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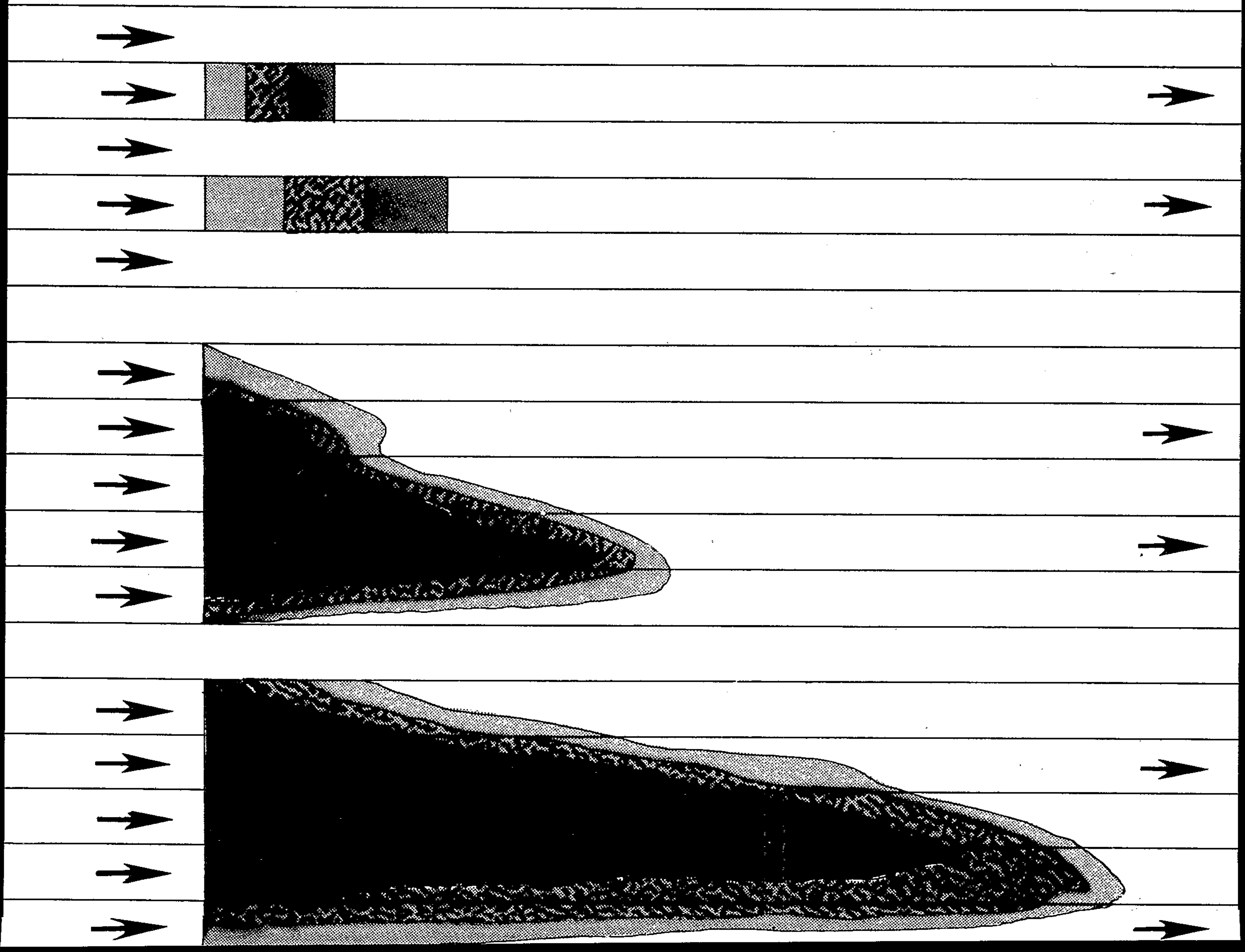
Seminar Publication

Transport and Fate of Contaminants in the Subsurface



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Seminar Publication

Transport and Fate of Contaminants in the Subsurface

Center for Environmental Research Information
Cincinnati, OH 45268

and

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NOTICE

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CONTENTS

ACKNOWLEDGEMENTS

This publication is based on a series of technology transfer seminars that were conducted in all ten EPA Regions between October 1987 and February 1988. The seminars provided regulators and technical specialists with a brief but intensive overview of the physical, chemical, and biological processes that govern the transport and fate of contaminants in the subsurface. A secondary purpose of the seminar was to provide a summary of modeling approaches used to make predictions about the transport and fate of contaminants in the subsurface and to describe the current and potential regulatory uses of such models.

The EPA Center for Environmental Research Information (CERI) and Robert S. Kerr Environmental Research Laboratory (RSKERL) developed this project to assist the technical support and technology transfer efforts of the EPA Office of Solid Waste and Emergency Response (OSWER) in the area of subsurface remediation. Seminar development and coordination were aided by numerous personnel, representing the EPA Office of Research and Development (ORD), OSWER, and the EPA Regions. Principal contributors to the project include:

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CHAPTER 1

INTRODUCTION

Joseph F. Keely

Congress requires that the U.S. Environmental Protection Agency (EPA), as well as other regulatory entities and the regulated community, meet four interrelated objectives for the protection of groundwater quality. These objectives are:

1. Assessment of the probable impact of existing pollution on ground water at points of withdrawal or discharge (Safe Drinking Water Act of 1974 & 1986 (SDWA)).
2. Establishment of criteria for location, design, and operation of waste disposal activities to prevent contamination of ground water, or movement of contaminants to points of withdrawal or discharge (Resource Conservation and Recovery Act of 1976 (RCRA), and the Hazardous and Solid Waste Amendments of 1984 (HSWA)).
3. Regulation of the production, use, and disposal of specific chemicals possessing an unacceptably high potential for contaminating ground water when released to the environment (Toxic Substances Control Act (TSCA), and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)).
4. Development of remediation technologies that are effective in protecting and restoring ground water quality without being unnecessarily complex or costly and without unduly restricting other land use activities (Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund), and the Superfund Amendments and Reauthorization Act of 1986 (SARA)).

To achieve these objectives, definitive knowledge of the transport and fate of contaminants in the subsurface environment is essential. Without this knowledge, regulatory agencies (such as EPA) run the twin risks of under-control and over-control. Regulatory under-control would result in inadequate prevention and cleanup of ground-water contamination. Regulatory over-control would result in costly preventative actions and remedial responses to contamination. However, gaining and using knowledge about contaminant transport and fate can be difficult because of the complexity of the subsurface environment. The activities of site characterization and remediation can be used to illustrate this complexity.

Site Characterization

Transport and fate assessments require interdisciplinary analyses and interpretations because the processes involved in these activities are naturally intertwined. Examining each process in isolation is much like taking photographs of an object from different perspectives and then trying to piece them together to describe the object. Each transport process must be viewed from the broadest of interdisciplinary viewpoints, and the interactions between them identified and understood. In addition to a sound conceptual basis, integrating information on geologic, hydrologic, chemical, and biological processes into an effective contaminant transport evaluation requires data that are accurate, precise, and appropriate at the intended problem scale.

The issues of contaminant transport and fate in the subsurface are particularly difficult to address at Superfund sites because of the complex array of the chemical wastes involved. The hydrogeologic settings of these sites are usually measured in hundreds of feet and, at this scale, are extremely complicated when characterized for a remediation plan. The methods and tools used for large-scale characterizations are generally applicable to the specialized needs at hazardous waste sites; however, the transition to smaller scale is fraught with scientific and economic problems. Some stem from the highly variable nature of contaminant distributions at hazardous waste sites, and other problems result from the limitations of available methods, tools, and theories.

Even though a given parameter, such as hydraulic conductivity, can be measured correctly and with great reproducibility, it is difficult to know how closely an observation actually represents the vertical and horizontal distribution of conductivities found at a site. Therefore, when using a conceptual model to interpret contaminant transport processes, it is crucial that special attention be given to the spatial and temporal variations of the collected data.

To circumvent the large numbers of measurements and samples needed to reduce uncertainties in dealing with subsurface parameters, more comprehensive theories are constantly under development. The use of these newly developed theories, however, is often frustrating because many call for data which are not yet practically obtainable, such as chemical interaction coefficients or relative permeabilities of immiscible solvents and water. Therefore, modern contaminant transport and fate studies necessarily involve a compromise between sophisticated theories, current limitations for acquiring data, and economics.

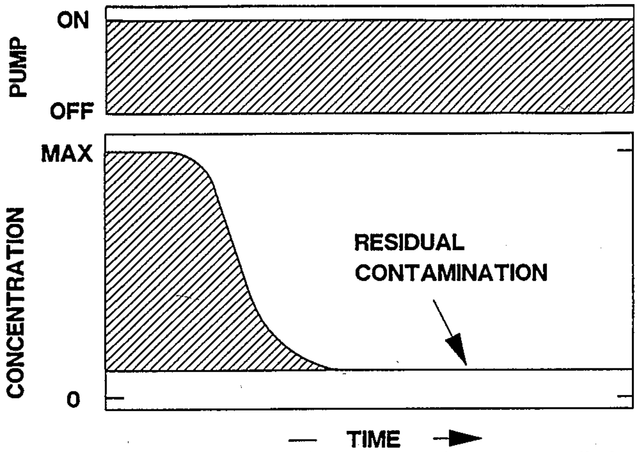


Figure 1. Apparent cleanup by pump-and-treat remediation.

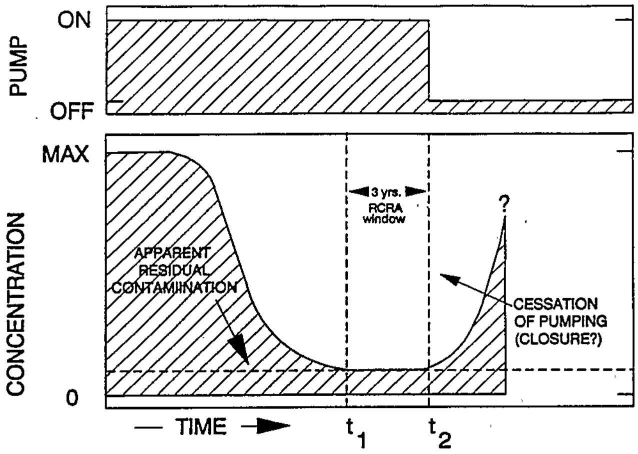


Figure 2. Contaminant rebound after remediation ceases.

Remediation

A major issue in cleaning up ground-water contamination is determining when remediation is complete. In remedial actions, the level of contamination measured at monitoring wells may be dramatically reduced after a moderate period of time, but low levels of contamination usually persist. In parallel, the contaminant load removed by extraction wells, for instance, declines over time and gradually approaches a residual level in the latter stages (Figure 1). A decision must be made whether to continue or end remediation. By continuing remediation, efforts will be made to clean up small amounts of residual contamination. However, if remediation is ended prematurely, an increase in the level of ground-water contamination may follow (Figure 2).

There are several contaminant transport processes that may be responsible for the persistence of residual contamination and the kind of effect depicted in Figure 2. In order to generate such an effect, releases of contaminant residuals must be slow relative to water movement through the subsurface caused by pumping. Transport processes that generate this kind of behavior include: (1) diffusion of contaminants within spatially variable sediments; (2) hydrodynamic isolation; (3) sorption-desorption; and (4) liquid-liquid partitioning.

Flow through the zones of highest hydraulic conductivity results in rapid cleansing of these zones by extraction wellfields, but cleanup of contaminants in low permeability zones can only occur after the slow process of diffusion takes place (Figure 3). The situation is similar, though reversed, for *in situ* remediations that require the injection and delivery of nutrients or reactants to the zone of intended action. Because the surface area of low-permeability sediments is greater than that for high-permeability sediments, greater amounts of contaminants accumulate on them. Hence, the majority of contaminant reserves may be available only under diffusion-controlled conditions in many heterogeneous settings.

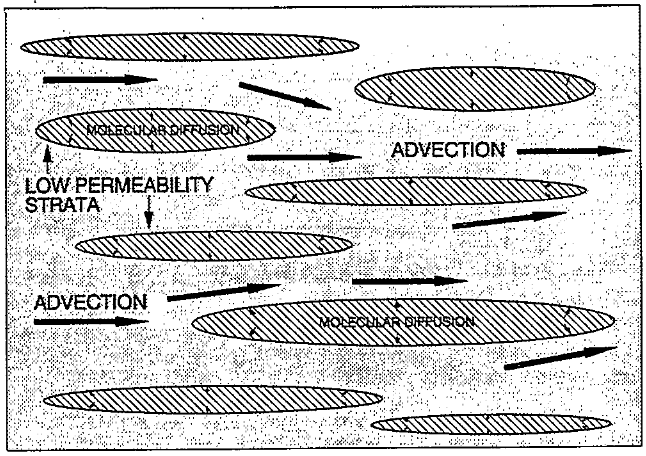


Figure 3. Remediation effectiveness limited by variations in permeability.

The operation of any remediation wellfield results in the formation of stagnation zones downgradient of extraction wells and upgradient of injection wells. These zones are hydrodynamically isolated so that mass transport within the isolated water will take place only by diffusion. Because of this, the portion of the contaminant plume lying within a wellfield's associated stagnation zones will not be effectively remediated.

For remediation efforts involving compounds that readily sorb to aquifer materials, the number of pore volumes to be removed depends not only on the sorptive tendencies of the contaminant, but also on whether flow rates during remediation are too rapid to allow contaminant levels to approach local equilibrium (Figure 4). If insufficient contact time is allowed, the affected water is advected away from sorbed contaminants prior to reaching equilibrium and is replaced by upgradient fresh water. This method of removal generates large volumes of mildly contaminated water where small volumes of highly contaminated water would otherwise result.

When non-aqueous phase liquid (NAPL) residuals, such as gasoline, are trapped in pores by surface tension, diffusive liquid-liquid partitioning controls dissolution of the toxic compounds within the NAPLs into the ground water. As with sorbing compounds, flow rates during remediation may be too rapid to allow saturation levels of the partitioned contaminants to be reached (Figure 5) and large volumes of mildly contaminated water will be generated.

The practical use of remediation wellfields and other ground-water cleanup technologies are highly dependent on site-specific knowledge of the influence of transport processes on contaminant levels. There is still much to be learned about highly specific and cost-effective remediations; however, far more could be accomplished if the processes that govern the behavior and treatability of contaminants were actively investigated at each site. In general, conventional field characterization efforts have not led to satisfactory remediations. Recent transport-process-oriented approaches of characterization are resulting in more permanent and cost-effective remediations.

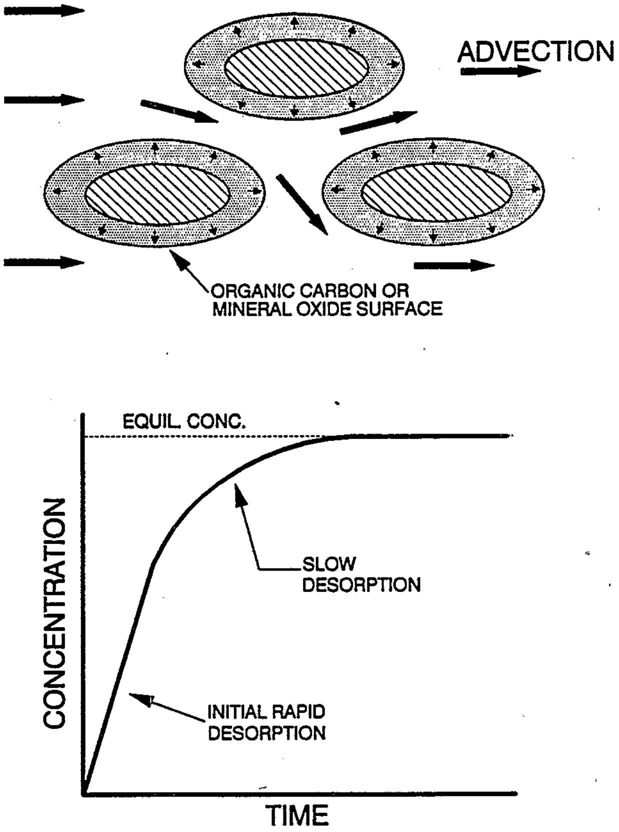


Figure 4. Sorption limitations on remediation effectiveness.

There are many misconceptions regarding the processes affecting the transport and fate of contaminants in the subsurface. Some of these are relatively easy to address by educational efforts while others can be addressed only by applied research. This document will describe some of the information known about transport and fate of contaminants in the subsurface. By understanding and using this information, as well as information derived from future research, the ground-water protection objectives required by Congress may be met.

EPA's Transport and Fate Research Program

The U.S. EPA Office of Research and Development (ORD) operates 12 national laboratories, several of which address various aspects of ground-water contamination. The Environmental Monitoring Systems Laboratory in Las Vegas, Nevada develops

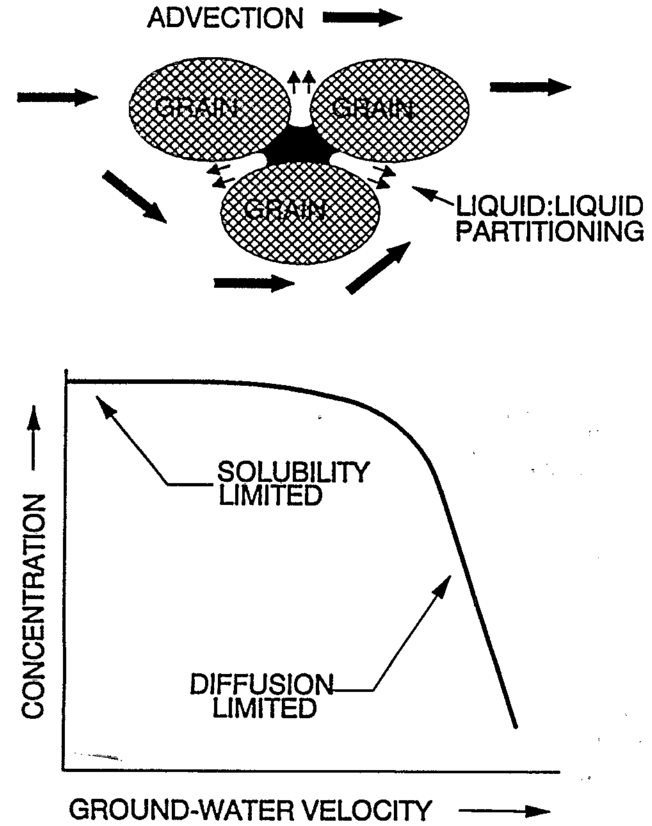


Figure 5. Liquid partitioning limitations on remediation effectiveness .

monitoring systems, with emphasis on hazardous waste site characterization, underground storage tank leak detection, and soil vapor monitoring. Engineering aspects of the prevention and remediation of ground-water contamination are addressed by the Risk Reduction Engineering Research Laboratory in Cincinnati, Ohio which develops source control measures (e.g., landfill covers and liners, and waste caps) and waste disposal techniques (e.g., solidification, pump-and-treat, and incineration). Other ORD laboratories also support research that is germane to ground-water contamination issues (notably, those laboratories in Ada, Oklahoma; Athens, Georgia; Edison, New Jersey; and Corvallis, Oregon).

The Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma focuses on these issues as its primary charge. The Kerr Laboratory serves as EPA's center for studies of the transport and fate of contaminants in the subsurface. The research program includes development of methodologies for protection and restoration of ground-water quality, and evaluation of the applicability and limitations of using natural soil and subsurface processes for the treatment of hazardous wastes. RSKERL's efforts in the 1980s have increasingly focused on improvement of site characterization and remediation methods, with special emphasis on identification and quantification of the mechanisms by which natural processes govern the transport and fate of contaminants in the subsurface.

Transport processes research at RSKERL is divided into three major areas:

1. Hydrologic processes, which act to influence the movement of water (the primary vehicle for subsurface contaminant movement).
2. Abiotic processes, which are the physical and chemical interactions that cause contaminants to move at different rates than those of the ground water.
3. Biotic processes, which are the microbially mediated transformations of contaminants in the subsurface to other compounds.

In the subsurface, however, these processes are inseparable, and RSKERL's comprehensive research goal is to ultimately have the knowledge to integrate the influences of these processes into a singular understanding of contaminant behavior in the subsurface.

CHAPTER 2

PHYSICAL PROCESSES CONTROLLING THE TRANSPORT OF CONTAMINANTS IN THE AQUEOUS PHASE

Carl D. Palmer and Richard L. Johnson

Introduction

Interest in the transport and fate of contaminants in terrestrial subsurface environments is based on concern for the protection and remediation of both ground- and surface-water resources. To achieve this protection, it is necessary to: (1) predict the time of arrival and concentration of contaminants at a receptor such as a monitoring well, a water-supply well, or a surface water body; (2) design safe, cost-effective waste facilities; (3) install effective monitoring systems; and (4) develop efficient and cost-effective strategies for remediation of contaminated aquifers. To attain these goals, the processes involved in the transport and transformation of contaminants in both porous and fractured media, and under either saturated or undersaturated conditions must be understood. This chapter will discuss some issues associated with the physical processes controlling contaminant transport in the subsurface. The advection-dispersion theory in saturated, porous media will be described as well as the issues pertaining to contaminant transport in the vadose zone and in fractured rock. This information can assist contractors, consulting engineers, and scientists in designing more efficient and cost-effective monitoring networks and remediation strategies, and safer waste facilities.

Contaminant Transport in Saturated, Porous Media

Advection-Dispersion Theory

If the concentration of a contaminant were measured in a monitoring well located between a contaminant source and a receptor such as a water supply well (Figure 6), a concentration breakthrough curve could be obtained (Figure 7). In the graph, the concentrations do not immediately increase in a step function but, instead, increase more gently in an S-shaped curve. In a one-dimensional, homogeneous system, the arrival of the center of mass is the result of advection while the spread of the breakthrough curve is the result of dispersion.

Advection is the transport of a non-reactive, conservative tracer at an average ground-water velocity. The average linear velocity, v, at which ground water flows through a porous aquifer is:

$$v = -(K/\theta_t)(dh/dx) \qquad (1)$$

where K is the hydraulic conductivity of the formation in the direction of ground-water flow, θ_t is the porosity of the formation, and (dh/dx) is the hydraulic gradient in the direction of ground-water flow (Freeze and Cherry, 1979). The velocity given by this equation can be substantially different for solutes that react through precipitation/dissolution, adsorption, and/or partitioning within the geologic media (see Chapter 5).

The study of dispersion phenomena is important for predicting the time when an action limit, a concentration limit used in regulations such as drinking water standards, will be reached and for determining optimal, cost-effective strategies for aquifer remediation. The classical mathematical approach used to determine solute transport in porous media is the advection-dispersion equation. This equation is written in its one-dimensional form as:

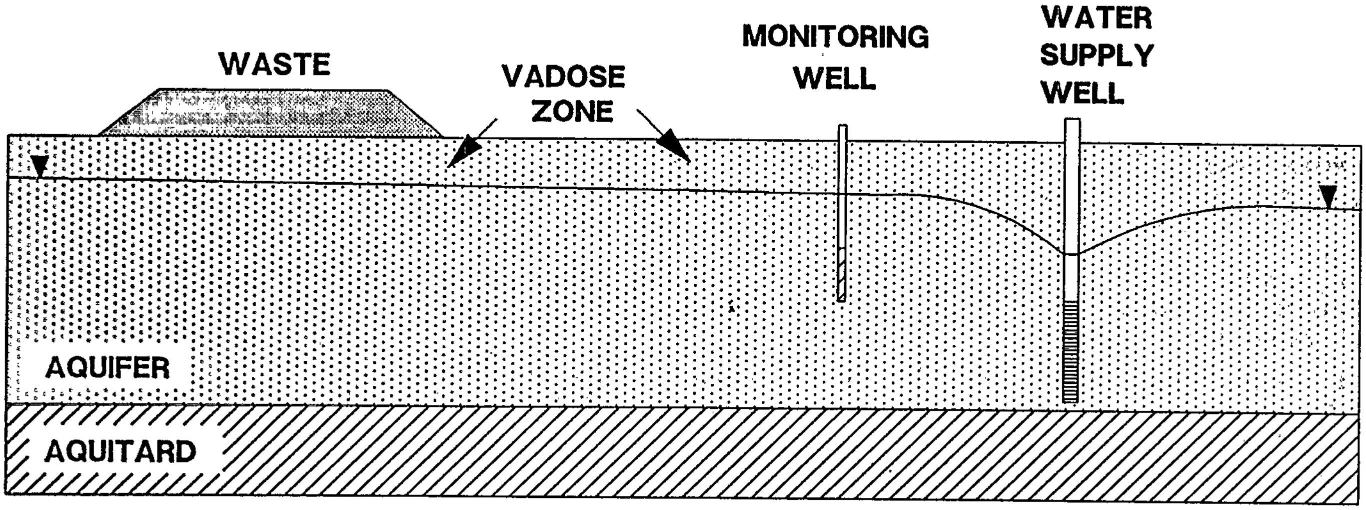


Figure 6. Site containing a monitoring well, contaminant source, and receptor.

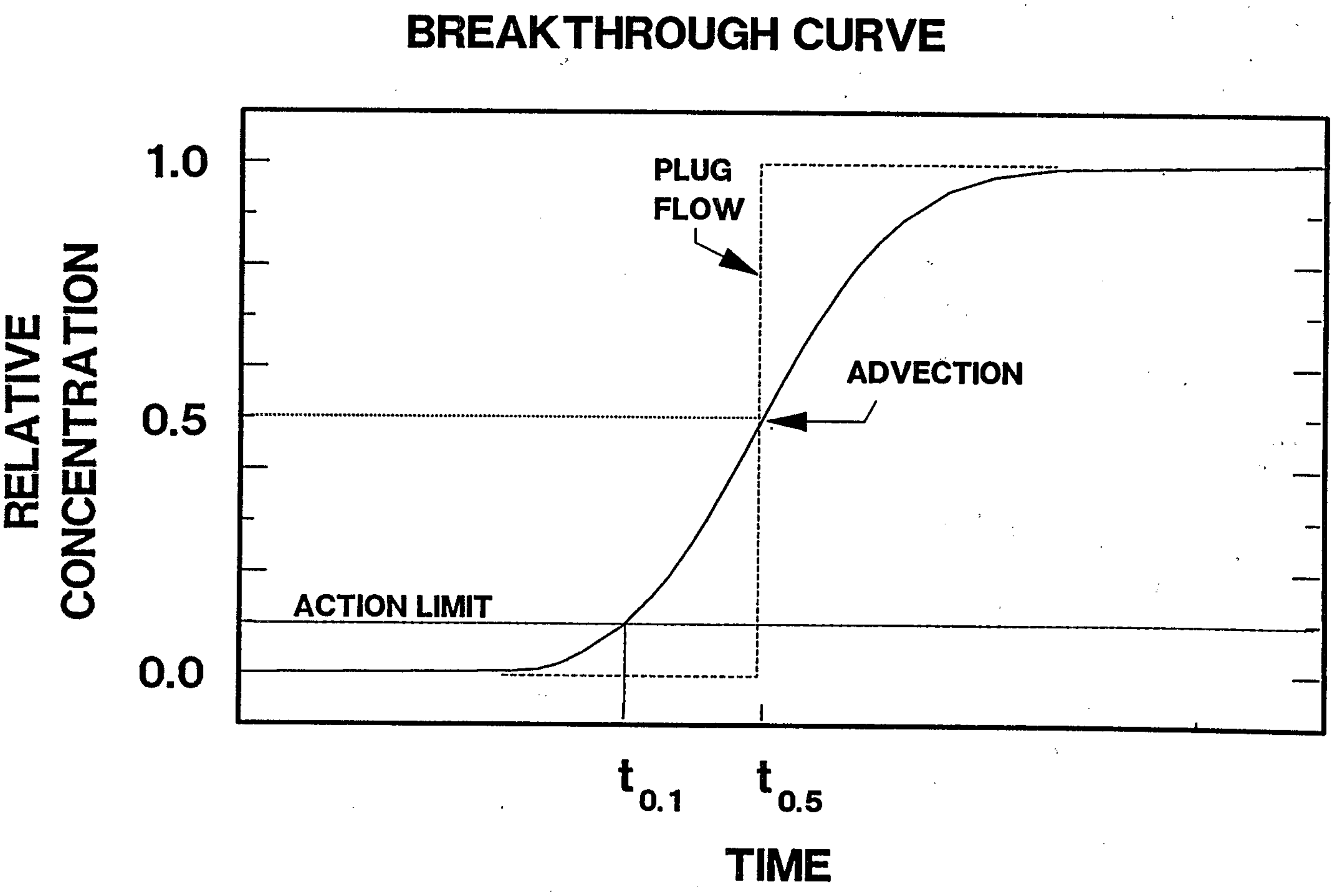


Figure 7. Concentration of a contaminant in a monitoring well.

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) - v\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (2)$$

where D is the dispersion coefficient, v is the groundwater velocity, C is the concentration of the solute, x is the spatial coordinate, and t is time. This equation is an expression of the mass balance of a contaminant within the aquifer as a result of dispersion, advection, and change in storage. These processes are represented respectively by the first, second, and third terms of Equation 2.

Early studies of the dispersion coefficient revealed that it varies with the ground-water velocity (Perkins and Johnston, 1963). A plot of the D/D_0 versus vd/D_0 (Figure 8) where D_0 is the molecular diffusion coefficient of the contaminant, v is the ground-water velocity, and d is the grain diameter of the porous medium, shows that the dispersion coefficient is relatively constant at low velocities, but increases linearly with velocity as the ground-water velocities increase. These experimental results led investigators to propose that the dispersion coefficient can be written as the sum of two terms: an effective molecular diffusion coefficient, D_d, and mechanical dispersion coefficient, D_m:

$$D = D_d + D_m \qquad (3)$$

The mechanical dispersion coefficient is proportional to the velocity:

$$D_m = \alpha v \qquad (4)$$

where α is the constant of proportionality and is known as the dispersivity parameter. This parameter continues to be the focus of a great deal of research and controversy. At a small scale of measurement, mechanical dispersion is the result of: (1) velocity variations within a pore; (2) different pore geometries; and (3) the divergence of flow lines around the sand grains present in a porous medium (Gillham and Cherry, 1982).

The effective molecular diffusion coefficient is a value for diffusion within the porous medium. It can be obtained from the solution diffusion coefficient, D_0, by:

$$D_d = \tau D_0 \qquad (5)$$

where τ is the tortuosity of the medium. Tortuosity is a factor that accounts for the increased distance a

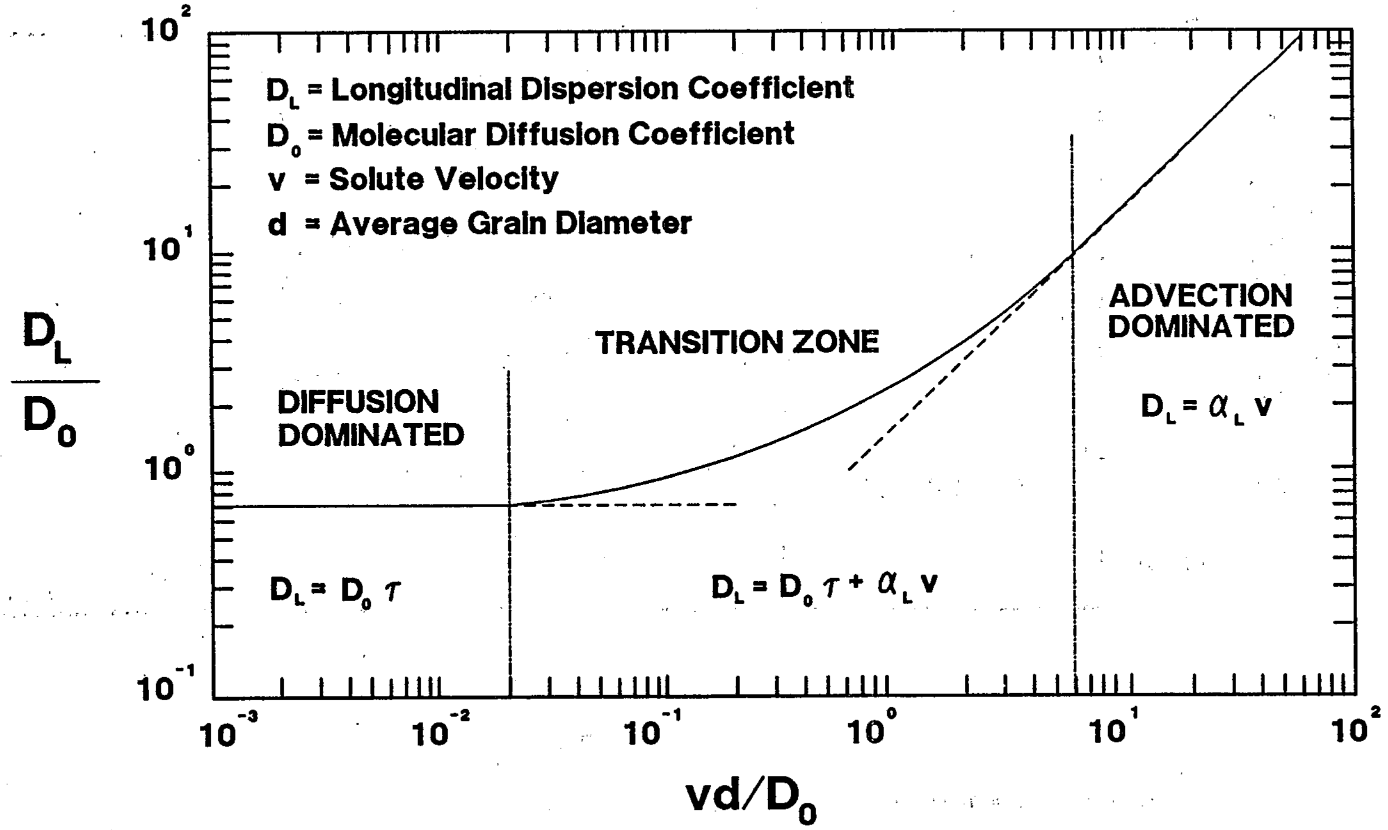


Figure 8.

Dispersion coefficient as a function of ground-water velocity, v, and grain diameter, d (after Perkins and Johnston,1963).

diffusing ion must travel to get around the sand grains. For granular, porous media, τ is typically in the range of 0.6 to 0.7 (Perkins and Johnston, 1963; Gillham, et al., 1984). A simple theoretical calculation indicates that, rather than travelling through a grain of diameter d, the solute must travel the distance around the grain or $\pi d/2$. Thus, the tortuosity should have a value of approximately 0.64.

The advection-dispersion equation (Equation 2) can be solved with appropriate boundary and initial conditions to yield the concentration breakthrough curves or concentration distribution curves. For a one-dimensional system with a constant concentration of solute at the boundary, the concentration at a given distance from the source results in an S-shaped curve (Figure 9). The concentration breakthrough curves arrive at points further from the source at later times and are more spread out. The concentration distribution curves look like a mirror image of the breakthrough curves with greater concentrations toward the source (Figure 10).

The discussion of the advection-dispersion equation has been limited thus far to the one-dimensional case. The same general principles can be applied to two- and three-dimensional problems. Figure 11 shows the transport of a contaminant slug through a porous aquifer in two dimensions. As the center of mass of the slug moves further from its initial location within the aquifer by advection with the ground-water flow, the slug spreads. The spreading in the direction of ground-water flow is the longitudinal dispersion, while the spread in the direction perpendicular to the ground-water flow is known as the transverse dispersion.

If the slug is viewed in three dimensions, there are three dispersion coefficients, one longitudinal and two transverse. In its general mathematical formulation, the dispersion coefficient is a second rank tensor. More mathematically detailed descriptions of the advection-dispersion equation can be found in the works of Bear (1979 and 1969).

