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Title: Bioremediation of Contaminated Sediments and Dredged Material

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Objectives/Hypothesis

The goal of this project was to develop the technical basis for evaluating the potential of bioremediation processes for cost-effective treatment and risk reduction of contaminated sediments (CS) and dredged material (DM).

Specific objectives of this project included:

- determine the unique properties of sediment-associated contaminants that influence their biodegradability.
- identify and quantify the factors that control the biodegradation of contaminants in sediments.
- assess the limits (how clean is clean?) of realistic field approaches to the bioremediation of CS and DM.
- use mass balance approaches to assess the potential risk reduction benefits of bioremediation systems.
- explore the feasibility of *in-situ* and in place bioremediation of CS and DM based on knowledge of sediment structure and mechanics and dredging and disposal operations.

Approach

The biodegradation of PAHs was studied in laboratory-scale slurry systems. Sediments for use in these experiments were collected on several occasions. Initially, sampling focused on four locations in the Houston Ship Channel - Turning Basin, Vince Bayou, San Jacinto Monument and Patrick Bayou. An additional sediment sampling location was identified approximately 30 miles south of the ship channel in Dickinson Bayou. Following sample collection, sediments were stored at 4E C in sealed wide-mouth glass containers. Prior to use in experimental systems, individual containers were homogenized and large debris (shells, sticks, etc.) were removed. Initially, studies were conducted to assess the ability of indigenous bacteria to mineralize PAHs. These experiments have clearly demonstrated mineralization of naphthalene, fluorene, and phenanthrene. In most cases, PAH degradation occurs without an observable lag (less than 24 hours). However, PAH mineralization rates are relatively slow - presumably due to their limited aqueous solubility. To develop an elevated population of indigenous PAH degraders for use in experimental systems, an enrichment culture was established using Dickinson Bayou sediments (10% to 15% solids) by routinely adding naphthalene, fluorene, and phenanthrene and other PAHs.

Slurry reactors were used to evaluate factors including: adsorption/desorption rates; the rate and extent of phenanthrene mineralization (by indigenous sediment bacteria); the rate and extent of contaminant biodegradation from sediments; and factors which may influence the design/operation of engineered bioreactors for use in remediation of contaminated sediments. Lab-scale slurry reactors ranged in size from 60 mL to 250 mL total volume depending on the requirements of an individual experiment. Mass balances were facilitated by the use of ^{14}C -labeled PAHs.

A focus of this project was to assess the ability to increase biodegradation rates through addition of surfactants. In theory, surfactants have the potential to increase degradation rates by enhancing hydrocarbon solubility and reducing interfacial tension, but there are conflicting reports on the effect of surfactants on biodegradation rates in the literature. Studies focused on non-ionic surfactants and their impact in the rate and extent of biodegradation were achieved.

Results

It can be concluded from this series of experiments that resuspension of anaerobic sediments can affect the degradation of phenanthrene sorbed to them. Sediments with contamination levels of 50 ppm phenanthrene were remediated in lab scale slurry reactors to the point that only trace phenanthrene (below GC-PID detection limit) was found after 7 days. Mixing and aeration, natural byproducts of the resuspension process, were the only treatment used.

Contaminant release from the sediments to the liquid phase is rapid under mixed conditions. Mixing was also found to be the main factor affecting rate and extent of compound mineralization. After a consistent 2-day lag period seen before appreciable activity, mineralization was rapid, reaching maximum extent within 3 days.

Mass balance analysis of radioactive carbon, in the radiolabeled phenanthrene added as a tracer, indicated that the PAH is used as a growth substrate and is biodegraded by bacteria indigenous to the sediments. Due to the time required to see complete degradation, it is unlikely that the mixing and aeration provided solely by dredging can be considered to be a remedial treatment.

The lab scale slurry reactors used, demonstrate that this type of reactor holds promise as a potential remediation methodology. A slurry reactor can be defined as an enclosed system where sediments and water are maintained in a homogeneous slurry over a period of time. It is envisioned that the reactors will be a batch treatment process. As such its size will be limited. *Ex-situ* reactors for sediment remediation could be built on barges or on shore. Both the bottom sediments and a liquid phase would have to be moved to the reactor to form the slurry. If hydraulic dredges are used, the sediments are removed in a slurry form and could be pumped directly to the reactors. *In-situ* reactors would isolate small areas of the contaminated bottom and utilize the overlying water to make the slurry. Potential methods of isolation include caissons, sheet piling, or other types of physical barriers.

