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# BIOREMEDIATION OF CONTAMINATED SEDIMENTS

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## INTRODUCTION

Contaminants in bottom sediments have historically been considered to have minimal environmental impact because they are buried, sorbed or electrostatically bound to clay particles, or incorporated into humus. Physical and chemical conditions such as alkalinity, pH, and redox of the sediments also play a part in sequestering contaminants. (2,3) As long as the sediments are undisturbed, the contaminants are considered stabilized and not an immediate environmental problem. Resuspension of bottom sediments makes contaminants more available for dispersal into the marine environment. Events that can cause resuspension include storm surges, construction activity, and dredging.

A conceptual model of the effect of a resuspension event on contaminated sediments is shown in Figure 1. During resuspension, sediment particles move from an anaerobic to aerobic environment, changing their redox characteristics, and allowing the indigenous aerobic bacteria to grow and utilize certain classes of contaminants as energy sources. The contaminants are also more available for use because the mixing energy imparted to the particles during resuspension enhances mass transfer, allowing contaminants to enter the aqueous phase more rapidly.

The contaminants targeted in this research are polynuclear aromatic hydrocarbons (PAHs), a class of contaminant commonly found in bottom sediments near highly industrialized areas. A major source of PAH contamination is the combustion of fossil fuels. (8,5) Other sources are industrial wastewater effluents, petroleum spills and oilfield produced brine disposal into waterways. PAHs consist of multiple benzene rings fused in linear, angular, and cluster arrangements. PAHs are non-ionic and hydrophobic and as such, are lipid soluble and can be bioaccumulated in the food chain. Exposure to polycyclic compounds has also been associated with higher risks for cancer.

Previous research has shown that PAHs can be biodegraded. Size and structure, i.e., number and configuration of condensed rings, can affect compound disappearance. (4,7) PAHs of up to three condensed rings have been shown to serve as growth substrates. Compounds with more than three rings may be subject to cometabolic degradation.(1) Probably the most important parameter affecting biodegradation is the redox character of the sediment or sediment/water system. Studies of sediment slurries under various redox conditions have shown that rates of compound disappearance and mineralization increase with increasing redox potential. (3,6)

The focus of this research was to examine the relationship between resuspension and biodegradation of PAHs in lab scale slurry reactors. The rate and extent of contaminant release from the sediments into an uncontaminated water column was determined. Oxygen demand of initially anaerobic sediments were investigated. Then rate and extent of phenanthrene biodegradation was examined. Final partitioning of the phenanthrene, after the degradation test, was determined based on mass balance calculations made on the radiolabeled carbon in the tracer. Several factors which may influence the design or operation of bioreactors used for remediation of contaminated sediments were also evaluated.

## METHODOLOGY

Sediments used in these experiments were collected from Dickinson Bayou, Galveston County, Texas. The natural environment is esutarine with total dissolved solids (TDS) of the water measuring

5,000 parts per million (ppm). An artificial seawater (ASW) medium based on Difco marine broth without the organics and diluted to the proper TDS was used in all tests. The sediments were artificially contaminated with phenanthrene (a 3-ring PAH). Special care was taken to keep the sediments anaerobic, with all handling done in a nitrogen atmosphere glove box.

Concentration in the various system compartments - liquid, solid, and vapor was monitored using a Hewlett Packard HP 5890 gas chromatograph with photo-ionization detector (GC-PID). Sediments were extracted using a modification of EPA Method 3550 (Sonication) with dichloromethane (DCM) as the solvent. Liquids were extracted by shaking with DCM. The sorbent of the ORBO hydrocarbon vapor traps were also extracted by shaking in DCM. $^{14}C$ labeled phenanthrene was added to trace mineralization in the biodegradation tests. Radiation levels were measured using a Beckman Model LS 3801 Scintillation counter.