Application of Advection-Dispersion Theory

One-, two-, and three-dimensional advection dispersion equations have been used to simulate the transport of contaminants. However, discrepancies between theory and laboratory experiments were observed. Investigators attribute these discrepancies to a variety of mechanisms including immobile zones of water within experimental columns, solution-solid

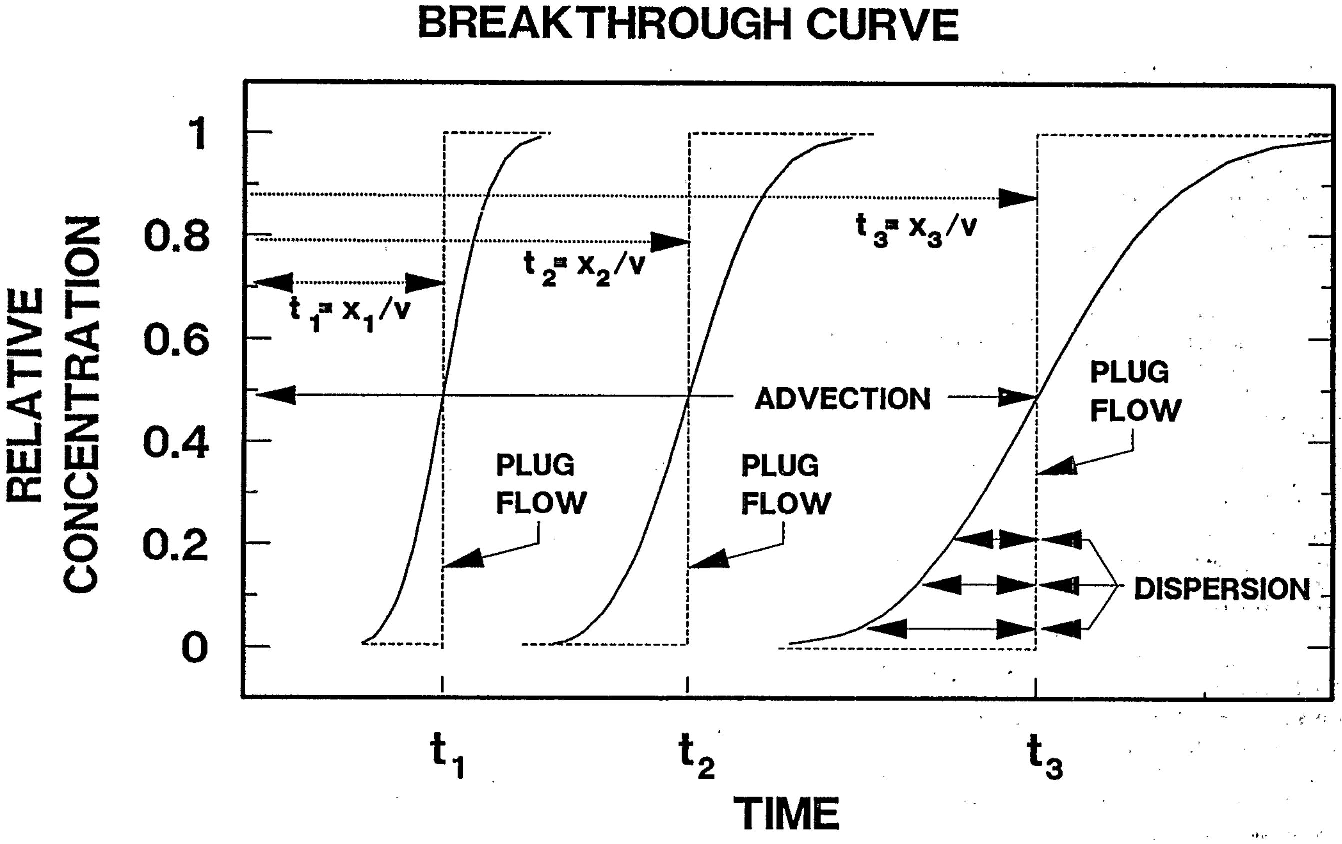


Figure 9. Concentration breakthrough curves derived from the advection-dispersion equation.

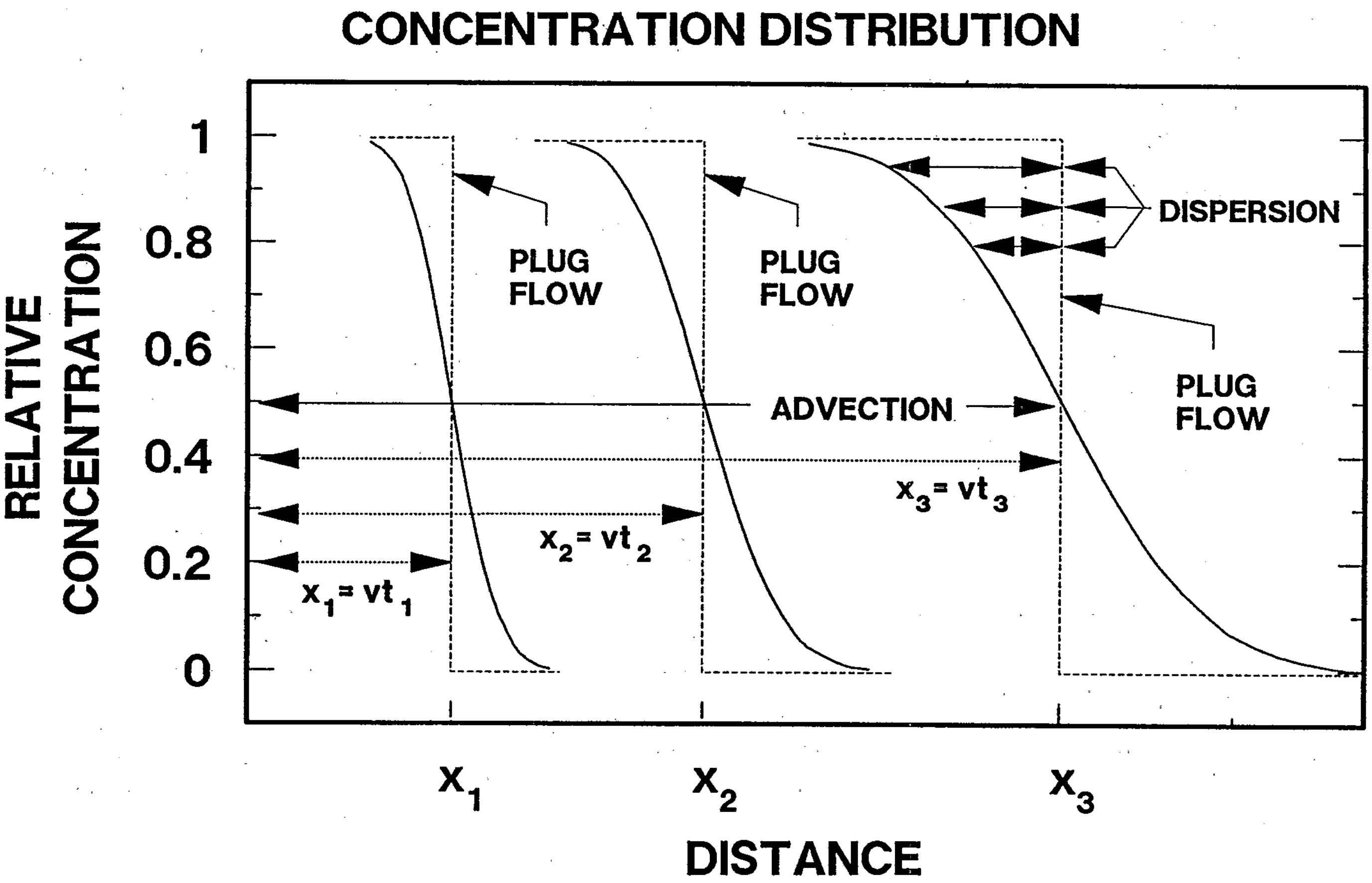


Figure 10. Concentration distribution curves derived from the advection-dispersion equation.

interface processes, anion exclusion, and diffusion in and out of aggregates. An apparent scale dependency of the dispersion coefficient also has been observed (Table 1). Laboratory scale experiments generally yield small values of longitudinal dispersivity (0.0001 to 0.01 m) while field tracer tests and model calibration of contaminant plumes yield longitudinal dispersivity values in the 10 to 100 m range. Even within a single tracer experiment, longitudinal dispersivity values are observed to increase with increasing transport distance (Figure 12). This apparent increase in the longitudinal dispersivity parameter with an increasing spatial or time scale indicates that the assumptions often used when applying classic advection-dispersion theory in natural geologic materials are not applicable.

Table 1. Longitudinal Dispersivity Values Obtained from Different Scale Experiments (After Gillham and Cherry, 1982)

Type of Test	Longitudinal Dispersivity
Laboratory Tests	0.0001 to 0.01 m
Natural Gradient Tracer Tests	0.01 to 2 m
Single Well Tests	0.03 to 0.3 m
Radial and Two Well Tests	0.5 to 15 m
Model Calibration of Contaminant Plumes	3 to 100 m

Furthermore, longitudinal dispersivity values generally were considered to be only 10 to 30 times larger than transverse dispersivity values. If transverse dispersivity values are large, contaminant plumes will spread over the entire thickness of an aquifer (Figure 13A). This is contrary to the long, thin plumes (Figure 13B) observed in the field where detailed three-dimensional monitoring was performed (MacFarland, et al., 1983; Kimmel and Braids, 1980). These observations indicate that transverse dispersivity must necessarily be very small and in many situations may even be close to zero (Sudicky, 1986; Frind and Hokkanen, 1987). If so, the transverse dispersion coefficient would be equal to the effective diffusion coefficient within the medium.

There is a growing consensus among contaminant hydrologists that the large longitudinal dispersion

ADVECTION AND DISPERSION

OF A CONTAMINANT SLUG

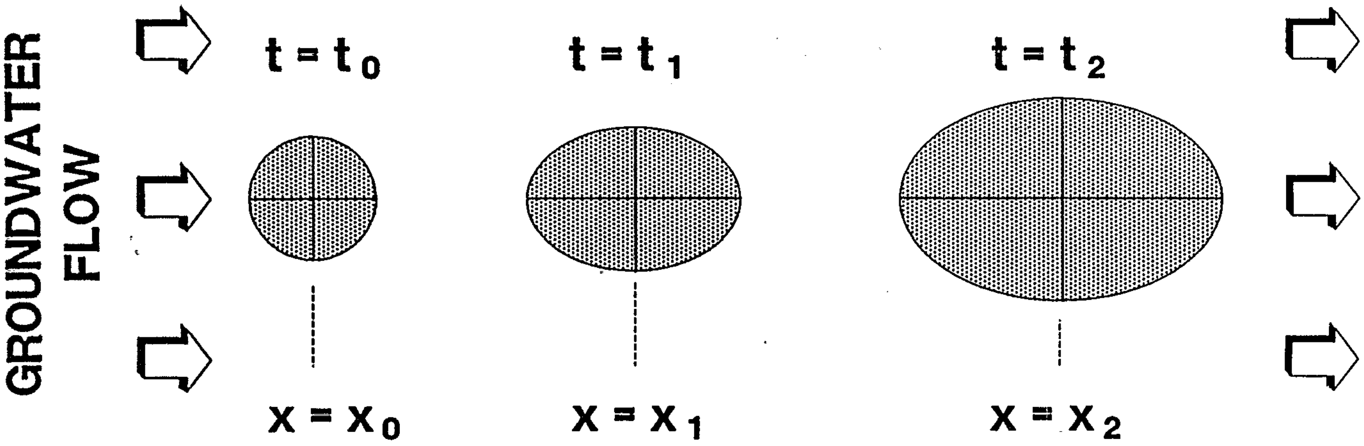


Figure 11. Transport of a contaminant slug through a porous aquifer.

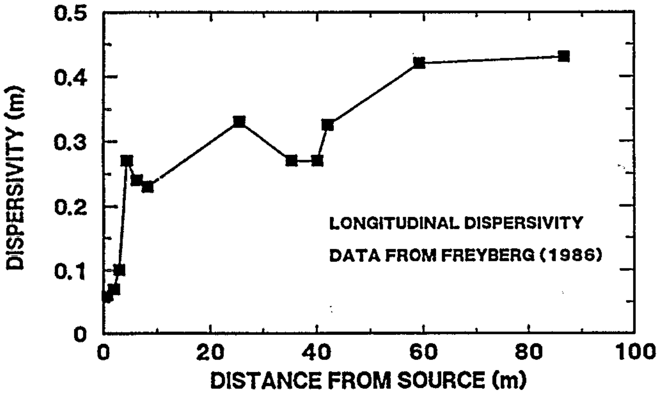
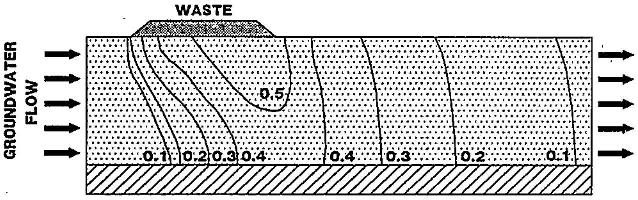


Figure 12. Increase in longitudinal dispersivity with transport distance.

A. HYPOTHETICAL CONTAMINANT PLUME
WITH A LARGE TRANSVERSE DISPERSIVITY



B. HYPOTHETICAL CONTAMINANT PLUME
WITH A SMALL TRANSVERSE DISPERSIVITY

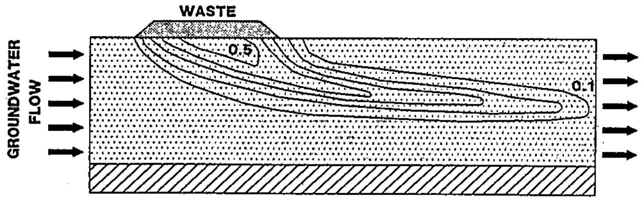


Figure 13. Hypothetical contaminant plumes for large (A) and small (B) dispersivities.

coefficients observed in field experiments and obtained by model calibration of contaminant plumes are the result of aquifer heterogeneity. The effects of heterogeneity on the spread of contaminants is easily illustrated in an ideally stratified aquifer with layers of sediment of different hydraulic conductivities (Mercado, 1967). Contaminants move rapidly along the layers with higher permeability and more slowly along the lower permeability layers (Figure 14). If water is sampled from monitoring wells that are screened through the various layers, the sample is an integration of the concentrations in each layer. Plotting concentration versus distance from the source reveals a curve with a large amount of spread even though only advection is considered. This macroscopic dispersion is the result of aquifer heterogeneity and not the pore-scale processes described above.

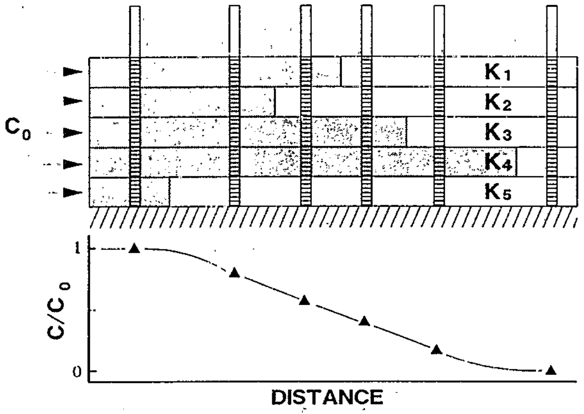


Figure 14.

Contaminant distributions and concentrations in an ideally stratified aquifer (after Gillham and Cherry, 1982).

Investigators can calculate contaminant transport rates through stratified aquifers by assuming that hydraulic conductivities follow a Gaussian distribution. When completed, these analyses indicate that the spread in the contaminant distribution is proportional to the mean distance travelled, L, rather than $L^{1/2}$ which is obtained for the classic advection-dispersion theory (Mercado, 1967). Thus, the spatial spread of the contaminant concentrations is greater than that predicted by the advection-dispersion theory. If the stratified medium is assumed to be homogeneous and if the advection-dispersion theory is applied, the apparent dispersivity parameters increase with distance from the source.

All geologic formations are heterogeneous and none are perfectly stratified. Bedforms are often lenticular and may contain cross-stratification or graded bedding. Detailing the distribution of hydraulic conductivity in the subsurface is a formidable task that cannot be done at waste sites on a routine basis. Heterogeneity can, nonetheless, be quantified by considering hydraulic conductivity to be a random process, and determining its important statistics such as the mean, variance, and autocorrelation function.

Such statistical analyses were performed on the Borden aquifer (Ontario, Canada) where permeameter measurements on more than 3,000 samples were analyzed (Sudicky, 1986). In an aquifer that is ostensibly described as homogeneous, hydraulic conductivity was found to vary by more than two orders of magnitude. Statistical analysis of this data further revealed that the hydraulic conductivity is log-normally distributed. Autocorrelation length-scales are 1.6 m in the horizontal direction and 0.10 m in the vertical direction. Using this information and applying the stochastic theory of Gelhar and Axness (1983), Sudicky (1986) calculated the asymptotic longitudinal dispersivity for the Borden aquifer to be 0.61 m, a value that is close to the 0.43 m reported by Freyberg (1986) for the large-scale tracer test conducted at the site The asymptotic transverse dispersivity values calculated by Sudicky (1986) are very close to zero, indicating that the transverse dispersion coefficient is on the order of the effective molecular diffusion coefficient.

Gillham, et al. (1984) proposed an advection-diffusion model for the transport of solutes in heterogeneous, porous media. This model recognizes that aquifers are heterogeneous and that advection is the key process controlling the rate of movement of solutes through the layers of higher permeability. As the front moves through those layers, some of the solute is lost to the lower permeability layers via molecular diffusion. This advection-diffusion model was tested in the laboratory (Sudicky, et al., 1985) using a sandbox model composed of a layer of sand sandwiched between layers of silt. If molecular diffusion in the transverse direction is ignored, the one-dimensional advection-dispersion equation can be applied (the dashed line in Figure 15). The experimental data, however, revealed retardation in the solute front and a much greater spread in the breakthrough curve. A mathematical solution that includes diffusion into the lower-permeability layers was able to simulate the experimental data. If the one-dimensional equation is used to analyze the experimental curves, a large apparent dispersivity would be obtained for the higher permeability layer.

While aquifer heterogeneity is a major factor contributing to the spread of contaminants, other processes contribute to contaminant transport characteristics as well. Diverging flow lines spread contaminants by advection over a larger cross-section of the aquifer. Temporal variations in the water table can change the direction of ground-water

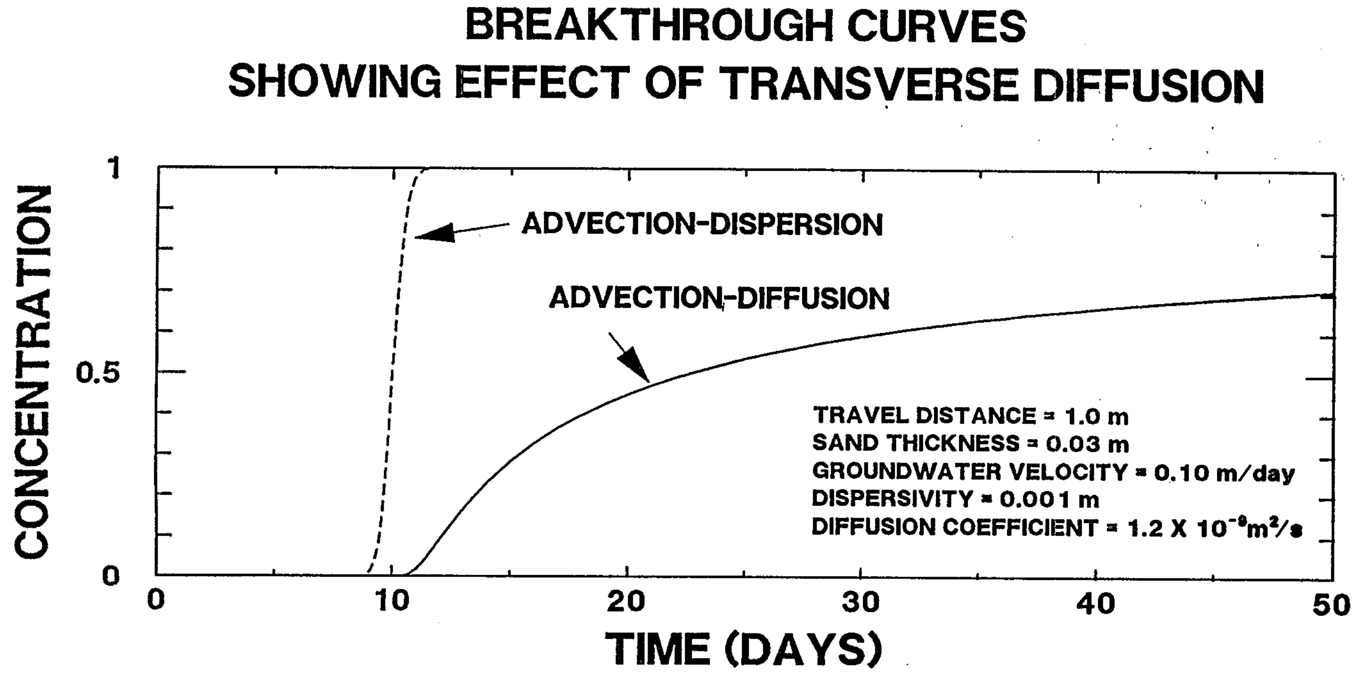


Figure 15. Breakthrough curves showing the effect of transverse diffusion.

flow and contribute to the lateral spread of contaminants. Also, variations in the contaminant concentrations at the source can cause apparent dispersion in the longitudinal direction (Frind and Hokkanen, 1987).

Apparent spreading in contaminant plumes also may be the result of ground-water sampling methods. Insufficient well purging may result in underestimation of contaminant concentrations at select locations within the aquifer. Monitoring wells with different screen lengths integrate ground water from disparate portions of the aquifer and may yield dissimilar contaminant concentrations.

Dispersion is a phenomenon that often is used as a mathematical convenience to correct for ignorance about the aquifer's heterogenous nature and a poor understanding of the processes occurring within the aquifer. As the fundamental processes controlling the distribution of contaminants in the subsurface are understood, better and more cost-effective techniques for aquifer remediation will be designed.

Diffusive Transport Through Low Permeability Materials

Unfractured clays and rocks often have hydraulic conductivities less than 10^{-9} m/s. A review of ground-water flow through such low-permeability formations is provided by Neuzil (1986). However, for such materials, the diffusive transport of contaminants is large compared to advective transport.

The diffusion of solutes through porous media has been studied in the laboratory (Gillham, et al., 1984; Robin, et al., 1987). Experiments confirm the applicability of Fickian diffusion models and Equation 5 for calculating the effective diffusion coefficient. Tortuosity factors in sand-clay mixtures were in the range of 0.59 to 0.84 for ^{36}Cl and 0.33 to 0.70 for tritium (Gillham, 1984).

A study of fine-grained Quaternary deposits in southern Ontario by Desaulniers, et al. (1981, 1986) established that the movement of Cl$^-$ and ^{18}O through the deposits occurred through molecular diffusion. The transport of inorganic ions through a clay beneath a municipal landfill also was shown to be predominantly by molecular diffusion (Goodall and Quigley, 1977; Crooks and Quigley, 1984). Similarly, a study of the transport of organic contaminants through a saturated clay beneath a hazardous waste site shows that the distribution of contaminants is controlled by Fickian diffusion (Johnson, et al., 1989).

Contaminants can contaminate aquifers by diffusing across natural aquitards or clay liners. The extent of ground-water contamination will depend on the diffusive flux, rate of ground-water flow in the aquifer, and length of the source area in the direction of ground-water flow. Diffusion of organic contaminants is discussed in more detail in Chapter 6.

Effects of Density

The discussion so far has been limited to cases where the contaminant plume does not have a density significantly different from the native ground water. In some cases, dissolved concentrations are large enough that the density of the contaminant plume may contribute to the direction of solute transport. The contribution of density to the vertical component of ground-water velocity, v_g, can be calculated using the concept of equivalent fresh-water head (Frind, 1982) by:

$$v_g = \frac{-K_{zz}}{\theta_t}\left(\frac{\rho}{\rho_0} - 1\right) \tag{6}$$

where K_{zz} is the hydraulic conductivity in the vertical direction, θ_t is porosity, ρ is the density of the contaminated water, and ρ_0 is the density of the native ground water.

As an example, assume that the density of ground water within an aquifer is 1.00, the natural horizontal gradient is 0.005, and the natural vertical gradient is 0.000. If the density of the contaminated water is equal to the density of the native ground water, the contaminant plume moves horizontally under the naturally existing hydraulic gradient. If the density of the contaminated water is 1.005, then the driving force in the vertical direction is the same as the driving force in the horizontal direction. If the aquifer is isotropic, then the resultant vector of these two forces plunges at 45° into the aquifer. Under these conditions, a contaminant plume moves deeply into the aquifer and may not be detected with shallow monitoring systems installed under the assumption of horizontal flow. The density of seawater, which contains 36,000 mg/L total dissolved solids, is 1.025 and the density of pure water is close to 1.000. Therefore, the density of 1.005 corresponds to approximately 7,000 mg/L.

Retardation of Contaminants

Not all solutes are transported through geologic material at the same rate. If solutes undergo chemical reactions while being transported, their rate of movement may be substantially less than the average rate of ground-water flow. Such chemical reactions include precipitation, adsorption, ion exchange, and partitioning into soil organic matter or organic solvents. While these topics are discussed in more detail in Chapter 5, the effect of this retardation on the breakthrough curves is introduced here.

One simple form of the differential equation for contaminant transport with retardation is:

$$\frac{\partial}{\partial x}\left(\frac{D}{R}\frac{\partial C}{\partial x}\right) - \frac{v}{R}\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{7}$$

where R is a constant known as the retardation factor and the other parameters are as defined above. If the retardation factor is equal to 1.0, the solute is nonreactive and Equation 2 is obtained. If R is greater than 1.0, the average velocity of the solute, v/R, is less than the velocity of the ground water and the dispersion of the solute, D/R, is likewise reduced. If a monitoring well is located at such a distance from a contaminant source that it takes time t_1 for a nonreactive solute to travel from the source to the well, it will take $2t_1$ for a contaminant with a retardation factor of 2 to reach that same well and $4t_1$ for a contaminant with a retardation factor of 4 (Figure 16).

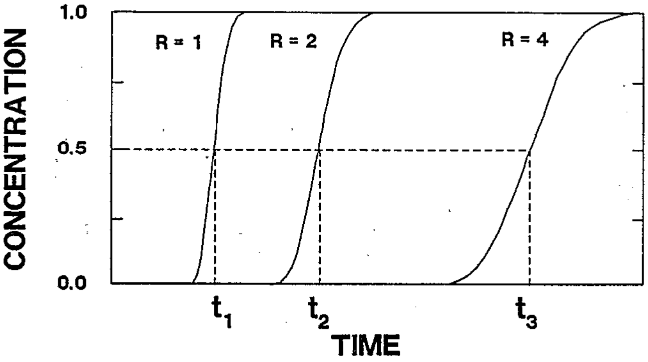


Figure 16. Time required for movement of contaminants at different retardation factors.

Contaminants with lower retardation factors are transported greater distances over a given time period than contaminants with larger retardation factors (Figure 17). A monitoring well network has a greater chance of encountering contaminants with low retardation factors simply because they occupy a greater volume of the aquifer. Thus, estimates of the total mass of a contaminant with a retardation factor of 1.0 may be more accurate than those for contaminants with greater amounts of retardation. Also, estimates of the time to remove nonreactive contaminants may, therefore, be more accurate than those time estimates for retarded contaminants. This is particularly important because the slow movement of retarded contaminants may control the time and cost necessary to completely remediate a site.

RETARDATION AND MONITORING

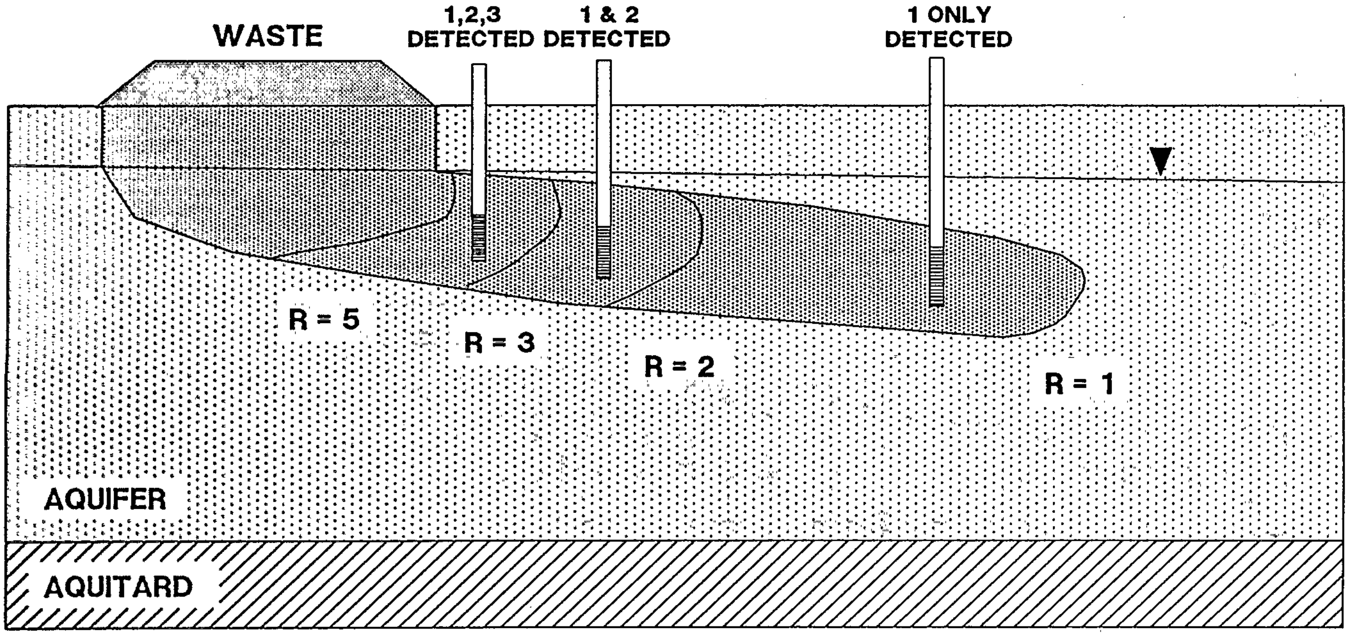


Figure 17. Transport of contaminants with lower retardation factors at a waste site.

Flow and Transport in the Vadose Zone

The vadose zone is that portion of the soil between the ground surface and the water table and includes the capillary fringe. More generally, the zone is defined as that region in which the pressure head is less than zero. Because it is part of the overall flow path, this zone can be very important to the transport of contaminants. Its length and the velocity of the contaminants passing through it, therefore, should be included in estimates of transport times.

The vadose zone often contains greater amounts of organic matter and metal oxides than the saturated zone. Contaminants can adsorb onto these materials, making their rate of movement substantially less than in the saturated zone. Further, materials adhering to these adsorbents can act as a source of contaminants to the saturated zone even after remediation. In addition, the activity of microorganisms in the vadose zone generally is considered to be much greater than below the water table. Finally, the unsaturated portion of the vadose zone can be a pathway for the transport of gases and volatile organics. These characteristics of the vadose zone can be important when predicting the transport of contaminants from a waste site and designing systems for remediation.

Transport of Water and Solutes

The flow of water through the vadose zone can be described by a differential equation that is analogous to the ground-water flow equation. The equation's one-dimensional form is:

$$\frac{\partial}{\partial z}\left(K(\psi)\,\frac{\partial \psi}{\partial z}\right) + \frac{\partial}{\partial z}\,[K(\psi)] = \Gamma(\psi)\,\frac{\partial \psi}{\partial t} \qquad (8)$$

where $K(\psi)$ is the hydraulic conductivity, $\Gamma(\psi)$ is the specific water capacity ($\partial\theta_w/\partial\psi$), θ_w is the volumetric water content, and ψ is the soil water pressure head. The key difference between this equation and the equation for one-dimensional ground-water flow is the dependence of the hydraulic conductivity on ψ and hence on θ_w. This makes Equation 8 nonlinear and more difficult to solve than the ground-water flow equation. If the hydraulic conductivity is constant and if the total head (h) is given as the sum of the pressure head and the elevation head (z), then Equation 8 simplifies to the one-dimensional ground-water flow equation.

The pressure head and the volumetric water content are related and often are plotted as a characteristic curve (Figure 18). If a saturated soil with zero pressure head is drained, ψ decreases while the volumetric water content remains constant and equal to the porosity of the soil. The volumetric water content is maintained at this level until sufficient negative pressure (the air entry value) is achieved to allow air to begin to enter the soil. At this point, the volumetric water content decreases in response to the decreasing pressure head. At low pressure head, the curve begins to level off and asymptotically approaches the residual water content of the soil.

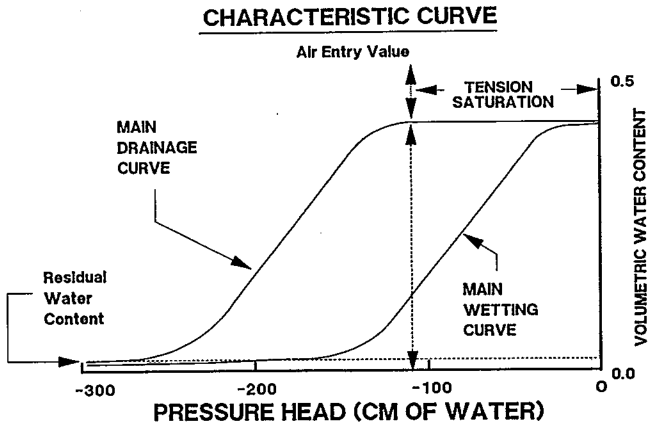


Figure 18 Volumetric water content versus pressure head.

If water is added to the drained soil, the plot of volumetric water content versus pressure head does not follow the main drainage curve described above but instead follows another path known as the main wetting curve. Thus, the relationship between pressure head and volumetric water content is not unique. If a soil is completely drained and then saturated again, the volumetric water content would initially plot along the main drainage curve and then along the main wetting curve. If the draining or wetting process is interrupted before the cycle is complete, the data plots between the two main curves along the primary scanning lines (Figure 19). If the wetting or drainage of the soil is reversed while the data is on the primary scanning lines, the data plots along yet a different path (secondary scanning lines). The dependence of volumetric water content (or any other soil property) at a given pressure head on the wetting and drying history of the soil is known as hysteresis.

If the hydraulic conductivity is a function of the pressure head, it also must be a function of the volumetric water content. For instance, the hydraulic conductivity of a soil may decrease by more than two orders of magnitude as the volumetric water content decreases from saturation to residual water content.

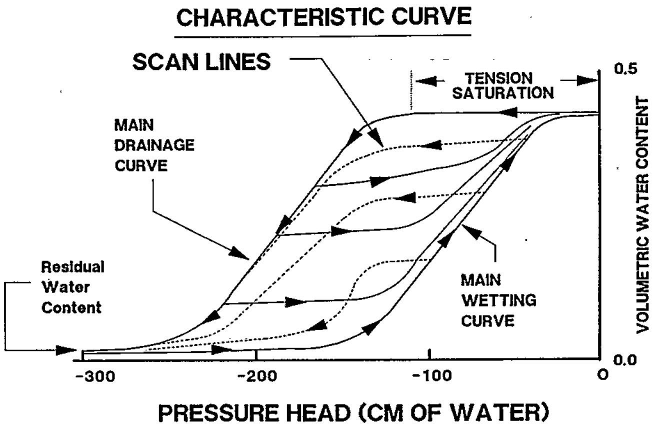


Figure 19. Volumetric water content versus pressure head showing primary scanning lines.

Solute transport in the vadose zone can be described by an advection-dispersion equation with an one-dimensional form of:

$$\frac{\partial}{\partial z}\left(\theta_w D \frac{\partial C}{\partial z}\right) - \frac{\partial (qC)}{\partial z} = \frac{\partial (\theta_w C)}{\partial t} \qquad (9)$$

where C is the solute concentration, D is the vadose zone dispersion coefficient, O_w is the volumetric water content, and q is the volumetric water flux. The dispersion coefficient has been assumed to be analogous to the dispersion term in the saturated zone:

$$D = D_o \tau + \alpha v(\theta_w) \qquad (10)$$

where $v(\theta_w)$ is the solute velocity and is equal to q/θ_w. Recent experiments by Bond (1986) demonstrate that Equation 10 is the correct form of the dispersion coefficient for transport in the vadose zone.

The application of Equations 9 and 10 to field situations is plagued by at least as many problems as those discussed earlier for Equation 2. Heterogeneity in the vadose zone may be the result of soil structure (aggregates) or macroscopic pores such as earthworm holes, decayed root channels, animal burrows, and fractures, all of which can substantially alter the flow of water and the transport of solutes through the vadose zone (White, 1985). Van Genuchten and Jury (1987) reviewed several modeling approaches being developed to investigate these situations.

Understanding the processes that control the movement of water and solutes in the vadose zone can provide insight into field observations of contaminant distributions and can be used to design storage facilities for wastes. Gillham (1984) used the general concepts of flow in the vadose zone to explain the role of the capillary fringe in the apparently disproportionate rise in shallow water tables with small amounts of recharge. Such water table changes help to explain stream-flow generation (Abdul and Gillham, 1984). Further, such a theory suggests that the characteristics of the capillary fringe and the vadose zone may contribute to the spreading of contaminants below the water table. Finally, Frind, et al. (1976) suggest that the differences in the unsaturated hydraulic conductivity between coarse- and fine-grained materials can be utilized in waste storage facilities.

Transport in the Gas Phase

Transport of gases and contaminants through the unsaturated zone can be an important consideration in certain field situations. Some organic contaminants are volatile and can partition from the liquid phase into the vapor phase. These vapors are transported through the unsaturated zone and eventually may diffuse into the atmosphere. The key physical processes that affect the transport of gases in the vadose zone are diffusion and advection, with diffusion playing the largest role. This is the result of the large diffusion coefficient for gases (10^{-5} m^2/s) compared to solutes (10^{-9} m^2/s). Many volatile organic chemicals have equilibrium concentrations that are high enough to increase the density of the vapor phase to 1.5 g/cm^3. This high density, in principal, should cause these vapors to sink to the capillary fringe. Cultural features, such as parking lots, streets, and foundations, can limit the exchange of gases with the atmosphere. The transport of volatile organics through the soil-gas phase also will be affected by the partitioning of the gas phase into the soil water, adsorption, and biodegradation (Johnson and Pankow, 1987).