Design factors that should be considered include mixing intensity, aeration, and the use of sequential treatment cells. The lab scale reactors used had minimal to insufficient mixing capacity. Any field or full scale test should be designed to provide adequate mixing for the desired slurry. Mixing not only enhances mass transfer of the contaminant from the sediment to the aqueous phase, but also helps to maintain oxygenation of the slurry when open to the atmosphere.

Tests conducted demonstrate that the intermittent aeration can substantially lower volatilization without detrimentally affecting mineralization. Optimum design will utilize intermittent aeration or some form of chemical oxidation, e.g., peroxide addition. The purpose will be to minimize contaminant loss due to volatilization or stripping. No tests have been made in slurry reactors using chemical oxidants. However, previous research looking at peroxide as a potential oxidant for injection into ground water aquifers has shown this chemical to be inhibitory at high concentrations.

It was shown that augmenting the reactor with aged slurry eliminated the lag period. Treatment times were reduced by 40% when the reactors were seeded, going from 5 to 3 days to reach maximum extent of mineralization.

Step desorption studies using the Dickinson Bayou sediments showed that desorption was fast and reversible. In sediment-slurry reactors desorption may not be a limiting factor to achieve biodegradation. PAHs in both liquid and sediment phases degraded in less than 10 days to below detection limits. This implies that PAHs were readily bioavailable. However, the current study has a lower limit on sediment concentration (1 ppm). Assuming one ppm is a reasonable value for environmentally acceptable end-point for practical purposes, bioremediation of contaminated sediments by slurry-type reactors can be considered to be a potential remedial technology.

A key element in mixing intensity is that it breaks up the sediment aggregates that entrap a fraction of the contaminant, and allowing for that fraction to be available for degradation by the microorganisms.

Sediments are strong adsorbents for nonionic surfactants as well as for PAHs. Sorption of surfactant molecules to sediment affected surfactant performance as a solubility enhancer by necessitating greater surfactant concentrations in order to achieve surface tension minima and micelle formation. When considering the use of surfactants in soil or sediment systems, a detailed consideration of surfactant sorption is necessary to evaluate the potential performance of the surfactant in enhancing contaminant solubilization and/or mobilization.

Sorption of low (less than 0.5 mg/L) phenanthrene concentrations to sediments may not limit the rate of phenanthrene biodegradation. The apparent lack of rate-limiting effect of desorption on biodegradation may be due to the relatively short (4 days) equilibration time used, since longer equilibration times have been implicated in increased degrees of sorption.

All but one of the nonionic surfactants tested at concentrations in excess of their CMC were inhibitory to the short-term (less than 6 days) extent of phenanthrene mineralization. As many nonionic surfactants are noted for their cellular membrane solubilizing characteristics, disruption of membrane-mediated cellular events or destruction of membrane integrity are likely explanations for inhibition of phenanthrene mineralization by nonionic surfactants.

Nonionic surfactants at concentrations greater than CMC, if not toxic or irreversibly inhibitory to the microbes capable of phenanthrene degradation, can enhance the extent of phenanthrene mineralization within short time periods when supplied with inorganic nutrients and oxygen. In the absence of sediment, addition of a nonionic surfactant in excess of its CMC reduced the initial rate of phenanthrene mineralization but enhanced the extent of mineralization after 1 week. The presence of as little as 2% sediment prevented this initial inhibitory effect, perhaps by acting as an adsorbent for surfactant molecules, reducing the free concentration of surfactant and thus its possible inhibitory effect on phenanthrene-degrading microorganisms. A greater concentration of micelles in the absence of sediment may have reduced the fraction of phenanthrene in molecular solution, thereby rendering the phenanthrene more difficult to degrade. This is a possibility since phenanthrene was at a concentration below its aqueous solubility. A sediment-specific property not relating to sorptive capacity for the surfactant may also be a factor in eliminating the initial inhibitory effect by the surfactant in the absence of sediment. Subtle structural differences among the surfactants within the same class may result in dramatically different biological effects, and any surfactant considered for use must be evaluated individually.

Supplemental Keywords

Bioavailability, volatile organics, and remediation

Students Supported

S.D. Chandra, M.S., 1995

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V. Jee, M.S., 1995

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