The slurry reactor used in the experiments is shown in Figure 2. $CO_2$ traps were used in the biodegradation tests. The traps were removed for the abiotic contaminant release experiments. Sediments and artificial seawater (ASW) medium were loaded into the reactors inside the glove box. Three solids loadings were tested - 5, 10, and 15% dry weight sediment. ASW used was purged for 30 minutes with $N_2$ gas before being brought into the anaerobic environment of the glove box.

The first experimental series determined the rate and extent of phenanthrene release from the sediments to uncontaminated liquid under various conditions of mixing and aeration. These were short term tests (48 hours) with an emphasis on early time measurements. Each solids loading was tested under three mixing conditions - (1) unmixed, (2) continuous mixing, and (3) initial mixing only, both with and without aeration.

Mineralization to $CO_2$ was tracked in the biodegradation tests using $^{14}C$ tracer and dual $CO_2$ traps containing 1N KOH. All reactors in this test series were continuously aerated. At the end of the 7 day biodegradation tests, the reactors were poisoned with mercuric chloride and samples of each system compartment (solid, liquid, and vapor trap) was extracted. A mass balance approach was utilized to determine final partitioning of carbon from degraded phenanthrene. Non-solvent extractable carbon was measured in the sediment fraction using a modified chemical oxygen demand (COD) test. Output gases from the oxidation were passed through dual $CO_2$ traps and the residual radiation measured by scintillation counting.

Additional tests were performed to evaluate the effect of various parameters on rate and extent of phenanthrene mineralization. Factors examined included intermittent aeration, nutrient amendment, and bioaugmentation. The objectives of these tests were to reduce volatilization losses and shorten degradation time.

## RESULTS

Contaminant release into the aqueous phase of sediment/water slurries was rapid in mixed reactors. Solids loading has no effect on rate of contaminant release and little effect on extent with mixing. All reactors reached 80 to 90% of theoretical aqueous concentration within 30 minutes. Mixing, itself, had the greatest effect on rate and extent. Rate of contaminant release was 2 to 4 times slower for unmixed systems. Maximum extent of release was also less than half that seen in mixed reactors. This is shown by Figure 3 which shows contaminant release in reactors loaded with 10% solids.

Aeration effects appear to be masked by mixing effects. No differences in release rates were seen between mixed reactors which were aerated and those that were not. In unmixed reactors, aerated systems showed faster rates of contaminant release than unaerated systems, indicating that the aeration process itself provides some degree of mixing.