There is an interest in using vapor monitoring wells to locate contaminant plumes in the saturated zone because these wells are much less expensive to install than standard ground-water monitoring wells. This concept is based on the premise that volatile organics within a contaminant plume located just below the water table will partition into the vapor phase in the overlying unsaturated zone where they then can be detected. In reality, the transport of volatile organics through the unsaturated zone is complicated by the chemical and physical processes discussed above and the general heterogeneous nature of soils. Vapors may be transported along high permeability layers to points distant from the ground-water source. Partitioning, adsorption, and biodegradation may reduce concentrations of contaminants in the vapor phase to levels that cannot be detected. Therefore, the use of vapor sampling to establish the existence of contaminant plumes in the subsurface is not always a reliable technology.

The volatility of certain organic contaminants can be exploited for the purpose of remediation. If there are residual solvents or petroleum products in the unsaturated zone, it is possible to remove the volatile fraction through vapor pumping. Wells are installed in the unsaturated zone and soil air extracted through a vacuum system. As the pressure drops and clean air passes through the soil, the organic contaminants partition into the vapor phase where they are then extracted by the vapor pumping well. The use of such systems is becoming more commonplace, and more efficient methods for their application are being developed.

In addition to volatile organic contaminants, the transport of the permanent gases, such as carbon dioxide and oxygen, also are of great interest. Oxygen can oxidize sulfide minerals (such as pyrite) to sulfuric acid, which can result in the degradation of ground-water quality. These problems can be particularly acute in disturbed lands where mining or construction has occurred. The presence of carbon dioxide also can alter ground-water quality by affecting mineral dissolution and the adsorption of metal ions. Both oxygen and carbon dioxide affect microbial activity and the rate of biodegradation in the vadose zone.

Contaminant Transport Through Fractured Media

The models for solute transport discussed up to this point only address porous media. While such models are applicable at sites located on recent alluvial deposits and glacial sediments, they are not necessarily appropriate when designing monitoring systems or planning remedial activities at waste sites on fractured rock.

Fractured rock has both primary and secondary porosity. Primary porosity is the pore space formed at the time of deposition and diagenesis of the rock mass. Secondary porosity is the pore space formed as a result of fracture of the rock.

As in porous media, the transport mechanisms in fractured media are advection and dispersion. In fractured rock, however, contaminants are advected only along the fractures. Dispersion phenomena within fractured rock is the result of: (1) mixing at fracture intersections; (2) variations in aperture across the width of the fracture; (3) variations in aperture width along stream lines; (4) molecular diffusion into microfractures penetrating the interfracture blocks; and (5) molecular diffusion into interfracture porous matrix blocks. Transport through fractured media can be described by one of four general types of models: continuum, discrete fracture, hybrid, and channel models.

In continuum models, the individual fractures are ignored and the entire medium is considered to behave as an equivalent porous medium. These models may be either single porosity or double porosity models. Single porosity models are applicable to fractured crystalline rocks such as granite and basalt where the only porosity of the rock mass is the fracture porosity. Double porosity models assume there is both primary porosity and secondary porosity. These models are applicable to media such as sandstones and shales.

Discrete fracture models attempt to describe flow and transport among individual fractures. These models require information about each fracture within the rock mass. The great difficulty of obtaining this information led to the development of stochastic models, which utilize information about the statistical distribution of fracture properties such as orientation and aperture widths.

Hybrid models are combinations of discrete fracture and continuum models. An example of this model is the "Multiple Interacting Continua" (MINC) model (Pruess and Narasimhan, 1985) in which transport takes place through a three-dimensional fracture network (the discrete portion) while diffusion into the interfracture rock matrix (the continuum) occurs.

Channel models (Tsang and Tsang, 1987) were developed from both laboratory (Witherspoon, et al., 1980) and field (Neretnieks, 1985) observations that the transport of solutes along fractures does not occur as a uniform front along the width of a fracture, but in many small fingers or channels. Such models are only now being investigated.

Studies of fractured rock often make use of the cubic law for the description of fluid flow and hydraulic conductivity. The hydraulic conductivity of a fracture, K_f, is:

$$K_f = (2b)^2 \rho g/(12\mu) \qquad (11)$$

where 2b is the fracture aperture, ρ is the density of the fluid, g is the acceleration of gravity, and μ is the dynamic viscosity of the fluid. The above equation can be modified for application in a continuum model:

$$K_m = (2b)^3 \rho g N/(12\mu B) \qquad (12)$$

where B is the thickness of the medium and N is the number of fractures through that thickness. An important consideration in the study of fractured rock is knowing when a fracture network can be considered to behave like an equivalent porous media. Numerical studies of single-porosity fracture networks suggest that such networks behave more like continua when: (1) fracture density is increased; (2) apertures are constant rather than statistically distributed; (3) the orientations of the fractures are statistically distributed rather than constant; and (4) larger sample sizes are tested (Long, et al., 1982).

Novakowski, et al. (1985) conducted a tracer test in a single fracture at about 100 m depth in gneiss at the Chalk River Nuclear Laboratories in Ontario, Canada. The fracture aperture of 510 μm obtained from their two-well tracer test does not agree well with the 60 μm aperture obtained from interference pumping tests. A survey of dispersivities in fissured rock obtained at various sites in Europe and in the United States reveals a range of four orders of magnitude (Neretnieks, 1985). Novakowski, et al. (1985) obtained a dispersivity of 1.4 m. Tracer tests at the Oracle, Arizona site are within the range from several tenths of a meter to a few meters (Cullen, et al., 1985). As in porous media, the dispersivity values obtained for fissured media become larger with increasing length of the flow path (Neretnieks, 1985).

Research into transport phenomena in fractured rock has been supported primarily by agencies interested in the potential for transport of radionuclides from high-level radioactive waste repositories. As a consequence, the bulk of the research performed has been of fractured crystalline rock such as granite. However, many hazardous waste sites are located on fractured sedimentary rocks such as sandstone and shale which have primary porosities of 5 to 25 percent in the rock matrix. Fractures increase the total porosity of these rocks and substantially increase their hydraulic conductivity, making them attractive for water supply aquifers. While contaminants are advected through these fracture systems, transport into and out of the porous matrix is primarily by molecular diffusion (Figure 20). This latter phenomena is much more important in fractured, porous rock than in fractured, crystalline rock.

Fractured, porous aquifers can be found throughout the conterminous United States. The 20 states with the greatest potential for ground-water contamination in fractured, porous media (FPM) are found primarily in the northeastern United States and around the Great Lakes (Figure 21). More than 1,500 Comprehensive Environmental Response and Liability Act (CERCLA) or Superfund sites located on

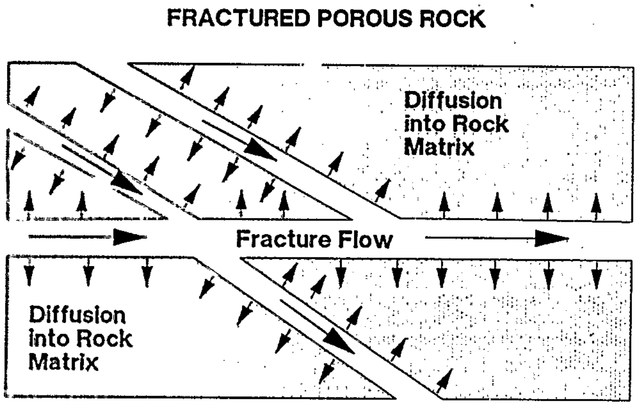


Figure 20. Transport in fractured porous rock.

FPM exist within these 20 states (Johnson and Pankow, 1987).

The use of porous media models can be appropriate in evaluating fractured, porous formations if the concentration of the contaminant can quickly reach equilibrium with the concentration found in the fracture (Pankow, et al., 1986). The rate of movement of a conservative tracer through such a fractured, porous aquifer (v_s) can be calculated from the rate of movement of the water through the fractures (v_f) by:

$$v_s = v_f/R_f \tag{13}$$

where R_f is a retardation factor that accounts for the loss of contaminant mass from the fracture to the matrix:

$$R_f = (b + nB')/b \tag{14}$$

where b is the half-width of the fracture and B' is the half-width of the matrix block.

These concepts have been applied to a site at Alkali Lake, Oregon, and at Bayview Park, Ontario (Pankow, et al., 1986). At Alkali Lake, the sediments are highly fractured, the matrix blocks are small (0.3 cm), and the matrix diffusion coefficient is 0.1 cm^2/day. In contrast, at Bayview Park, the matrix blocks are 5 to 35 cm and the matrix diffusion coefficients are only 0.0032 cm^2/day. At Alkali Lake, the concentrations in the matrix approach equilibrium with the concentrations in the fractures in

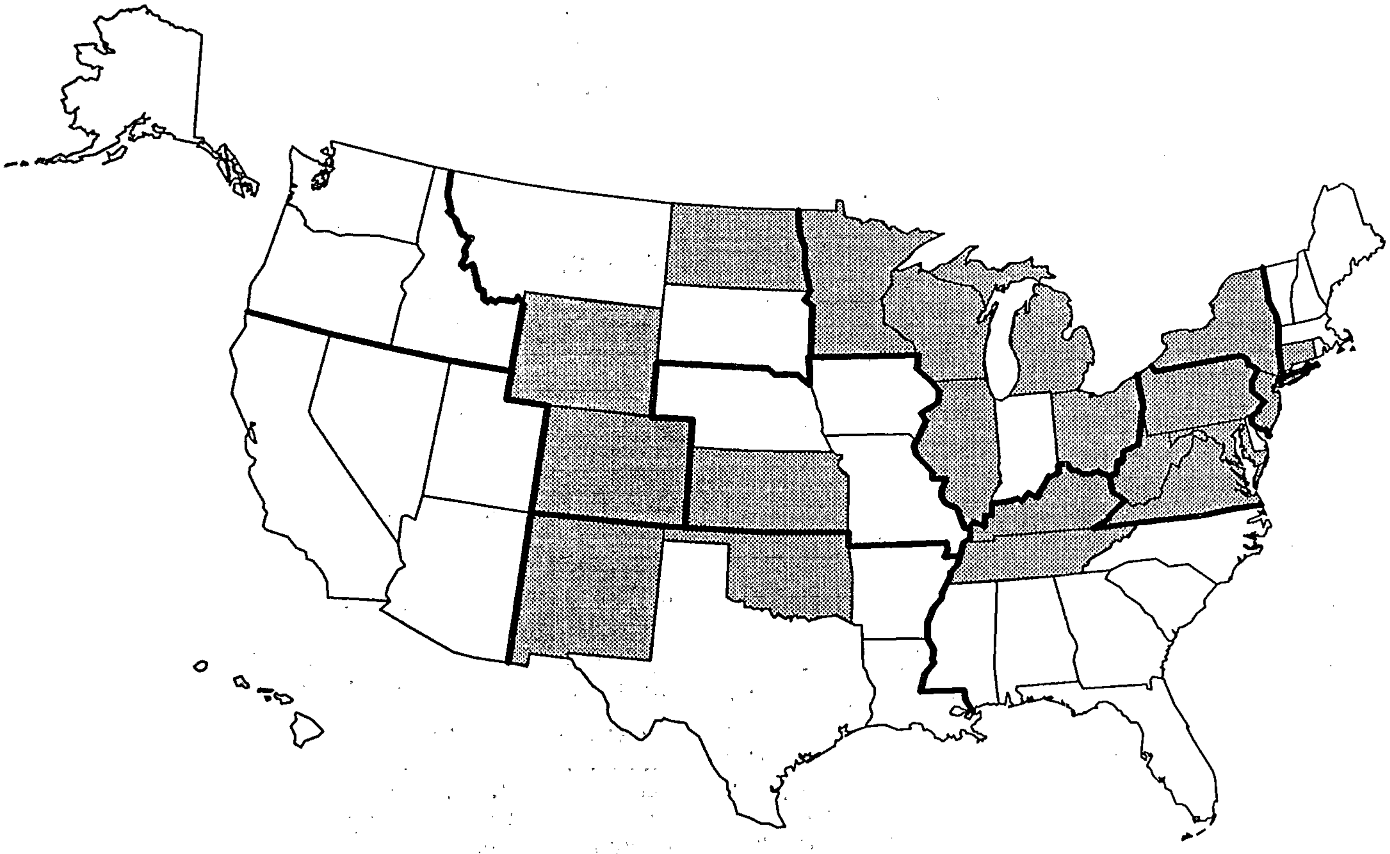


Figure 21. States with a high potential for ground-water contamination in fractured, porous rock (bold line outlines EPA Regions).

about 5 days, while more than 6,000 days are required at Bayview Park. As a result, the equivalent porous media model works well at Alkali Lake but not at Bayview Park. Thus, simple calculations of the time needed for the matrix block to reach equilibrium within the fracture can be used as a guide for the applicability of the equivalent porous media model for fractured, porous media.

Particle Transport Through Porous Media

So far, this chapter has only considered the transport of solutes through porous and fractured media. However, particles also may be of interest to contaminant hydrologists. The term "particle" can be used very broadly to include bacteria, viruses, inorganic precipitates, natural organic matter, asbestos fibers, or clay.

Particles can be removed from solution by three major processes: (1) surface filtration; (2) straining; and (3) physical-chemical processes (McDowell-Boyer, et al., 1986). Determining which of these processes is the most effective depends on the size of the particles (Figure 22). If the particles are larger than the largest pore diameters, they cannot penetrate into the porous medium and will be filtered at the surface of the medium. If the particles are smaller than the largest pores but larger than the smallest, the particles are transported into the porous medium along the larger pore channels. Eventually, the particles encounter a pore channel with a smaller diameter and are removed by straining. If the particles are smaller than the smallest pore openings, the particles can be transported great distances through the porous medium.

The rate at which the particles move through the porous medium depends on a variety of physicochemical processes. For example, the particles may undergo random collisions with sand grains. A certain percentage of such collisions result in particles adhering to the solid matrix (interception). Chemical conditions also may affect particle transport. For example, if the pH changes, aggregates may result due to changes in the particles' surface properties. These larger aggregates then can be strained or filtered from the water.

Microorganisms are particles that can be transported through geologic media. The movement of bacteria and viruses in the subsurface is a significant problem. More than 50,000 individuals in the United States suffered from waterborne disease between 1971 and 1979 (Craun, 1984) and about 45 percent of all reported cases involved ground-water sources. In addition, increasing interest in the use of microorganisms for *in situ* remediation of aquifers contaminated with organic chemicals necessitates a greater understanding of the transport and fate of microorganisms within the subsurface.

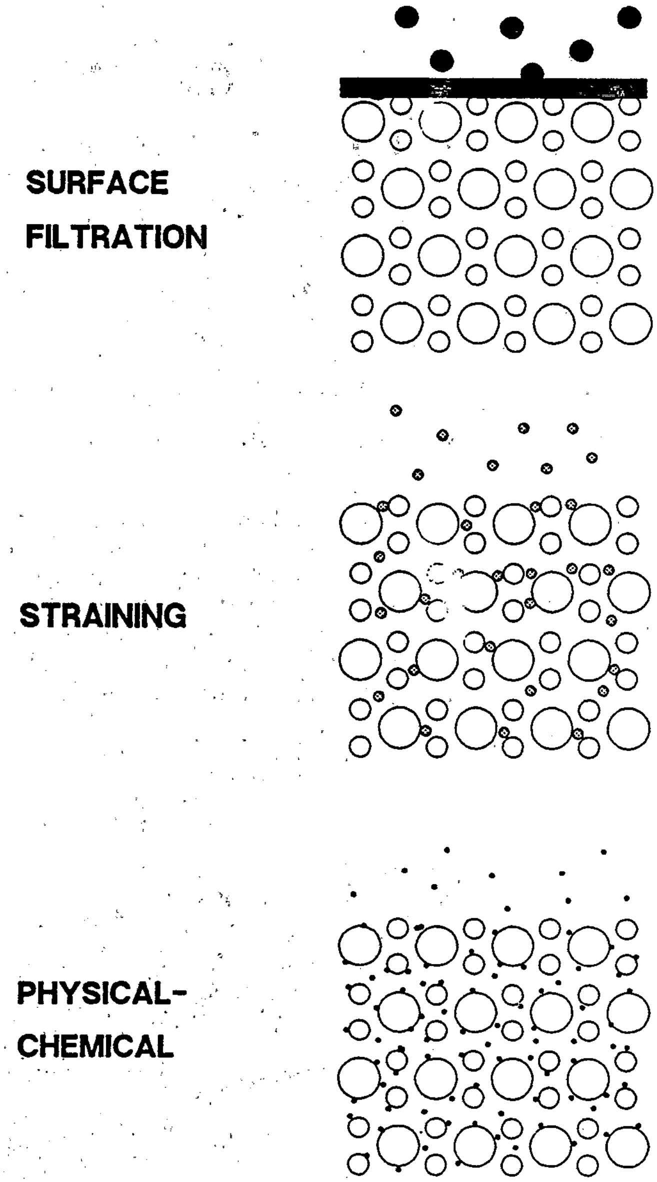


Figure 22. Filtration mechanisms.

There are many processes that limit the movement of microorganisms through geologic materials. Some bacteria are large enough to be strained from the water. In comparison, the smaller viruses can pass through the pores, but their surfaces are charged and, like charged ions, may undergo adsorption under the proper chemical conditions. Like molecules, microorganisms are transported by diffusion.

Some microorganisms are motile and move in response to changes in chemical concentrations. Like other living organisms, microbes grow and die, and the rates of these processes must be included in the description of the transport of microbes in the subsurface. All of these processes are reviewed in detail by Yates, et al. (1987) and Matthess and Pekdeger (1981).

Field tracer tests using baker's yeast (*Saccharomyces cerevisiae*) were conducted at a field site in Stanton, Texas (Wood and Ehrlich, 1978). The baker's yeast was injected into a sand and gravel aquifer containing clay lenses. In two separate tests where bromine and iodine (Br^- and I^-) ions were used as chemical tracers, the baker's yeast arrived at the monitoring well before the chemical tracers. Wood and Ehrlich (1978) explain these observations by suggesting that: (1) the chemical tracers were retarded because of their adsorption onto the aquifer material; and (2) the yeast traveled only through solution channels in caliche deposits within the aquifer while the chemical tracers flowed through both the solution channels and the intergranular pore structure. As the chemical tracer moves through the larger solution pores, it loses mass to the smaller pores by molecular diffusion, thereby retarding the rate of movement of the chemical front. The larger yeast particles have smaller diffusion coefficients and are excluded from the smaller pores. Without the mass loss to the adjacent pores, the yeast arrives more quickly at the observation well.

Champ and Schroeter (1988) used field tracer tests to show that non-reactive particle tracers and bacteria (*Escherichia coli*) can be rapidly transported through fractured, crystalline rock. Similar to the results of Wood and Ehrlich (1978), Champ and Schroeter (1988) observed that the *E. coli* arrived before the bromine tracer. Tracer experiments using native bacteria and different sizes and types of microspheres were conducted at a Cape Cod site in Massachusetts (Harvey, et al., 1987). The results indicate that both size and surface characteristics of particles affect their movement through the aquifer.

Field evidence of the transport of inorganic particles in the subsurface was obtained at the Otis Air Force Base site on Cape Cod in Massachusetts (Gschwend and Reynolds, 1987). Secondarily treated sewage containing phosphates was recharged to a sand and gravel aquifer through rapid infiltration beds over a 30-year period. Downgradient from the rapid infiltration beds, ground-water samples are found to contain 100 nm-diameter particles. These particles, composed of phosphate and iron, may be the mineral vivianite. The phosphate comes from the recharged water while the iron is derived from the dissolution of naturally existing iron within the aquifer.

Another example of particle transport exists at the Nevada Test Site where particle transport was identified as a mechanism for the movement of lanthanide and transition element isotopes from subsurface nuclear explosion cavities (Buddemeier, 1986).

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CHAPTER 3

PHYSICAL PROCESSES CONTROLLING THE TRANSPORT OF NON-AQUEOUS PHASE LIQUIDS IN THE SUBSURFACE

Carl D. Palmer and Richard L. Johnson

Introduction

Liquids that do not readily dissolve in water and can exist as a separate fluid phase are known as non-aqueous phase liquids (NAPLs). Generally, NAPLs are subdivided into two classes: those that are lighter than water (LNAPLs); and those with a density greater than water (DNAPLs). Most LNAPLs are hydrocarbon fuels such as gasoline, heating oil, kerosene, jet fuel, and aviation gas. Most DNAPLs are chlorinated hydrocarbons such as 1,1,1-trichloroethane, carbon tetrachloride, chlorophenols, chlorobenzenes, tetrachloroethylene, and PCBs.

Concern about NAPLs exists because of their persistence in the subsurface and their ability to contaminate large volumes of water. For example, 7 L (10 kg) of trichloroethylene (TCE) can contaminate 10^8 L of ground water at 100 ppb (Feenstra and Cherry, 1987). NAPLs are ubiquitous throughout North America and have been identified at 4 out of 5 hazardous waste sites in the United States (Plumb and Pitchford, 1985). Greater understanding of the transport and dissolution of NAPLs is necessary to implement cost-effective techniques for the cleanup of these contaminants.

Transport and Dissolution of NAPLs

As NAPLs move through geologic media, they can displace water and air. Because water is the wetting phase relative to both air and NAPLs, it tends to line the edges of the pores and cover the sand grains. The NAPL is the non-wetting phase and tends to move through the central portions of the pores. Neither the water nor the NAPL phase occupies the entire pore. Because of this, the permeability of the medium with respect to these fluids is different than when the pore space is entirely occupied by a given phase. This reduction in permeability depends on the medium and often is described in terms of relative permeability, k_{ri}, for phase i, which is defined as:

$$k_{ri} = k_i(S_i)/k_{si} \tag{1}$$

where S_i is the fraction of pore space occupied by phase i, $k_i(S_i)$ is the permeability of the medium to phase i at saturation S_i, and k_{si} is the permeability of the medium at complete saturation with phase i. Thus, the relative permeability varies from 1.0 at 100 percent saturation to 0.0 at 0 percent saturation.

A plot of relative permeability versus water saturation for a hypothetical medium (Figure 23) reveals some important features about multiphase flow. At 100 percent water saturation, the relative permeability of the water and the NAPL are 1.0 and 0.0, respectively. As the fraction of the pore space occupied by the NAPL (S_n) increases, a corresponding decrease occurs in the fraction of water within the pore space (S_w). As S_w decreases, the relative permeability with respect to the water phase decreases to zero. Zero relative permeability is not obtained at zero S_w, but at the irreducible water saturation (S_{rw}). At this water saturation, the water phase is effectively immobile and there is no significant flow of water. These concepts are similar to those discussed for unsaturated flow in Chapter 2. The relative permeability of the NAPL behaves in a similar manner. At 100 percent NAPL saturation, the relative permeability for the NAPL is equal to 1.0, but as the NAPL saturation decreases, so does the relative permeability. At the residual NAPL saturation (S_{rn}), the relative permeability for the

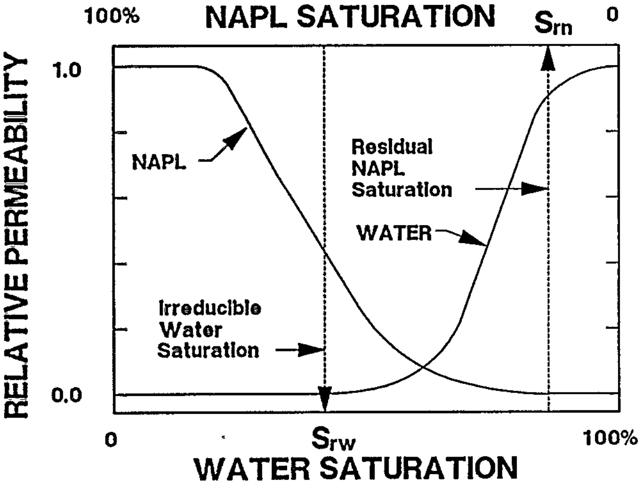

Figure 23. **Relative permeability as a function of saturation.**

NAPL is effectively zero and the NAPL is considered to be immobile.

These immobile fractions of NAPL cause great concern because they cannot be easily removed from the pores except by simple dissolution by flowing ground water. An example of this could be a cubic meter of soil with a 35 percent porosity and containing TCE at a 20 percent residual saturation. This situation implies that there is 0.07 m^3 or 103 kg of TCE within the soil. If the solubility of the TCE is 1,100 mg/L and if ground water flows through the soil at a rate of 1.7 cm/day, it would take 15.4 years for the TCE to be removed by dissolution. If the contaminated aquifer is twice as long (2 m), 30.8 years are necessary. If a NAPL with a lower solubility than TCE is spilled, the rate of mass removal is lower, requiring even more time for dissolution. Thus, NAPLs that enter the subsurface can remain for decades and can contaminate large volumes of ground water. Some of the key aspects of NAPL dissolution are considered in more detail in Chapter 6.

Understanding how an NAPL moves within a porous aquifer can be useful. The movement of petroleum products in the subsurface is described in detail by Schwille (1967), and the movement of DNAPLs is examined closely by Schwille (1988), Feenstra and Cherry (1987), Kueper and McWorter (1988), and Anderson (1988).

Light Non-Aqueous Phase Liquids (LNAPLs)

As a spilled LNAPL enters the unsaturated zone, it flows through the central portion of the unsaturated pores. If the amount of product released is small, the product flows until residual saturation is reached (Figure 24A). Therefore, a three-phase system consisting of water, product, and air is created within the vadose zone. Infiltrating water dissolves the components within the LNAPL (e.g., benzene, toluene, and xylene) and carries them to the water table. These dissolved constituents then form a contaminant plume emanating from the area of the residual product. Many of the components commonly found in LNAPLs are volatile and, as a consequence, can partition into the soil air and be transported by molecular diffusion to other portions of the aquifer. As these vapors diffuse into adjacent soil areas, they partition back into the water phase and spread contamination over a wider area. If the surface is not covered with an impermeable material, these vapors diffuse across the surface boundary and into the atmosphere. However, if a relatively impermeable boundary covers the area, no mass transfer occurs with the atmosphere and the concentrations of contaminants in the soil atmosphere may build up to equilibrium concentrations.

If large volumes of product are spilled (Figure 24B), the product flows through the pore space to the top of the capillary fringe. The dissolved components of the infiltrating product precede the product and may change the wetting properties of the water, causing a reduction in the residual water content and collapse of the capillary fringe.

The LNAPL product is lighter than water and tends to float on top of the capillary fringe. As the head created by the infiltrating product increases, the water table is depressed and the product begins to accumulate in the depression. If the source of the spilled product is then turned off, the LNAPL within the vadose zone continues to flow under the influence of gravity until reaching residual saturation. As this drained product continues to recharge the product pool, it spreads laterally on the top of the capillary fringe (Figure 24C). The draining of the upper portions of the vadose zone also reduces the total head at the interface between the product and the ground water, causing the water table to rebound slightly. The rebounding water can only displace a portion of the product because the latter remains at residual saturation. Ground water passing through this area of residual saturation dissolves the components within the residual product, creating a contaminant plume. Water infiltrating from the surface also can dissolve the residual product and vapors within the vadose zone, thereby contributing to the overall contaminant load to the aquifer.

If the water table drops because of seasonal variations or pumping, the pool of product also drops. If the water table rises again, part of the product is pushed upward, but a portion remains at residual saturation below the new water table. Thus, variations in the water table can spread the product

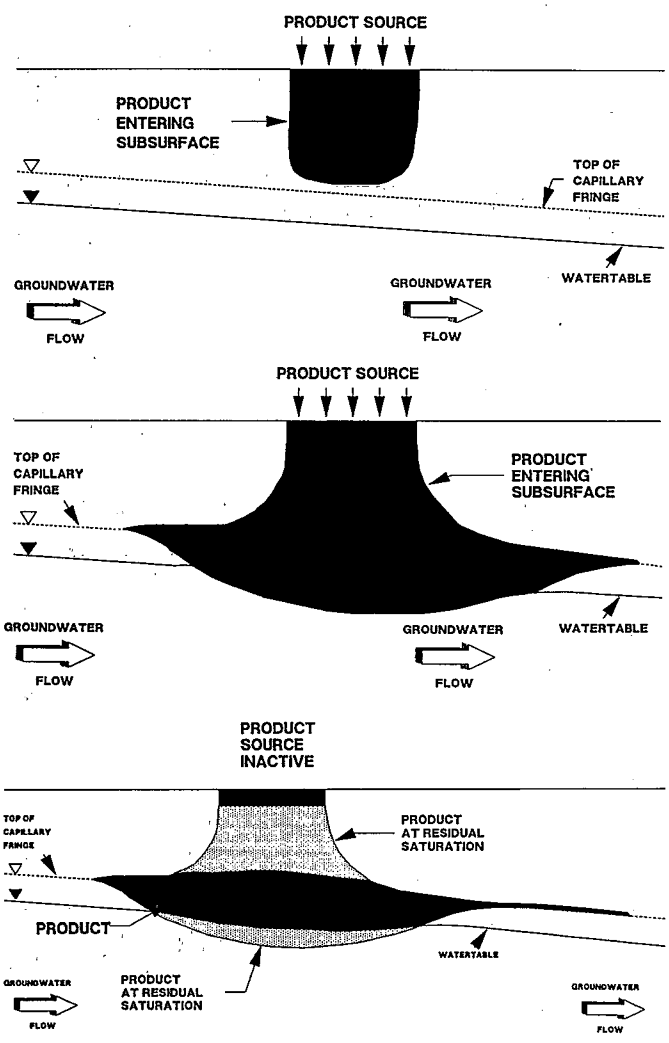

Figure 24. **Movement of LNAPLS into the subsurface: (a) distribution of LNAPL after small volume has been spilled; (b) depression of the capillary fringe and water table; (c) rebounding of the water-table as LNAPL drains from overlying pore space.**

over a greater thickness of the aquifer, causing increased volumes of soil to be contaminated. Cleanup methods for LNAPLs in the subsurface should take this principle into account and avoid moving the product into uncontaminated areas where more product can be held at residual saturation.

Dense Non-Aqueous Phase Liquids (DNAPLs)

DNAPLs can have great mobility in the subsurface as a result of their relatively low solubility, high density, and low viscosity. The sparingly soluble DNAPLs do not readily mix with water and therefore remain as separate phases. The relatively high density of these liquids provides a driving force that can carry product deep into aquifers. The combination of this high density and low viscosity is particularly important with regard to the transport of DNAPLs in the subsurface. When a high density, low viscosity fluid (DNAPL) displaces a lower density, higher viscosity fluid (water), the flow is "unstable" and viscous fingering occurs (Saffman and Taylor, 1958; Homsy, 1987; Chouke, et al., 1959; Kueper and Frind, 1988).

During a spill (Figure 25A), DNAPL flows through the unsaturated zone under the influence of gravity toward the water table. If only a small amount of DNAPL is spilled, it flows until reaching residual saturation in the vadose zone. If there is water within the unsaturated zone, the DNAPL exhibits viscous fingering during infiltration. No viscous fingering is observed if the vadose zone is dry. The DNAPL can partition into the vapor phase and these dense vapors may sink to the capillary fringe. Infiltrating water can dissolve the residual DNAPL or the vapors and transport these contaminants to the water table, creating a dissolved chemical plume within the aquifer.

If a greater amount of DNAPL is spilled (Figure 25B), the DNAPL flows until it reaches the capillary fringe and, once there, begins to penetrate into the aquifer. However, to do this, the DNAPL must displace the water by overcoming the capillary forces between the water and the medium. The critical height of DNAPL required to overcome these capillary forces (z_c) can be calculated from:

$$z_c = 2\gamma \cos(\theta)(1/r_t - 1/r_p)/(\Delta\rho\, g) \qquad (2)$$

where γ is the interfacial tension between the water and the DNAPL, θ is the contact angle between the fluid boundary and the solid surface, r_t is the radius of the pore throat, r_p is the radius of the pore, $\Delta\rho$ is the difference in the density between the water and the DNAPL, and g is the acceleration of gravity (Villaume, et al., 1983). As an example, calculated critical heights required for perchloroethylene to penetrate saturated porous media of different grain size range from a few centimeters for coarse grains to tens of meters for clays (Table 2). Thus, unfractured, saturated clays and silts can be effective barriers to the migration of DNAPLs, provided the critical heights are not exceeded.

After penetrating the aquifer, the DNAPL continues to move through the saturated zone until it reaches residual saturation. The DNAPL then is dissolved by ground water passing through the contaminated area, resulting in a contaminant plume that can extend over a great thickness of the aquifer. If finer-grained strata are contained within the aquifer, the

Table 2. Critical Height for Perchloroethylene to Penetrate Water Saturated Media (Anderson, 1988).

Material	Diameter	Critical Height (cm)[1]
Coarse Sand	1.0	13
Fine Sand	0.1	130
Silt	0.01	1,300
Clay	0.001	13,000

[1] Calculated for $\Delta\rho = 0.62$ g/cm^3.
$\gamma = 47.5$ dynes/cm, $\cos\theta = 1$.

infiltrating DNAPL accumulates on top of the material, creating a pool. At the interface between the ground water and the DNAPL pool, the solvent dissolves into the water and spreads vertically by molecular diffusion. As water flows by the DNAPL pool, the concentration of the contaminants with the ground water increases until saturation is achieved or the downgradient edge of the pool is reached. The relative density of pools and fingers of DNAPL within the aquifer is important when controlling the measured concentrations of dissolved contaminants derived from DNAPLs. The existence of fingers and pools of the DNAPL, rather than relatively continuous distributions, in the subsurface accounts for the observation that the concentration of many of the DNAPL compounds in ground water are far below their saturation limit (Anderson, 1988).

If even larger amounts of DNAPL are spilled (Figure 25C), the DNAPL can, in principle, penetrate to the bottom of the aquifer, forming pools in depressions. If the impermeable boundary is sloping, the DNAPL flows down the dip of the boundary. This direction can be upgradient from the original spill area if the impermeable boundary slopes in that direction. The DNAPL also can flow along bedrock troughs, which may be oriented differently from the general direction of ground-water flow. This flow along low permeability boundaries can spread contamination in directions that would not be predicted on the basis of hydraulics.

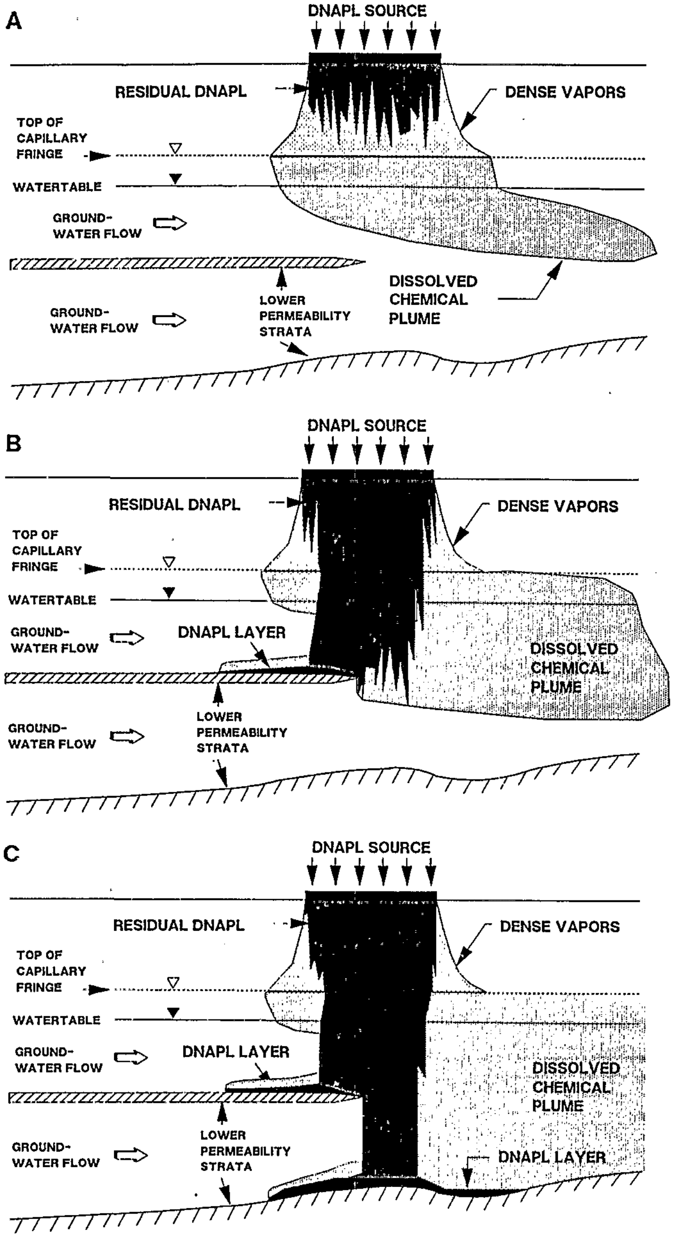

Figure 25. **Movement of DNAPLs into the subsurface: (a) distribution of DNAPL after small volume has been spilled; (b) distribution of DNAPL after moderate volume has been spilled; (c) distribution of DNAPL after large volume has been spilled (After Feenstra and Cherry, 1988).**

The transport of DNAPLs in physical models of fractures illustrates the importance of fracture aperture and roughness. Schwille (1988) found that if fracture apertures are greater than 0.2 to 0.5 mm, the DNAPL moves directly to the capillary fringe where it spreads out. Eventually the DNAPL penetrates the capillary fringe and is transported to the bottom of the aquifer. There is very little residual DNAPL for fractures larger than 0.2 mm. If the fracture aperture is less than 0.2 mm and is smooth, the DNAPL spreads out near the surface and a few fingers migrate down to the capillary fringe. At the capillary fringe, the DNAPL spreads out further and a few relatively wide fingers penetrate below the capillary fringe. If the fracture is rough, there is a great amount of fingering and the DNAPL penetrates below the capillary fringe in small, scattered fingers. Thus, for fractures with apertures less than 0.2 mm, there can be a large volume of DNAPL that remains at residual saturation in the fractures both above and below the capillary fringe. While similar behavior is expected to occur in fractured rock, the statistical distribution of fracture aperture and fracture roughness may preclude the use of such a simple categorization based on the mean apertures.

