United States
Environmental Protection
Agency

Envirogen Propane Biostimulation Technology for In-Situ Treatment of MTBE-Contaminated Ground Water

Innovative Technology Evaluation Report

EPA/600/R-02/092
November 2002

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NOTICE

The U.S. Environmental Protection Agency (EPA) through its Office of Research and Development funded the information described here by Ann Keeley, the EPA TPM and WAM for this demonstration, under contract 68-C-98-138 to ManTech Environmental Research Services Corp. and 68-C-00-179 to SAIC. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

All research projects making conclusions or recommendations based on environmental data funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project was conducted under an approved Quality Assurance Project Plan. The procedures specified in this plan were used without exception. Information on the plan and documentation of the quality assurance activities and results are available from the principal Investigator.

FOREWORD

The U.S. Environmental Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

The purpose of this publication is to present information that will assist decision-makers in evaluating an innovative remedial technology for application to cleanup of sites with contaminated ground water. This ITER, which has been produced as part of the Laboratory's strategic long-term research plan, describes the effectiveness and applicability of the propane biostimulation technology developed by Envirogen as a potential in-situ remedial alternative for the mineralization of MTBE from contaminated ground water. This technology was demonstrated and evaluated at the Naval Base Ventura County at Port Hueneme, California. Spatial and temporal data to evaluate the technology were collected from a dense network of in-situ monitoring points over a period in excess of 300 days. This comprehensive evaluation of the Envirogen technology demonstrated that its application at this site did not meet the State of California's treatability criteria.

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ABSTRACT

The primary objective of the Biostimulation Technology Evaluation was to determine if enhanced biodegradation was occurring in a ground-water Test Plot to a sufficient degree to reduce intrinsic methyl tertiary butyl ether (MTBE) to the State of California's treatability criteria of 5 μg/L or below. The project was carried out at the National Environmental Technology Test Site (NETTS) at the (NBVC) Naval Base Ventura County, Port Hueneme, California where a hydrocarbon release into ground water occurred between September 1984 and March 1985 involving approximately 4,000 gallons of leaded and 6,800 gallons of unleaded premium gasoline.

The geology at the site consists of unconsolidated sediments composed of sands, silts, clays and minor amounts of gravel and fill material. A shallow, perched, unconfined aquifer is the uppermost water-bearing unit. The water table is generally encountered at depths between 6 to 8 feet below ground surface (BGS), and has a saturated aquifer thickness of 16 to 18 feet.

The evaluation was carried out between June 2001 and March 2002 using Control and Test Plots and a cadre of primary and secondary analytes through 15 sampling events. The goals of the project were approached with the use of deuterated MTBE (d-MTBE) and ground-water tracers including bromide and iodide.

An analysis of intrinsic MTBE, deuterated MTBE, daughter products, and geochemical parameters demonstrated that the technology did not meet the State of California's treatability criteria.

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ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ALSI	Analytical Laboratory Services, Inc.
ARAR	Applicable or relevant and appropriate requirement
BIPT	Bacterial injection point in the Test Plot
Br^-	Bromide ion
BGS	Below ground surface
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CAA	Clean Air Act
CERCLA	Comprehensive Emergency Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CFU	Colony Forming Units
Cl^-	Chloride ion
CO_2	Carbon dioxide
COC	Chain-of-Custody
CPT	Cone Penetrometer Technology
CWA	Clean Water Act
DBPR	Disinfection By-Product Rule
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOE	Department of Energy
d-MTBE	Deuterated methyl tert-butyl ether
EPA	U.S. Environmental Protection Agency
ITER	Innovative Technology Evaluation Report
LCS/LCSD	Laboratory control samples and laboratory control sample duplicates
MCL/MCLG	Maximum Contaminant Level and Maximum Contaminant Level Goal
MDL	Method detection limit
µg/L	Microgram per liter
mg/L	Milligram per liter
MS/MSD	Matrix spike/matrix spike duplicate
MTBE	Methyl tert-butyl ether
NAAQS	National Ambient Air Quality Standard
NETTS	Department of Defense National Environmental Technology Test Site

ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)

NBVC	Naval Base Ventura County
NEX	Naval Exchange
NFESC	Naval Facilities Engineering Service Center
NRMRL	National Risk Management Research Laboratory
OIPC	Oxygen injection point in the Control Plot
OIPT	Oxygen injection point in the Test Plot
OSWER	Office of Solid Waste and Emergency Response
PIPT	Propane injection point in the Test Plot
PMO	Propane monooxygenase
POB	Propane oxidizing bacteria
ppm	Part per million
PQA	Pre-Quality Assurance Project Plan Agreement
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
RCRA	Resource Conservation and Recovery Act
RRF	Relative response factor
RPD	Relative percent difference
SAIC	Science Applications International Corporation
SDWA	Safe Drinking Water Act
SPRD	Subsurface Protection and Remediation Division
STDEV	Standard Deviation
SVE	Soil vacuum extraction
SVOC	Semi-volatile organic compound
TBA	*tert*-butyl alcohol
TCE	Trichloroethene
TPM	Technical Project Manager
TOC	Total organic carbon
TSCA	Toxic Substance Control Act
TSA	Technical system audit

ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)

UCL	Upper confidence limit
VMP	Vapor monitoring point
VOA	Volatile organic analysis
VOC	Volatile organic compound
WAM	Work Assignment Manager
WQCB	Water Quality Control Board
WQS	Water quality standard

ACKNOWLEDGMENTS

This report was prepared for the U.S. Environmental Protection Agency (EPA) by Ann Keeley, the EPA Technical Project Manager and Work Assignment Manager for this demonstration, at the National Risk Management Research Laboratory (NRMRL) in Ada, Oklahoma. The technology evaluation process was a cooperative effort that involved personnel from the EPA Office of Research and Development (ORD), EPA Region 9, U.S. Navy, California Water Quality Control Board (WQCB), and Envirogen.

The extensive effort of the following personnel during this project is gratefully acknowledged:

- Fran Kremer, Annette Gatchett, Bob Olexsey, and Steve Schmelling of NRMRL and Arlene Kabei of Region 9 for the composition of an outstanding management team for the overall MTBE demonstration evaluation program;
- The NRMRL QA Managers Ann Vega and Steve Vandegrift for their crucial roles in association with the various aspects of the quality assurance and quality control of this demonstration;
- Drs. Carl Enfield, John Wilson, and Randall Ross for their technical advice;
- Peter Raftery as well as the WQCB management for their technical and administrative efforts in granting the project permits;
- ManTech, a SPRD contractor for performing various tasks including system installation, sampling execution, and laboratory analytical services; and
- SAIC, a NRMRL contractor for the development of the project QAPP.

Special thanks are offered to the employees at the U.S. Navy, Naval Facilities Engineering Service Center (NFESC) host site for their hospitality and assistance throughout this demonstration, especially, Ernie Lory, Dorothy Cannon, and James Osgood.

EXECUTIVE SUMMARY

The primary objective of the Biostimulation Technology Evaluation was to determine if biodegradation was occurring in a ground-water Test Plot to a sufficient degree to reduce intrinsic MTBE to the State of California's treatability criteria of 5 µg/L or below. The evaluation was carried out using Control and Test Plots and a cadre of primary and secondary analytes through 15 sampling events over a 38-week test period. An analysis of intrinsic MTBE, deuterated MTBE, daughter products, and geochemical parameters demonstrated that the technology did not meet the State of California's treatability criteria.

The National Environmental Technology Test Site (NETTS) at the (NBVC) Naval Base Ventura County, Port Hueneme, California is the site of a hydrocarbon release into ground water (Everett et al., 1998) between September 1984 and March 1985 involving, according to inventory records, approximately 4,000 gallons of leaded and 6,800 gallons of unleaded premium gasoline. The resulting ground-water plume consists of approximately 9 acres of BTEX and approximately 36 additional acres of methyl tertiary butyl ether (MTBE) contamination, extending approximately 4,500 feet downgradient from the site of the release. The Port Hueneme NETTS facility is located approximately 40 miles northwest of Los Angeles.

The geology at the site consists of unconsolidated sediments composed of sands, silts, clays and minor amounts of gravel and fill material. A shallow, perched, unconfined aquifer is the uppermost water-bearing unit. The shallow aquifer is comprised of three depositional units: an upper silty-sand, an underlying fine- to coarse grained sand and a basal clay layer. Based on CPT pushes, the upper silty-sand unit ranges between 8 to 10 feet thick and the underlying sand is approximately 12 to 15 feet thick. The water table is generally encountered at depths between 6 to 8 feet below ground surface (BGS), with seasonal fluctuations ranging between 1 and 2 feet, yielding a saturated aquifer thickness of 16 to 18 feet near the test area.

Methyl *tert*-butyl ether (MTBE) has become the most widely used automobile fuel oxygenate (Gullick and leChevallier, 2002). As a consequence of fuel spills and leaking storage tanks, MTBE has become a ubiquitous and recalcitrant ground-water contaminant (Pankow et al., 1997; Rice et al., 1995; Reuter et al., 1998).

In an attempt to demonstrate ground-water remedial alternatives for MTBE, the U.S. Environmental Protection Agency (EPA) and the U.S. Navy entered into a memorandum of understanding (MOU) to conduct a demonstration of a treatment technology for MTBE in ground water. Technology vendors were

chosen through an open solicitation requesting proposals for processes to treat MTBE. Proposals were then selected using external and internal peer review. Envirogen was selected to demonstrate their propane biostimulation barrier technology as a mechanism to inhibit the migration of MTBE through ground water. The potential remedial action proposes the stimulation of cometabolism by the injection of oxygen and propane into the aquifer along with MTBE degrading bacteria.

