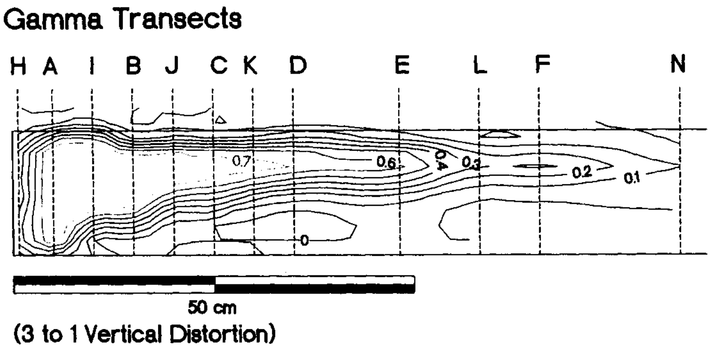

FIGURE 3-8. NAPL saturation determined from gamma-spectroscopy before recovery (after Okeson et al. 1995).

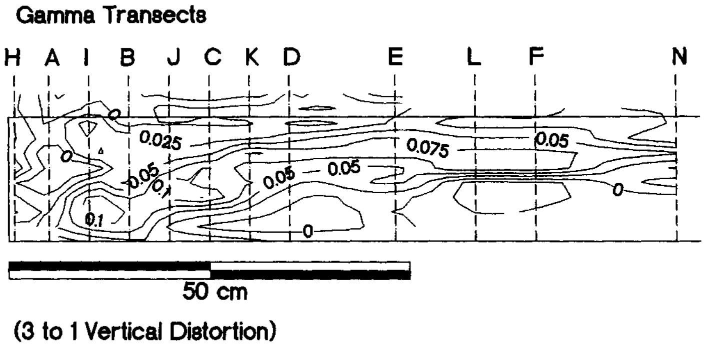

FIGURE 3-9. NAPL saturations determined from gamma-spectroscopy after recovery (after Okeson et al. 1995).

NAPL using a tube inserted to the end of the no. 8 sand lens. Recovery continued for 83 min until the recovery of NAPL completely stopped, indicating residual entrapment within the lens. A total of 165 mL of NAPL was recovered (75% of initial spill volume). The residual saturation distribution as measured using the gamma system is shown in Figure 3-9. Aqueous samples containing benzene were collected at six sampling ports during the spill, during recovery, and after recovery. Figure 3-10 illustrates the breakthrough curves of relative concentrations of benzene at five ports in which the dissolved chemical was detected.

The analysis of the breakthrough curves will provide some insight into the problem of NAPL dissolution under micro- and macroscale entrapment in a two-dimensional flow field. Results show that the aqueous concentration of benzene declined over time both before and after recovery. This is predicted by Eq. 3-10, which states that the maximum concentration of benzene contributed by the NAPL source will decline as the mole

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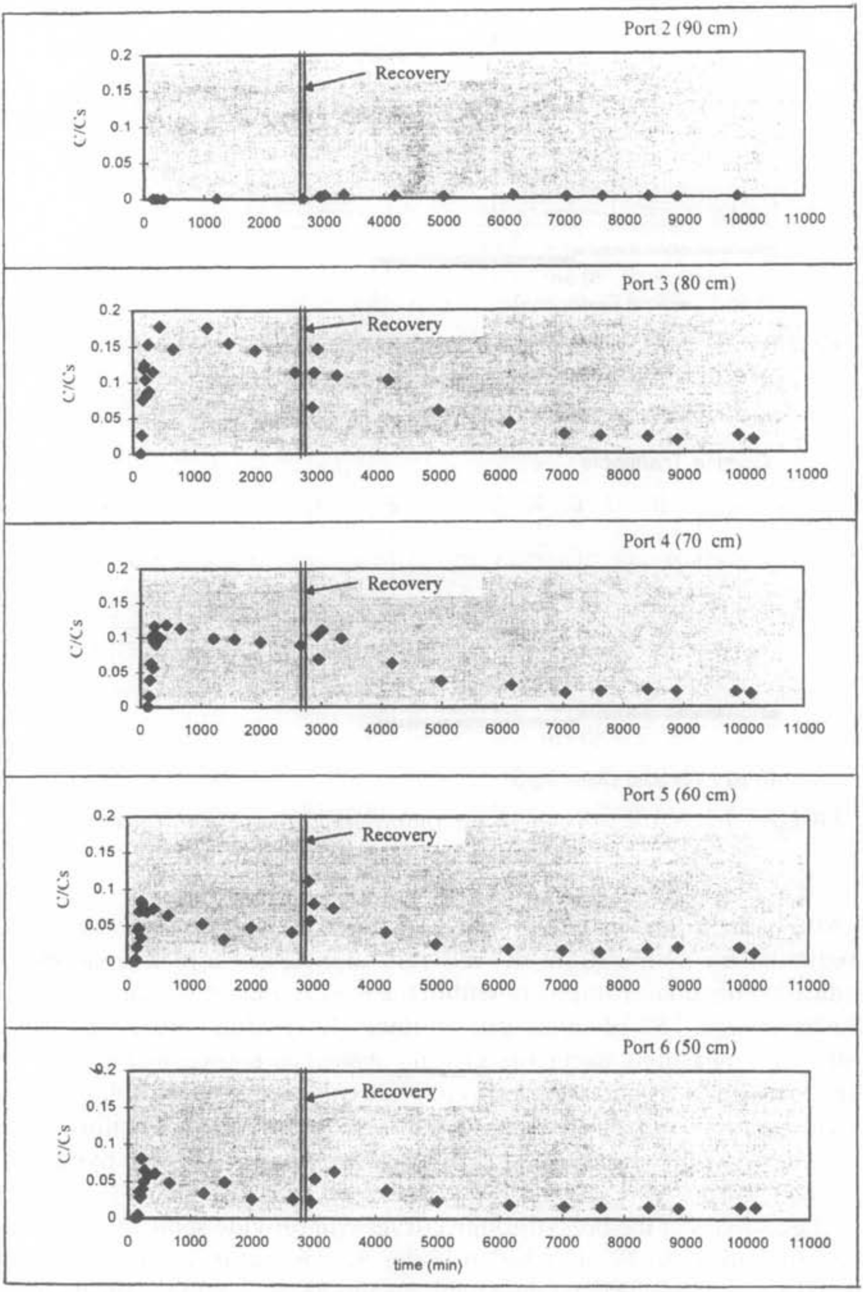

