NATURAL ATTENUATION OF CHLORINATED SOLVENTS AT MULTIPLE AIR FORCE BASE DEMONSTRATION SITES

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ABSTRACT

Natural attenuation treatability studies (TSs) were conducted at 14 U.S. Air Force bases. Only sites where biodegradation of chlorinated aliphatic hydrocarbons (CAHs) was suspected were selected for the study. The major initiative was to evaluate the effectiveness of monitored natural attenuation (MNA) at sites contaminated with chlorinated solvents and associated daughter products (CAHs). The study was designed to evaluate naturally occurring degradation mechanisms for CAHs and migration limitations of groundwater plumes. The degree and rate of natural bioremediation of CAHs were highly site specific and depended on prevailing biochemistry and geochemistry of groundwater at the site. All sites where petroleum hydrocarbons were commingled with CAHs were actively methanogenic and reductive dechlorination was occurring. Field-scale biodegradation rate constants for potentially stable plumes ranged from 0.00005/day to 0.013/day. Modeling results using first-order kinetics showed that groundwater quality standards will not be achieved throughout the plumes within 100 years unless a more aggressive remediation program than MNA is implemented. Natural attenuation processes at only two of the 14 sites studied were sufficient to use MNA as the sole remediation. Some form of engineered remediation such as source reduction at the other sites was recommended in conjunction with MNA.

Key words: *bioremediation, chlorinated, field*

INTRODUCTION

This report summarizes the results of natural attenuation treatability studies conducted at some U.S. Air Force base sites from 1993 to 1999.

Natural attenuation is the decrease in concentration or mass of groundwater contaminants by natural physical, chemical, and biological processes. Reductive dechlorination is the primary process for CAHs. Generally, reductive dechlorination occurs in anaerobic conditions, reducing environments by sequential dechlorination from the parent CAH to successively less-chlorinated daughter products. MNA can provide nonintrusive groundwater remediation and avoids the transfer of contaminants to another phase in the environment. MNA generally is a less costly remedial technology. Long-term monitoring (LTM) and land use control measures usually are required to ensure protection of potential human and ecological receptors.

OBJECTIVE

The study was conducted to evaluate the effectiveness and potential applicability of MNA for dissolved CAH plumes at Air Force facilities. The procedures followed can be found in the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater (USEPA, 1998)*.

SITE LOCATIONS

Studies for CAH natural attenuation were completed at 14 spill sites at 11 Air Force bases in 10 states.

PROTOCOL TASKS

- Groundwater monitoring wells were installed and sampled for contaminant concentrations and geochemical indicators such as pH, temperature, conductivity, ORP, DO, nitrate, sulfate, sulfide, ferrous iron, methane, ethene, alkalinity, chloride, and dissolved hydrogen.
- Groundwater flow direction and hydraulic gradient were measured by water table levels.
- Slug tests were performed to estimate aquifer hydraulic conductivity.
- Models were applied to predict migration trends for contaminant plumes.
- Implementability of MNA both alone and with an engineered remediation technology was assessed.
- A long-term monitoring plan was developed.

PLUME BEHAVIOR RESULTS

The stabilization or decline of dissolved contaminant concentrations is the most convincing evidence for natural attenuation. Two sets of groundwater quality data for most of the sites showed that only two were expanding. The remaining were either stable or receding. TCE was the most pervasive chlorinated ethene at most sites followed by daughter product, cis-1,2-DCE.

GEOCHEMICAL RESULTS

Contaminant biodegradation will cause geochemical changes in the groundwater system as microbial metabolism utilizes an electron donor. Three types of plume behavior were detected and are described as follows:

Type 1—Occurred under anaerobic groundwater conditions where the primary microbial electron donor is anthropogenic carbon such as BTEX or landfill leachate and CAHs are electron acceptors.

Type 2—Occurred in plumes under anaerobic conditions with high concentrations of biological available native organic carbon that served as an electron donor in reductive CAH dechlorination. Type 2 was generally slower in biodegradation than Type 1.

