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LETTER TRANSMITTING BIODEGRATION AS A REMEDIATION ALTERNATIVE TO GASOLINE CONTAMINATION AT NAVY EXCHANGE SERVICE STATION PROPOSAL AND REQUESTING COMMENTS MILLINGTON SUPPACT TN
4/23/1992
U S DEPARTMENT OF THE INTERIOR

United States Department of the Interior

GEOLOGICAL SURVEY

Water Resources Division
Stephenson Center, Suite 129
720 Gracern Road
Columbia, SC 29210-7651
April 23, 1992

Commanding Officer, Southern Division
Naval Facilities Engineering Command
2155 Eagle Drive
P.O. Box 10068
Charleston, South Carolina 29411
attn: 18236 John Karlyk

Dear Mr. Karlyk:

Enclosed is a copy of the proposal "Biodegradation as a remediation alternative to gasoline contamination at the Naval Exchange, NAS, Memphis, Tennessee". This proposal addresses two specific issues:

(1) Are ongoing microbial processes proceeding at a sufficient rate to effect remediation within a reasonable period of time?
(2) If presently occurring rates of biodegradation too slow to be acceptable, can rates be effectively stimulated to achieve a workable biodegradation rate?

As indicated in the proposal, there is a high probability that there is sufficient oxidant (Fe(III) oxyhydroxides) in the system to oxidize the amount of gasoline that has spilled. Therefore, the relevant question is how fast does this occur and can it be stimulated.

The approach outlined in this proposal, first documenting existing rates of microbial degradation and then documenting the potential for increasing those rates via enhanced biodegradation, is one that is applicable to many sites. Each site for which the no-action option can be rigorously defended will save considerable resources. Furthermore, each site to which enhanced bioremediation can be applied may result in additional savings.

We look forward to your comments.

Francis H. Chapelle, Ph.D.
Hydrologist

#212

BIODEGRADATION AS A REMEDIATION ALTERNATIVE TO GASOLINE CONTAMINATION AT THE NAVAL EXCHANGE, NAS, MEMPHIS, TENNESSEE

by

Francis H. Chapelle

PROJECT PROPOSAL SC92J

U.S. Geological Survey
Water Resources Division
Columbia, South Carolina

April 23, 1992

BIODEGRADATION AS A REMEDIATION ALTERNATIVE TO GASOLINE CONTAMINATION AT THE NAVAL EXCHANGE, NAS, MEMPHIS, TENNESSEE

PROBLEM

Background

In 1986 approximately 5,000 gallons of regular unleaded gasoline leaked from a faulty pipe joint at a Naval Exchange gasoline station, Naval Air Station (NAS), Memphis Tennessee. Follow up investigations confirmed gasoline contamination of soil and ground water near the site. A study by Harding Lawson Associates (HLA) in 1987 described local hydrologic conditions and showed the approximate areal extent of the contamination. HLA recommended that enhanced biodegradation be considered as a remediation alternative at the site. A follow-up study by ERC Environmental And Energy Services Company (ERC) further refined delineation of the contamination and recommended that vacuum extraction be applied as the remediation strategy. However, a subsequent study of the feasibility of vacuum extraction by ERC concluded that, due to the low hydraulic conductivity of the water-table aquifer, the cost of lowering the water table sufficiently would be prohibitive. For this reason, ERC recommended that vacuum extraction not be applied as a remediation alternative. For these reasons, Southern Division Naval Facilities Engineering Command (SouthDiv) is

presently considering biodegradation as a remediation alternative at this site.

Biodegradation as a Remediation Alternative

Petroleum hydrocarbons are readily degraded by soil and aquifer microorganisms under a variety of environmental conditions. The relatively light hydrocarbons associated with unleaded gasoline are particularly susceptible to biodegradation processes. Because of this, it is likely that some fraction of the contamination present at the NEX has been degraded by indigenous microorganisms. It is possible that natural biodegradation is proceeding at a rate that will lower contamination levels in ground water and soil below regulatory threshholds within a few years. However, it is also possible that the lack of appropriate electron acceptors, (such as oxygen and Fe(III) hydroxides), essential nutrients (organic nitrogen), or trace growth factors (vitamins, metals etc) may be limiting rates of metabolism to the point that it will take decades for complete oxidation can take place.