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CHAPTER 4

DETERMINATION OF PHYSICAL TRANSPORT PARAMETERS

Carl D. Palmer and Richard L. Johnson

Introduction

The models used for the simulation and prediction of contaminant transport in the subsurface are only as good as the data input used in those models. The range of important variables for contaminant transport are tabulated (Mercer, et al., 1982), but ultimately site-specific values must be obtained. Hydrogeological parameters such as hydraulic conductivity, porosity, bulk density, ground-water flux, and dispersion are important for modeling; methods for determining these parameters are discussed below.

Both laboratory and field methods are useful for determining hydrogeological parameters. Although parameters measured in the laboratory are applicable in small-scale situations, they may not be representative of the bulk properties of the formation. Still, if many such measurements are taken, not only can the average, larger scale properties of the formation be estimated, but other important statistical properties also can be calculated. For example, Sudicky (1986) applied such techniques to determine the mean and variance of the saturated hydraulic conductivity of the Borden aquifer in order to calculate the macroscopic scale dispersivity.

Field methods represent an increase in the scale of measurement relative to most laboratory methods. This increase does not mean that such methods are inherently better than laboratory methods, but simply that the field-measured variables represent average properties over a larger volume. The key advantage of field methods is the potential for measuring less disturbed materials, thereby giving more accurate representations of the relevant parameters. The disadvantage to using such methods is that during the data analysis, ideal models are applied to non-ideal media. To reduce this discrepancy, field and laboratory methods should be developed or modified to complement one another.

Hydraulic Conductivity

Hydraulic conductivity can be measured both in the laboratory and the field. Laboratory methods include estimation from grain-size analysis, permeameter tests, and soils-engineering tests. Slug tests, aquifer tests, and flow net analyses are field methods that provide increasing scales of measurement.

Laboratory Methods

Hydraulic conductivity, K, can be estimated from grain-size distribution curves using either the Hazen method (Freeze and Cherry, 1979) or the Masch and Denny method (1966). Sieve, pipet, hydrometer, and settling tube methods can be used to analyze grain size, and light scattering techniques have been developed to look at micron- and submicron-sized particles. Sample preparation and methods for particle-size analysis are described in detail by Gee and Bauder (1986). In addition to its use for estimating hydraulic conductivity, grain-size analysis can be used to properly size filter packs and screens for monitoring, extraction, and injection wells (Driscoll, 1986).

Saturated hydraulic conductivity is measured with either constant-head or falling-head permeameter tests. Constant-head tests are useful for measuring hydraulic conductivity in the range of 10^0 to 10^{-5}

cm/s. Falling-head tests work best over a range of 10^{-3} to 10^{-7} cm/s. Undisturbed samples used in permeameter tests offer the best results. If the soil structure is disturbed, errors can be minimized by repacking the soil to its original bulk density.

Soils-engineering tests in consolidometers and triaxial cells provide coefficients of compressibility and consolidation of soils. These properties are related to the hydrogeologic parameters of hydraulic conductivity, K, and specific storage, S_s (Jorgensen, 1980). Parameters K and S_s for fine-grained materials have been successfully calculated from the coefficients of compressibility and consolidation (Desaulniers, et al., 1981; Paul, 1987). In fractured tills, these calculated values of K and S_s represent values for the matrix.

Unsaturated hydraulic conductivity can be measured using steady-state head control methods, steady-state flux control methods, non-steady state methods, or sorptivity methods. Details of methods for both saturated and unsaturated media are provided by Klute and Dirksen (1986). Empirical models for predicting unsaturated hydraulic conductivity as a function of water content or pressure head are described by Mualem (1986).

Field Methods

Slug tests are the most common method for obtaining hydraulic conductivity in the field. These tests are conducted by instantaneously changing the hydraulic head within a well and measuring its return to the static level. Different types of slug tests include: (1) falling head; (2) rising head; (3) bail; and (4) pressure/packer.

In a falling-head test, the water level is instantaneously increased by adding a slug of water, or, preferably, some displacing volume of material such as a metal rod. The head is then measured as it falls back to its static level. In a rising head test, a volume (e.g., a metal rod) is removed from the well, causing the water level to instantaneously drop. The rising hydraulic head is then measured over a time interval.

A bail test is a type of rising head test where the water is removed using a bailer. This technique is suitable in low-permeability material where the time needed to remove the water is short relative to the overall time needed for recovery in the well. In a pressure/packer test, an interval of the well is isolated by packers and a pressure pulse is applied to that area. The decay of the pressure pulse can be measured with a pressure transducer and the data interpreted in the same manner as the other test methods. In principle, these data are used to calculate the hydraulic conductivity and the specific storage of the geologic material.

Several techniques used for analyzing slug test data are described by Hvorslev (1951), Bouwer and Rice (1976), Cooper, et al. (1967), and Nguyen and Pinder (1984). Both the Hvorslev (1951) and the Bouwer and Rice (1976) methods are based on steady-state flow equations. If the specific storage of the medium is small, these techniques can provide a good estimate of the hydraulic conductivity. In theory, the relative recovery in the well should plot as a linear function of time for both of these methods. The slope of this recovery-time curve is used to calculate hydraulic conductivity. If the formation has a non-zero specific storage, a curve rather than a straight line is obtained and application of steady-state equations results in over-estimation of the hydraulic conductivity.

The Cooper, et al. (1967) and the Nguyen and Pinder (1984) methods are based on transient ground-water flow equations and, therefore, better represent the physical conditions within the soil. The Cooper, et al. (1967) method assumes that the well fully penetrates the aquifer while the Nguyen and Pinder (1984) method accounts for partial penetration of the well. The Cooper, et al. (1967) method is a curve-fitting technique and is not very sensitive to the value of the specific storage. The Nguyen and Pinder (1984) model is the most general and, in principle, should be the best technique for interpreting slug test data. Instead of being a curve-fitting technique, the model uses the slopes of two different plots to calculate the specific storage and the hydraulic conductivity.

Many factors contribute to errors in the calculation of hydraulic conductivity from slug test data (Table 3). Most of these factors affect the estimation of hydraulic conductivity by a factor of 2 or 3. An important exception is when a low-permeability skin forms at the well-bore interface. Under these circumstances, order of magnitude errors can result (Palmer and Paul, 1987; Faust and Mercer, 1984). In addition, simulated recovery data from wells that have low permeability skins of finite thickness at the well-bore interface can produce straighter lines on a Hvorslev plot than simulated data for ideal wells without a skin. Because of this, a straight-line Hvorslev plot is not necessarily a valid criterion for a "good" slug test.

Aquifer tests can provide larger scale information about hydraulic properties than laboratory methods or slug tests, and can be used to determine hydraulic conductivity, specific storage, leakage, aquitard diffusivity, anisotropy, and the general location of boundaries. Also, aquifer tests can be constant rate, variable rate, or constant head. Many different types

Table 3. Potential Sources of Error in Slug Tests (Palmer and Paul, 1987)

- Bridging of Seals
- Leaky Joints
- Formation of Low Permeability Skins
- Entrapped Air
- Presence of Fractures
- Stress Release Around Borehole
- Partial Penetration of Well
- Anisotropy of Formation
- Varying Regional Potentiometric Surface
- Boundary Conditions
- Sand Pack Effects
- Uncertainty in Initial Head
- Radius of Influence of Test
- Thermal Expansion

of methods are used to analyze aquifer test data and the choice of method depends on the conditions under which the data were collected (steady-state flow or non-steady-state flow) and the type of aquifer (confined, unconfined, or semi-confined). Methods for analyzing aquifer test data can be found in Kruseman and de Ridder (1970), Walton (1962, 1970, and 1984), Lohman (1972), and Hantush (1964).

The classic test method of Theis (1935) can be used for confined aquifers. However, this method is limited to fully penetrating wells in isotropic media. If the wells partially penetrate the aquifer, a variety of methods by Hantush (1964) can be used. These methods also can be applied to leaky aquifers. If monitoring wells are installed in the aquitard, then the ratio method (Neuman and Witherspoon, 1972) is useful for obtaining the hydraulic diffusivity of the aquitard.

Investigators have long debated the nature of "delayed yield" observed in aquifer tests conducted in unconfined aquifers (Neuman, 1972 and 1979). The methodology presented by Neuman (1975) has a stronger physical basis than other methods and accounts for anisotropy and partial penetration. Neuman's (1975) method is highly recommended for use in unconfined aquifers.

Although the methods described above for analyzing aquifer test data were derived for porous media, they also can be applied to aquifer tests conducted in fractured rock if the aquifer behaves like a single porosity medium. However, such fractured media are often highly anisotropic, and the methods by Weeks (1969) or by Way and McKee (1982) may be more appropriate in these situations.

If the test is conducted in a fractured, porous aquifer, then the double porosity methods by Barenblatt, et al. (1960) or by Boulton and Streltsova (1977) may be applied. Determining whether an aquifer is a single or double porosity system can be accomplished using a simple method (Gringarten, 1984), where a plot of $\partial s/\partial\,[\ln(t)]$ versus t is made on log-log paper (Figure 26). In a single porosity aquifer, the plot should increase to a maxima, then decrease and become constant. In a double porosity aquifer, the plot should go through a maxima, and then decrease and pass through a minima before finally becoming constant.

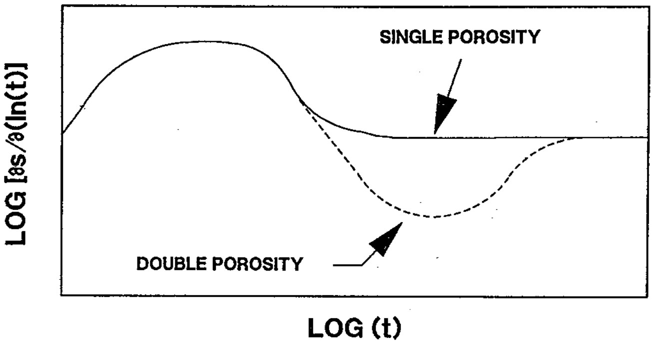

Figure 26. Differentiating double porosity media from single porosity media (after Gringarten, 1984).

Flow-net analysis can provide a larger scale estimate of hydraulic conductivity than aquifer tests. While regional scale values may not be directly applicable to a specific site, they may prove useful in regional scale models to define local boundary conditions. Methods of flow-net analysis are described in Freeze and Cherry (1979) and Cedergren (1967).

Unsaturated hydraulic conductivity can be measured in the field using either steady-state or non-steady-state flux methods. Such techniques are described in detail by Green, et al. (1986).

Bulk Density, Porosity, and Volumetric Water Content

Bulk density, porosity, and volumetric water content also are required for transport models. Porosity is necessary to estimate the ground-water velocity from the Darcy flux while both the porosity and the bulk density are needed to calculate a retardation factor from a partition coefficient (see Chapter 5). The volumetric water content is required to estimate water and contaminant movement through the vadose zone. Laboratory techniques exist for measuring these parameters (Danielson and Sutherland, 1986; Blake and Hartage, 1986; Gardner, 1986). Field methods used to estimate these parameters include neutron logs for porosity and water content, gamma-gamma logs for bulk density, and electrical capacitance for water content. In addition, the porosity can be calculated from the average linear velocity, v, and the ground-water flux, q, by q/v.

Ground-Water Flux and Average Linear Velocity

Potentiometric Surface Data

The most common method for estimating the magnitude and direction of ground-water flux is with potentiometric surface data and hydraulic conductivity. The direction of ground-water flow in isotropic media is downgradient orthogonal to the equipotential lines. The flux rate, q, can be calculated directly from Darcy's equation and the product of hydraulic conductivity and gradient. If the porosity, θ_t, is known, the average linear velocity, v, is calculated as the ratio, q/θ_t. If the aquifer is anisotropic, the flow lines and the equipotentials are not orthogonal and the direction of flow must be estimated from flow nets constructed in the transformed section or through use of the inverse hydraulic-conductivity ellipse (e.g., Freeze and Cherry, 1979).

Borehole Dilution

Borehole dilution is a relatively simple technique to determine the magnitude and, in principle, the direction of ground-water flow. In a borehole dilution test, an interval within a well is isolated with packers and a tracer is injected and continuously mixed. During the test, ground water enters the well bore and dilutes the tracer. The rate at which the tracer is diluted within the well bore is a measure of the rate of ground-water flow. The relationship between the concentration and ground-water flux is:

$$\ln\left[\frac{(C - C')}{(C_0 - C')}\right] = -\frac{A\beta q}{W}(t - t_0) \qquad (1)$$

where C' is the background concentration, C_0 is the concentration in the injected slug, A is the cross-sectional area of the borehole, W is the volume in the isolated section of the borehole, and q is the ground-water flux. The β parameter accounts for the convergence of flow lines on the open borehole and is often called the borehole factor. This convergence of flow lines results in a greater flux through the borehole than through the aquifer. For an ideally installed well with no sandpack and with the screen permeability much greater than the formation, β has a value of 2.0. Methods for estimating β are discussed by Drost, et al. (1968) and by Halvely, et al. (1966).

According to Equation 1, a plot of the logarithm of relative concentration versus time should produce a straight line with a slope of - Aβq/W. Thus, if A, β, and W are known, the ground-water flux, q, can be calculated. Experiments conducted in a sandbox by McLinn and Palmer (1988) show that the logarithm of relative concentration versus time is linear and that the flux rates calculated from the borehole dilution test agree with the measured flux values (Figure 27).

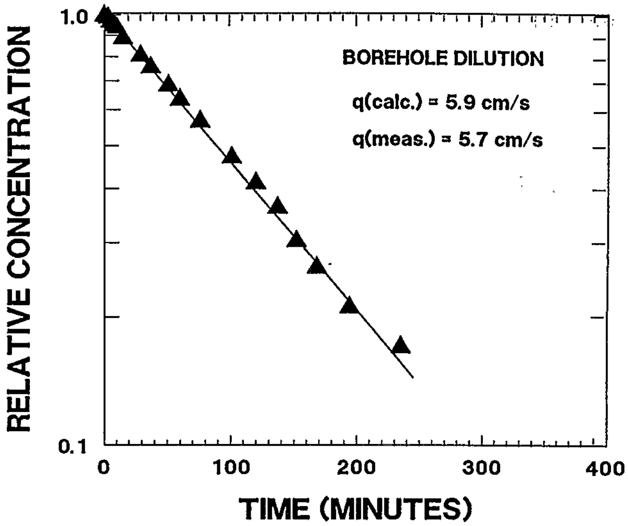

Figure 27. Results of borehole dilution test illustrating linear relationship between the logarithm of relative concentration and time.

There are several different types of borehole dilution devices. For example, early investigators used radioisotopes with scintillation counters (Halvely, et al., 1966), as well as specific ion electrodes (Grisak, et al., 1977) and specific conductance electrodes (Bellanger, 1985). Currently, a thermal device is commercially available (Kerfoot and Skinner, 1980; and Kerfoot, 1982), and an electrical resistivity device has been developed (McLinn and Palmer, 1988). One key advantage of borehole dilution is its potential to profile the distribution of velocities along the length of the well screen. Under appropriate conditions, therefore, the device can be used to discern velocity variations within the aquifer and to describe aquifer heterogeneity.

Seepage Meters

Seepage meters can be an extremely useful tool for measuring fluid flux at the ground-water/surface-water interface (Lee, 1977; Lee and Cherry, 1978).

The seepage meter consists of an inverted section of a 55-gallon drum with a hole in the top that is covered with a plastic bag (Figure 28). After a measured period of time (Δt), the bag is removed and the volume of water collected, V, is measured. The flux of ground water through the sediments and into the surface water is simply $V/(A\Delta t)$ where A is the area of the drum. If a mini-piezometer is used in conjunction with the seepage meter, the hydraulic gradient between the sediments and the surface water can be calculated. If the hydraulic gradient and the flux rate are known, a simple calculation using Darcy's equation yields the hydraulic conductivity of the sediments. The seepage meter works best in materials that are not easily compressed; if the sediments are compressed during installation, the hydraulic conductivity will be underestimated.

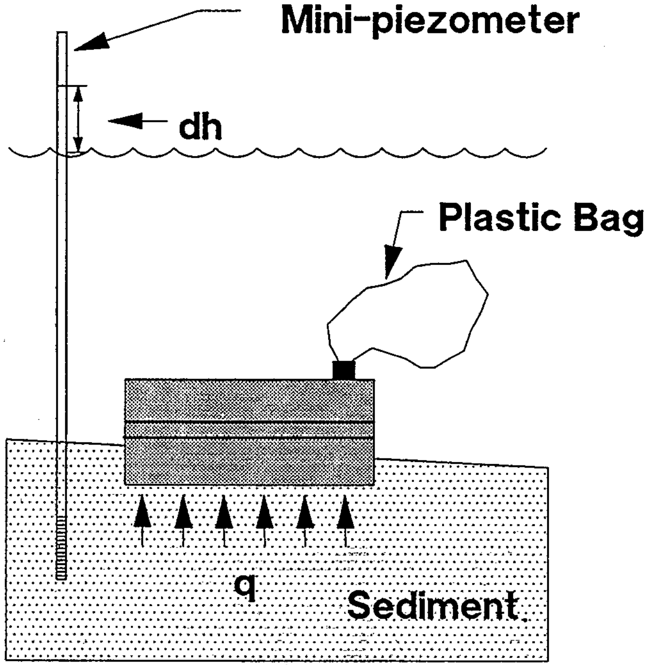

Figure 28. Seepage meter.

Dispersion Coefficient and Aquifer Heterogeneity

Tracer Tests

Tracer tests have been used to study physical, chemical, and biological processes in the subsurface. Physical parameters such as dispersion, average linear velocity, porosity, and variation in hydraulic conductivity have been obtained from tracer tests. The tracer tests by Sudicky, et al. (1983) and Sutton and Barker (1985) show that ground-water velocity can vary substantially over small scales. In their experiments, small slugs of contaminants broke into discrete parts that moved at different velocities. Also, Sudicky, et al. (1983) and Freyberg (1986) used tracer tests to describe how the apparent dispersivity value increases with the scale of the problem. Pickens and Grisak (1981) were able to demonstrate that when the concentration breakthrough curves obtained with point samplers are analyzed, the dispersivity parameter is small (0.007 m). In addition, Palmer and Nadon (1986) and Taylor, et al. (1988) suggest that electrical resistivity can be coupled with the execution of single-well injection tracer tests to obtain information about variation in hydraulic conductivity.

Tracer tests can be conducted in several ways. Natural-gradient tracer tests are commonly used for research purposes. In these tests, a slug of tracer is injected into an aquifer and traced as it moves along with the natural hydraulic gradient. Such tests were used by Sudicky, et al. (1983), Sutton and Barker (1985), and MacKay, et al. (1986).

Forced-gradient tracer experiments involve the injection of a tracer over a prolonged period of time and measurement of the arrival of the tracer at one or more monitoring wells during the injection period. Forced-gradient wells may be either single-well or double-well tests. In single-well tests, only one "active" well is used for injecting and withdrawing the tracer. The fluid is injected into the aquifer and monitored at one or more sampling wells at some radius from the active well (Figure 29). Two-well tests (Figure 30) use two active wells, one to inject the tracer and the other for withdrawal. These types of forced gradient tests were used by Pickens and Grisak (1981), Molz, et al. (1986), Palmer and Nadon (1986), and Taylor, et al. (1988).

Experiments by Molz, et al. (1986) demonstrate that tracer tests can be applied as an engineering tool and numerical models can be used to predict the transport of solutes in the subsurface. Molz, et al. (1986) initially conducted a single-well tracer test in a confined aquifer to measure the variation in hydraulic conductivity over the thickness of the aquifer. These tests were on a scale of approximately 5.5 m. A two-well tracer test with travel distances of 38 to 90 m was also conducted. Using the hydraulic conductivity distribution for the single-well test, the concentration-versus-time curve of a pumping well in a two-well test could be reasonably simulated without recourse to model calibration (Figure 31). Two models were used: (1) a three-dimensional advection-dispersion model using small dispersivity values; and (2) an advection model. The results of the two models are indistinguishable. If the aquifer is assumed to be homogeneous and the concentrations

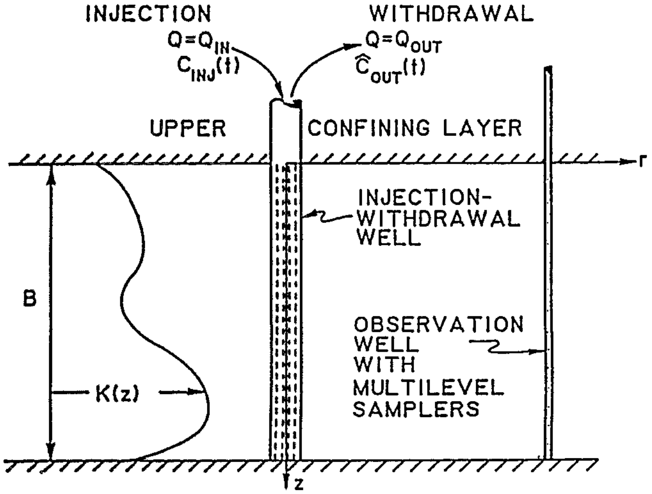

Figure 29. Vertical cross-section showing single-well test geometry (Molz, et al., 1986).

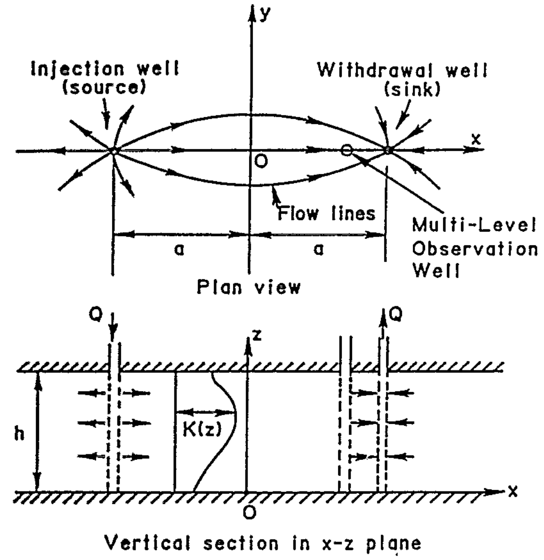

Figure 30. Two-well test geometry in a stratified aquifer (Molz, et al., 1986).

in the pumping well are calculated using average hydraulic properties, poor replication of the experimental data is obtained (Figure 32). These results emphasize the importance of heterogeneity and advection to the transport of solute through porous media.

Geophysical Techniques

While geophysical techniques are recognized as useful tools in characterizing waste sites, a detailed discussion of geophysical techniques is beyond the scope of this chapter. Surface geophysical techniques used include gravity, infrared imagery, ground-penetrating radar, induced electrical polarization, resistivity, magnetometer, reflection seismics, and electromagnetic surveys. Borehole methods include geothermetry, electrical methods, acoustic methods, and nuclear logging techniques. Surface geophysical techniques such as resistivity, conductivity, seismic refraction, and VLF can be useful in identifying lithology changes in the subsurface, depth to water table, and depth to bedrock. Ground-penetrating radar, electromagnetic methods (EM), and resistivity are effective in locating buried drums and containers. Borehole geophysical techniques are used to estimate hydraulic conductivity (resistivity), lithology (natural gamma), bulk density (gamma-gamma), and porosity (neutron). Discussions of these topics can be found in Keys and MacCary (1971), Benson, et al. (1983), and Rehm, et al. (1985). As described in the discussion of tracer tests, borehole resistivity logs can be coupled with tracer tests to obtain information about subsurface heterogeneity (Taylor, et al., 1988; Palmer and Nadon, 1986).

Plume Detection

Ground-Water Monitoring

The most common method for detecting contaminant plumes in the subsurface is by direct sampling of the subsurface fluid. However, the common practice of "plume chasing" may not be the most efficient method for determining the extent of ground-water contamination (Dowden and Johnson, 1988). Greater use of hydrogeologic data can greatly improve the design of ground-water monitoring systems and the quality of information provided.

Although ground-water monitoring networks can provide the greatest certainty about the extent of contamination, there are important factors that control the quality of this information, including the amount of well purging done prior to sampling (Barcelona and Helfrich, 1986), the method of sampling (Stolzenburg and Nichols, 1985), and the method of well construction and installation (Keely and Boateng, 1987). Methods for ground-water sampling are discussed in detail by Scalf, et al. (1981), Ford, et al. (1984), and Barcelona, et al. (1985).

Geophysical Techniques

Geophysical methods can be used to locate contaminant plumes with high dissolved solids. For example, surface resistivity methods have been successful at some sites (e.g., Stollar and Roux, 1975; Kelly, 1976; Rogers and Kean, 1980), and electromagnetic methods are useful for obtaining some estimate of water quality changes in the subsurface

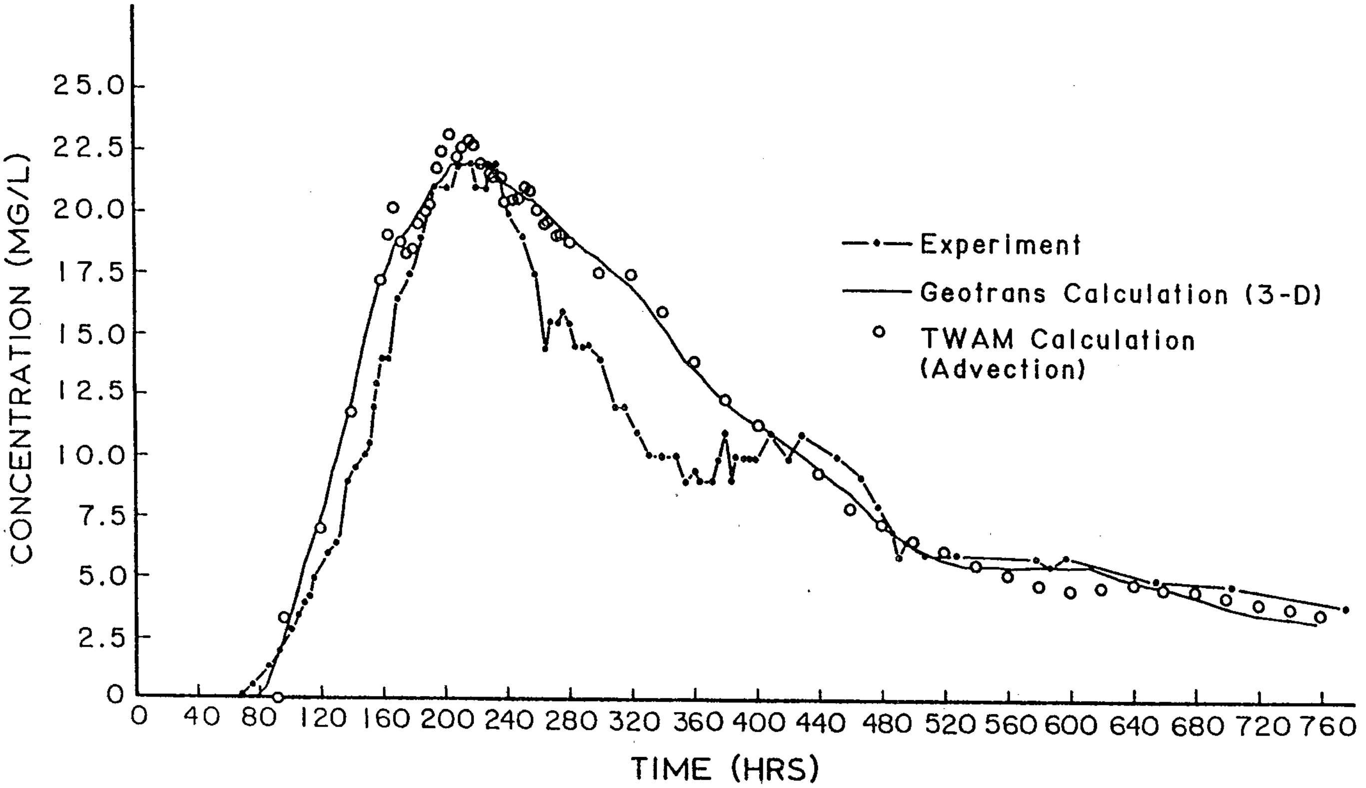

Figure 31. **Comparison of predicted and modeled concentrations in the pumping well of a two-well tracer test (Molz, et al., 1986).**

(Stewart, 1982; Slaine and Greenhouse, 1982; Glaccum, et al., 1982; Ludwig, 1983). The borehole counterparts to these surface geophysical methods should work equally as well in determining variations in water quality over the thickness of the aquifer. Detailed discussions of these methods and their limitations can be found in Keys and MacCary (1971), Benson, et al. (1983) and Rehm, et al. (1985).

Chemical Time-Series Sampling Tests

Chemical time-series sampling tests are conducted by repeatedly sampling wells that are continuously pumped (Keely, 1982). The concentration data can then be plotted as a function of time, volume removed, or an equivalent radius from the well bore. The particular shape of the curve obtained from such a test varies according to the distribution of contaminants in the subsurface. Some suggested interpretations are provided in Figure 33. Data from the time-series test have been used to determine the proper amount of well purging that should be performed before collecting water samples at the site, and to identify the source of a contaminant entering a water-supply well (Keely and Wolf, 1983). While there is no unique interpretation of the resultant curve, its general shape can provide information that must be reconciled with hypotheses concerning the distribution of contaminants near the well bore.

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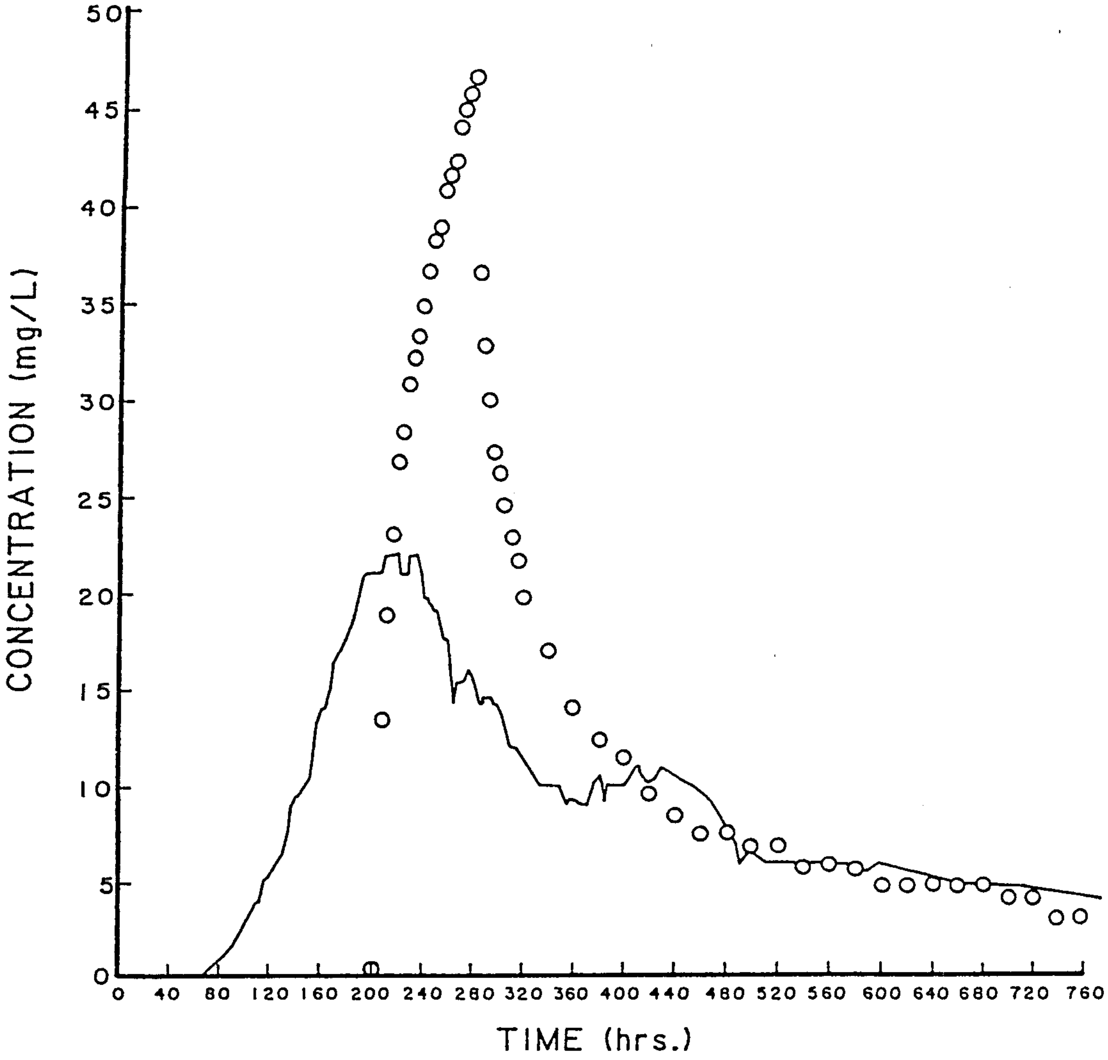

Figure 32. Comparison of predicted and modeled concentrations in the pumping well of two-well tracer test assuming a homogeneous aquifer (Molz, et al., 1986).

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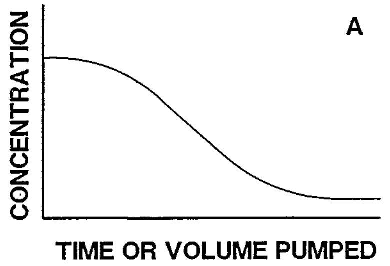

Figure 33A. Hypothetical curve obtained from chemical times-series sampling test. (The results may be interpreted as data from a monitoring well placed at the edge of a plume where the concentrations are reduced due to increasing amounts of uncontaminated water entering the borehole.) (After Keely, 1982).

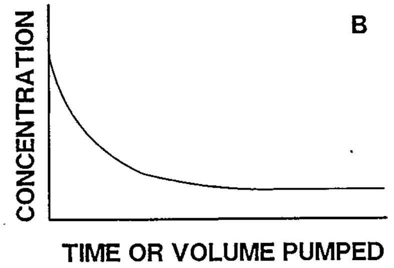

Figure 33B. Hypothetical curve obtained from chemical times-series sampling test. (The results may be interpreted as data from a monitoring well that may have been contaminated during drilling or installation. The concentrations rapidly decrease as uncontaminated water from the aquifer enters the well bore.) (After Keely, 1982).

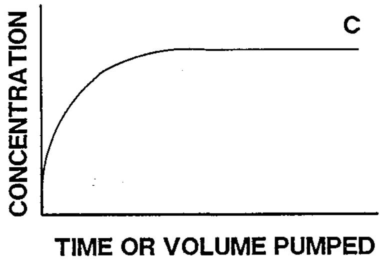

Figure 33C. Hypothetical curve obtained from chemical times-series sampling test. (The results may be interpreted as data from a monitoring well in which chemical reactions have reduced concentrations in the stagnant water column. When pumping is started, contaminated ground water from the aquifer enters the well and contaminant concentrations rapidly increase.) (After Keely, 1982).

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CHAPTER 5

SUBSURFACE CHEMICAL PROCESSES

Richard L. Johnson, Carl D. Palmer, and William Fish

Introduction

Risk assessment and remediation of ground-water contamination require an understanding of how chemicals move through and interact with the subsurface environment. However, subsurface transport of contaminants is often controlled by complex interactions between chemical, physical and biological processes. This means that mathematical models often must be used to predict chemical movement. Models for ground-water systems are frequently based on the advection-dispersion equation described in Chapter 2 and shown here in one-dimensional form:

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (1)$$

This equation requires *quantitative* information to simulate all subsurface processes. In the context of the advection-dispersion equation, chemical processes important in controlling contaminant transport and fate usually take the form of reaction terms (RXN) added to the basic equation:

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \pm \mathrm{RXN} \qquad (2)$$

This chapter will discuss the chemical processes that affect the movement of organic and inorganic contaminants in ground-water systems and how those processes can be represented in the advection-dispersion equation. Methods and limitations of experimental data for modeling chemical processes also will be examined.

