-CO₂, produced from utilizing [¹⁴C]-labeled organic contaminant by indigenous microorganisms was used to measure respiratory processes.

For site sediments with addition of radiolabeled compounds (acetone, benzene, chlorobenzene and 1,4-dichlorobenzene), only acetone was mineralized to ¹⁴CO₂, under anaerobic conditions. No CO₂-mineralization of benzene, chlorobenzene and 1,4dichlorobenzene was observed.

Mineralization of acetone is a direct evidence of biodegradation. Acetone is decomposed by bacteria for metabolism and energy with a fairly rapid rate. Ten days of acclimation period (i.e., no degradation of chemicals) was observed on methane production and ¹⁴CO₂ production.

No CO₂-mineralization was observed for benzene and chlorobenzene and they are believed to be recalcitrant under methanogenic conditions. 1,4-Dichlorobenzene was not mineralized or degraded in the studies using labeled and unlabeled compounds. Degradation of trichloroethylene (TCE) was observed by a rapid disappearance of unlabeled TCE. TCE (-10 mg/L) was degraded in 30 days under methanogenic conditions.

Based on the current observations, it can be concluded that if the site is contaminated with water-immiscible hydrocarbons, yet microorganisms generally will reside in the aqueous phase. For effective biodegradation to occur, it is therefore essential that the contaminant substrate be "bioavailable" to the degrading microbial communities. Many microorganisms possess an ability to overcome partitioning effects and utilize water-insoluble substrates (i.e., 1,4-dichlorobenzene, etc.). In some cases, the production of extracellular, surface active agents are produced that may solubilize hydrocarbons into the aqueous phase (Miller, 1994). In other cases, hydrophobic cell walls may actually partition with hydrocarbons present in the soil or attach to water-hydrophobe interface. The mechanisms by which hydrocarbon transport into, and assimilation by, microorganisms is not entirely understood (Bossert and Compeau, 1995).

Moreover, the chemical structure of a contaminant has both direct and indirect impacts on how well the substrate will be metabolized, i.e., biodegraded. First, metabolic or physiological constraints including nutrient or metabolic limitation and bioavailability of the contaminant substrate by microorganisms will directly impact how readily substrate can be degraded. Second, type and size of chemical structure may directly affect biodegradation by altering the bioavailability of the contamination to the biodegrading microorganisms. Biodegradability of hydrocarbons in soils has been demonstrated to correlate to their water solubility, which are generally inversely proportional to their respective molecular weight. Other structural attributes, such as degree of unsaturation, can affect water solubility and ultimately uptake and availability to the degrading microorganisms (Bossert and Compeau, 1995).

The effect of hydrocarbon contamination on microbial populations in soil therefore varies considerably, depending on the type, amount, and age of the contaminant, as well as the prevailing environment conditions. Unlike surface bodies of water or groundwater, which will diffuse the effects of contamination through dilution and migration, the contamination in soils will remain localized, potentially exerting pronounced effects on the immediate soil microcosms. However, because of physical matrix and chemistry of soil, most soils are actually good mitigators for toxic effects. By (ionic or covalent) binding, and/or sorption onto the soil organic materials which provide a solid, physical support as well to help protect and stabilize microorganisms and their cellular components, contamination quickly becomes immobilized and less bioavailable. Moreover, the solid soil structure aids in maintaining cell membrane integrity in the presence of contaminants exhibiting solvation effects (Bossert and Compeau, 1995).

Sorption described the partitioning of contaminants between aqueous phase and the solid aquifer matrix is not directly examined in the laboratory. However, quantity of sorbed contaminant in each bioreactor can be determined by direct counting of radiolabeled material on sediment or recovered throughout solid-liquid extraction from sediment. Sorption processes as-we believed tend to reduce the dissolved contaminant concentrations and limits the migration of the aqueous phase plume, however, they do not result in a loss of contaminated mass from the aquifer.

Supplemental Keywords

Biodegradation, fate and transport, and wetland sediments

References

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Students Supported

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Publications and Presentations

Saunders, M., "Sediment-Based Intrinsic Bioremediation at Robins Air Force Base", Final Report submitted to the Hazardous Substance Research Center/S&SW, August 1998

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