The possibility that natural biodegradation processes may be sufficient to remediate the contamination should be thoroughly investigated. For example, Fe(III) reduction has been documented to degrade petroleum hydrocarbons. Furthermore, all of the descriptions of the sediments on-site refer to "tan" or "brown" sediments, which indicate the

presence of Fe(III) oxyhydroxides in the sediment. The 5,000 gallons of gasoline is approximately equivalent to 10^5 moles of decane. Assuming that the "brown" aquifer sediments contain 200 umoles/g of Fe(III) oxyhydroxides (a conservative estimate), than the area of contamination (~30x30x5 meters) contains about 10^7 moles of Fe(III) oxyhydroxides. Assuming an overall stoichiometry for decane oxidation of:

$$C_{10}H_{22} + 10Fe(OH)_3 \text{ -----> } 10Fe^{2+} + 10\ CO_2 + 10H_2O + 10H^+$$

it is evident that there may be a sufficient mass of oxidant to completely oxidize the gasoline <u>in situ</u>.

The availability of electron acceptors, however, is only one potential constraint on microbial oxidation of hydrocarbons. For example, the release of H^+ may lower ground water pH to the point that Fe(III) reduction is inhibited. Therefore, the <u>rate</u> microbial hydrocarbon oxidation coupled to Fe(III) reduction is as critical as the availability of Fe(III). If this rate can be demonstrated to be sufficient to degrade most of the contaminants within a reasonable time frame, then a no-action option may be reasonable.

If natural biodegradation rates are shown to be insufficient to be considered as a remediation alternative, then an enhanced biodegradation system may be appropriate. Experience at the Hanahan, SC, DFSP site has shown that simply increasing the flux of fresh water by means of well pumping can increase biodegradation rates several fold. Addition of nutrients can increase biodegradation rates as much as ten fold. In this case, it is necessary to experimentally determine optimum conditions to significantly enhance biodegradation rates.

Evaluation of Bioremediation Alternatives

There are two distinct bioremediation alternatives available at the NEX site. First, is that natural biological processes (the no-action option) may be the most efficient remediation strategy available. Alternatively, an enhanced bioremediation system may be the most feasible alternative. While extensive information on site hydrogeologic conditions is available, information on indigenous and potential rates of petroleum hydrocarbon biodegradation is lacking. This information is necessary in order to either defend the no-action option or to design a workable enhanced bioremediation system.

OBJECTIVES

The objectives of this project are to:

(1) Evaluate rates of ongoing microbial oxidation of petroleum hydrocarbons at the NEX site under existing (non-enhanced) conditions.

(2) Evaluate what conditions are presently limiting microbial oxidation of petroleum hydrocarbons at the NEX site, and how these limitations can be relieved by an enhanced bioremediation system.

(3) If enhanced bioremediation is determined to be feasible and if this strategy presents significant advantages over the non-enhanced option, use existing hydrogeologic data to form a conceptual design for enhanced biodegradation at the NEX site.

APPROACH

Rates of non-enhanced hydrocarbon biodegradation

A combination of field and laboratory studies will be conducted to evaluate indigenous rates of hydrocarbon biodegradation. Ground water at existing monitoring wells will be sampled for concentrations of dissolved hydrogen gas

and major anions and cations to determine the zonation of predominant microbial processes such as oxygen reduction, nitrate reduction, Fe(III) reduction, sulfate reduction, and methanogenesis. Ground water will also be sampled for concentrations of organic acids. Our previous studies have shown that high (greater than 0.5 molar) concentrations of organic acids are indicative of substantial inhibition of hydrocarbon oxidation. This approach will give a qualitative estimate of relative rates of hydrocarbon oxidation.

In situ rates of hydrocarbon oxidation will be determined by two independent methods.

(1) Concentration changes of BTX compounds along the hydrologic gradient will be measured. Based on observed concentration changes along flowpaths and the time of travel (calculated from Darcy's Equation) associated with each flowpath, an approximate degradation rate that includes biologic and non-biologic processes will be calculated.