Reactions of Organic Compounds

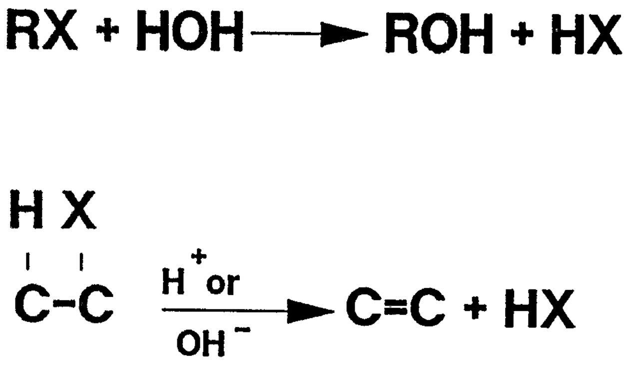
Hundreds of thousands of organic chemicals are currently used in industrial and domestic applications in the United States. These chemicals represent an extremely broad range of physical and chemical properties and are subject to different physical, chemical, and biological processes in the subsurface. For example, because chlorinated solvents are only slightly soluble and are more dense than water, they can penetrate deep into aquifers and remain as an immiscible phase for prolonged periods of time. In contrast, a spill of acetone will not penetrate into the ground water because of its low density. Also, because of its miscibility with water, the acetone will dissolve quickly and become available for further chemical and biological reactions.

Organic reactions may transform one compound into another, change the state of a compound, or cause a compound to combine with other organic or inorganic chemicals. In the context of the advection-dispersion equation, these reactions represent changes in the distribution of mass within the elementary volume through which the movement of the chemicals is modeled. Although, many of these reactions have been studied in the laboratory and observed in the field, there is a lack of good quantitative information about the processes under complex, real-world conditions.

Chemical reactions in the subsurface are frequently characterized on a kinetic basis as equilibrium or zero- or first-order, depending upon how the rate is affected by the concentrations of the reactants. For example, a zero-order reaction is one that proceeds at a rate independent of the concentration of the reactant(s). In a first-order process, the rate of the reaction is directly dependent on the concentration of one of the reactants. In many cases, grouping a chemical process into one of these classes over-simplifies the actual process. However, more realistic, higher-order processes often are difficult to measure and/or model in complex environmental systems. The following example of hydrolysis illustrates some of the difficulties in obtaining quantitative kinetic information and applying it to the advection- dispersion equation.

Hydrolysis

Hydrolysis is the direct reaction of dissolved compounds with water molecules, and can be an important abiotic degradation process in ground-water systems (Mabey and Mill, 1978). For example, hydrolysis of chlorinated hydrocarbons is significant because many chlorinated compounds are not readily degraded by reactions such as biodegradation (Siegrist and McCarty, 1987). This hydrolysis of chlorinated compounds often yields an alcohol or an alkene (Figure 34).



$$RX + HOH \longrightarrow ROH + HX$$

$$\overset{H}{\underset{|}{}}\overset{X}{\underset{|}{}} \qquad C{-}C \xrightarrow[OH^-]{H^+ \text{ or}} C{=}C + HX$$

Figure 34. Schematic hydrolysis reactions for halo-carbons.

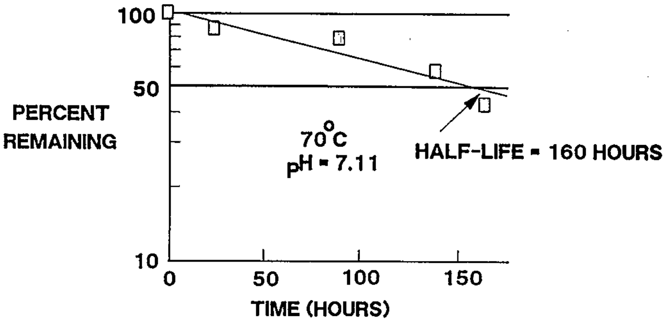


Figure 35. Hydrolysis data for 1,2,4-trichlorobenzene (adapted from Ellington, et al., 1986).

$$\frac{dC}{dt} = -KC$$

$$\ln\left[\frac{C}{C(0)}\right] = -Kt$$

$$\text{at the half-life:} \quad \left[\frac{C}{C(0)}\right] = 0.5$$

$$t = 160 \text{ hours}$$

$$\text{thus, } K = 0.69/160$$

$$\boxed{K = 4.3 \times 10^{-3} \text{ hr}^{-1}}$$

Figure 36. Calculation of the first-order hydrolysis rate constant for the degradation of 1,2,4-trichlorobenzene.

Hydrolysis rates are typically difficult to measure in the field due to other competing reactions and slow degradation rates, and as a result, most hydrolysis data come from laboratory studies. Even in the laboratory, conditions must be optimized to minimize other reactions and provide good quantitative data. For example, data in Figure 35 (Ellington, et al., 1986) for the hydrolysis of 1,2,4-trichlorobenzene were collected at 70°C to speed the reaction and eliminate competing microbial degradation. The data then were fitted as a first-order reaction, which assumes a straight line on a semi-log plot, even though the data suggest some higher-order effects. From these data, the hydrolysis rate constant (K) at the elevated temperatures was estimated (Figure 36). The extrapolation of K at ambient temperatures from this data could potentially result in additional error.

After estimating K, the behavior of a specific compound can be modeled using a form of the advection-dispersion equation that includes a first-order degradation term:

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + KC \qquad (3)$$

Although first-order reactions are not always the most realistic, they are easy to incorporate into transport models. Hydrolysis and other chemical process data on the EPA priority pollutants can be found in Mabey, et al. (1982).

Sorption

Of all the chemical processes discussed in this chapter, sorption is probably the most important and the most studied. In ground-water applications, sorption of non-polar organics often can be treated as an equilibrium-partitioning process between the aqueous phase and the porous medium (Chiou, et al., 1979). When solute concentrations are low (e.g., either $\leq 10^{-5}$ Molar, or less than half the solubility, whichever is lower), partitioning often is described using a linear Freundlich isotherm (Karickhoff, et al. 1979; Karickhoff, 1984):

$$S = K_p C \quad (4)$$

where S is the sorbed concentration (mg/g), C is the aqueous concentration (mg/mL), and K_p is the partition coefficient. K_p typically is measured in the laboratory using batch equilibrium tests, and the data are plotted as the concentration in the aqueous phase versus the amount sorbed onto the solid phase (Figure 37) (Chiou, et al., 1979). Under conditions of linear equilibrium partitioning, the sorption process can be represented in the advection-dispersion equation as a "retardation factor," R:

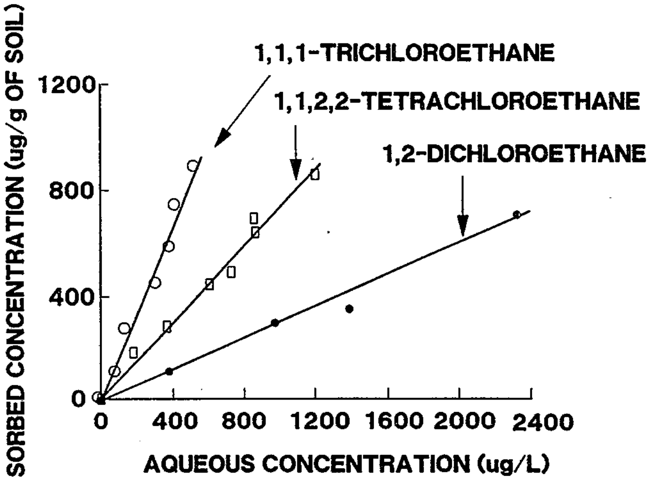


Figure 37. Batch equilibrium data for 1,1,1-TCA, 1,1,2,2-TeCA and 1,2-DCA (adapted from Chiou, et al., 1979).

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \quad (5a)$$

where

$$R = 1 + \frac{\rho_b K_p}{\theta_t} \quad (5b)$$

and ρ_b = soil bulk density (g/cm^3) and θ_t = porosity.

The dominant mechanism of organic sorption is the hydrophobic bond between a chemical and natural organic matter associated with aquifers (Karickhoff, et al., 1979; 1984; Tanford, 1973; MacKay and Powers, 1987; Chiou, et al., 1985). The extent of sorption can be reasonably estimated if the organic carbon content of the soil is known (Figure 38) (Karickhoff, et al., 1979; Karickhoff, 1984) by using the expression:

$$K_p = K_{oc} f_{oc} \quad (6)$$

where f_{oc} is the fraction organic carbon content of the soil and K_{oc} is a proportionality constant characteristic of the specific chemical. This approach works reasonably well for a wide range of soils, providing the soil organic content is sufficiently high (e.g., $f_{oc} > 0.001$). For lower carbon-content soils, sorption of the neutral organics onto the mineral phase can cause important errors in the estimate of K_p (Chiou, et al, 1985). Still, the K_{oc} relationship allows estimations of sorption-based retardation developed from measured f_{oc} values, rather than the more expensive batch equilibrium tests.

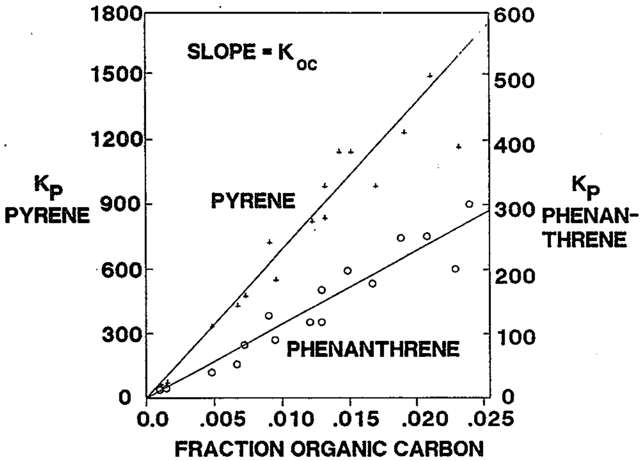


Figure 38. Sorption of pyrene and phenanthrene on various soils as a function of soil f_{oc} (after Karickhoff, 1981).

K_{oc} values for many compounds are unknown. Because of this, numerous researchers have developed correlation equations to relate K_{oc} to more commonly available chemical properties, such as solubility or octanol-water partition coefficient (Chiou, et al., 1982 and 1983; Schwarzenbach and Westall, 1981; Karickhoff, 1981; Kenaga and Goring,

1980) (Figures 39 and 40). Some of these correlations cover a broad range of compounds, in which case the errors associated with the K_{oc} estimates can be large. However, within a compound class, K_{oc} values derived using these expressions often provide reasonable estimates of sorption.

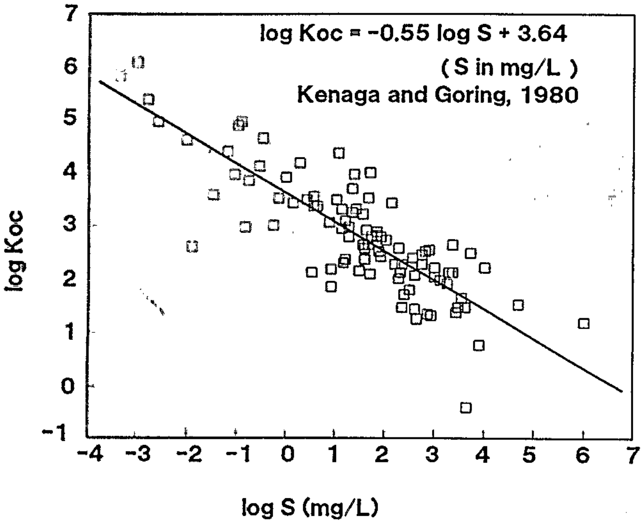


Figure 39. Correlation of K_{oc} and solubility data (adapted from Kenaga and Goring, 1980).

Regression Equations

$\log K_{oc} = -0.55 \log S + 3.64$

$\log K_{oc} = 0.544 \log K_{ow} + 1.377$

$\log K_{oc} = 0.681 \log BCF + 1.963$

Figure 40. Regression equations for K_{oc} versus solubility (S in mg/L), octanol/water partition coefficient (K_{ow}), and bioconcentration factor (BCF) (after Kenaga and Goring, 1980).

Unfortunately, the linear equilibrium approach to sorption is not adequate for some real-world situations. For example, trichloroethylene (TCE) sorption onto a glacial till shows a change in K_p of more than 50-fold over the parts per billion range (Figure 41) (Johnson, et al., 1989; Myrand, et al., 1989; McKay and Trudell, 1987). In addition, for many very hydrophobic organics, adsorption and desorption occur over time scales of many months (Figure 42) (Karickhoff and Morris, 1985; Witkowski, et al., 1988; Coates and Elzerman, 1986; Wu and Gschwend, 1986). The importance of non-ideal sorption will be discussed again in Chapter 6.

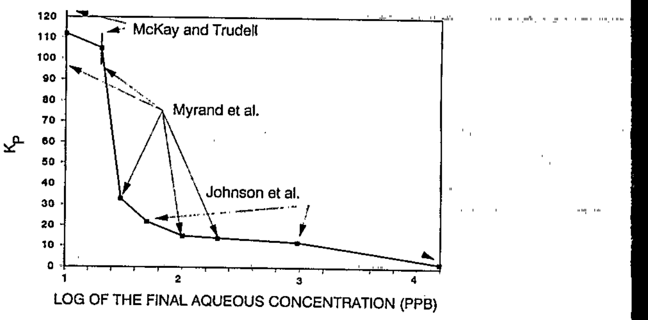


Figure 41. TCE sorption on a glacial till from near Sarnia, Ontario (after McKay and Trudell, 1987; Myrand, et al. 1989; Johnson, et al., 1989).

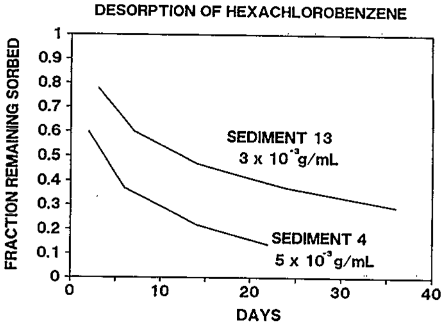


Figure 42. Desorption of hexachlorobenzene from two sediments (after Karickhoff and Morris, 1985).

Field data or field-scale experiments also can provide good measures of sorption-based retardation. Field data have the advantages of operating on more realistic scales, time frames, and conditions than those typically reproduced in the laboratory. For example, data on chlorophenol transport collected downgradient from a hazardous chemical disposal site at Alkali Lake, Oregon (Figure 43) (Johnson, et al., 1985), demonstrate compound-specific retardation that can be explained by equilibrium-partitioning sorption. Also, numerous large-scale tracer experiments were conducted in recent years to demonstrate and quantify certain physical and chemical processes (Figure 44) (LeBlanc, et al., 1987; MacKay, et al., 1986; Barker, et al., 1987; Molz, et al., 1986). However, field data are often expensive, as well as difficult and time-consuming to gather.

Cosolvation and Ionization

Cosolvation and ionization are processes that can decrease sorption and, therefore, increase transport velocity. Cosolvents decrease the entropic forces that favor sorption of hydrophobic organics by increasing the interactions between the solute and the solvent (Nkedi-Kizza, et al., 1985; Zachara, et al., 1988). The thermodynamic basis for the cosolvation effect was described by Rao, et al. (1985), and Woodburn, et al. (1986). For many of the more hydrophobic priority pollutants, the presence of biologically derived or anthropogenic compounds in the range of 20 percent by volume or greater can increase the solubility of those pollutants by an order of magnitude or more. As seen in Figure 45, this results in a log-linear decrease in sorption that inversely parallels changes in the solubility of the solute in the mixed solvent system (Nkedi-Kizza, et al., 1985). The data for three soils in Figure 45 clearly show that the cosolvent concentration must be large in order for the solute velocity to be substantially increased. For this reason, cosolvation is important primarily near sources of ground-water contamination.

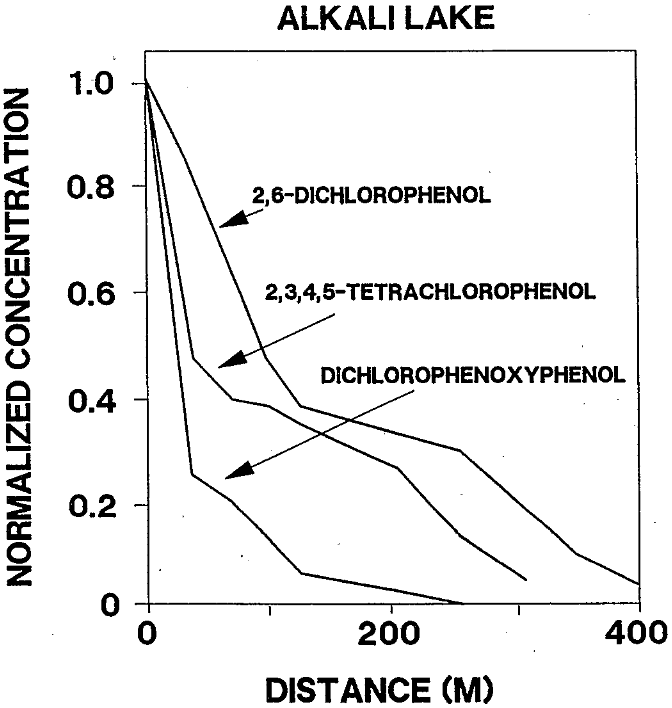


Figure 43. Chlorophenol distributions downgradient of the chemical disposal site at Alkali Lake, Oregon (adapted from Johnson, et al., 1985).

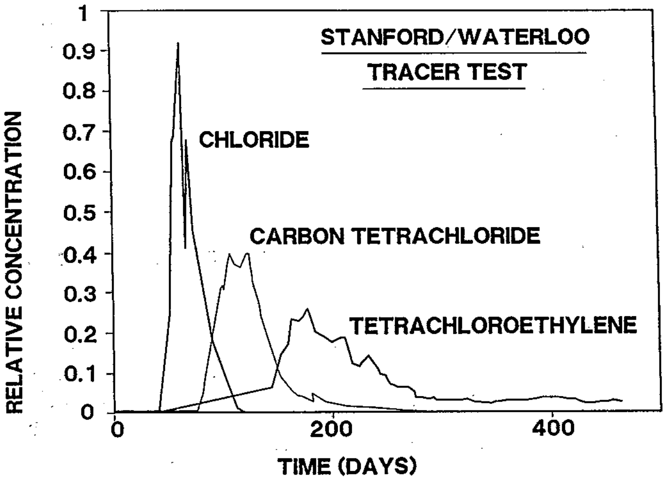


Figure 44. Tracer distribution data from the Stanford/Waterloo tracer experiment (adapted from Mackay, et al., 1986).

Acidic compounds, such as phenols or organic acids, can lose a proton in solution to form anions (Figure 46) that, due to their charge, tend to be very water soluble (Zachara, et al., 1986). Thus, the K_{oc} of a compound like 2,4,5-trichlorophenol can decrease from 2,330 for the phenol, to near zero for the phenolate (Figure 47). Acidic compounds tend to ionize more as the pH increases. However, for many compounds like the chlorophenols, substantial ionization can occur at neutral pHs. Positively charged organic ions also can be present in ground-water systems. Zachara, et al. (1986) and Ainsworth, et al. (1987) demonstrated that in low-carbon soils and

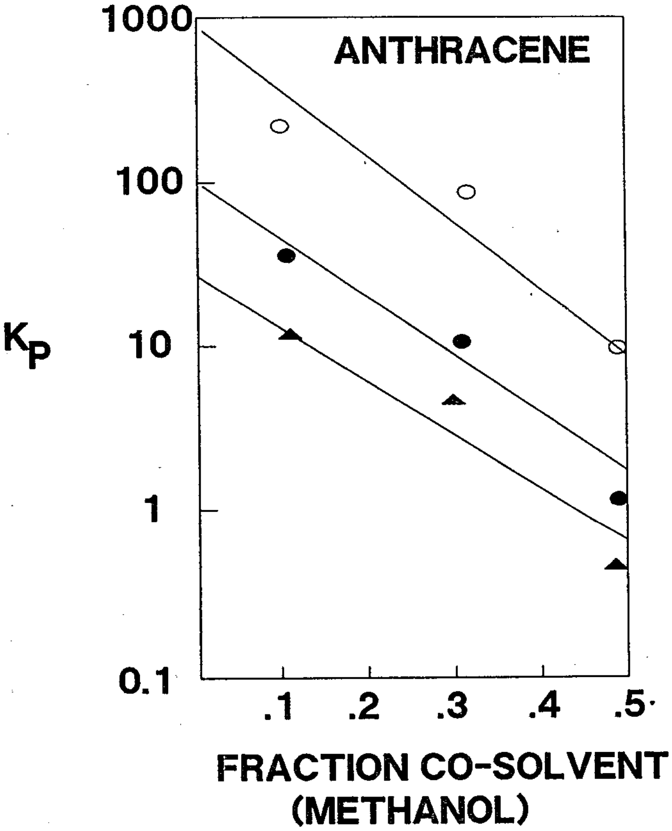


Figure 45. Effect of methanol as a cosolvent on anthracene sorption for three soils (Adapted from Nkedi-Kizza, et al., 1985).

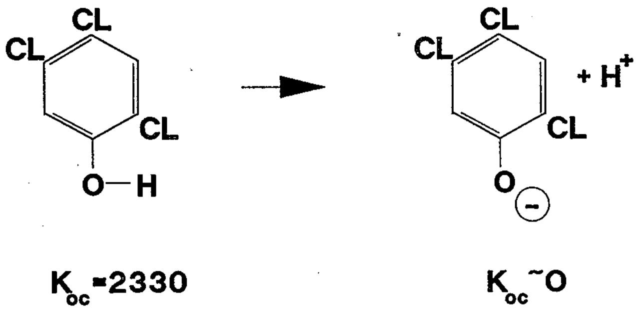


Figure 46. K_{oc} values for 2,4,5-trichlorophenol and 2,4,5-trichlorophenolate.

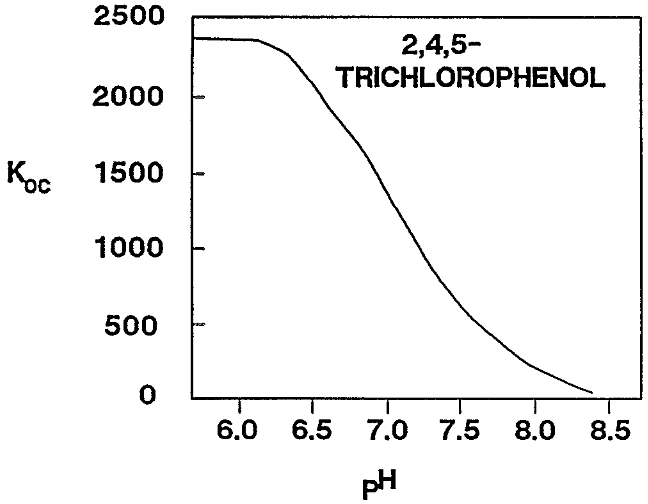


Figure 47. K_{oc} versus pH for 2,4,5-trichlorophenol.

soils containing clays, quinoline is sorbed primarily by ion exchange.

Zachara, et al. (1988) and Fu and Luthy (1986a, 1986b) examined the combined processes of ionization and cosolvation using quinoline as a model. They found that sorption decreased in a log-linear fashion when methanol and acetone were used as cosolvents. Zachara, et al. were able to relate the increased cosolvent effect of acetone, relative to methanol, to the greater solvating properties of acetone.

Biodegradation

Although biodegradation is described in greater detail in Chapters 7 and 8, two chemical-reaction-related aspects of biodegradation are discussed in this section. The first aspect is that biodegradation in natural systems often can be modeled as a first-order chemical reaction. Both laboratory and field data suggest that this is true when none of the reactants are in limited supply. For example, data from the Stanford/Waterloo tracer experiment (Figure 48) (Roberts, et al., 1986) show a reasonably good fit to a first-order degradation process.

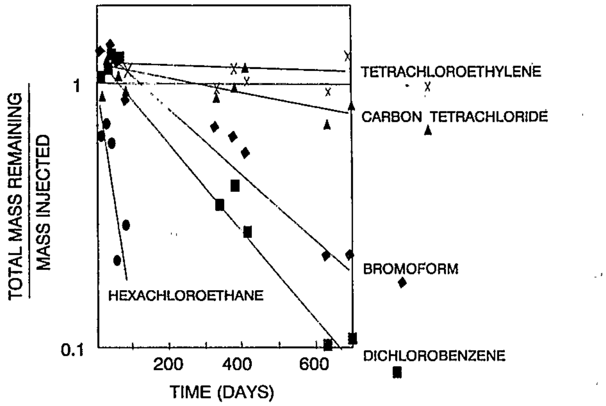


Figure 48. Degradation of chlorinated organics in the Stanford-Waterloo natural-gradient tracer experiment (adapted from Roberts, et al., 1986).

The second chemically related aspect of biodegradation is that, like most abiotic reactions, not all biodegradation reactions result in complete mineralization of the reactants. In many cases, the microorganisms that degrade the contaminants produce an intermediate chemical which they do not or cannot degrade. Other organisms or other conditions may allow degradation to continue, but the lifetime of the intermediate chemical may be significant. Perhaps the best known example of this is the sequential degradation of tetrachloroethylene to the more toxic vinyl chloride (Figure 49) which is not readily degraded and tends to accumulate. In the process, the original moderately sorbing contaminant is transformed to a weakly sorbing compound with a partition coefficient lower than the original chemical by a factor of approximately eighty.

Volatilization and Dissolution

Spills of volatile organic compounds (solvents or petroleum-based liquids) are very common in all parts of the United States. Two important transport

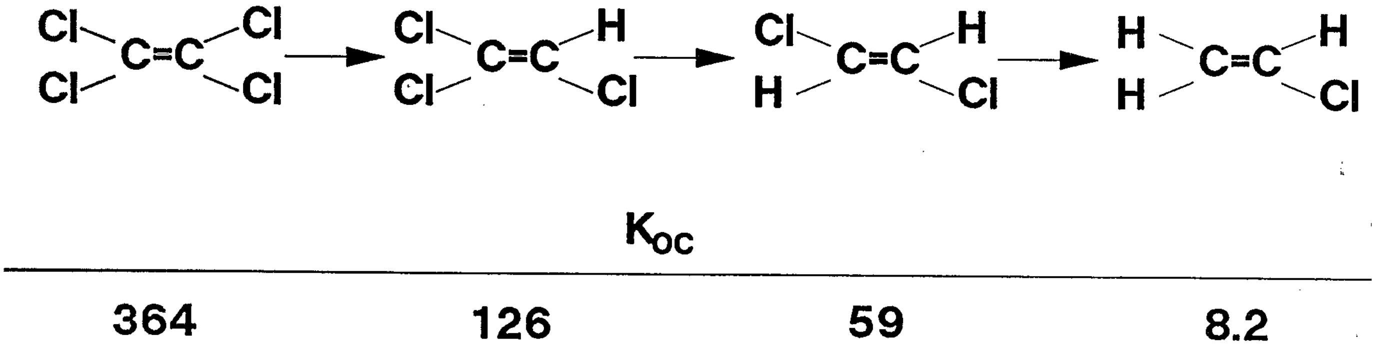


Figure 49. Schematic of the sequential degradation of tetrachloroethylene to vinyl chloride.

pathways for these materials are volatilization into the unsaturated zone and dissolution into the ground water. In addition to being important transport pathways, volatile organic compounds also carry the contaminants from the free-product phase into the aqueous and vapor phases where they are more amenable to degradation.

The importance of volatilization is determined by the area of contact between the free product and the unsaturated zone, the vapor pressures of the spilled compounds, and the rate at which the compound diffuses in the subsurface. The contact between a compound and the unsaturated zone is determined by the nature of the medium (e.g., grain size, depth to water, water content, etc.) as well as of the compound (e.g., surface tension and liquid density). As discussed in Chapter 3, when immiscible liquids move downward through unsaturated porous media, portions of the liquid are left behind as "trapped residual." This residual provides a very large surface area for volatilization. Laboratory experiments suggest that vapor concentrations in the vicinity of the residual are maintained at saturation concentrations. Movement of the vapor away from the residual is typically controlled by molecular diffusion, as described by Fick's Second Law:

$$D_e \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad (7)$$

Mass transfer is controlled by the effective diffusion coefficient, D_e, of the compound in the porous medium. D_e is defined as:

$$D_e = D_a \tau \qquad (8)$$

where D_a = free-air diffusion coefficient, and τ = tortuosity factor. Tortuosity factors for moist porous media can be determined experimentally or calculated theoretically. Millington (1959) developed the most widely used theoretical expression for τ:

$$\tau = \frac{\theta_a^{2.33}}{\theta_t^2} \qquad (9)$$

where θ_a is the air-filled porosity of the medium. Thus, diffusion is significantly reduced in high water-content (low θ_a) soils (Figure 50).

In addition to the effect of tortuosity, diffusion may be further reduced by the partitioning of the vapors out of the gas phase and into the solid or aqueous phases. This process can be described in a manner that is very analogous to retardation due to sorption in the saturated zone, with the addition of a term to describe the partitioning between the vapor and aqueous phases (Baehr, 1987):

$$R = 1 + \frac{\theta_w K_w}{\theta_a} + \frac{\rho_b K_H K_p}{\theta_a} \qquad (10)$$

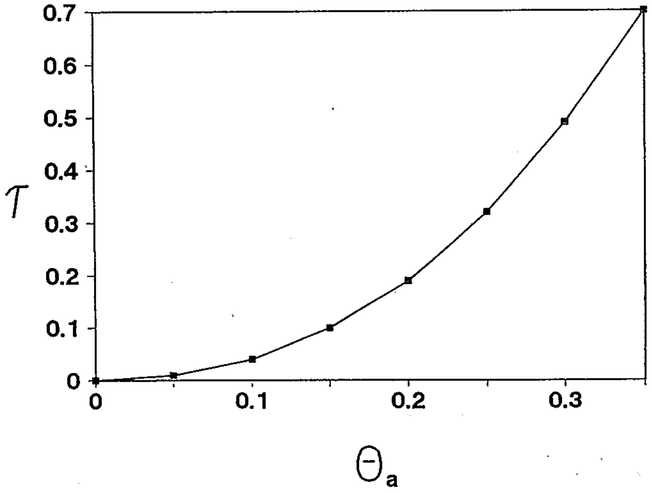


Figure 50. Tortuosity as a function of air-filled porosity (total porosity = 0.35) (adapted from Millington, 1959).

where K_H = dimensionless water-air partition coefficient and θ_w = volumetric pore-water content. Equation 7 can be modified to the form:

$$\frac{D_e}{R} \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad (11)$$

As with the saturated zone R (Equation 5b), this formulation of the retardation factor assumes that partitioning is at equilibrium and the factors K_p and K_H are not functions of solute concentration. These assumptions are probably valid for most unsaturated zone conditions.

When immiscible fluids reach the capillary fringe, their behavior is dictated by the fluids' density relative to water (Schwille, 1988; Scheigg, 1984). As discussed in Chapter 3, fluids less dense than water (LNAPLs) pool up on the water table while dense fluids (DNAPLs) penetrate into the ground water. Floating pools of LNAPL also can provide substantial surface area for volatilization. Again, diffusion frequently controls the mass transfer of organics into the vapor phase.

The transport and fate of DNAPLs that penetrate into the ground-water zone is controlled by dissolution. Anderson (1988) and Anderson, et al. (1987) conducted a series of dissolution experiments in a three-dimensional physical model (Figure 51). A cylindrical volume of sand laden with tetrachloroethylene (TeCE) was surrounded by identical sand without the TeCE. Ground water flowing through the tank dissolved the TeCE, and concentrations downgradient of the source quickly rose to saturation values. Experiments at higher ground-water velocities showed that saturation values were maintained, even when the flow rate was 1 m/day (Figure 52). These data suggest that ground water is flowing relatively unimpaired through the zone of residual, and that the dissolution process should be effective, even at the high ground-water velocities present during remediation.

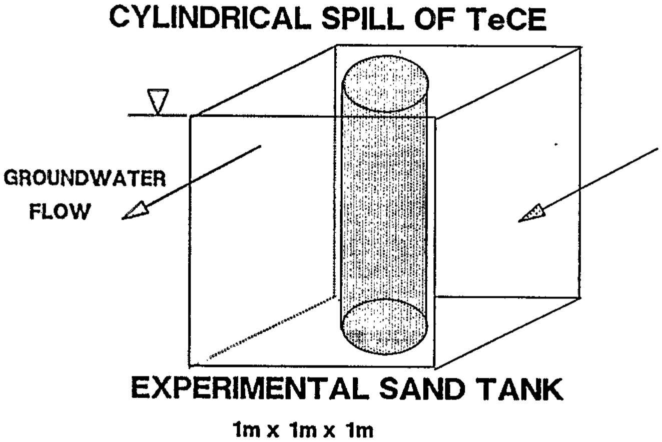


Figure 51. Schematic of the experimental apparatus for measuring dissolution from DNAPL residual in saturated porous media used by Anderson (1988).

Chemical Reactions of Inorganic Components

Speciation

For organic contaminant studies, researchers are primarily interested in the total concentration of the compound in a given phase (e.g., in water vs. in the aquifer matrix). Study of inorganic compound behavior, on the other hand, is greatly complicated by the lack of sufficient knowledge of the total concentration of material. Inorganic materials can occur in many chemical forms, and knowing these forms or "species" is critical to predicting the behavior of inorganic compounds (Morel, 1983; Sposito, 1986).

In ground water, an element may occur in any of the following six categories of species:

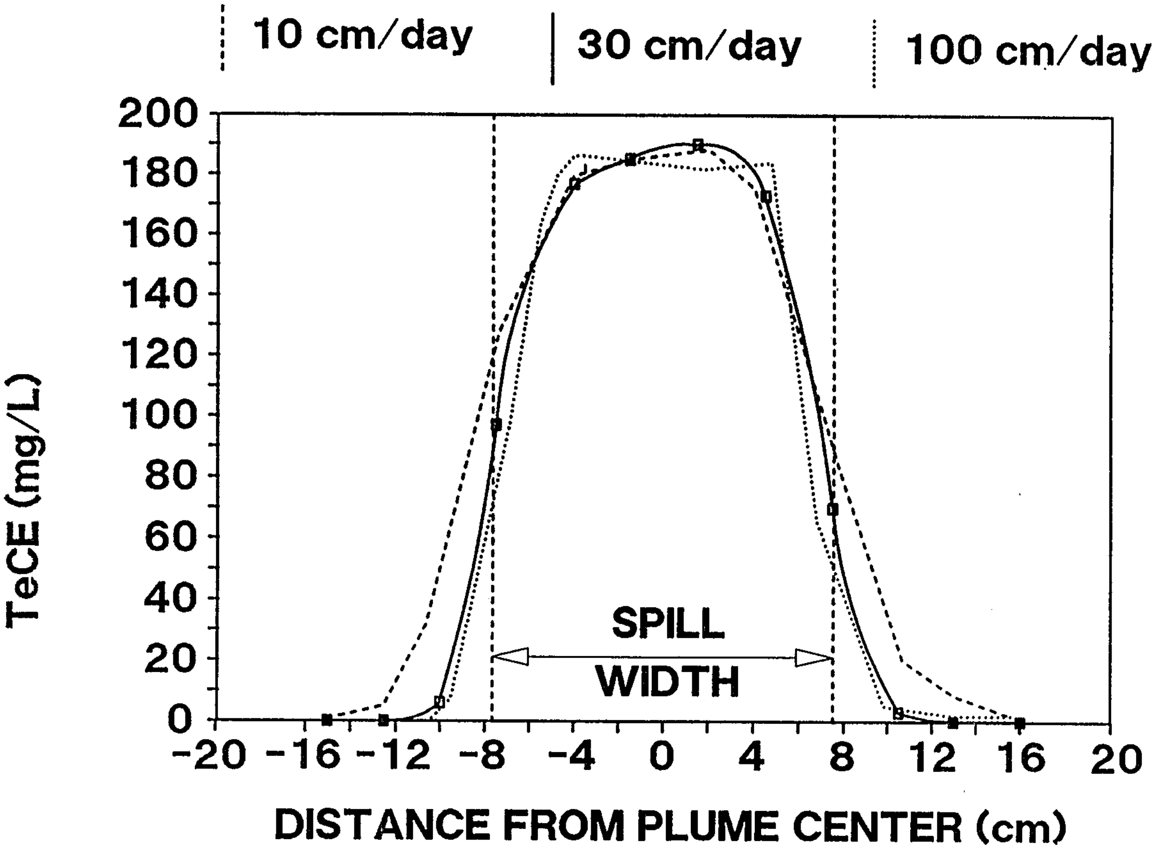


Figure 52. Tetrachloroethylene dissolution data for ground-water velocities of 10 cm/day, 30 cm/day, and 100 cm/day (adapted from Anderson, et al., 1987).