Type 3—Dominated in plume areas of low carbon and concentration of DO was more than one mg/L. Under this condition, reductive dechlorination was very low or not at all. Vinyl chloride can be rapidly oxidized under these conditions.

Most of the sites exhibited some type of mixed behavior with most of Type 1 coupled with either of the other types. Three sites had primarily Type 1 behavior. Most sites were either actively sulfate-reducing or methanogenic. All sites where petroleum hydrocarbons/ solvent mixtures were present were actively methanogenic and reductive dechlorination was occurring.

BIODEGRADATION RATE RESULTS

Rate constants are needed to predict the fate and transport of groundwater-dissolved CAHs. Assuming biodegradation is controlled by concentration of the contaminant, use of first-order kinetics is appropriate if dilution, sorption, and volatilization can be normalized. Several methods were used to estimate first-order rates as follows:

1. Use of a recalcitrant compound such as trimethylbenzene.
2. Use of the one-dimensional, steady state analytical solution by the Buscheck and Alcantar (1995) method.
3. Computation of field-scale reduction dechlorination rates using the method of Moutoux et al. (1996).
   - Rates using Method 1 were 0.0003 to 0.00074 / day.
   - Rates using Method 2 were 0.00005 to 0.013 / day.
   - Rates using Method 3 were 0.00000004 to 0.0025 / day.

MODELING RESULTS

Groundwater flow and solute fate and transport modeling were done at all 14 spill sites. A number of characterization and software-related limitations were apparent during modeling activities that increased the uncertainty of predictions. The estimated length of time required for MNA alone to achieve federal groundwater standards for CAHs ranged from 17 to more than 200 years.

LONG-TERM MONITORING

A network of monitoring wells was recommended at each site to monitor natural attenuation trends, verify model predictions, and protect downgradient receptors. The recommended number of wells ranged from 8 to 30 with an average of 17. Annual sampling was recommended most frequently.

COST ANALYSIS

The average cost for CAH natural attenuation sites was $122,000 per site. If additional engineered remediation is needed, the estimated averaged remedial cost was $876,000, but did not always reduce the time to achieve federal groundwater standards.

DISCUSSION

Results of the site characterization studies at the 14 spill sites indicated that natural attenuation of CAHs was occurring to some degree at all sites. However, biodegradation at most sites was very localized. The most direct evidence for natural attenuation was historical groundwater data that showed stabilization or decline of dissolved contaminant concentrations. Also important is evidence that biodegradation daughter products or altered geochemical trends are present to support occurrence of biological attenuation.

Before investing in a detailed study of natural attenuation at a site, an accurate assessment of the potential for natural biodegradation of chlorinated compounds should be made. It should be determined if natural bioattenuation of CAHs is likely to be a remedial alternative before time and money are expended for a more active form of remediation. The bioattenuation screening process described in USEPA (1998) and Wiedemeier et al. (1999) is designed to recognize geochemical environments where reductive dechlorination is possible. Solute transport models such as the BIOCHLOR natural attenuation model (Aziz et al., 1999) can be used during the screening process to evaluate whether the efficiency of natural attenuation is sufficient to prevent contaminant transport to sensitive receptors.

Most states are now receptive to the use of monitored natural attenuation for dissolved BTEX plumes, but acceptance of MNA for CAHs has not been as pervasive. Important factors to consider when proposing MNA are the required level of groundwater modeling, the proximity of downgradient receptor exposure points, the value of source reduction technologies in reducing monitoring time frames, and obtaining early acceptance of a site closure strategy.

ACKNOWLEDGEMENTS

Development of the research report into a manuscript for publication was done by Kathy Tynsky of CSC. The U.S. Environmental Protection Agency through its Office of Research and Development collaborated in the research described here under Interagency Agreement, RW-57-93863101, from the Air Force Center for Environmental Excellence at Brooks AFB, Texas. It has not been subjected to agency review and therefore does not necessarily reflect the views of the agency, and an official endorsement should not be inferred.

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