(2) Cores of sediments will be collected at the NEX site using a hand auger, aseptically placed in vials, flushed with nitrogen gas, and returned to the laboratory. In the laboratory, the vials will be amended with radiocarbon-labeled toluene. At

appropriate intervals, duplicate vials will be acidified, the evolved CO_2 collected in basetraps, and total evolved $^{14}CO_2$ quantified on a scintillation counter. Rates of evolved $^{14}CO_2$ are directly proportional to rates of toluene oxidation.

Toluene oxidation rates determined by methods (1) and (2) can then be compared to the mass of this compound observed in the aquifer to determine how long the contaminant may persist in the system.

Enhanced biodegradation

Laboratory studies will be conducted to determine how degradation of target compounds can be enhanced in sediments from the NEX site. Sediments from three locations within the contaminant plume will be subjected to three treatments, hydraulic flushing, hydraulic flushing with nutrient addition, and no amendment:

(1) Two to three pore volumes of non-contaminated aquifer water (collected on site) will be used to flush contaminated sediments. Then, rates of toluene oxidation will then be quantified as described earlier.

(2) Contaminated sediments will be flushed with aquifer water amended with 10 mg/L nitrate and 1 mg/L phosphate, and rates of toluene oxidation quantified.

(3) Splits of the contaminated sediments used in (1) and (2) will be used to quantify rates of toluene oxidation without treatment. These sediments will serve as controls so that enhancement of degradation rates can be separated from experimental effects.

Conceptual Design of Enhanced Biodegradation System

If the results of the field and laboratory studies indicate that enhanced biodegradation is feasible, available hydrogeologic data will be used to recommend a system design.

The ground-water system at the NEX site is characterized by relatively low hydraulic conductivities (~ 1 ft/day) and this must be taken into account in designing a remediation system. The overall strategy will be to introduce fresh water and nutrients in the up-gradient part of the plume, and recover contaminated ground water in the down-gradient portion of the plume. Two nutrient delivery mechanisms will be evaluated by a combination of field testing and hydrologic modeling:

(1) A subsurface "sprinkler" system, consisting of horizontal perforated pipes extending along the upgradient boundary of the plume and buried approximately two feet below grade.

(2) A line of gravity-feed injection wells extending along the upgradient boundary of the plume.

For both delivery mechanisms, extraction wells will be used along the downgradient boundary of the plume to maintain the flux of nutrient-bearing water and to facilitate removal of hydrocarbons.

Standard percolation tests will be used to evaluate the feasibility of the "sprinkler" delivery system. The feasibility of gravity-feed injection wells will be evaluated by performing a long-term constant-rate injection slug test at an existing well at the site.

Design of an optimal injection/withdrawal design will be evaluated using a digital flow model of the site. This flow model will be constructed using existing hydrologic data and will be calibrated against the results of a 24-hour pumping test that was performed at the site in 1990 by ERC. The model will be used to estimate rates of injection and withdrawal that will maximize delivery of fresh water and

nutrients to the contaminated sediments and minimize spreading of the contaminant plume.

Consultation With Environmental Protection Agencies

Prior to initiating evaluation of microbial processes at this site, a meeting will be scheduled with the Tennessee Department of Health and Environment in order to inform them of the work being undertaken, the kinds of data to be developed, and the expected utility of the results. Following completion of the work, another meeting will be held to inform the agency of the results. If a no-action strategy appears feasible, the detailed reasons for this determination will be presented for their review and approval. If enhanced biodegradation is indicated, the agency will be asked to provide input on the design and operation of the bioremediation system.

Time Frame and Reports

This project will be completed six months after initiation. At that time, a draft report will be submitted to SouthDiv for review. Following review, the report will be published as a U.S. Geological Survey Water Resources Investigations (WRI) report.

BUDGET

Budget Narrative

The project will require a half-time hydrologist and a half-time microbiologist for six months. Two one-week sampling trips to the site will be required. All of the equipment needed for the experimental work is available. Laboratory expenses will include routine supplies, the purchase of appropriate radiolabled compounds, and the disposal of toxic and radiological wastes.

Salaries	$ 29,000
Travel	$ 10,000
Equipment and Laboratory Supplies	$ 11,000
Total	$ 50,000