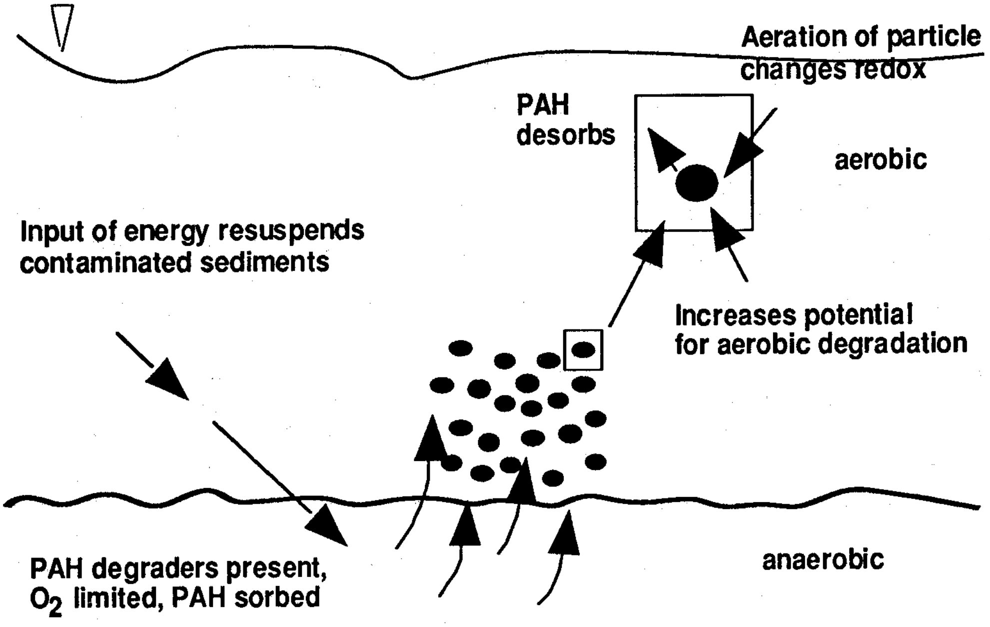

Figure 1. Conceptural model of the resuspension of process and the effect it has on the ability of indigenous bacteria to biodegrade polynuclear aromatic hydrocarbons (PAHs).

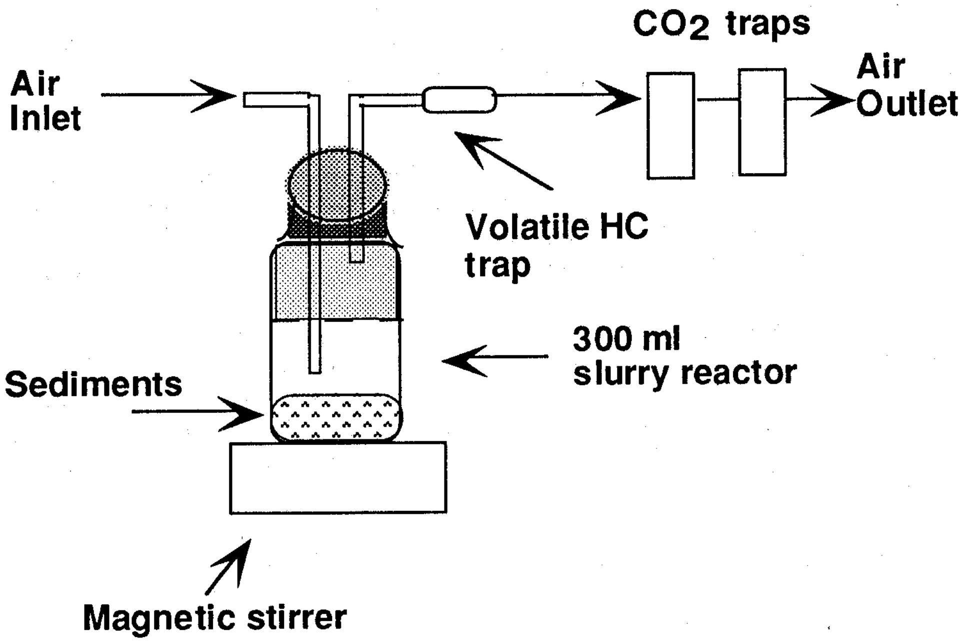

Figure 2. Slurry reactor used in experiments. $CO_2$ traps are included only in biodegradation tests where radiolabeled $CO_2$ is a byproduct of phenanthrene mineralization.

Several observations can be made about the biodegradation experiments. Volatilization over the 7 day test period was considerable. A two (2) day lag period was seen before significant mineralization occurred in all reactors. Maximum extent of mineralization appeared to be reached within five (5) days in mixed systems. The effect of mixing on mineralization is clearly evident. Figure 4 shows mineralization in reactors loaded with 10% solids. Significantly higher mineralization was seen in reactors which were mixed.

Mass balance calculations were performed based on tracking of the radiolabeled carbon. Table 1 shows the mass balance for mixed reactors at the end of the biodegradation test. Analysis of the mass balance partitioning in relationship to expected partitioning based on stoichiometry indicates that the phenanthrene was being used as a growth substrate by the indigenous bacteria.

The amount of phenanthrene lost to volatilization is much higher than might be expected from low vapor pressure ($6.8 \times 10^{-4}$ torr.). Therefore the effect of intermittent aeration on mineralization and stripping was tested. The test results show that not only does mineralization still occur without continuous aeration, but also that the final extent of mineralization is higher for the intermittently aerated reactor.

