SERDP Strategic Environmental Research and Development Program
Improving Mission Readiness Through Environmental Research

Subsurface Bioremediation Process Monitoring Indicators

Cleanup
CU-383

LEAD AGENCY: Environmental Protection Agency

LAB: National Risk Management Research Laboratory (NRMRL)

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PROBLEM STATEMENT: The application of in-situ, active or passive bioremediation of fossil fuel contamination holds promise of achieving both detoxification and source removal of regulated compounds such as benzene, toluene, ethylbenzene and xylene (BTEX). BTEX as well as other mobile constituents of fuels and solvents are a major category of subsurface contaminant mixtures present at DoD installations. These contaminant mixtures entered the subsurface as a result of spills or releases from fuel tanks, pipelines, maintenance areas, and fire-training installations. The scope of known problems, in a variety of hydrogeologic settings, requires a systematic, cost-effective approach to monitoring the progress of bioremediation processes and plume transport. In most cases, methods applied to the detection or assessment of specific subsurface contaminant distributions in aqueous or solid matrices have been applied to long-term monitoring during remedial action operations. However, disappearance of source-related compounds from ground water alone is insufficient evidence for removal. Reliable indicators of the progress of bioremediation actions, including the monitoring of metabolic intermediates in aquifer solids and water are needed in order to evaluate the performance of remediation schemes and to complement source contaminant monitoring efforts. (National Research Council, In-Situ Bioremediation When Does It Work?, National Academy Press, 1993.)

The major problem we intend to address is the need to identify biochemical pathway metabolites and critical substrates so that engineered mass-balances can be approached. In this way it may be possible to link net contaminant destruction or transformation to both hydrogeochemical conditions and specific biodegradation pathways. With this process level understanding, we should be able to more easily apply bioremediation to other sites. Acceptance of passive or "low-technology" bioremediation schemes can be achieved when mass-balances and definable endpoints for contaminant removal are achieved.

The needs for these monitoring improvements are recognized in several SERDP Thrust Areas: 1.B: Site Characterization and Analysis Penetrometer System, 1.III.1.e. Improved Standards and Analytical Techniques for Defining "Clean"; 1.C: Characterization/Monitoring, 1.III.3.a. Improved Subsurface Condition Description and Simulation; 1.D: Chemical Analytical Systems, 1.III.1.o. Improved Chemical Analysis Technology for Finger-Printing Organic Contaminants; 1.J: Treatment of Fuels in Groundwater, 1.I.1.e. Process to remediate Groundwater Contaminated with Hydrocarbon Fuels; and 1.T: Bioassay/Biomonitoring Methods; 1.III.1.j. Long-term, In-place Monitoring of Remediation Effectiveness and 2.II.2.e. Improved Biomonitoring Capability.

The specific applied research needs addressed by this project are: (1) the correspondence between apparent oxidation-reduction and hydrogeochemical conditions with major organic metabolite concentration distributions in source, transitional and downgradient zones, (2) the identification of mass distributions (i.e. including solid-associated and aqueous) of the principal electron acceptors, metabolites of regulated compounds and potential organic substrates present in the media (e.g. microbially derived: such as, acetate, formate, etc., and background organics, fatty acids, hydrocarbons and fire-fighting foam constituents), and (3) the temporal and spatial variability in: critical geochemical indicators (e.g. O2,

NO_3^-, NO_2^-, NH_3, FeTotal, Fe^{2+}, MnTotal, MnDiss, CO_2, CH_2 and CH_4) and major metabolites (e.g. formate, acetate, propionate, as well as, benzoic, toluic, salicylic acids and isomers).

This applied research project builds on the basic work begun with USEPA-NRMRL support (Barcelona, Tomczak, Lu & Virkhaus, Petroleum Hydrocarbons in the Subsurface Conf, In- Press, 1993) which had the general goal of redox-specific characterization of organic matter in both contaminated and uncontaminated aquifers. In this work, major fractions of soluble organic matter and acidic metabolites from the microbial decomposition of hydrocarbon fuels were determined. It showed the importance of hydrogeologic and oxidation-reduction (i.e. redox) potential control over major transformation pathways and that significant degradation of fuel constituents occurs even under anoxic or reducing conditions. The methods developed in this work and that of Cozzarelli et al. (Geochimica Cosmochimic Acta, In-Press, 1993; Environ. Geol. Wat. Sci., 16, 293-297, 1990) are directly applicable to monitoring the progress of microbial processes which occur under a variety of subsurface remediation measures (e.g. air sparging, bioventing, solvent or surfactant flushing). The project's emphasis on both inorganic and organic indicators of bioremediation will aid in the definition of cleanup benchmarks and endpoints. It directly addresses the approach to answering the question of "how clean is clean"?

PROJECT DESCRIPTION: The overall goal of the project is to determine those hydrogeochemical conditions under which hydrocarbon fuels can be degraded in the subsurface with an emphasis on: major transformation conditions and pathways, mass distributions of both source-related compounds and metabolic products, and the spatial and temporal variability in these distributions which bear on the extent of bioremediation efficiency. It directly relates to the Cleanup Thrust Area's R & D objectives which aim at both verifiable and cost-effective site investigation, characterization and remediation technologies.