FIGURE 3-10. Solute breakthrough curves at five monitoring ports before and after recovery of NAPLs (after Okeson et al. 1995).

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fraction of benzene decreases within the mixture. However, none of the samples reached the maximum relative concentration of 0.21 that was determined independently in a batch test and would be predicted by Eq. 3-10. The benzene concentrations increased for a short time after the recovery of free product and then rapidly declined and reached an asymptotic value. This increased concentration after recovery can be attributed to the change in the mode of entrapment from macro to residual. Under macroscale entrapment, the relative permeability of the water phase is much lower in the high-saturation zones, resulting in lower water velocities within the zone of entrapment. After recovery, when the saturation dropped to residual, the relative water permeability increased, resulting in the water easily getting into the interior of the entrapment zone. These results suggest that diffusion of benzene within the NAPL-entrapped zone is the primary limiting factor to benzene dissolution under macroscale entrapment.

A comparison of the observed vertical distribution of relative concentrations show near-equilibrium benzene concentrations in the higher ports and much lower concentrations below the lens. This phenomenon appears to be directly attributed to the local flow field in the NAPL-contaminated area that is controlled by the changes in relative permeability due to NAPL entrapment.

3.5 SUMMARY AND CONCLUSIONS

The two case studies identified some of the complexities and limitations of pump-and-treat as a containment and a treatment method for NAPL-contaminated sites. The complexities arise from the fact that the aquifers are naturally heterogeneous, and the flow and entrapment behavior of the NAPLs are controlled by these heterogeneities. As indicated by experiences at the two sites, the fundamental problem hindering the successful application of pump-and-treat approaches for remediation or hydraulic containment is the lack of detailed knowledge about the waste or the geological setting in which it resides. The behavior of NAPLs, in particular, depends on soil and waste characteristics at a scale far smaller than routinely available at even the most-studied hazardous waste site. As long as NAPLs remain in the subsurface, they constitute source areas for aqueous-phase contamination. Because small zones of NAPLs may not be identified or appropriately characterized in sampling activities, the kinetics of mobilization or dissolution of these phases cannot be estimated. The kinetics of mobilization or dissolution and the removal of these source areas could be enhanced by the proper placement of withdrawal wells, but without intimate knowledge of the form and distribution of these areas, proper well placement is not possible. The disso-

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lution of these compounds is limited by their low solubility and further reduced by a low mass transfer area or slow diffusion or mass transfer rate constants, should they be applicable, because of limited contact between the nonaqueous phase and the flushing water. A nonaqueous phase distributed within a zone of soil also reduces the relative permeability of the flushing water phase, causing flow maldistribution or bypassing. These problems are even more important if the nonaqueous-phase waste source area is present in a fractured bedrock environment, in which the permeability of the surrounding media is effectively negligible and flushing of the fractures is effectively impossible.

Because these source areas are poorly flushed by the groundwater flow, concentrations in the effluent water can be reduced by eliminating contaminants from the well-flushed areas. However, if the flow is stopped due to the appearance of a successful remediation (because the effluent water will be relatively clean), slow mass transfer and diffusion processes from the poorly flushed source areas ultimately result in returning groundwater contamination. Restarting the groundwater withdrawal system under these circumstances gives rise to a rebound effect; that is, produced waters again exhibit high contaminant concentrations.