Reactors were amended with various amounts of fertilizer to determine if the low nutrient (nitrogen and phosphorus) content of the ASW could be causing the lag period seen before mineralization. Nutrient amendment had no effect on rate and extent of mineralization. Augmenting the slurry reactor with an aged slurry (2 - 3 days), however, did eliminate the lag time.

## CONCLUSIONS

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 was found after 5 days. Mixing and aeration, natural byproducts of the resuspension process, were the only treatment used. Due to the time required to see complete degradation, it is unlikely that the mixing and aeration provided solely by dredging can be considered a remedial treatment.

The lab scale slurry reactors used in this project show 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 fixed 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 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. Optimum design will utilize intermittent aeration or some form of chemical oxidation, for example addition of peroxide. The purpose will be to minimize contaminant loss due to volatilization or stripping.

Since it was shown that augmenting the reactor with aged slurry eliminated the lag period, an

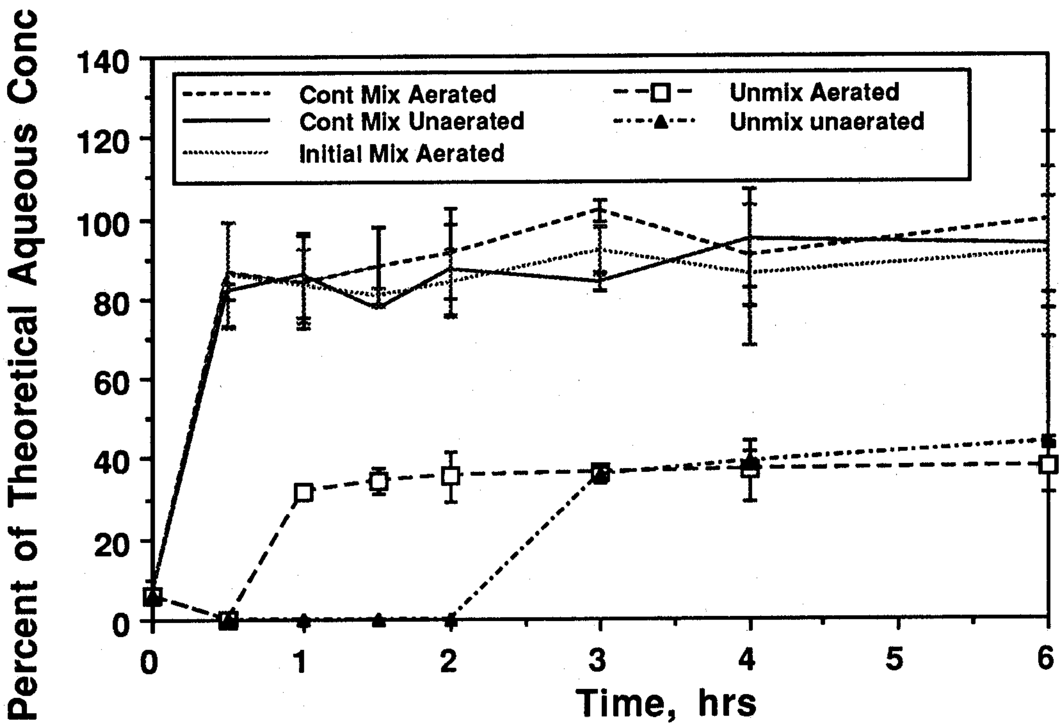

Figure 3. The effect of mixing and aeration on contaminant release in slurry reactors loaded with 10% solids. Error bars represent one standard deviation.