The objectives of the work include: (1) Hydrogeochemical Zonation; determination of the correspondence between redox and hydrogeochemical zones of the subsurface with loci of microbial transformation, (2) Contaminant Distributions; determination of the fractionation of critical inorganic and organic transformation indicators in water and aquifer solids, and (3) Spatial and Temporal Variability; determinations of the variability in the mass distributions to evaluate techniques for volumetric averaging and performance criteria for bioremediation operations. The project has been designed to be conducted in parallel with either operational or experimental remediation efforts at sites where hydrocarbon fuels constitute a contamination problem. As such, the project can be conducted at any number of DoD or DOE installations where access can be assured. The Wurtsmith AFB, Oscoda, MI, would be an excellent candidate site given our familiarity with the hydrologic setting, hydrogeochemistry and the focus on bioremediation at the site. It represents a "fast" site characterized by potentially high fluxes of both nutrients and water, as well as high hydraulic conductivity which facilitate high biodegradation rates and potential options for engineered enhancements (Hickman et al. J.W.P.C.F. 61, 9, 1564-1575, 1989).

The three main objectives of the project will be approached in a phased manner building on the existing array of monitoring points and initial site data review. Overall scheduling is flexible based on a FY94 or FY95 start.

Phase 1. Initial Reconnaissance and Delineation of Hydrogeochemical Zones. The existing array of monitoring wells will be sampled and preliminary borings will be made taking water and solid samples at alternate depths for the initial delineation of redox-zones. Field analyses will include: O_2, temperature, pH, conductance, Fe^{2+}, NO_3^-, NH_4^+, alkalinity, CH_4, CO_2, and volatile organic compounds (VOC's). Solid and H_2O samples will be returned to the lab for determination of: total VOC's, inorganic and organic carbon, extractible acid metabolites and intermediates, non- volatile organic compounds (e.g. hydrocarbons, fatty acids, surfactants, fire-fighting foam agent), total Fe and Mn. Appropriate microcosm experiments will be run to evaluate biological activity in selected redox zones. On the basis of these results the initial hydrogeochemical zones and loci of bioactivity will be located and geostatistical estimations of sources and downgradient plume composition will be done. Selected areas for supplemental borings will be determined to expand the biomonitoring array in Phase 2.

Phase 2. Development of Optimized Biomonitoring Network and Long-Term Microcosm Experiments. The geostatistically (kriging) based distributions of redox/hydrogeochemical zones and loci of bioactivity include levels of confidence in estimating concentrations between known points. Supplemental borings and water sampling points will be located to reduce uncertainty within regions of the subsurface and the field and lab work in Phase 1 will be repeated with improved resolution. Refined estimates of background conditions and total contaminant mass per unit volume of aquifer will be developed and the network will be optimized (i.e. minimizing uncertainty) for the evaluation of spatial and temporal variability in critical indicators of contaminant removal. The approximate rates of biotransformation of the principal contaminants from microcosm experiments will be evaluated with respect to increases in metabolic products and correlated with the distributions found in the field.

Phase 3. Evaluation of Variability and Net Bioremediation Over Time. The network will be sampled at intervals (e.g. quarterly) to evaluate temporal and spatial variability in redox/hydrogeochemical zonation and progress of contaminant removal/metabolite production. It is anticipated that the methods we have used in past work (Barcelona et al., Environmental Science and Technology 25, 5, 991-1003, 1989) will serve to control sampling and analytical error so that actual subsurface variability can be determined at known levels of confidence. Seasonal effects on nutrient supply, dispersion and transport will be evaluated at selected intervals simulating the field results with stepwise applications of two-dimensional flow and transport models. It is likely that at least eight quarters of data collection will be needed to evaluate these effects. Borings will be taken and characterized as before to benchmark the progress of bioremediation and estimate time frames for net contaminant removal.

EXPECTED PAYOFF: The results of the work will provide a conceptual model for the design and operation of cost- effective remediation efforts. Minimizing the number of wells/borings at such sites and uncertainties in contaminant distributions while providing known levels of confidence in net contaminant removal will reduce the life-cycle costs of remediation efforts. Also, definable benchmarks for evaluating the performance of remediation efforts will serve to better allocate fiscal and human resources at DoD and DOE installations.

In order for benchmarks for the evaluation of the potential success for intrinsic bioremediation to be useful and valid, standard procedures must be developed for contractual use. An additional payoff of this project is the development of analytical procedures that will be reviewed for approval by the EPA to be designated as Standard Methods for contractor use. Personnel on this project are collaborating with Dr. John Wilson and the Air Force in developing protocols for fuel hydrocarbons and chlorinated hydrocarbons. We are actively participating in refining methods for microcosm tests, field quantification of hydrogen gas and quantification of biologically available iron III in core samples. These procedures will become routine characterization methods in standard protocols that are in development as both screening tools and actual implementation of intrinsic bioremediation protocols.

TRANSITION PLAN: In addition to peer-reviewed papers and reports which will issue from the project it is clear that technology transfer must occur within DoD, DOE and the environmental restoration community. Public presentation at conferences, short-courses, and workshops which we support will be enriched in the future by the results of the project. We would welcome the opportunity to offer focused short-courses for DoD and DOE personnel as well as contractors to broaden the communication of results. It is likely that a pilot course could be offered at the experimental site(s) during the project period if logistics can be arranged. A two-day monitoring short-course with field exercises has been budgeted for Year 2 of the work (FY96). The pilot course could be made part of the project review process involving DoD or DOE project officers, AFIT staff and others as participants.