1. "Free" ions (i.e., surrounded only by water molecules)
2. Insoluble species (e.g., Ag_2S, $BaSO_4$)
3. Metal/ligand complexes (e.g., $Al(OH)^{2+}$, Cu-humate)
4. Adsorbed species (e.g., lead sorbed onto a ferric hydroxide surface)
5. Species held on a surface by ion exchange (e.g., calcium ions on clay)
6. Species that differ by oxidation state (e.g., manganese (II) and (IV); iron (II) and (III); and chromium (III) and (VI)

The mobility, reactivity, biological availability, and toxicity of metals and other inorganics depend upon the speciation; knowing only the total concentration of an inorganic compound is frequently of little use. The primary reactions governing these six categories of inorganic chemicals are discussed below.

Solubility and Dissolution

The dissolution and weathering of minerals determines the natural composition of ground water. A useful distinction can be drawn between these two related phenomena. "Dissolution" refers to the dissolving of all components within a mineral, for example:

halite (NaCl) → Na^+, Cl^-

gypsum ($CaSO_4 \cdot 2H_2O$) → Ca^{2+}, $SO_4^{=}$

calcite/aragonite ($CaCO_3$;limestone) → Ca^{2+}, $CO_3^{=}$, HCO_3^-

quartz (SiO_2) → H_4SiO_4

Dissolution of such minerals is the source of most inorganic ions in ground water. The extent of the dissolution can be estimated from calculations using thermodynamic constants known as the solubility products, K_{sp}. In principal, a mineral can dissolve up to the limits of its solubility; however, in many cases, the reactions occur at such a slow rate that true equilibrium is never attained (Morgan, 1967).

Natural systems are further complicated by the simultaneous presence of many minerals containing common ions. The contribution of ions from one mineral affects the solubility of other minerals containing the same ion. This is the so-called "common-ion effect." Computer calculation schemes, such as MINTEQ (Felmy, et al., 1984), MINEQL (Westall, et al., 1976), or WATEQ2 (Ball, et al., 1980), yield the equilibrium distribution of chemical species in the ground water and indicate if the water is undersaturated, supersaturated, or at equilibrium with various mineral phases. Some of these programs also can be used to predict the ionic composition of ground water in equilibrium with assumed mineral phases (Jennings, et al., 1982).

"Weathering" is a partial dissolution process in which certain elements leach out of a mineral, leaving others behind. The weathering of aluminosilicates (such as feldspars) contributes cations, primarily Ca^{2+}, Mg^{2+}, K^+, Na^+, and silica, to water and forms secondary weathering products such as kaolinite and montmorillonite. This weathering of silicate minerals increases the alkalinity of the water; hence, natural ground water often is more alkaline than its rainwater origins. Weathering and dissolution also can be sources of contaminants. Leachates from mine tailings (Hem, 1970) can yield arsenate, heavy metals, and strong mineral acids. Also, leachates from fly-ash piles yield selenium, arsenate, lithium ions (Li^+), and heavy metals (Honeyman, et al., 1982; Murarka and MacIntosh, 1987; Stumm and Morgan, 1981).

The converse of dissolution reactions is the precipitation of minerals or contaminants out of aqueous solution. During precipitation, the least-soluble mineral is removed from solution as shown for iron in Figure 53 (Stumm and Morgan, 1981; Williams, 1985). A thermodynamic restriction known as the Gibbs Phase Rule limits the number of solid phases that can form from a given solution (Sillen, 1967). An element is removed by precipitation when its solution concentration saturates the solubility of one of its solid compounds. If the solution concentration later drops below the solubility limit, the solid will begin to dissolve until the solubility level is attained again. Thus, contaminants may initially precipitate, then slowly dissolve later after "remediation" reduced the

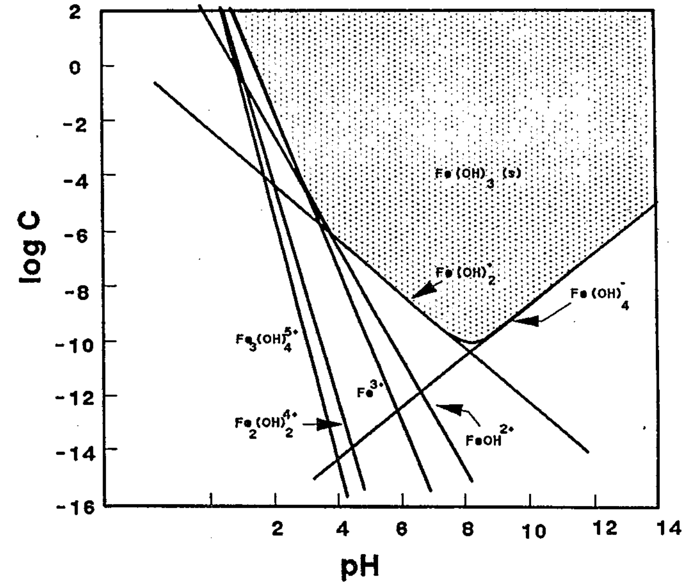


Figure 53. Log C-pH diagram for iron (adapted from Stumm and Morgan, 1981).

solution concentration. Remediation may take years to complete under such conditions.

In another scenario, a contaminant initially may be soluble, but later precipitates after mixing with other waters or after contact with other minerals (Williams, 1985; Drever, 1982; Palmer, 1989). For example, pumping water from an aquifer during remediation might cause dissolved lead to be mobilized until it converges and mixes with high carbonate waters from a different formation. At that point, much of the lead would precipitate as $PbCO_3$ solid. Changes in the oxidation state of an element also can cause contaminants to precipitate or dissolve; this topic is addressed later in this chapter in the discussion on redox chemistry.

Complexation Reactions

In a complexation reaction, a metal ion reacts with an anion that functions as a so-called ligand. The metal and the ligand bind together to form a new, soluble species called a complex. Transition metals are the most important metals involved in complexation (Stumm and Morgan, 1981); alkaline earth metals only form weak complexes while alkali metals essentially do not form complexes at all (Dempsey, et al., 1983). The approximate order of complexing strength of metals is:

Fe(III) > Hg > Cu > Pb > Ni > Zn > Cd > Fe(II) > Mn > Ca > Mg

Important inorganic ligands include most of the common anions (Hanzlik, 1976), and their strength depends highly on the metal ion with which they are complexing. Common ligands are OH^-, Cl^-, $SO_4^=$, $CO_3^=$, $S^=$, F^-, NH_3, PO_4^{3-}, CN^-, and polyphosphates. Inorganic ligands frequently are in great excess compared to the "trace" metals they bind and, therefore, affect metal chemistry, not vice versa (Morel, 1983).

Organic ligands generally form much stronger complexes than inorganic ligands. Important organic ligands include synthetic compounds from wastes such as amines, pyridines, phenols, and other organic bases and weak acids. Natural organic ligands are mostly humic materials (Stevenson, 1982 and 1985; Hayes and Swift, 1978; Schnitzer, 1969), and the complexation behavior of these diverse substances is difficult to predict (Dzombak, et al., 1986; Fish, et al., 1986; Perdue, 1985; Sposito, 1984; Perdue and Lytle, 1983). Humic materials are generally found in significant concentrations only in shallow aquifers, but in such systems they may dominate the metal chemistry of the ground water (Thurman, 1985).

Equilibrium among reactants and complexes for a given reaction is predicted by an equilibrium (or "stability") constant (K) which defines a mass-law relationship among the species. For example:

Reaction: $Hg^{2+} + Cl^- = HgCl^+$

Described by: $[HgCl^+]/[Hg^{2+}][Cl^-] = K_{HgCl^+} = 107.2$

For given *total* ion concentrations (measured by analysis), stability constants can be used to predict the concentration of all possible species (Figure 54) (Smith and Martell, 1976).

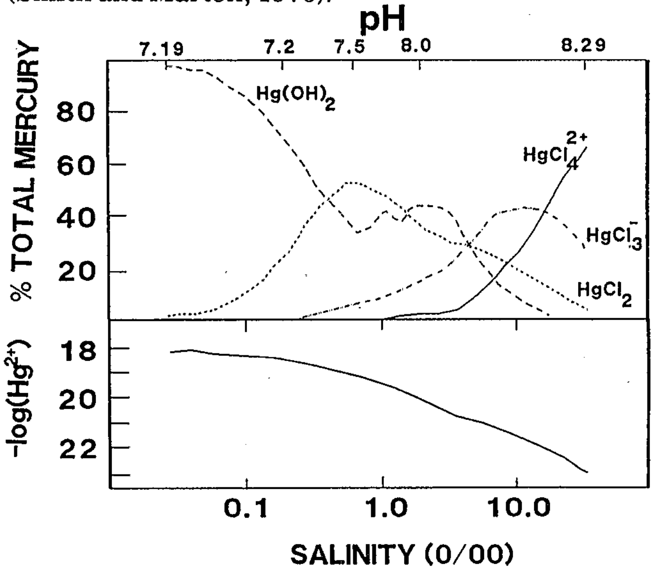


Figure 54. Speciation of mercury as a function of salinity (adapted from Smith and Martell, 1976).

Because complexes decrease the amount of *free* ions in solution, less metal may adsorb onto aquifer matrix or precipitate. That is, the metal is more soluble because it is mostly bound up in the soluble complex. Rueter, et al. (1979) found that a metal undergoing complexation may be less toxic to aquifer microbes.

Adsorption and Surface Chemistry

A vast amount of surface area exists in an aquifer and, in many cases, surface adsorption is the most important process governing toxic metal transport in the subsurface. Changes in metals concentration, as well as pH, can have a significant effect on the extent of adsorption (Figure 55). Unfortunately, a general model of ionic adsorption on natural surfaces still has not been developed (Dzombak, 1986; Dzombak and Morel, 1986). Numerous theories and models of adsorption exist, but no truly general principles have been defined. Current models still are highly

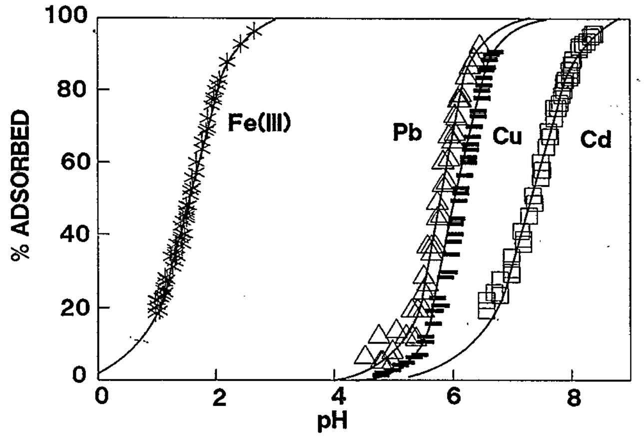


Figure 55. Adsorption of metal ions on amorphous silica as a function of pH (adapted from Schindler, et al., 1976).

empirical and therefore are calibrated to specific data (Westall, 1980). Because of this, it is difficult to base generalized regulations or remediation plans on the computer-predicted behavior of metal ions.

Despite these shortcomings, some useful approaches to the problem have been developed. Adsorption data usually are presented graphically as "isotherms" (called this because they represent data collected at a fixed temperature). Isotherms can be fitted to mathematical representations; the two most common forms are the Freundlich and the Langmuir isotherms (Figure 56). The Freundlich isotherm:

$$S = K C^N \tag{12}$$

is purely empirical, and sorbed (S) and aqueous (C) concentration data are fitted by adjusting the parameters K and N. The Langmuir formulation, in contrast, is based on the theory of surface complexation (Morel, 1983):

$$S = S_{max} \frac{KC}{1+KC} \tag{13}$$

where S_{max} is the maximum amount which can be sorbed, and K is the partition coefficient.

Surface complexation models represent adsorption as ions binding to specific chemical functional groups on a reactive surface. All surface sites may be identical or may be grouped into different classes of sites (Benjamin and Leckie, 1981), and each type of surface site has a set of specific adsorption constants, one for each adsorbing compound. Electrostatic forces at the surface also contribute to the overall adsorption constant (Davis, et al., 1978) and sometimes are explicitly included in the adsorption constant as the Coulombic term (Stumm and Morgan, 1981). The binding of ions to the surface is computed from constants with mass-law equations identical to those used to calculate solution-complex formation (Stumm, et al., 1976; Schindler, et al., 1976; Dzombak and Morel, 1986).

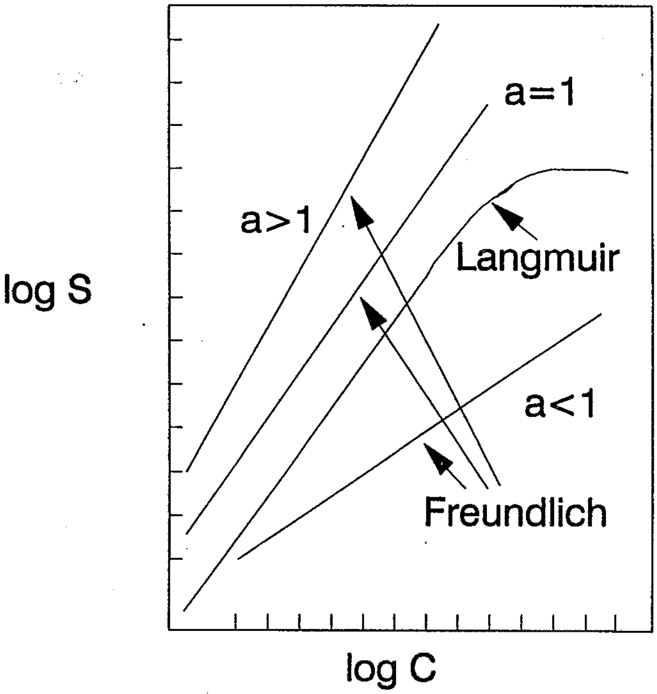


Figure 56. Schematic drawing of Freundlich and Langmuir isotherm shapes for batch equilibrium tests.

Although this approach is conceptually simple, there are practical problems in using the models. Model parameters are effectively data-fitting parameters. The parameters can fit a specified set of data to a particular model, but have no true thermodynamic meaning and, therefore, no generality beyond the calibrating data set (Westall, et al., 1980). Some models contain many "knobs" that can be adjusted to get the best fit of the experimental data. However, once a model is calibrated for one set of conditions, lack of generality may preclude dynamic predictions for changing aquifer conditions. Parameters calculated using one model should not be used in another model unless modified according to each model's assumptions.

Ion-Exchange Reactions

Ion-exchange reactions are similar in effect to adsorption, but have some key distinctions. Adsorption is viewed as the coordination bonding of metals (or anions) to specific surface sites considered to be two-dimensional. In contrast, an ion-exchanger is visualized as a three-dimensional, porous matrix containing fixed charges. Ions are held by electrostatic forces rather than by coordination bonding (Helfferich, 1962). Surface complexation uses fixed stability constants for mass law calculations whereas ion-exchange "selectivity coefficients" are strictly empirical (Reichenberg, 1966) and vary with the amount of ion present. Ion exchange best describes the binding of alkali metals, alkaline earths, and some anions to clays and condensed humic matter (Sposito, 1984; Helfferich, 1962).

Knowledge of ion exchange in soils and aquifers is very important for understanding the behavior of major (natural) ions. In principle, ion exchange theory also is useful for understanding low-level contaminant ions. In practice, this theory is very empirical when applied to these types of ions, and surface complexation models probably are better choices for trace metals. Ion exchange models need further development, but may be the most useful representation of competition among metals for surface binding (Sposito, 1984).

Redox Chemistry

Reduction-oxidation (redox) reactions involve a change in the oxidation state of elements. The level of that change is determined by the number of electrons on the element transferred during the reaction (Stumm and Morgan, 1981.) Redox reactions can greatly affect contaminant transport. For example, in slightly acidic to alkaline environments, Fe(III) precipitates as a highly adsorptive solid phase (ferric hydroxide), whereas Fe(II) is very soluble and does not retain other metals. The reduction of Fe(III) to Fe(II), therefore, releases not only Fe^{2+} to the water, but also any contaminants that were adsorbed to the ferric hydroxide surfaces (Evans, at al., 1983; Sholkovitz, 1985). The behavior of chromium and selenium also illustrates the importance of redox chemistry to contaminant movement. Cr(VI) (hexavalent) is a toxic, relatively mobile anion whereas trivalent Cr(III) is inert, relatively insoluble, and strongly adsorbs to surfaces. Selenate (Se(VI)) is mobile, but less toxic; however, selenite (Se(IV)) is more toxic, but less mobile.

The redox state of an aquifer usually is closely related to the microbial activity and the type of substrates available to the organisms. Organic contaminants provide the reducing equivalents for the microbes. Because of the inherently "enclosed" nature of aquifers, oxygen is readily depleted and chemically reducing (anaerobic) conditions form. The redox reactions that occur depend entirely on the dominant electron potential, which is defined by the primary redox-active chemical species. For example, the combination of Fe(II)/Fe(III) defines a particular, narrow range of electron potentials, whereas S(+IV)/S(-II) defines a more broad range. These pairs of chemical species are called redox couples.

After oxygen is depleted from the water, the most easily reduced materials begin to react and, along with the reduced product, dictate the dominant potential. After that material is more or less completely reduced, the next most easily reduced material begins to react, and so on. Microbes typically catalyze this series of reactions, and an aquifer is described as "mildly reducing" or "strongly reducing," depending on where it is in the chemical series (Stumm and Morgan, 1981).

The electron potential of a water body can be given in volts (as the E_H), or expressed by the "pe," which is the negative logarithm of the electron "activity" in the water. The pe sounds complex but is exactly analogous to pH (negative log of hydrogen ion activity). A convenient way to summarize a set of reactions is on a pH-pe (or pH-E_H) diagram, sometimes called a Pourbaix diagram. Inspection of the diagram yields the predominant redox species at any specified pH and E_H (Figure 57).

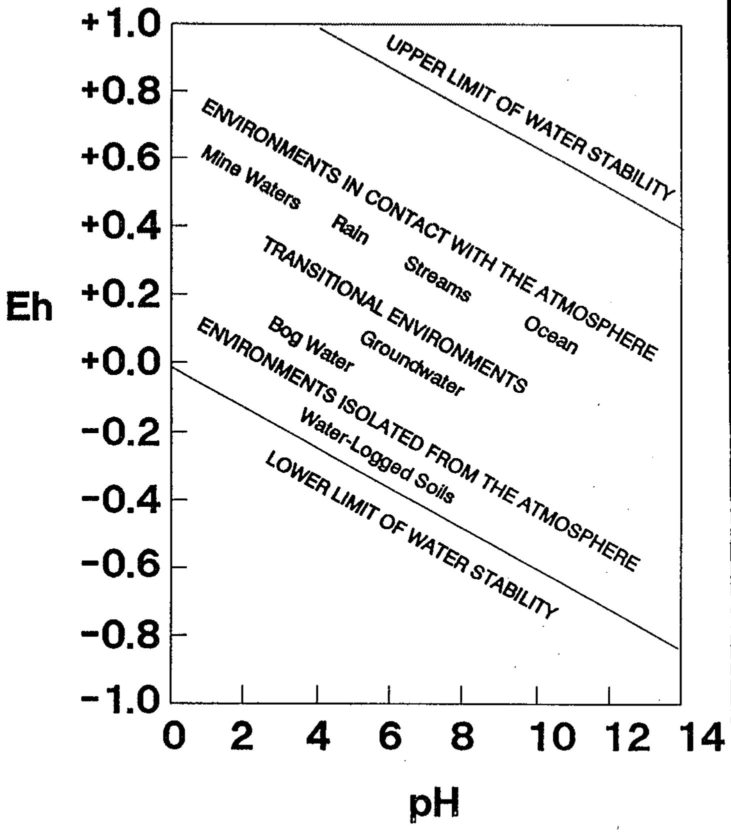


Figure 57. pH-Eh diagram showing the ranges of various aquatic environments.

In this theoretical approach, only one redox couple should define the redox potential of the system at equilibrium. In practice, this series of events is not clearly defined and many redox couples not in equilibrium can be observed simultaneously (Lindberg and Runnels, 1984). Hence, it can be nearly impossible to predict redox behavior of chemicals in aquifers from equilibrium predictions. However, the redox status of an aquifer cannot be ignored because of the effects discussed above and the potential effects on biodegradation of organic contaminants. Anaerobic (reducing) conditions are inefficient for the degradation of hydrocarbons, but reducing conditions favor dehalogenation of chlorinated and other halogenated compounds.

Much more research is needed in the area of redox chemistry in aquifers because researchers only now are realizing the importance of these phenomena in controlling contaminant behavior. Among the areas for future research are the development of better measuring techniques for redox potentials, microbiological studies, and new approaches for computational models.

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CHAPTER 6

SUBSURFACE CHEMICAL PROCESSES: FIELD EXAMPLES

Richard L. Johnson, Carl D. Palmer, and William Fish

Introduction

Understanding chemical processes in the subsurface is essential for accurate site characterization and for the design and implementation of efficient remediation systems. This chapter will focus on examples of how chemical processes can control transport and fate in the subsurface.

Petroleum Hydrocarbons in the Unsaturated Zone

Gasoline in the subsurface has been examined from both experimental and theoretical points of view. For example, theoretical analyses of spills by Baehr (1987), Corpacioglu and Baehr (1987), and Baehr and Corpacioglu (1987) demonstrate that volatilization is a dominant mechanism of transport for many hydrocarbon spills (Figure 58). Gasoline is a complex mixture of hundreds of compounds, some of which are more amenable to volatilization than to dissolution, and vice versa. Also, other components within gasoline are not particularly prone to either and will tend to persist in the subsurface.

As discussed in Chapter 5, the importance of volatilization is determined by the composition of the free-product, the vapor pressure of the specific compound, and the rate at which the chemical diffuses in the vapor phase. For example, aromatic hydrocarbons in gasoline are moderately volatile, but also dissolve readily into the pore water. Therefore, they diffuse more slowly and may persist in the unsaturated zone longer than the less-soluble alkanes and alkenes (Baehr, 1987).

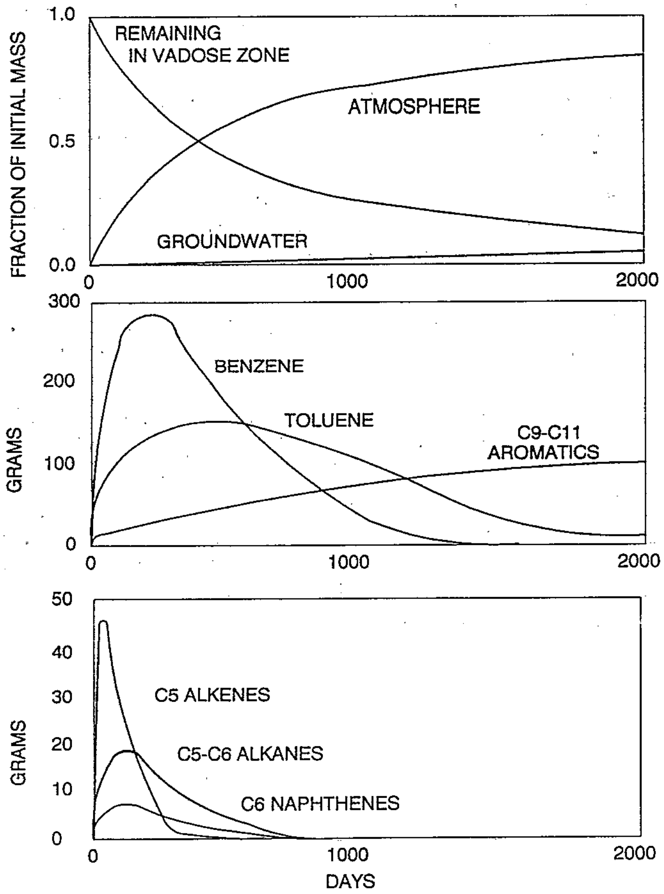


Figure 58. (a) Transport pathways for subsurface gasoline; (b) masses of aromatics in the unsaturated zone after a hypothetical spill; and (c) masses of hydrocarbons in the unsaturated zone after a hypothetical spill (after Baehr, 1987).

Biodegradation also plays an important role in the fate of gasoline. Many components of gasoline are readily degraded by subsurface microorganisms. In the saturated zone, biodegradation frequently makes the aquifer anaerobic, resulting in much slower rates of degradation. This trend towards anaerobic conditions is demonstrated in data collected by Wilson, et al., (1986) and others at a Traverse City, Michigan site (Figures 59 and 60).

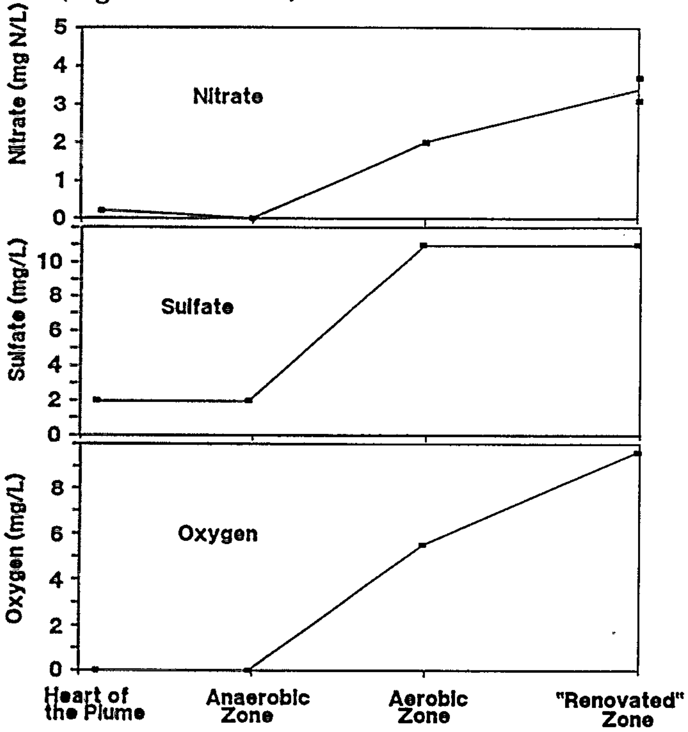


Figure 59. Ground-water quality parameters downgradient from a hydrocarbon spill at Traverse City, Michigan (after Wilson, et al., 1986).

In the unsaturated zone, vapor-phase molecular diffusion can maintain an oxygen supply even at distances of tens of feet below the ground surface (Figure 61) (Hult and Grabbe, 1985). The data of Hult, et al. also show elevated carbon dioxide and methane concentrations (Figures 61 and 62) which are the result of biodegradation. In field experiments, Allen, et al. (1987) infiltrated water containing simple aromatics into unsaturated porous media.

Naturally present microorganisms quickly degraded all of the components. These data, when contrasted with the fact that the aromatics are widely observed in the unsaturated zone, suggest that the interactions between gasoline and the subsurface environment are complex.

Indicator Compounds

RCRA regulations identify a number of indicator parameters to be used as an early warning system for ground-water contamination, including specific conductance, pH, chloride, bromide, total organic carbon (TOC), and total organic halides (TOX). In general, these parameters were selected because they are conservative and non-reactive, more or less unique to and commonly found in contaminated ground water, and easily analyzed. Also, compounds detectable at the leading edge of a contaminant plume were emphasized.

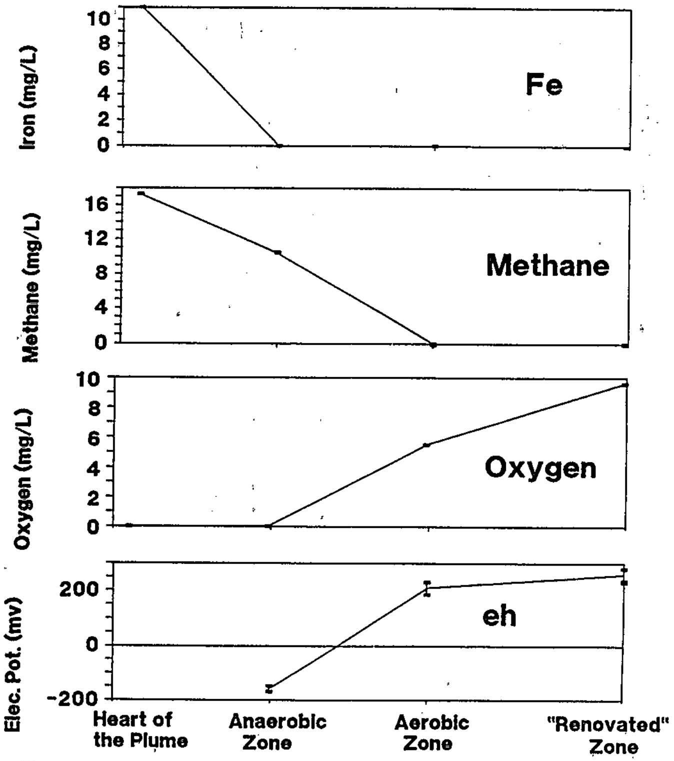


Figure 60. Additional ground-water quality parameters downgradient from a hydrocarbon spill at Traverse City, Michigan (after Wilson et al., 1986).

Most of the RCRA-specified indicator parameters, however, only partially satisfy the criteria listed above. Changes in specific conductance, pH, chloride, and bromide are typically not unique to contaminated ground water. Similarly, some natural total organic carbon (TOC), chloride, and bromide are present in virtually all ground water. TOC is particularly problematic in that natural TOC is often found in ground water in the range of 1 to 10 mg/L, whereas it is often desirable to measure organic contaminants at the µg/L level. Total organic halides (TOX) determinations have a much lower detection limit than TOC, but are prone to analytical difficulties.

Plumb (1985), Plumb and Fitzsimmons (1984), and Plumb and Pitchford (1985) examined leachate data from a large number of RCRA and Superfund sites to determine if other components of leachate would better serve as indicator parameters. These studies show that purgeable priority pollutants (PPP) were found at a high percentage of these sites. The PPP have low detection limits and are not normally present in ground water; therefore, they seem an excellent alternative to the bulk TOC and TOX

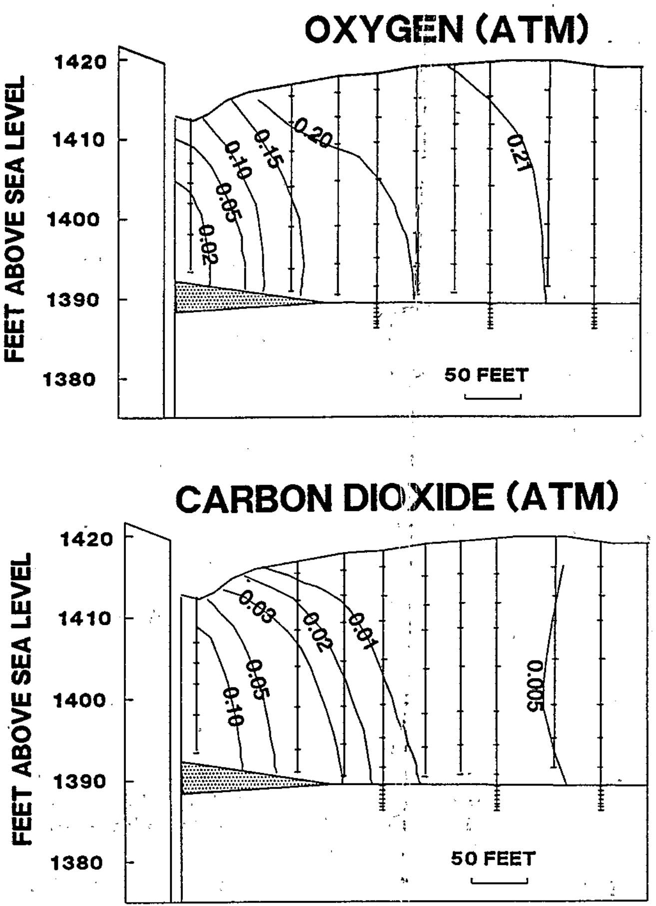


Figure 61. Oxygen and carbon dioxide concentrations in the unsaturated zone above an oil spill at Bemidji, Minnesota (after Hult, et al., 1985).

analyses. However, the sum of all priority pollutants in landfill leachates often represent only 1 to 5 percent of the total dissolved organic material present in the ground water (e.g., Reinhard, et al., 1984; Johnson, et al., 1989). The bulk of the unidentified organic contaminants are made up of a wide variety of primarily hydrophilic compounds (Figure 63). An examination of major chemicals produced in the United States (Webber, 1986) indicates that 7 of the top 35 are priority pollutants and only 5 are purgeable priority pollutants (PPP). Furthermore, many of the top 35 chemicals are significantly more hydrophilic than the PPP (Figure 64). This means that if sorption plays a role in retarding chemical movement, there are many common compounds that will move more rapidly than the PPP. Many of those non-PPP compounds cannot be detected by standard EPA methods. Nevertheless, they may have significant impacts on ground-water quality due to their mobility, solubility, degradability, toxicity, etc. A better understanding of the complexity of landfill leachate is necessary before an accurate assessment of the transport and fate of the wide range of compounds found there can be made.

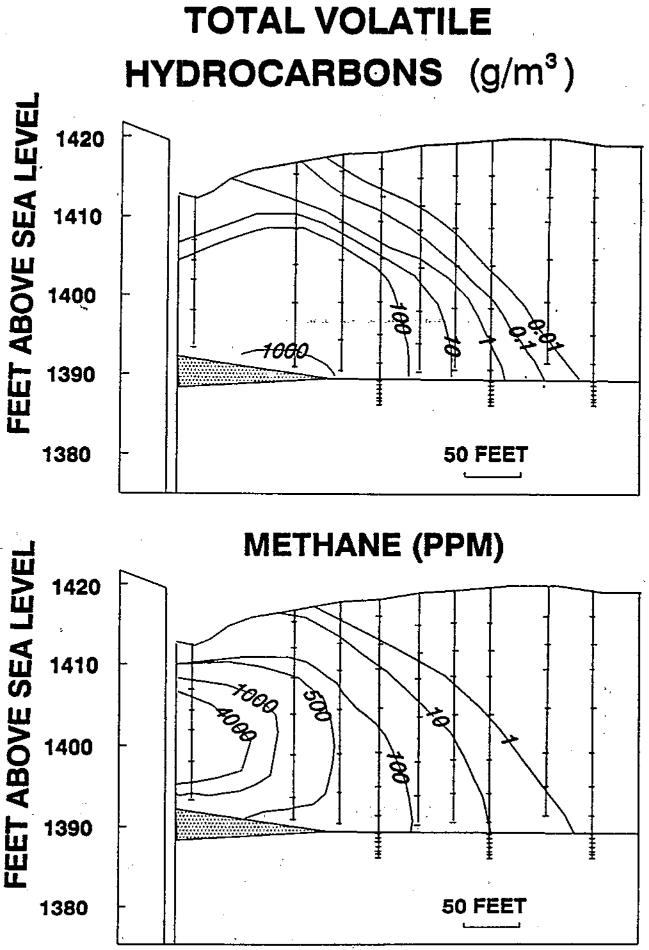


Figure 62. Hydrocarbon and methane concentrations in the unsaturated zone above an oil spill in Bemidji, Minnesota (after Hult, et al., 1985).

- ■ Alcohols
- ■ Analines
- ■ Acetates
- ■ Amines
- ■ Thiols
- ■ Furans
- ■ Nitriles
- ■ Phenols
- ■ Aldehydes
- ■ Ketones
- ■ Acids

Figure 63. Polar and ionizable compound classes commonly present in leachates.

Organic Transport on Microparticles

A growing number of field data suggest that very hydrophobic compounds can be transported in the subsurface at rates which are significantly greater

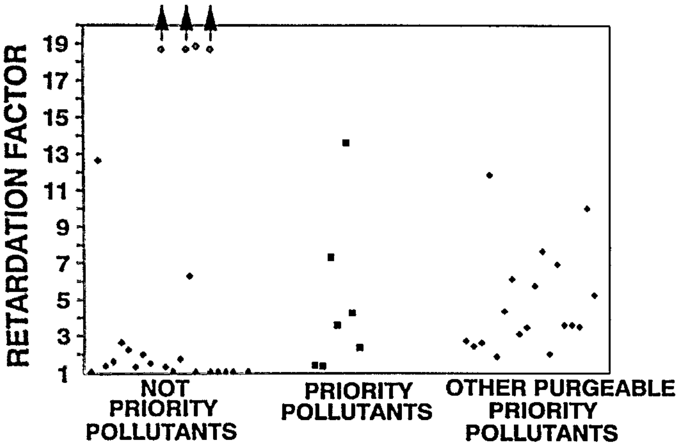


Figure 64. Estimated retardation factors for common organics and priority pollutants (f_{oc} = 0.01).

than would be predicted by equilibrium sorption (Means and Wijayaratne, 1982). In addition, nearly all ground water contains some levels of "dissolved" organic carbon (DOC) as microparticles. (DOC levels are commonly 0.1 to 10 mg/L, but may be significantly higher in the vicinity of landfills or other waste disposal facilities.)