Source areas also may not be effectively flushed by groundwater because of the drawdown that occurs with groundwater withdrawal. Water is withdrawn from a well only if the water table gradient is reversed in the vicinity of a well. Although this method provides the containment that is sought from a pump-and-treat system, it also means that contaminants present at the original water table either have been isolated from the flushing water or have fallen by gravity as the water table dropped, smearing contamination over a larger area.

Although the changes in groundwater table slope and direction associated with groundwater withdrawal may isolate or further spread a contaminant, it is necessary to the achievement of the objective of hydraulic containment. Remember that hydraulic containment is often the primary feasible objective of a pump-and-treat system. The problem of water table drawdown and the degree of success of hydraulic containment again requires adequate characterization of contaminant form and location and the water table response to the water withdrawal. Special care must be taken to achieve hydraulic containment everywhere—a difficult task in light of incomplete geological and hydrological characterization.

Hydraulic containment is even more difficult to achieve in the vertical direction. Often, this is the most important direction in which containment is desired to avoid the movement of a dense nonaqueous phase from the near-surface environment down to a drinking water aquifer. Vertical hydraulic gradients are often difficult to measure and control. It is frequently assumed that the presence of an apparently continuous clay layer will preclude significant vertical interaction of groundwater and contami-

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nants. Often, however, pumping for groundwater withdrawal in one layer can affect hydraulic heads in a layer below. In such conditions, the hydraulic connection between the two layers is obvious, and vertical containment must be achieved hydraulically rather than through dependence on low-permeability strata.

The theoretical models presented here, in combination with the understanding of the NAPL behavior discussed elsewhere in this volume, will allow engineers to develop the necessary tools to help reduce some of the guesswork in designing pump-and-treat schemes that can be combined with more recent technologies such as bioremediation and thermally and chemically enhanced dissolution.

3.6 ACKNOWLEDGMENTS

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Chapter 4

NATURAL BIOATTENUATION OF ANAEROBIC HYDROCARBONS AND CHLORINATED SOLVENTS IN GROUNDWATER

Robert C. Borden

Abstract

Natural attenuation is an approach to groundwater cleanup whereby the naturally occurring processes of dispersion, sorption, volatilization, chemical transformation, and biodegradation are used to manage contaminant plumes released into the subsurface. The major processes controlling the natural attenuation of aromatic hydrocarbon and chlorinated solvent plumes are reviewed along with current assessment protocols and mathematical modeling approaches. The major focus of this work is on anaerobic and aerobic biotransformation processes, although other physical and chemical processes are briefly reviewed.

4.1 INTRODUCTION

In recent years, natural attenuation has become accepted as an alternative for the management of organic compounds dissolved in groundwater. The U.S. Environmental Protection Agency (EPA) Office of Research and Development and Office of Solid Waste and Emergency Response defines natural attenuation as "the biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem" (Wiedemeier et al. 1996a).

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This approach requires an assessment of those factors that influence the attenuation capacity of an aquifer and the potential human and environmental risks. This assessment typically includes a detailed hydrogeologic, chemical, and biological characterization; data analysis to determine whether contaminants are being attenuated and/or removed from the aquifer; modeling of the fate and transport of the dissolved groundwater plume; and, finally, long-term monitoring to confirm and ensure protection of human health and the environment. In most cases, natural attenuation is used to supplement other conventional engineered remediation techniques. The type and extent of conventional remediation techniques used depend on the environmental conditions in the aquifer, the extent of contamination, and the risk to the public and environment.

4.2 PROCESSES CONTROLLING CONTAMINANT DISTRIBUTION, TRANSPORT, AND ATTENUATION IN THE SUBSURFACE

In the absence of human intervention, many contaminant plumes will develop until they reach a quasi-steady-state condition. At steady state, the contaminant plume is no longer growing in extent and may shrink somewhat over time. Major processes controlling the size of the steady-state plume include release of dissolved contaminants from the source area, downgradient transport of the contaminants and mixing with uncontaminated groundwater, volatilization, and abiotic and biologically mediated transformations.

Organic contaminants may enter groundwater dissolved in recharge water or as nonaqueous-phase liquids (NAPLs). These NAPLs may be composed of a single organic compound (e.g., perchloroethylene) or a wide variety of organic compounds with different physical, chemical, and biological properties (e.g., gasoline, coal tar). NAPLs that enter the subsurface will flow downward under the influence of gravity. During movement through the soil, a portion of the NAPL will become entrapped within the individual soil pores. If the release is large, the amount of NAPL present will exceed the amount that can be trapped in the soil, and the NAPL will continue downward until it reaches the capillary fringe. If the NAPL is less dense than water (lighter-than-water NAPL [LNAPL]), the spilled liquid will float on the capillary fringe and may migrate horizontally with the local groundwater flow. As the water table rises and falls, a portion of the LNAPL may become trapped below the water table and become available for dissolution by flowing groundwater. Denser-than-water NAPLs (DNAPLs) flow downward through the saturated zone until a low-permeability confining layer is reached or the NAPL becomes entrapped within the aquifer pore spaces.

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