Project objectives were addressed through the establishment of treatment and control plots, a network of conventional upgradient and downgradient monitoring points in the aquifer and vadose zone, and a ground-water tracer mixing and injection system. The treatment plot received the vendor's biostimulation technology consisting of oxygen, propane, and bacterial amendments. The control plot received only oxygen.

The goals of the project were multifaceted with the end result being the determination of the efficacy of using propane and/or oxygen biostimulation and bioaugmentation as a potential remedial alternative for the removal of MTBE from ground water. Achieving these objectives was approached with the use of deuterated MTBE (d-MTBE) and ground-water tracers including bromide and iodide. The ratios of ground-water tracers between downgradient transects were designed to provide evidence concerning the relative losses in MTBE concentrations resulting from dilution and degradation. Likewise, the use of d-MTBE ratios in downgradient transects served as a tracer of anthropogenic MTBE. More importantly, the use of d-MTBE was selected to provide evidence of biodegradation by the realization of d-MTBE daughter products.

Bromide was used in a preliminary study to determine the velocity as well as the distribution of ground-water flow, and the degree of communication between the tracer injection system and each of the downgradient monitoring locations. Bromide injection was started on February 1, 2001, and was stopped on February 28, 2001. Monitoring continued in order to observe the return of bromide to background concentrations.

Based on the results of the pre-demonstration bromide tracer study, the final project plan was developed concerning the application rate of conservative and non-conservative tracers from the injection wells, and called for 15 sampling events rather than the original 7 because it was determined that little ground-water flow was taking place in other than the bottom portion of the aquifer. Periodic samples were taken from the middle and upper monitoring screens, however, to assure that flow remained predominantly at the bottom of the aquifer through the evaluation period.

During the latter part of May 2001, the performance evaluation phase of the project was begun with the addition of amendments of oxygen, propane, and bacteria. The injection of iodide started on June 8, 2001. Iodide was selected for use in this phase of the project because of its low level of detection and to avoid possible problems associated with residual bromide concentrations. The first sampling event took place on June 14, 2001.

Some significant observations were made concerning the period during the pre-characterization investigation, beginning in late 2000, up to the beginning of the evaluation period in June 2001. For example, the overall intrinsic MTBE concentration in the vicinity of the plots dropped about 500 µg/L between October 4 and November 11, 2000, and MTBE concentrations in the Control Plot were significantly higher than those in the Test Plot. Most significantly, MTBE concentrations in the downgradient Test Plot dropped from over 5,000 µg/L in January 2001 to less than 1,000 µg/L by the first sampling event in June. This meant the remediation technology had to be effective in reducing the MTBE concentration from less than 1,000 µg/L to 5 µg/L or below rather than starting with a MTBE concentration of over 5,000 µg/L.

During the 38-week period between June 14, 2001, and March 8, 2002, 15 sampling events took place, occurring biweekly for the first ten events and monthly thereafter. Although sampling was concentrated at the bottom well screens, the middle and upper screens were sampled periodically at each well location. In the Test Plot the sampling locations included 6 upgradient wells, 14 downgradient wells, and 19 injection wells. The Control Plot consisted of 4 upgradient wells, 10 downgradient wells, and 19 injection wells.

In addition to the primary parameters of MTBE, d-MTBE, and iodide, samples were also analyzed for appropriate secondary parameters in order to test for both MTBE and d-MTBE daughter products as well as changes in geochemistry. Following the evaluation period it was determined that geochemical parameters in the upgradient and downgradient Test and Control Plots were unchanged. There was no evidence of increases in alkalinity in the downgradient Test Plot as would be expected, nutrients were not reduced, and most importantly, the total and dissolved organic carbon (electron donors) were not reduced.

The daughter products which were analyzed included: acetone; acetone-d6; 2-propanol; 2-propanol-d6,d8; formaldehyde; *tert*-butyl alcohol; and *tert*-butyl alcohol-d9,d10. Very low levels of daughter products were detected in both the Test and Control Plots. While only TBA was detected at the

upgradient wells, both d-TBA and TBA were detected in the downgradient wells. It was not determined whether biotic or abiotic processes produced these products.

The d-MTBE in both the Test and Control Plots increased throughout the evaluation period. Although the concentrations were slightly higher in the Control Plot because of its higher hydraulic conductivity, the increase in both Plots was the same as determined by a least squares fit of the data.

The intrinsic MTBE concentrations in the upgradient Test Plot and both upgradient and downgradient portions of the control Plot decreased gradually through the evaluation period. In the downgradient Test Plot, the most significant site of the evaluation, the data remained between 300 – 600 μg/L with a small positive slope as determined by a least squares calculation.