The importance of microparticle transport of organics in ground water depends upon the extent of partitioning to the microparticles. For example, when the carbon associated with non-settling particles (NSP) is 1 mg/L, a compound with a K_{oc} of 10^6 will only experience a decrease in retardation factor of approximately two. Given the very large retardation values common for many of these compounds, a factor of two increase in velocity generally will not be important. However, if desorption occurs more slowly than adsorption onto the microparticles, the relatively rapid movement of the microparticles could result in significantly enhanced transport velocities for the hydrophobic organics. Laboratory data suggest that desorption times can be quite long, however, the processes controlling the sorption kinetics of hydrophobic organics on microparticles currently are not well-understood.

In a related observation, several investigators reported that the partition coefficients of hydrophobic organics appear to increase at low sediment/water ratios (Figure 65) (Voice, et al., 1983; Voice and Weber, 1985; Gschwend and Wu, 1985). The most satisfactory explanation for this phenomena is that the process of separating microparticle-bound organics from the aqueous phase is incomplete (Gschwend and Wu, 1985). This effect increases with increasing soil/water ratio, thus (somewhat counter-intuitively), the K_p values observed at low soil/water ratios may be more representative of partitioning in the undisturbed medium. This observation is important because batch tests are frequently used to estimate retardation factors for many very hydrophobic compounds at sediment/water ratios at or above those in Figure 65. In those cases, K_p values could be underestimated by an order of magnitude or more, leading to a corresponding overestimation of transport velocity and an underestimation of the time required for remediation.

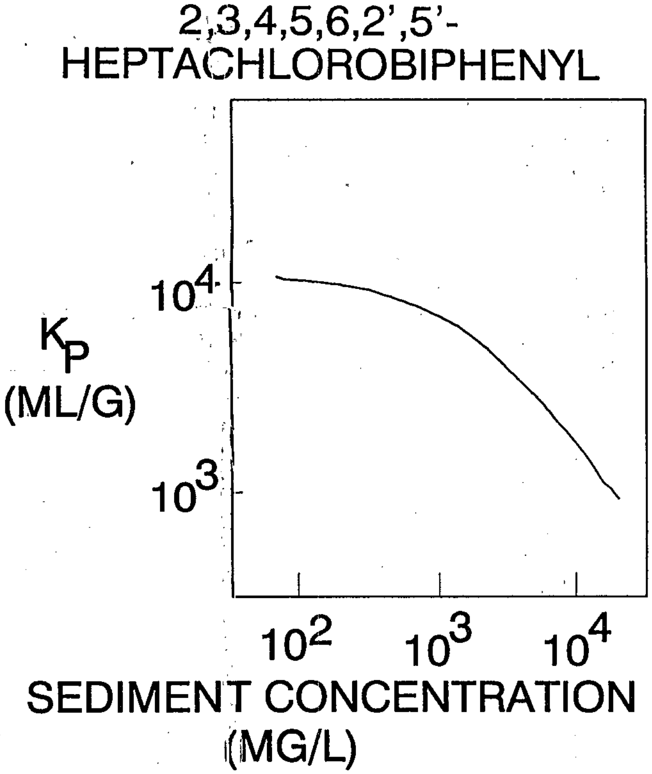


Figure 65. Apparent decrease in K_p with increasing solids concentration in batch equilibrium tests (adapted from Gschwend and Wu, 1985).

Clay Liner Failure

Although clay liners have been a standard method of containment for land-filled wastes, questions persist as to their suitability and durability. Three possible mechanisms of clay-liner failure are advective transport, waste-induced changes in permeability, and molecular diffusion. Advective transport through the liner can occur if the liner has mechanically failed, or if a very large hydraulic gradient exists across the liner. An example of the latter is a landfill filled with water, located in the unsaturated zone. Under these conditions, gradients of 10 or higher may make transport velocities significant, even for a "tight" liner. In such cases, installation of a gravel sump between two liners can minimize the hydraulic gradient across the lower liner. Advective velocities for a landfill sited in a saturated medium are expected to be of relatively minor importance, except where breaks in the barrier exist.

There is some experimental evidence that solvents present in landfills can degrade otherwise impermeable clay liners (Anderson, et al., 1985; Brown and Thomas, 1984; Brown and Anderson, 1983; Green, et al., 1983). The main question is whether or not organic solvents can cause the clay to shrink and crack. Experiments indicate that if pure solvents penetrate into the clay, they may be able to displace water within the clay structure, leading to shrinkage, cracking, and an increase in permeability. In these experiments, the solvents were forced into the clay at high pressures equivalent to many tens of meters of fluid head. This behavior is consistent with the critical pressure required for entry of the solvents into the clay (estimated from the grain diameter of the clay) (Chapter 3; Villaume, et al., 1983), but is probably not realistic in most landfill situations.

In the absence of sufficient pressure, entry of the solvents occurs by simple Fickian diffusion in the aqueous phase. However, the extent of entry is limited by the solubilities of the solvent in the water and vice versa. For many solvents, solubilities are thousands of milligrams per liter or less, in which case, the impact of the solvents on the clay is expected to be minimal.

The presence of mechanical failures or other imperfections in the clay may provide focal points for degradation of the clay liners. Miscible liquids, such as alcohols, acids, bases, and ketones, also have the potential to affect clay structure. Because they are not limited by solubility, large concentrations can diffuse into the clay. Miscible compounds generally are polar molecules which can interfere with the electrostatic forces within the clay (Fernandez and Quigley, 1985). This interference can result in a breakdown of the clay structure and subsequent failure of the liner.

Even though chemical concentrations of thousands of milligrams per liter within clay liners are not expected to affect the hydraulic properties of the clay, such concentrations could have a major impact on ground-water quality because of the diffusive movement of chemicals through the liner. In the absence of advection, mass transport is controlled by Fick's Second Law:

$$D_e \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad (1)$$

As seen in Chapter 5, for sorbing compounds, Fick's Law can be modified to handle equilibrium partitioning:

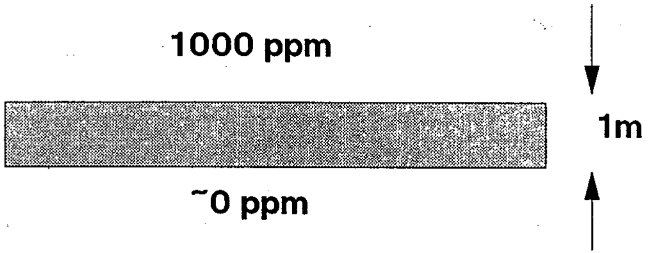
$$\frac{D_e}{R} \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad (2)$$

A number of field studies demonstrated the importance of simple Fickian diffusion (Johnson, et al., 1989; Goodall and Quigley, 1977; Crooks and Quigley, 1984; Desaulniers, et al., 1981). Johnson, et al. collected clay cores from beneath a five-year-old waste disposal cell and determined concentration profiles for chloride and several organic contaminants. The chloride diffused nearly one meter while the organics moved much shorter distances. The principal reason for the slower diffusion of the organics was their sorption onto the clay (f_{oc}~0.01). For non-sorbed contaminants (including organics when the f_{oc} is low), breakthrough of a one-meter liner could occur in less than 10 years. Within a few decades, steady-state concentrations could develop across the clay, possibly resulting in significant mass transfer into the underlying aquifer.

Under steady-state conditions, mass flux follows Fick's First Law:

$$J = -D_e \theta_t \frac{\partial C}{\partial x} \qquad (3)$$

As the calculation in Figure 66 suggests, the mass flux through a liner via diffusion can be on the order of 1 gram per square meter per year. For a large liner, a mass transfer of thousands of grams of individual contaminants per year to the aquifer



$$\text{FLUX} = -nD_{pm} \frac{dC}{dX}$$

$$= -0.37 \times 1.5\times10^{-6}\ \text{cm}^2/\text{sec} \times 1\text{g/L-m}$$

$$= 5.55\times10^{-12}\ \text{g/cm}^2/\text{sec}$$

$$= 1.75\ \text{g/m}^2/\text{year}$$

Figure 66. **Example calculations of steady-state diffusive mass flux through a one-meter thick clay liner.**

could occur. Similar conditions can exist across natural aquitards as well, and the large contact area between aquifers could result in significant mass transfer into an uncontaminated aquifer.

"Plume Sniffing"

Because soil vapor samples are relatively easy to collect from the subsurface, interest has grown in using soil-gas sampling or "plume sniffing" to search for ground-water contamination (Marrin and Kerfoot, 1988). Shallow soil-gas sampling detects vapors emitted into the unsaturated zone by ground-water contaminant plumes that contain volatile organics. Many factors affect vapor concentrations in the unsaturated zone. For example, vertical transverse dispersion in the saturated zone may control mass flux into the unsaturated zone. Because air-diffusion coefficients are much greater than the values typically reported for vertical dispersion (10^{-2} cm^2/s vs. 10^{-6} cm^2/s), unsaturated zone vapor concentrations might be expected to be low. Nevertheless, substantial unsaturated concentrations have been reported at several sites. Swallow and Gschwend (1984) examined the steady-state distribution of volatile organic vapors in the ground water and unsaturated zones (Figure 67). For vertical transverse dispersivities (α_{tv}) in the ground water of 1 cm or less, concentrations at steady-state were found to be near zero through the unsaturated zone. A limitation of the steady-state approach is that data are not provided during the time required for the system to reach steady-state. For the 10-meter aquifer in the Swallow and Gschwend model system, with $\alpha_{tv} = 1$ cm, hundreds of years would be required before the system reached the steady-state.

As previously mentioned, vapor concentrations in the unsaturated zone may deviate from idealized values due to environmental conditions or biodegradation. Data from Hult and Grabbe (1985) (Figure 68) for the Bemidji, Minnesota site show that vapor concentrations at the depths typically used for plume sniffing (3 to 6 feet) are very low because of biodegradation. This is the case even though a large organics source is present as free-product at the capillary fringe. Vapors from ground-water plumes also can be masked by clean water which forms a cap over the plume. This occurs if local recharge displaces the contaminants from the capillary fringe, or if the plume moves downward into the ground water.

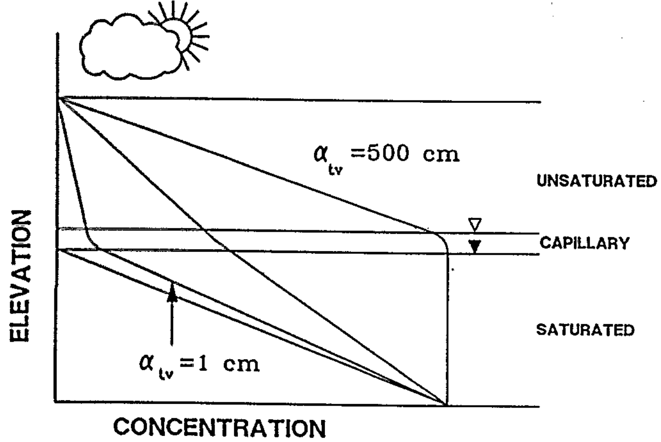


Figure 67. Schematic drawing of steady-state concentration profiles for several vertical dispersion values (adapted from Swallow and Gschwend, 1984).

Numerous case histories demonstrate the usefulness of plume sniffing (Marrin and Thompson, 1987; Marrin and Kerfoot, 1988), especially for chlorinated solvents. As a result, plume sniffing continues to receive a great deal of attention, despite the fact that its general applicability has not been thoroughly demonstrated. As Marrin and Kerfoot (1988) correctly point out:

> Conventional technologies available for subsurface investigation (e.g., monitoring wells and soil borings) always will be required to confirm and monitor subsurface contamination; however, quicker and less expensive techniques are useful for preliminary site evaluations.

They also suggest that, while positive results generally suggest detection of ground-water plumes, failure to detect plumes does not assure that ground-water contamination is not present.

Ground-Water Contamination by Chromium

Chromium (Cr) in the environment causes great concern because of its wide use in industry and its potentially high toxicity. Although chromium can exist in oxidation states ranging from -2 to +6, the trivalent (Cr(III)) and hexavalent (Cr(VI)) species are the common stable forms found in the environment. Three recent surveys of the environmental significance of chromium (U.S. EPA, 1983; Radian Corp., 1983; the American Petroleum Institute, 1981) emphasize that the chemical form of this metal determines its environmental behavior and toxicity. Cr(III) is relatively insoluble and exhibits little or no toxicity (van Weerelt, et al., 1984), while Cr(VI) usually occurs as the highly soluble CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$ anions.

Cr(III) is the most common form of chromium in the earth's crust; the predominant source of hexavalent chromium in the environment is anthropogenic activities. For example, industry has used Cr(VI)

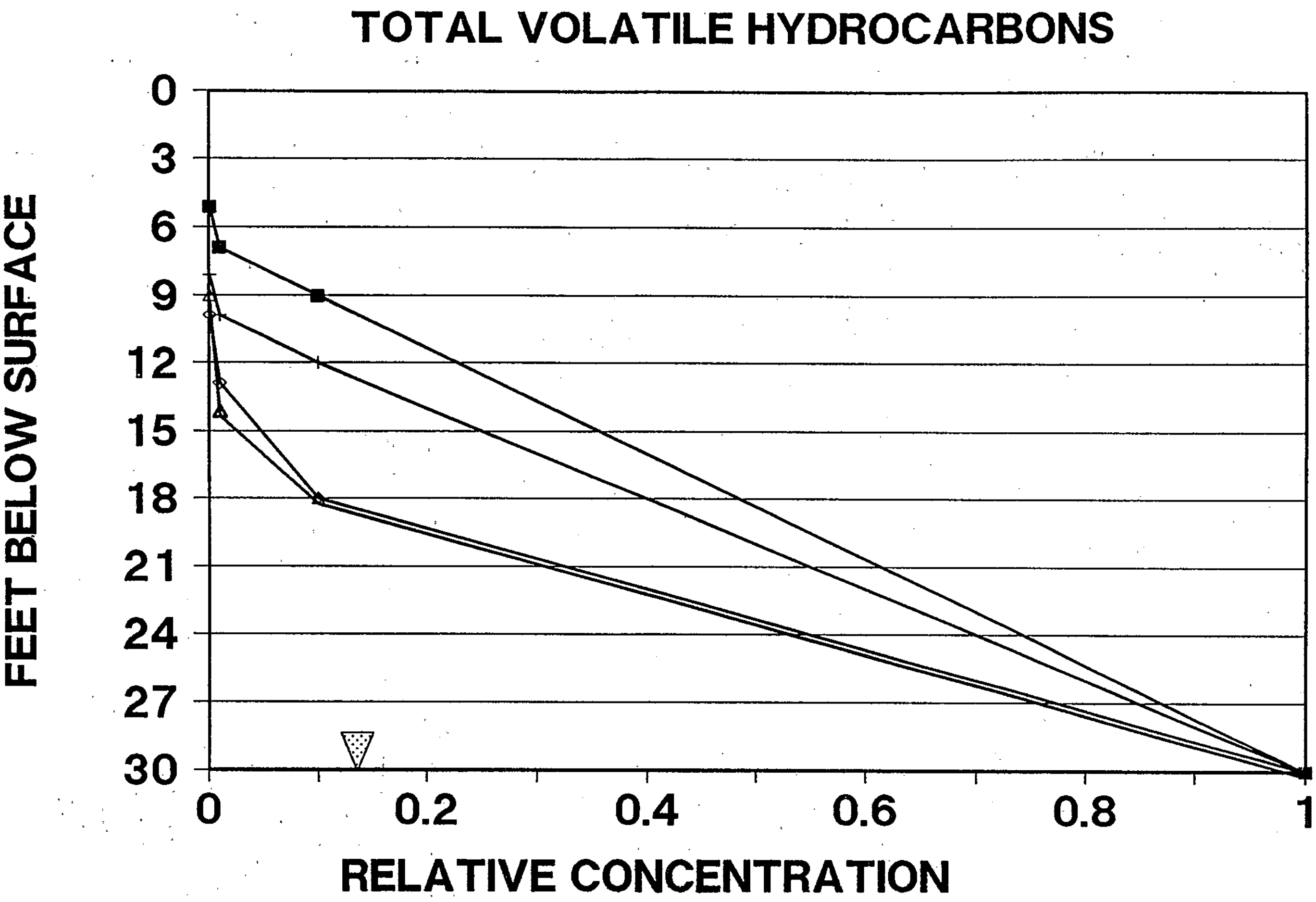


Figure 68. Vertical hydrocarbon profiles in the unsaturated zone above an oil spill near Bemidji, Minnesota site (adapted from Hult, et al., 1985).

primarily in metal plating and leather tanning applications for over 100 years. As a result, numerous waste lagoons, dumps, and landfills are contaminated with chromate wastes (Black and Heil, 1982; Cook and DiNitto, 1982; Owen, 1982; Massachusetts Department of Environmental Quality Engineering, 1981; Keely and Boateng, 1987). At many sites, the chromium coexists with a variety of other inorganic and organic wastes, and under these conditions, a wide range of chemical interactions are possible.

Chromium transport in aqueous systems strongly depends on sorption, chelation, and redox reactions. The redox reactions are only poorly understood, yet, they are of key importance because the redox state of chromium dictates its sorptive and chelation behavior. Despite the strong tendency for chromium to partition to many mineral surfaces, there are reports of extensive chromium migration (Keely and Boateng, 1987).

Surface sorption is an important element of chromium behavior. Electrostatic forces near the solid-liquid interface form a transition range near neutral pH in which both positively and negatively charged surface sites coexist (Swallow, et al., 1980). Several published studies discuss adsorption of chromium species at oxide interfaces (Bartlett and Kimble, 1976; Bartlett and James, 1979; Huang and Wu, 1977). If the mineral composition of the aquifer is known, appropriate sorption parameters for Cr(III) or Cr(VI) can be roughly estimated. Unfortunately, the redox state of the chromium also must be known and this is difficult to predict because natural redox chemistry of Cr(III)/Cr(VI) is not well understood.

Although Cr(III) and Cr(VI) are each quite stable and tend to be kinetically inhibited from undergoing redox transformations, there are systems which catalyze oxidation-reduction reactions of chromium. In strong acid solutions, Cr(VI) will oxidize organic compounds and be reduced to Cr(III) (Bartlett and Kimble, 1976). This reaction eliminates toxic Cr(VI) and generates the relatively insoluble trivalent species. The reverse reaction can be driven by MnO_2 in a process in which the MnO_2 appears to act as both an oxidizing agent and a catalytic surface (Bartlett and James, 1979). James and Bartlett (1983) reported the oxidation of Cr(III) in a mixture of tannery sludge and moist soil containing MnO_2. Thus, Cr(VI) may be generated at waste sites in which only Cr(III) is deposited. It is possible that at an actual waste disposal site, the organic oxidation and MnO_2 reduction reactions may form a cycle.

Another chromium/organic association that is largely unexplored yet potentially important to chromium behavior at waste sites is the solvation of chromate by organic phases. Essentially all studies of chromium in the environment focus on the solid- or aqueous-phase chromium. However, chromate is typical of a class of relatively large inorganic anions that dissolve to an appreciable extent in certain organic solvents. This phenomenon is well documented for highly acidic conditions in analytical solvent extraction studies (Zolotov, et al., 1967). Recent studies show that organic solvation of chromate occurs even near neutral pH; the phenomenon, therefore, has wider environmental significance than would be deduced from the solvent extraction literature. Reactions also may be enhanced by the close association of the chromate with the solvent.

Partitioning of chromate into non-aqueous phases may actually increase the mobility of chromium in the environment. Both Cr(VI) and dense chlorinated solvents are frequently associated with plating operations. This suggests that the chromate could become stabilized in the dense solvents and be transported well below the water table.

In summary, reactions between solvated Cr(VI) and organic compounds may affect the composition and behavior of ground-water contaminants by: (1) removing more hexavalent chromium from the aqueous phase than would occur by simple solvation; (2) stabilizing Cr(VI) in organic phases; and (3) mediating the oxidation of organic waste components into new compounds with greater or lesser toxicity and mobility.

Ground-Water Contamination by Leaded Gasoline

The subsurface movement of lead is expected to be minimal in most aquifers because of its low solubility and strong tendency to sorb to aquifer materials. However, studies have found that gasoline-derived lead can be transported over hundreds of meters. The mechanism(s) of this transport remain unclear, although transport as the alkyl lead, on microparticles, and/or in the free-product gasoline may be involved. An example case history of lead movement was conducted at the site of a large gasoline spill in Yakima, Washington (Fish, 1987). Up to 20,000 gallons of leaded and unleaded gasoline were released over several years. At the time of sampling, the lead had been transported over 100 meters in a heterogeneous alluvial aquifer.

At least three hypotheses have been made to explain these data. The first is that some of the lead is associated with fine-colloidal particles transported through the aquifer. The presence of large quantities of lead in the solid phase would support this possibility. However, the relatively low concentrations observed in ground water filtered through a 0.1 µm filter suggests that if particle transport is the mechanism, the bulk of the particles must be greater than 0.1 µm.

A second hypothesis is that the bulk of the lead transport occurred when the lead existed in less strongly sorbed alkylated forms. However, no alkylated lead could be found in the aquifer at the time of sampling.

A third hypothesis is that the bulk of the transport of the lead, as well as the organics, took place while both were associated with the free-product gasoline. The volume of the spill is such that the product could have extended over significant distances. However, as discussed in Chapter 3, the erratic behavior of immiscible phases in the subsurface is poorly understood. At the time of sampling, free product could be observed in wells at distances of up to 100 m from the source. The highly heterogenous, interbedded nature of the aquifer also might allow relatively narrow, preferential pathways for free-product movement that could enhance traveling distances.

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CHAPTER 7

MICROBIAL ECOLOGY AND POLLUTANT BIODEGRADATION IN SUBSURFACE ECOSYSTEMS

Joseph M. Suflita

Introduction

Interest in ground water-related sciences is growing, and individuals involved with all facets of ground-water use and protection are developing a greater awareness of the chemistry, physics, hydrology, geology, and biology of the terrestrial subsurface. Information gathered from ground-water contamination sites helps to focus questions regarding the possibility that aquifers possess natural attenuation mechanisms for pollutant abatement. Consideration of this possibility has led investigators to realize that natural physico-chemical processes may, at best, only partially transform aquifer contaminants.

Parallel to the general interest in ground water came the beginnings of serious study of ground-water microbiology. Because of the biochemical versatility of natural microbial communities, investigators thought that the microflora indigenous to aquifers might function to remove problem contaminants. In fact, microbial metabolism of ground-water pollutants is the only technology that has the potential to completely degrade pollutants *in situ* and convert them to more environmentally acceptable forms.

This chapter will introduce the historic and current scientific perspectives regarding microbial ecology of the terrestrial subsurface and will focus on how these perceptions evolved. Examples will be given of the diverse types of subsurface microorganisms, microbial communities, and associated metabolic activities. Also, the metabolic principles governing pollutant biodegradation in other habitats will be extrapolated to ground water. Limits to pollutant biodegradation will be considered in the context of existing environmental conditions, physiology of the indigenous microflora, and chemical structure of the contaminants. Finally, this chapter will discuss how these principles can be applied to either the *in situ* or above-ground bioremediation of contaminated aquifers.

Historical Perceptions

Several historical misconceptions about ground-water microbiology hindered the use of bioreclamation and probably contributed to the abuse of aquifers. First, ground water was perceived as a safe water source, protected by a metabolically diverse "living filter" of microorganisms in the soil root zone which functioned to convert organic pollutants to innocuous endproducts. However, recent evidence indicates that, in many instances, ground water may be at least as contaminated as surface waters (Council on Environmental Quality, 1981; Page, 1981). In retrospect, the historical perspective is somewhat understandable since ground-water flow is generally slow (10 to 100 m per year) and transport processes are complex (McKay, et al, 1985). A significant time lag for the movement of chemicals from their subsurface source to even nearby wells is common, and many years can pass before environmental or health impacts of ground-water contamination become evident.

Secondly, aquifers were considered abiotic environments since early studies indicated that microbial numbers decreased with soil depth (Waksman, 1916), and later studies showed that the vast majority of cells were attached to soil particulates (Balkwill, et al., 1977). In addition, by estimating the time required for surface water to vertically penetrate subsurface formations, investigators reasoned that microbes traveling with the water would quickly exhaust available nutrients and rapidly die off. These beliefs led to the perception that aquifers were sterile and essentially irretrievably lost when contaminated by polluting chemicals. Now, however, microscopic, cultivation, metabolic, and biochemical investigations, often using aseptically obtained aquifer material, reveal that the terrestrial subsurface harbors a surprisingly rich assemblage of procaryotic and some eucaryotic life forms. The evidence supporting this perception is described in the following sections.

Ground-Water Contamination

The sources of ground-water contamination have important implications for the design of biorestoration techniques. Contaminants can originate from non-point sources, such as agricultural chemicals and road salts, and from point sources including residential septic systems, leaking underground storage tanks, surface impoundments, landfills, and transportation losses. Comprehensive reviews of the sources and types of ground-water pollution are presented by Keswick (1984); Craun (1984); and Zoetman (1985).

It is important to point out that ground-water pollution is not just a water pollution problem. As shown in Figure 69, a spill of gasoline hydrocarbons tends to exist in multiple phases. The gasoline free product represents the most severe form of contamination, but also is the most limited in terms of area affected. As gasoline moves from a spill site, it contaminates soil in the vadose zone. Since its components are largely water-insoluble and less dense than water, hydrocarbon free product tends to reside and spread along the water table boundary. Hydrocarbon free product can easily pollute wells within the zone of contamination, and also can sorb to and contaminate those soil areas influenced by water table fluctuations. This sorbed material tends to be another more subtle source of secondary contamination. In addition, free product can contaminate surface waters, and gasoline vapors can collect in basements of buildings and create inhalation or explosion risks.

As discussed in earlier chapters, the severity of soil contamination tends to be a function of the properties of the soil. Water, too, affects the amount of contamination because it is an excellent solvent and can even dissolve, to some extent, those substances deemed insoluble. The concentrations of hydrocarbons in the water phase are generally low, but the amount of area affected by such contamination can be very high. Consequently, this form of contamination has the highest potential for human exposure. All remediation technologies must consider where the contaminant resides in the subsurface; treatment of only the water phase may provide a temporary solution to an immediate problem, but also may effectively ignore the more subtle and, many times, more important problem areas.

Evidence for Subsurface Microbiota

Microbiological investigations of the terrestrial subsurface have revealed that all aquifers examined thus far possess a sometimes surprisingly rich microflora. Such studies include direct microscopic, cultivation, metabolic, and biochemical evidence for microorganisms in aseptically obtained aquifer material. Table 4 is only a partial listing of the typical numbers of bacteria detected in various geological settings. This table illustrates that relatively high numbers of microorganisms can be detected in both contaminated and pristine aquifers of varying depth and geological composition. There is

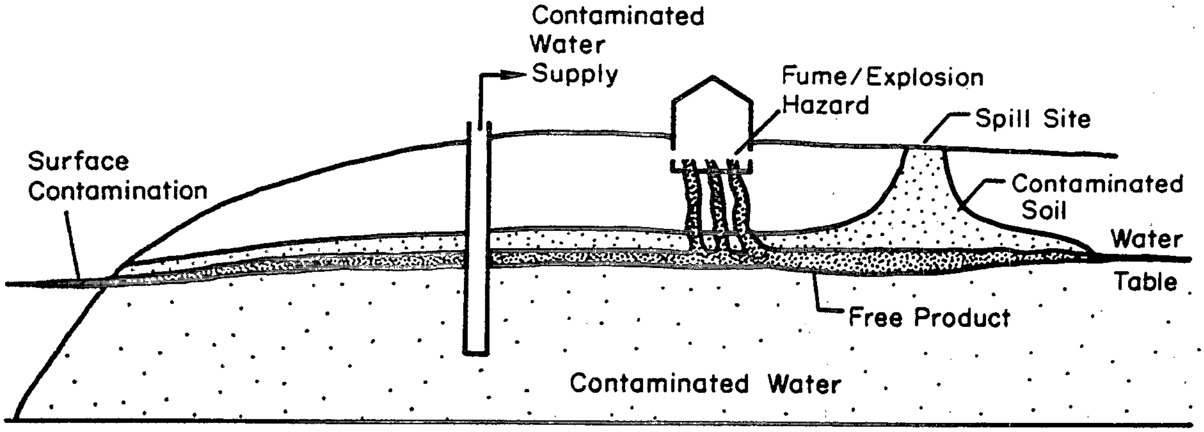


Figure 69. Multiple problems associated with hydrocarbon release to the terrestrial subsurface.

Table 4. Microbial Numbers in Various Geological Settings and Depths

Aquifer Site	Sample Type[a]	Depth (m)	Aquifer Contaminant	Total Count[b] x 10^6 Cells/gdw or Cells/ml	Viable Count[c] x 10^4 CFU/gdw or Cells	References
Sand/Gravel Lula, OK	S	5	None	3.8-9.3	20-110	Wilson, et al., 1983; Balkwill and Ghiorse, 1985
Sand Pickett, OK	S	5.5	None	5.2	250	Balkwill and Ghiorse, 1985; Ghiorse and Balkwill, 1985
Loamy Clay Fort Polk, LA	S	5	None	9.8	-	Ghiorse and Balkwill, 1983; White, et al., 1985
	S	5.5	None	1-10[d]	-	
Sand/Clay Conroe, TX	S	7.5	Creosote	5-49	-	Webster, et al., 1985
Burn Cavern Tenn. Colony, TX	W	91	Phenolics	-	4.2	Humenick, et al., 1982
Carrizo Aquifer TX	W	76	None	-	0.04	Humenick, et al., 1982
Mogothy Aquifer Long Island, NY	W	146	Treated sewage	-	0.01-5	Godsey and Ehrlich, 1978
Sand Ontario, Canada	W	10	Septage	0.14	0.031	Ventullo and Larson, 1985
Gravel Dayton, OH	W	10-12	None	0.036-0.06	0.052-0.06	Ventullo and Larson, 1985
Glacial Till St. Louis Pk., MN	W	25-35	Creosote	0.07-10	0.09-400[e]	Ehrlich, et al., 1983
Marmot Basin Alberta, Canada	W	1.5	None	0.05-2.5	-	Ladd, et al., 1982
Bacatunna, Clay Pensacola, FL	S	410	Acid waste	10[d]	-	White, et al., 1983
Sand/Gravel Cape Cod, MA	S	12-32	Sewage	11-34	-	Harvey, et al., 1984
Sand Norman, OK	S	1.8	Landfill leachate	11-17	-	Beeman and Suflita, 1987

[a] Aquifer Solids
[w] Ground Water
[b] Acridine Orange Direct Count (Unless Otherwise Noted)
[c] Plate Count Assay (Unless Otherwise Noted)
[d] Signature Lipid Analysis
[e] Most Probable Number Assay

good evidence that even deep geological formations can be suitable habitats for bacteria (Kuznetsov, et al., 1963; Updegraff, 1982).

The picture that emerges from microbiological studies is that subsurface microorganisms tend to be small, capable of response to the influx of nutrients, and primarily attached to solid surfaces. Although detectable, eucaryotic microorganisms are few in number relative to surface soil microorganisms and presumably of minor importance in the terrestrial subsurface. Microeucaryotes (such as fungi and protozoa) probably exist in most aquifers as metabolically inert resting structures. These data reinforce information published in a recent book (Bitton and Gerba, 1984) which reiterates that there is little to preclude microbial growth in the terrestrial subsurface (McNabb and Dunlap, 1975). This conclusion is important because it shows that those aquifers that are most susceptible to contamination by chemicals (those less than 100 meters deep), do possess diverse microbial communities.

Sample Procurement

The development of suitable sampling technology has helped to show the existence of a sizable subsurface microbiota. Any microbiological probe of the terrestrial subsurface is critically dependent on the quality, integrity, and representativeness of the samples obtained. To make valid interpretations of the data resulting from subsurface investigations, the samples received must not be contaminated with nonindigenous microorganisms. Potential sources of contamination include organisms present on the drilling machinery, in surface soil layers, in drilling muds, and in water used to make up the drilling muds. Since most subsurface biology is associated with the solid matrix, the discussion of sampling will be limited to aquifer sediments. However, McNabb and Mallard (1984) have published an excellent review of all the requirements for microbiological sampling of aquifers.

No sampling effort can be performed without some microbiological contamination, regardless of whether drilling tools are employed to reach deeper regions of the subsurface or if excavation pits are dug in relatively shallow areas. With this realization, most current sampling efforts rely on the recovery and subsequent dissection of cores to remove microbiologically compromised portions. This dissection can be performed in the field or, if the sampling sites are nearby, when the cores are returned to the laboratory. In all cases, the outer few centimeters and the top and bottom portions of aquifer cores are removed because of possible contamination by nonindigenous bacteria, and only the center portions of an aquifer core are used for subsequent analysis.

Ideally, this dissection process occurs as soon as possible after the core is removed from the ground so that nonindigenous microorganisms do not have a chance to penetrate to the inner portions of the core. In the field, an alcohol-sterilized paring device is used in the dissection process (McNabb and Mallard, 1984). The paring device has an inner diameter that is smaller than the diameter of the core itself. The aquifer material is extruded out of the core barrel used for sampling and over the sterile paring device to strip away the potentially contaminated material. For anaerobic aquifers, this field paring procedure is performed inside plastic anaerobic glovebags while the latter is purged with nitrogen to minimize exposure of the microflora to oxygen (Beeman and Suflita, 1987). Samples received in this manner are termed "aseptically obtained" and are suitable for microbiological analysis.

Metabolic Activity in Aquifers

Many of the studies cited in Table 4 employed aseptically obtained aquifer material and, thus, provide direct and conclusive evidence for the existence of subsurface bacteria. Several questions immediately become apparent: (1) Are the indigenous ground-water organisms metabolically active; (2) How diverse is their metabolism; (3) What factors serve to limit and/or stimulate the growth and metabolism of these organisms; and (4) Can one take advantage of the inherent metabolic versatility of aquifer communities to remediate contaminated areas?

The answers to the first two questions can be gleaned from a review of the scientific literature (Table 5). Even though many of the studies cited in the table were conducted prior to the development of aseptic sampling procedures, the list does illustrate that subsurface microbial activity can be detected, and major and minor elements may potentially be recycled in subsurface ecosystems. The metabolic processes referred to in the table include a variety of aerobic and anaerobic carbon transformations, many of which are pertinent to the biodegradation of aquifer contaminants. In this respect, the recent reviews by Ghiorse and Wilson (1988) and Lee, et al. (1988) are very illuminating. Other metabolic processes noted are those required for the cycling of nitrogen, sulfur, iron, and manganese.

The various metabolic processes listed in Table 5 are not mutually exclusive. As shown schematically in Figure 70, as labile organic matter enters an oxygenated aquifer, microbial metabolism will likely degrade the contaminating substrate. That is, the indigenous microorganisms utilize the pollutant as an electron donor to support heterotrophic microbial respiration. The aquifer microbiota use oxygen as a co-substrate and as an electron acceptor to support their respiratory activities. This demand on oxygen often results in its depletion and the establishment of anaerobic conditions. When oxygen becomes limiting, aerobic respiration slows, but other groups of microorganisms may then come into play and continue to degrade the contaminating organic matter. Under conditions of anoxia, anaerobic bacteria can use organic chemicals or several inorganic anions as alternate electron acceptors.