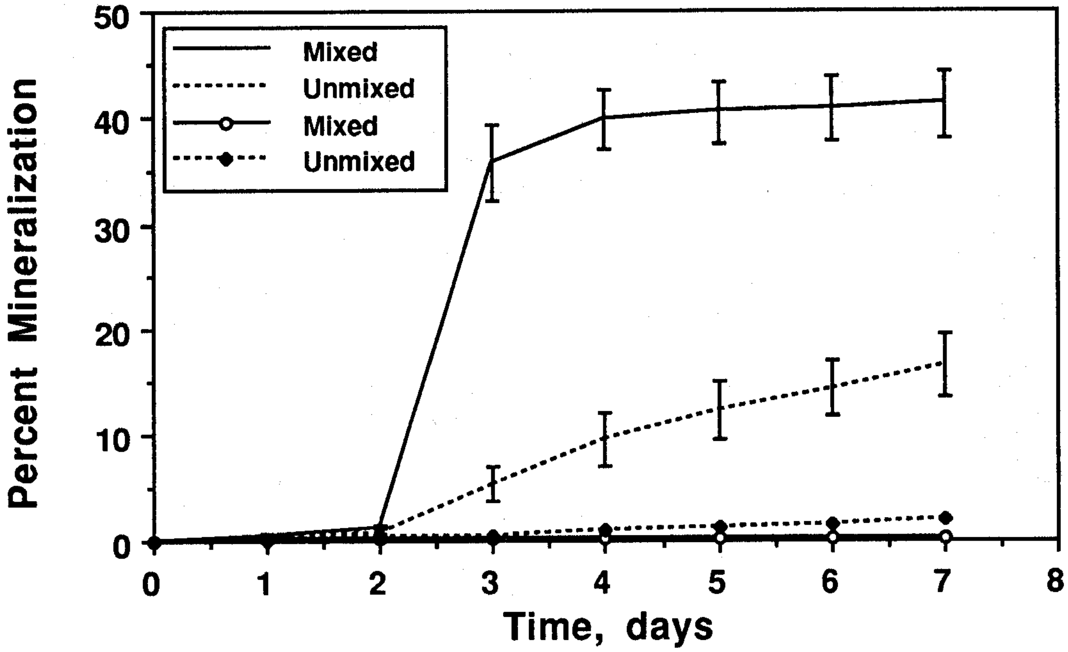

Figure 4. Phenanthrene mineralization in slurry reactors loaded with 10% solids. Error bars represent one standard deviation. Curves with symbols are for the abiotic controls.

overall treatment scheme utilizing some form of sequential treatment seems prudent. Treatment times were reduced by 40% when the reactors were seeded, going from 5 to 3 days to reach maximum extent of mineralization. Ex-situ treatment would require two reactors. Slurry from the initial reactor would be used to seed the second reactor which then would be used to seed the first reactor, etc. In-situ treatment cells could be built so that each successive cell would be seeded by the previously built cell. Removable barriers for only two cells would be required. Cell construction could be timed so that the materials from the first cell would be moved to build the third cell, etc.

From the research conducted, it appears that engineering intervention would be most effective in treating small areas of highly contaminated sediments before dredging. This assumes that in-situ reactors would be more cost effective than ex-situ reactors. Since batch biological treatment requires, at minimum, 3 days, an in-situ approach also eliminates problems associated with sediment storage that would arise if the sediment were treated after dredging.

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Table 1 Mass balance and partitioning of radiolabeled carbon for mixed reactors after 7 day biodegradation tests.

| | 5% Solids | | 10% Solids | | 15% Solids | |
|---|---|---|---|---|---|---|
| | % Initial | % STDV | % Initial | % STDV | % Initial | % STDV |
| Mineralized | 26.8 | 20.9 | 41.1 | 7.5 | 30.5 | 12.8 |
| NS Extract | 26.9 | 36.4 | 33.7 | 19.9 | 59.4 | 7.4 |
| Volatilized | 44.1 | 25.2 | 15.2 | 59.9 | 8.5 | 17.6 |
| Sediment | 2.3 | 95.7 | 0.8 | 175.0 | 5.2 | 61.5 |
| Liquid | 8.3 | 24.1 | 6.5 | 61.5 | 2.6 | 73.1 |
| Total | 108.4 | 6.1 | 97.4 | 3.5 | 106.1 | 4.6 |