Nitrate present in the ground water, as indicated in Figure 70, generally is not rapidly depleted until oxygen is utilized. Organic matter can still be metabolized, but, instead of oxygen, nitrate serves as the terminal electron acceptor during the process of denitrification. Similarly, sulfate can serve as a terminal electron acceptor when nitrate is limiting. This information supports microbial metabolism linked to sulfate-reduction. When this occurs, hydrogen sulfide often can be detected in the ground water as a metabolic endproduct. When very highly reducing conditions prevail in aquifers, carbon dioxide also can serve as an electron acceptor and metabolism is linked to methane formation. Sometimes a spatial separation of dominant metabolic processes can occur in aquifers, depending on the availability of electron acceptors, the presence of suitable microorganisms, and the energy benefit of

Table 5. Selected Microbial Metabolic Processes and Oxygen Requirements in Subsurface Environments

Metabolic Process	Oxygen Requirement	Reference
I. Biodegradation of Organic Pollutants		
a. Petroleum Hydrocarbons	Aerobic	Jamison, et al., 1975 Lee and Ward, 1985 McCarty, et al., 1984 Raymond, et al., 1976 Roberts, et al., 1980 Wilson, et al., 1983 Wilson, et al., 1985
b. Alkylpyridines	Aerobic/Anaerobic	Rogers, et al., 1985
c. Creosote Chemicals	Aerobic/Anaerobic	Ehrlich, et al., 1983 Smolenski and Suflita, 1987 Wilson, et al., 1985
d. Coal Gasification Products	Aerobic	Humenick, et al., 1982
e. Sewage Effluent	Aerobic	Aulenbach, et al., 1975 Godsey and Ehrlich, 1978 Harvey, et al., 1984
f. Halogenated Organic Compounds	Aerobic/Anaerobic	Gibson and Suflita, 1986 McCarty, et al., 1984 Suflita and Gibson, 1985 Suflita and Miller, 1985 Ward, 1985 Wilson, et al., 1983 Wood, et al., 1985
g. Nitrilotriacetate (NTA)	Aerobic/Anaerobic	Ventullo and Larson, 1985 Ward, 1985
h. Pesticides	Aerobic/Anaerobic	Gibson and Suflita, 1986 Suflita and Gibson, 1985 Ventullo and Larson, 1985 Ward, 1985
II. Nitrification	Aerobic	Barcelona and Naymic, 1984 Idelovitch and Michail, 1980 Preul, 1966
III. Denitrification	Anaerobic	Ehrlich, et al., 1983 Lind, 1975 Ward, 1985
IV. Sulfur Oxidation	Aerobic	Olson, et al., 1981
V. Sulfur Reduction	Anaerobic	Beeman and Suflita, 1987 Bastin, 1926 Hvid-Hansen, 1951 Jacks, 1977 Olson, et al., 1981 van Beek, et al., 1962
VI. Iron Oxidation	Aerobic	Olson, et al., 1981 Hallburg and Martinell, 1976
VII. Iron Reduction	Anaerobic	Godsey and Ehrlich, 1978 Ehrlich, et al., 1983
VIII. Manganese Oxidation	Aerobic	Hallburg and Martinell, 1976
IX. Methanogenesis	Anaerobic	Beeman and Suflita, 1987 Belyaev and Ivanov, 1983 Davis, 1967 Gibson and Suflita, 1986 Godsey and Ehrlich, 1978 Suflita and Miller, 1985 van Beek, et al., 1962

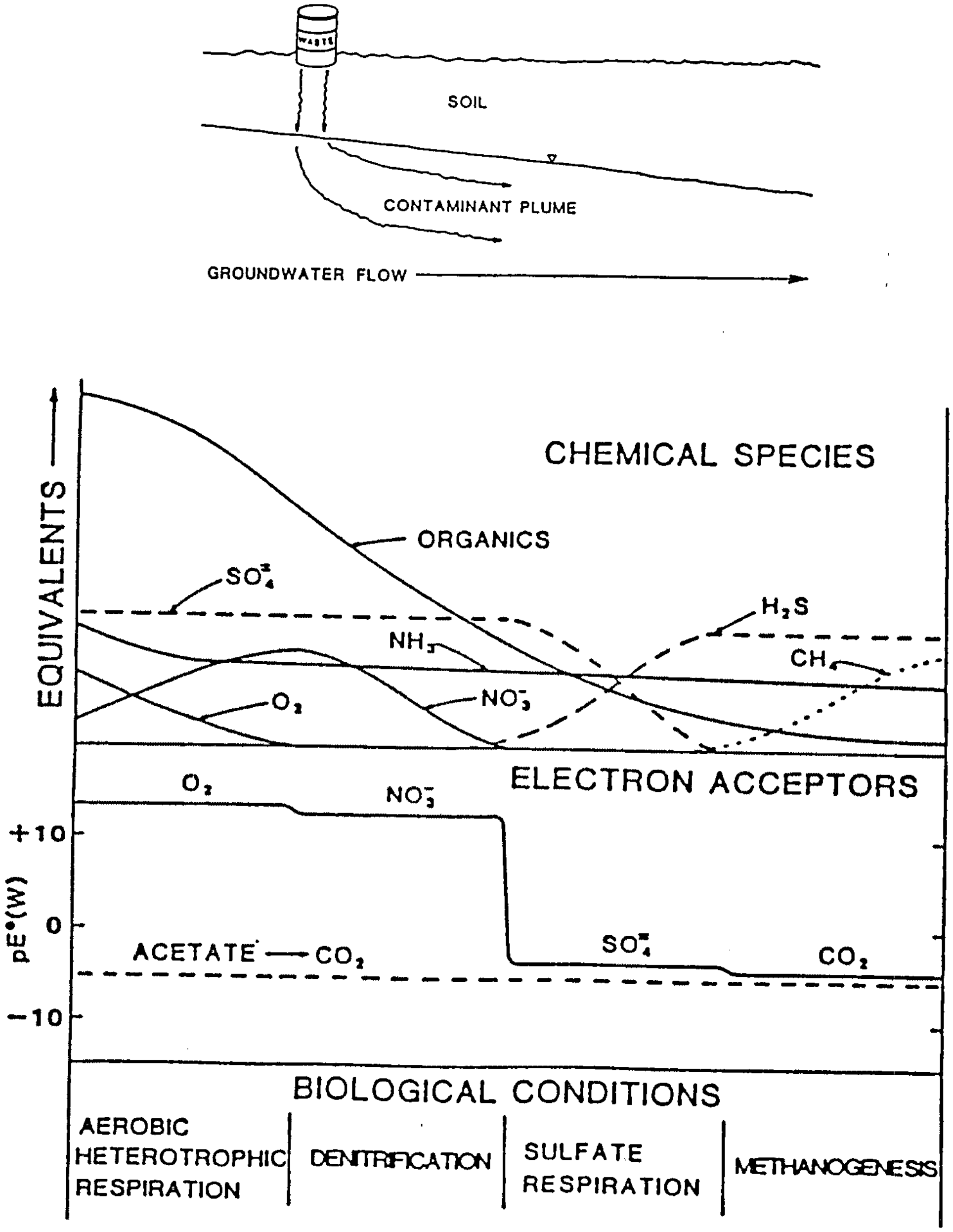
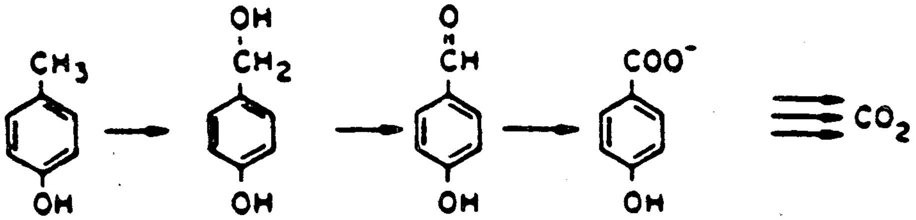
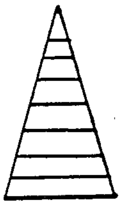
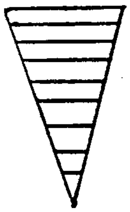


Figure 70. Microbially mediated changes in chemical species, redox conditions, and spatial regions favoring different types of metabolic processes along the flow path of a contaminant plume (adapted from Bouwer and McCarty, 1984).

the metabolic process to the catalyzing microbial communities. As organic matter is transported in a plume, a series of redox zones can be established which range from highly oxidized to highly reduced conditions. The biodegradation potential available under these various conditions and the expected rates of metabolism will be very different in each instance.

The biodegradation of a known ground-water contaminant, p-cresol, can be used as an example (Figure 71). This compound is reported to be



Redox Conditions	Biodegradability	Lag Time	Relative Rate	Ref.
Aerobic	+			1
Denitrifying	+			2
Sulfate Reducing	+			3,4
Methanogenic	+			4,5,6

(1) Hopper, 1976, 1978; (2) Bossert & Young, 1986; (3) Bak & Widdel, 1986; (4) Smolenski & Suflita, 1987; (5) Godsy et al., 1983; (6) Senior & Balba, 1984.

Figure 71. Proposed degradation pathway for *p*-cresol under various redox conditions.

degradable under aerobic, dinitrifying, sulfate-reducing, and methanogenic conditions. Moreover, the initial stages of the metabolism of p-cresol are similar under the various redox conditions. Under aerobic conditions, the initial conversion of the substrate to aromatic alcohol requires molecular oxygen. However, oxygen inhibits the anaerobic metabolism of p-cresol, so, presumably, a water molecule is employed to effect this transformation during the catalysis of this substrate under the other conditions. Comparing the length of the lag time before the onset of biodegradation and the rate of metabolism once it begins, aerobic decomposition is relatively fast, especially compared to methanogenic incubation conditions. Thus, if rapid biotransformation is the goal, then aerobic incubation conditions should be maintained in an aquifer in any sort of a bioremediation strategy. However, considering the often slow rates of ground-water movement, even anaerobic removal may effectively compete with the faster aerobic metabolism of this substrate.

This does not imply that aerobic transformation mechanisms are always faster than the anaerobic counterparts. Some compounds may biodegrade at faster rates when anaerobic conditions prevail. For example, several halogenated aliphatic substrates prove amenable to microbial metabolism under reducing conditions, but persist in comparable aerobic incubations (Bouwer and McCarty, 1984; Bouwer, et al., 1981). Similarly, the haloaromatic pesticide 2,4,5-T often is considered recalcitrant under aerobic conditions. Although specialized, genetically manipulated microorganisms now exist that aerobically degrade this substance (Kilbane, et al., 1982), 2,4,5-T can be completely mineralized without genetic manipulations when incubated under methanogenic conditions (Gibson and Suflita, 1986).

When assessing microbial metabolism in aquifers, the existing scientific literature must be used as a guidepost for determining the types of biotransformations to expect. For some substances, existing information will be available and instructive; however, for more exotic substances, the available literature will prove disappointingly small. In either case, laboratory experimentation is required to evaluate a pollutant's susceptibility to biotransformation.

Microcosms

Even when the bulk of scientific literature indicates that a pollutant chemical is likely to biodegrade easily in most environments, an assay should be used to confirm that contention. This is necessary because, while a specific ground-water contaminant may be the same as that encountered in other environments, the particular physical, chemical, and hydrological site characteristics can be quite different and can influence biodegradation processes. A reliable tool or method is required for evaluating the susceptibility of a ground-water contaminant to biodegradation. In addition, the experimental system should be scientifically rigorous, yet flexible enough to facilitate a critical evaluation of various bioremediation strategies. In this respect, the use of microcosms seems to hold great promise. Some examples of microcosm technology are discussed by Pritchard (1981) and Pritchard and Bourquin (1984). Also, Wilson and Noonan (1984) have analyzed the specific application of microcosms to aquifer systems.

The term microcosm means different things to different individuals. In the strictest sense, a microcosm is:

> ...a calibrated laboratory simulation of a portion of a natural environment in which environmental components, in as undisturbed a condition as possible, are enclosed within definable physical and chemical boundaries and studied under a standard set of laboratory conditions (Pritchard, 1981).

Implicit in this definition is that microcosms may be used as surrogates for ground-water field studies without the associated logistical, financial, administrative, and regulatory problems. In addition, when properly employed, microcosms incorporate the site-specific variables of the area under investigation and allow for the assessment of risk and prediction of the transport and fate characteristics of a contaminant. Further, such systems help to evaluate the waste assimilative capacity of an environment (Pritchard and Bourquin, 1984). This evaluation can be achieved without a detailed knowledge of those endogenous environmental factors that may stimulate or retard microbial metabolism.

The design of microcosms depends a great deal on the nature of the question being posed (Wilson and Noonan, 1984; and Pritchard and Bourquin, 1984). Microcosms range from simple batch incubation systems to large and complex flow-through devices, and all can be used in a variety of studies on the transport and fate of subterranean contaminants influenced by microorganisms. Microcosms are used to help identify biodegradable pollutants and those pollutants that tend to persist. Often, by following the fate of a pollutant in a microcosm, the predominant pathways of biotic or abiotic transformation can be described. Lastly, the decay of a particular contaminant in a microcosm may relate to the rate of biotransformation *in situ* without relying on indirect measures of microbial biodegradation for rate predictions such as the enumeration of catalytic microorganisms.

This last point can be illustrated with an example. An assay for the anaerobic biodegradation of the pesticide 2,4,5-T was conducted with microcosms made of sediments and ground water sampled from two distinct sites within the same aquifer (Gibson and Suflita, 1986). Microorganisms from one site were able to completely mineralize this substrate while parallel experiments revealed that the pesticide persisted in microcosms made from the other site. Further experimentation showed that the requisite microorganisms were present at both sites, but their activity at the second site was at least partially inhibited by locally high levels of sulfate in the ground water. Predictions of the rate of substrate utilization in the sulfate-rich ground water would have been overly optimistic if based primarily on assays for the number of degrading microorganisms. Conversely, predictions of transport and fate behavior based on microcosm experimentation would likely prove more realistic, even without the appreciation for the role of sulfate in a portion of the aquifer. This example also illustrates how site-specific aquifer characteristics can drastically influence the evaluation of biodegradation results.

Microcosms possess several experimental advantages. For example, microcosms are replicable and allow appropriate controls to be employed. This advantage cannot be overstated since it allows the resulting data to be statistically evaluated. Further, such experiments can meet the usual requirements for scientific rigor. While environmental simulation is a goal of microcosms, such systems may be subject to controlled perturbations of their chemical or physical parameters. In that manner, the influence of such perturbations can be quantitatively evaluated for effects on biotransformation processes. Similarly, the trophic structure of microcosms can be varied in order to study complex biological interactions. However, this advantage may not exist since microeucaryotes tend to be of minor importance in most aquifers examined thus far. Microcosms are accessible and containable laboratory tools with which the experimenter controls inputs (water, substrate, nutrients, etc.) as well as exports (cells, metabolites, etc.). When properly employed, microcosms avoid field pollution, yet provide a time-efficient way of evaluating the likely fate of environmental contaminants.

Conversely, microcosms also suffer from several limitations that should not be ignored at the onset of experimentation and during an evaluation of the resulting data. One limitation is that the start-up and operating costs for complex microcosms can be high. Also, microcosms can disturb the normal structural and functional features of an ecosystem and generally possess abnormally high surface to volume ratios. The simple sampling and containerization of microbial communities within altered physical limits causes the initiation of rapid population shifts that may influence biodegradation estimates. However, the advantages of microcosm techniques outweigh the inherent limitations (Pritchard and Bourquin, 1984), and such studies can provide useful and environmentally reliable information.

Extrapolation of Metabolic Information

Although microcosms provide a tool that can be used to address some of the questions regarding metabolic proficiency of ground-water microorganisms, other questions remain. For example, is the information collected from microcosm studies reliable, and can the metabolic information obtained from microcosm studies be reliably extrapolated to terrestrial subsurface environments? These questions stem from a consideration of the basic principles that generally govern biodegradation. Although subsurface microbes may or may not prove to be unusual, metabolism tends to be a unifying feature of life. As Dagley (1984) has pointed out, diverse life forms often exhibit similar metabolic pathways, and information pertinent to even human physiology often can be obtained from microbiological studies (Dagley, 1984). Therefore, metabolic principles gleaned from the study of xenobiotic compound metabolism in surface habitats are useful for subsurface site evaluations and the design of aquifer remediation strategies. The existing literature provides an excellent scientific foundation that can be used to make cautious extrapolations of metabolic principles observed in surface environments to those that regulate microbial activities in the subsurface.

Microorganisms play prominent roles in the transformation and degradation of contaminating organic chemicals in virtually every major habitat except the atmosphere. Microbial communities in nature are able to metabolize many types and quantities of synthetic organic compounds (Alexander, 1981; Kobayashi and Rittman, 1982). At the extremes, some xenobiotic compounds can supply the carbon and energy requirements associated with microbial growth, while other substrates tend to resist significant biotransformation. Still other chemicals are "cometabolized" to form degradation products that are usually structurally similar to the parent molecule (Alexander, 1981). By definition, the latter process does not result in growth of the catalyzing microorganism, but does result in the transformation of a substrate such that the molecule can be available for subsequent utilization by other microorganisms. In an ecological sense, it is common that several microbes act in a combination to effect some overall degradation of a substrate (Slater and Lovatt, 1984). In anaerobic ecosystems, this concerted metabolic activity is essential for the normal cycling of carbon and energy on earth (McInerney and Bryant, 1981).

Knowledge of the mechanisms of energy and materials cycling in the terrestrial subsurface, however, is limited and reflects the difficulties in sampling and studying a complex and unfamiliar environment (McNabb and Mallard, 1984). As pointed out earlier, the likely metabolic fate of contaminating chemicals sometimes can be predicted if the governing microbial ecology and the limits of extrapolation are understood.

Recalcitrance

Researchers have learned that there are limits to the metabolic versatility of microorganisms. Many xenobiotic substrates are transformed so slowly under most conditions that some degradation of environmental quality occurs. These chemicals are referred to as recalcitrant. However, recalcitrance or resistance to biodegradation is not a feature strictly associated with anthropogenic chemicals. Many naturally occurring materials also can persist for long periods of time (Alexander, 1965 and 1973). For example, entire portions of human corpses (i.e., hair) were recovered from various environments (peat bogs, desert cemeteries, etc.) and estimated to be hundreds to thousands of years old. Similar ages have been ascribed to proteolytic enzymes recovered from permafrost soils. Microbial spores can persist for tens of thousands of years. These spores are useful to help "date" geological deposits. Finally, most of the world economies are based on petroleum deposits that have managed to persist for many millennia within subterranean environments.

In aquifers, as in other environments, organic matter decomposition should be considered in the context of: (1) existing environmental conditions; (2) physiology of the requisite microorganisms; and (3) chemical structure of the particular substance(s) under consideration. The general principles of these interrelated topics are considered below; detailed reviews can be found in Alexander's publications (1965 and 1973).

Environmental Barriers to Biodegradation

In order to grow, microorganisms need a suitable physical and chemical environment. Extremes of temperature, pH, salinity, osmotic or hydrostatic pressures, radiation, free water limitations, contaminant concentration, and/or the presence of a heavy metal or other toxicant materials can adversely influence and even limit the rate of microbial growth and/or substrate utilization. Often, two or more environmental factors interact to limit microbial decomposition processes, and, in fact, environmental barriers can act to render normally labile substances persistent. This explanation was used by Woods Hole researchers (Jannasch, et al., 1971) who found food substances from an accidentally sunken and subsequently recovered submarine to be almost preserved after 10 months exposure to deep-sea conditions. However, when the food was incubated in sterile seawater at *in situ* temperatures (3°C), the materials putrefied after only a few weeks. The authors suggested that the hydrostatic pressures of the sea (150 ATM) effectively raised the minimal temperature necessary for microbial proliferation. Once this increase exceeded incubation temperatures, microbial activity slowed 10 to 100 fold.

Recognition of the nature of the limiting environmental factor(s) and a consideration of its practical application in subsurface environments will help dictate which type of bioreclamation procedures to use. For example, the temperature of aquifers probably could not be significantly altered to stimulate *in situ* microbial growth and metabolism. However, the same is not true for a surface biological treatment process.

Physiological Barriers to Biodegradation

In addition to the immediate environment, various microbial physiological factors can influence the biotransformation of pollutant chemicals. Like all forms of life, the requisite microorganisms present in an aquifer are primarily composed of carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, and a variety of trace elements. These substances are required in varying degrees for aquifer microorganisms to proliferate. Aquifer microorganisms can utilize such substances to the point where one or more of the requirements are exhausted and effectively limit further microbial growth or metabolic activity. For aquifer remediation efforts to succeed, these materials must already be present in the aquifer or be supplied in the proper form.

Ideally, the organic pollutants in the aquifer represent an appropriate supply of carbon and energy necessary for heterotrophic microbial growth. However, that supply can be too high or too low. Too high a substrate concentration can limit microbial metabolism due to the toxicity of the substrate to the requisite microflora. In contrast, ground-water contaminants also can be present at concentrations that are too low to allow microbial response and/or may not be suitable growth substrates. Growth and energy sources need not come from the same carbon substrate. The growth and metabolism of degrading microbes sometimes can be stimulated by providing them with a non-harmful primary carbon substrate so that the rate and extent of pollutant decomposition can be proportionally increased (McCarty, 1985; McCarty, et al., 1981; McCarty, et al., 1984).

A chemical also will be metabolized poorly if it is unable to enter microbial cells. This may occur with either natural or anthropogenic polymers. While the monomeric units may be inherently amenable to microbial destruction, the larger molecular weight polymers persist because they often fail to gain access to intracellular catabolic enzymes. A substrate also will persist if it fails to derepress the enzymes necessary for its destruction. It may be possible to induce the appropriate enzymes with an alternate chemical compound. Occasionally, initial biochemical reactions result in metabolites that tend to inhibit the degradation of even the parent molecule and can adversely affect the biodegradation of some pollutants.

Lastly, the absence of other necessary microorganisms can limit the destruction of a contaminant. Often, several microbial groups are needed for the destruction of a pollutant. In anaerobic environments, this type of relationship is a prerequisite for completion of the carbon cycle (McInerney and Bryant, 1981). The anaerobic mineralization of organic matter is critically dependent on obligate microbial consortia; if any of the individual members of a consortium are absent, the biodegradation of the parent material effectively ceases.

Chemical Barriers to Biodegradation

One of the most important factors that influence the degradation of a contaminant in aquifers is the contaminant's structure, which can dictate the pollutant's physical state (i.e., soluble, adsorbed, conjugated, etc.) and thereby alter its tendency to biodegrade. However, it is important to be specific when referring to biodegradation. When a compound undergoes primary attack, initial metabolic events often result in reaction products with their own environmental impact and persistence characteristics. An example of this is the fate of the pesticide carbaryl (Sevin). Carbaryl is widely used as a substitute for DDT and is touted as being readily degradable. However, this pesticide is known to have a myriad of environmental fates (Figure 72). An examination of Figure 72 reveals that some metabolic routes do lead to the ultimate conversion of carbaryl to carbon dioxide, while others result in the production of complex aromatic metabolites, the fate of which is still unknown. Therefore, when

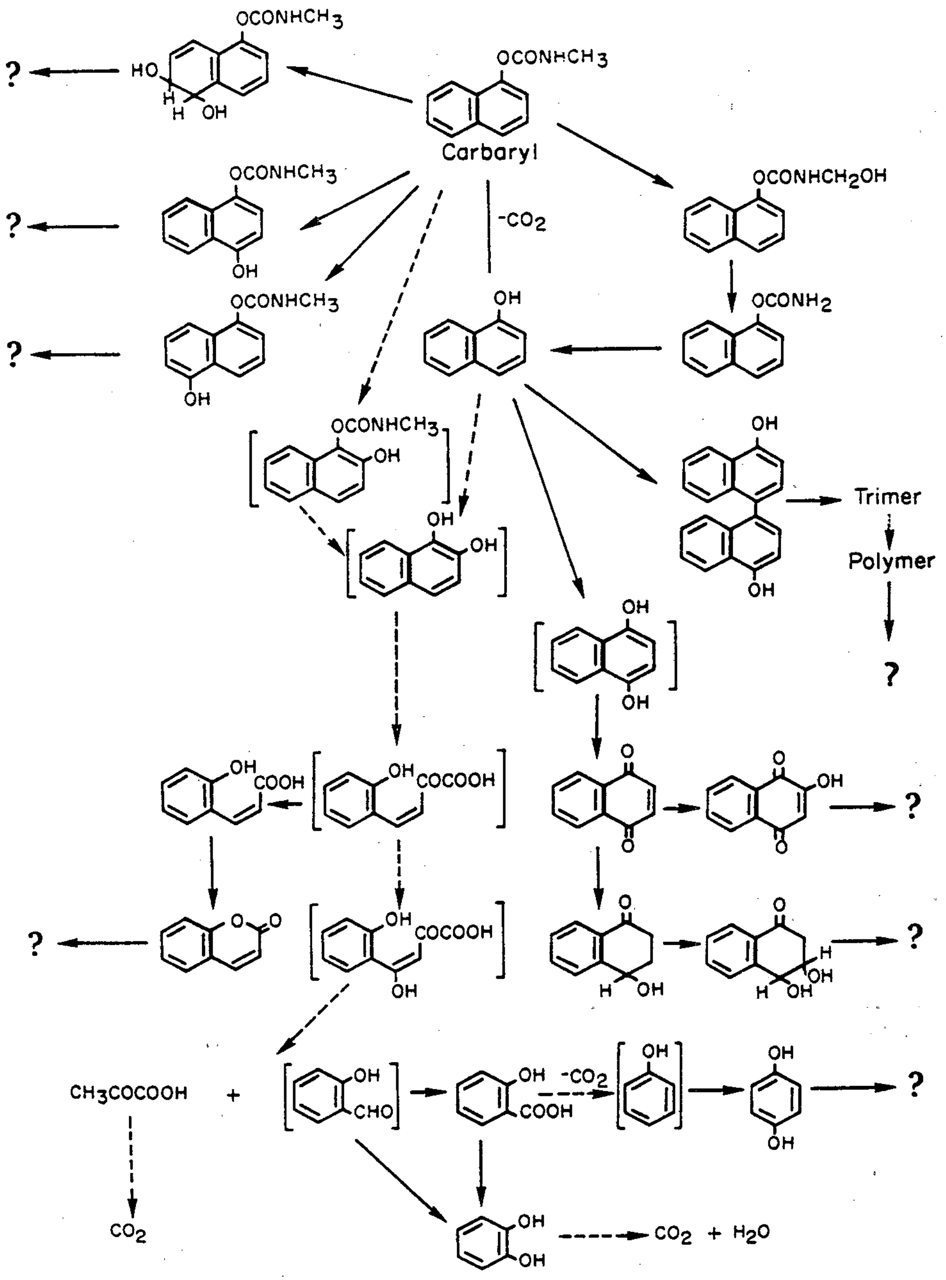


Figure 72. **Proposed pathway of carbaryl degradation in soils and microbial cultures (adapted from Rajagopal, et al., 1984).**

evaluating the scientific literature, the distinction must be made between "biodegradation" and "mineralization." The mere loss of a chemical from an environment may or may not be a desirable consequence of biotransformation processes. If biodegradation results in the production of undesirable metabolites, it may be best to choose a non-biological strategy for aquifer cleanup. The example above illustrates the need to understand the overall fate of a contaminating chemical in an aquifer and how informed decision-making must be based on solid metabolic information.

Aquifer pollutants may contain various chemical linkages that tend to favor or hinder microbial attack. However, broad generalizations on the biodegradability of various linkages tend to be of limited value since substitute effects drastically alter the susceptibility of even simple organic molecules to biotransformation. The number, type, and position of substituents must be considered when evaluating the metabolic fate of particular contaminants in aquifers.

The effect of branching is illustrated in Table 6 which is adapted from the work of McKenna and Kallio (1964). Approximately 15 bacterial strains from several different genera were evaluated for their ability to use a series of structurally related substrates. Cultures exhibiting profuse growth, slight growth, or no growth on a particular substrate were assigned a qualitative index of 2, 1, or 0, respectively. All cultures grew well with 1-phenyldecane. The organisms most likely initiated their attack on this molecule through the oxidation of the terminal methyl group in order to convert the molecule to a fatty acid derivative. Continued metabolism of the molecule would likely be by β-oxidation of the side chain. However, a single methyl substituent on the side chain drastically influenced the susceptibility of the resulting structure to metabolism by the test organisms. All the mycobacteria and nocardia were able to grow on 1-phenyl-4-methyldecane. However, the pseudomonads and micrococci were no longer able to do so. When the substrate contained an "internal" quaternary carbon atom, as is the case for 1-phenyl-4,4-dimethyldecane, the molecule proved available to only a few organisms and permitted minimal growth at best. Very often, when a quaternary carbon atom occurs at the terminal end of an alkane chain, the resulting molecule is quite resistant to aerobic microbial attack.

Structural effects also can be observed with anaerobic microorganisms. A comparison of the rate of aryl-reductive dehalogenation by an anaerobic consortium of bacteria revealed that the type and position of the halogen substituent influenced the degradation of the resulting molecules. Table 7 shows that all brominated and iodinated benzoates were transformed by these bacteria, but no fluorinated benzoates and only one chlorinated benzoate

Table 7. The Rate of Anerobic Monohalobenzoate Metabolism Exhibited by an Enrichment of Dehalogenating Bacteria (DeWeerd, et al., 1986)

	Dehalogenation Rate (µmoles/L/hr)			
Position	F	Cl	Br	I
Ortho	n.d.	0	1.20	0.50
Meta	**0**	**4.63**	**3.70**	**0.89**
Para	0	0	0.05	0.66

Table 6. Microbial Growth Response to Phenyldecanes: 0 = No Growth; 1 = Questionable or Slight Growth; 2 = Moderate or Abundant Growth (Adapted from McKenna and Kallio, 1964)

Organism	Strain	1-Phenyldecane	1-Phenyl-4-methyldecane	1-Phenyl-4,4-dimethyldecane
Micrococcus cerificans	H.O.1-N	2	0	0
	H.O.3	2	0	0
	H.O.4	2	0	0
	S-18.2	2	0	0
	S-14.1	2	0	0
Pseudomonas aeruginosa	119 JWF	2	0	0
	191 JWF	2	0	0
	Sol 20 JS	2	0	0
Mycobacterium phlei	No. 451	2	2	0
M. fortuitum	No. 389	2	2	0
M. rhodochrous	No. 382	2	2	0
M. smegmatis	No. 422	2	2	1
Nocardia opaca		2	2	1
N. rubra		2	2	1
N. erythropolis		2	2	1
N. polychromogenes		2	2	1
N. corallina		2	2	1

were transformed. For transformed compounds, slower rates of dehalogenation were correlated with increasing halogen size. However, the rate of *ortho*, *meta*, and *para* dehalogenation differed less with increasing halogen size. Most importantly, the *meta*-substituted halobenzoates always exhibited the fastest rates of biodegradation when compared to their isomeric counterparts. Thus, when halobenzoates are considered, the *meta*-substituted molecules are the most susceptible to anaerobic biotransformation.

These few examples illustrate that the chemical structure of a contaminant also influences its susceptibility to biodegradation. Despite the difficulty in generalization, the scientific literature shows that the closer a contaminant structurally resembles a naturally occurring compound, the better the possibility that the former will be able to enter a microbial cell, derepress the synthesis of catabolic enzymes, and be converted by those enzymes to central metabolic intermediates. In addition, biodegradation is less likely, but not entirely precluded, for those molecules having unusual structural features only infrequently encountered in nature. Ease of biodegradation can be viewed as a continuum ranging from very labile compounds to those that are recalcitrant (Figure 73).

Labile		Recalcitrant
Structural Analogs of Natural Materials	← - - - →	Chemicals with No Natural Counterpart

Figure 73. The continuum of biodegradation ease.

When viewed in this context, it should not be surprising that xenobiotic compounds tend to persist in nature because microorganisms have not evolved the necessary metabolic machinery to attack those compounds. However, as a group, microorganisms are nutritionally versatile, have the potential to grow rapidly, and possess only a single copy of DNA. Consequently, any genetic mutation or recombination is immediately expressed. If the alteration is of adaptive significance, new species of microorganisms can arise and proliferate. The polluted environment supplies selection pressure for the evolution of organisms with novel metabolic potential. Ultimately, the organisms may not only survive in the polluted environment, but also may be capable of growing at the expense of the contaminating substance.

Bioremediation of Aquifers

Once an aquifer contaminant is recognized as being susceptible to biodegradation, the goal of bioremediation/bioreclamation efforts is to utilize the metabolic capabilities of the indigenous microflora to destroy and eliminate that contaminant. Currently, enhanced bioreclamation is the use of common aquifer bacteria to degrade organic contaminants. This practice generally does not require the innoculation of the terrestrial subsurface with foreign bacteria.

Bioremediation attempts to impose particular conditions in an aquifer that encourage microbial proliferation and the development of desirable microorganisms. With knowledge of the chemical and physical needs of microorganisms and the predominant metabolic pathways, a strategy can be developed to stimulate biodegradation. Most often, microbial activity is stimulated by supplying the nutrients necessary for microbial growth. These efforts can take place either above ground or *in situ*.

An example of above-ground bioreclamation is schematically shown in Figure 74. In the illustration, ground water and the associated contaminant are pumped to the surface through a series of recovery wells. On the surface, the water is treated in a series of steps, which include the supply of appropriate nutrients. The treated (i.e., decontaminated) water is then reinjected into the aquifer. Injection and recovery wells are positioned so that they intersect a zone of contamination within the aquifer along natural ground-water flow paths. If excess nutrients are in the treated water, it is conceivable that this system also will stimulate the *in situ* biotransformation of the contaminants.

Moving the contaminant to the surface for treatment is often impossible or impractical since even mildly adsorbing chemical species may require many decades of pumping before being reduced to sufficiently low levels. In this case, an *in situ* approach may be more feasible. Figure 75 shows two such systems.

Figure 75A illustrates a system in which the microbial nutrients are mixed with ground water and circulated through the contaminated portion of the aquifer via a series of injection and recovery wells. In this case, air compressors are used to impose aerobic conditions on the indigenous microflora. Nutrients also can be circulated via an infiltration gallery as depicted in Figure 75B. This method provides a potential mechanism for the microorganisms to attack contaminants trapped in the pore spaces of the unsaturated zone. Each of the examples

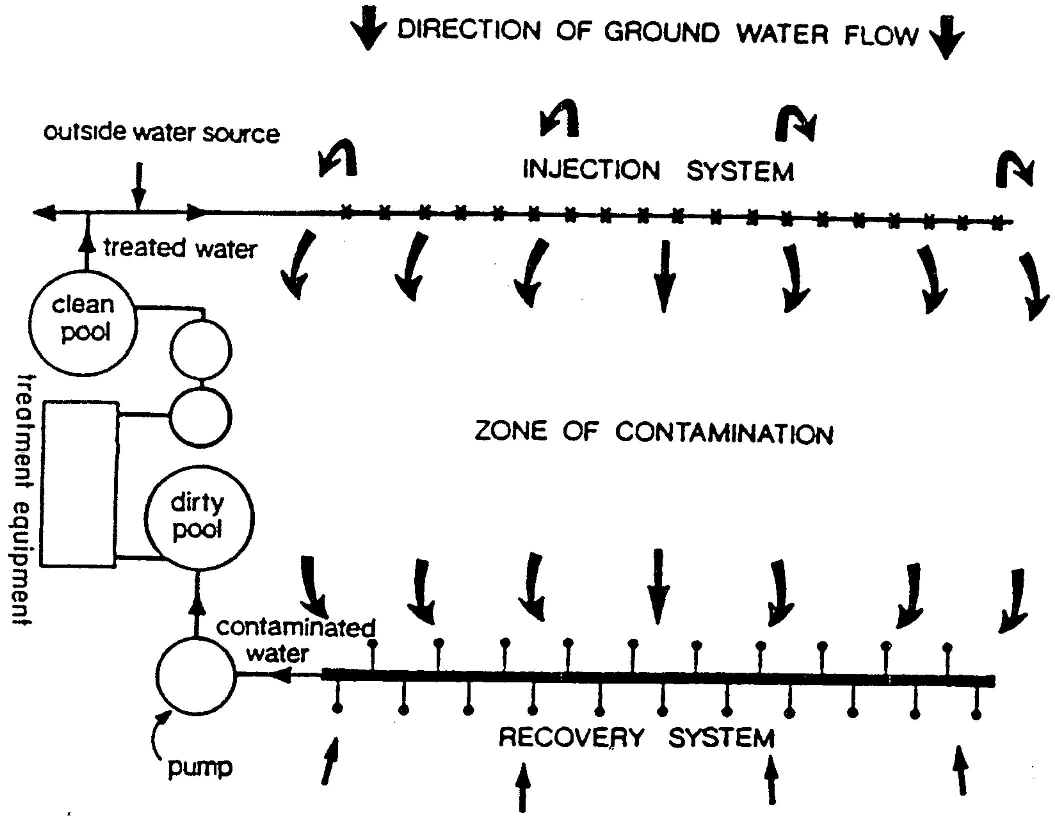


Figure 74. Above-ground treatment system design for the biorestoration of a contaminated aquifer (adapted from Lee, et al., 1988).

discussed above presume an adequate understanding and control of the hydrogeology of the area under treatment. This topic will be dealt with more specifically in Chapter 8.

Biorestoration approaches have several advantages over other potential cleanup strategies. First, these approaches can be used to treat some common aquifer pollutants, as described in Chapter 8. Bioremediation is environmentally sound in that it results in the complete destruction of a contaminant. This is not to imply that the technology can remove 99.999 percent of the material, but rather, it results in the complete change in the chemical properties of the parent contaminant. Aquifer biorestoration approaches utilize the indigenous microflora so that mass inoculation efforts are often unnecessary. There is insufficient scientific evidence to suggest that the intentional addition of desirable microorganisms actually aided an aquifer biorestoration effort (Lee, et al., 1988; Chapter 8). Finally, compared to other technologies, biorestoration also is economical.

However, biorestoration also suffers from several drawbacks (Lee, et al., 1988). At some sites, many types of wastes (acids, bases, and organic and inorganic materials) are co-disposed and any of these wastes alone or in combination could inhibit microbial growth and metabolism. Incomplete degradation of some substances may lead to taste and odor problems in the ground water. Also, the operation of biorestoration programs can be maintenance- and analytically intensive. Further, to date, the technology has generally been limited to aquifers possessing high permeabilities. Despite these limitations, the cost of competing technologies will likely insure that bioreclamation efforts will continue and assume an increasingly larger role as a viable aquifer cleanup strategy.

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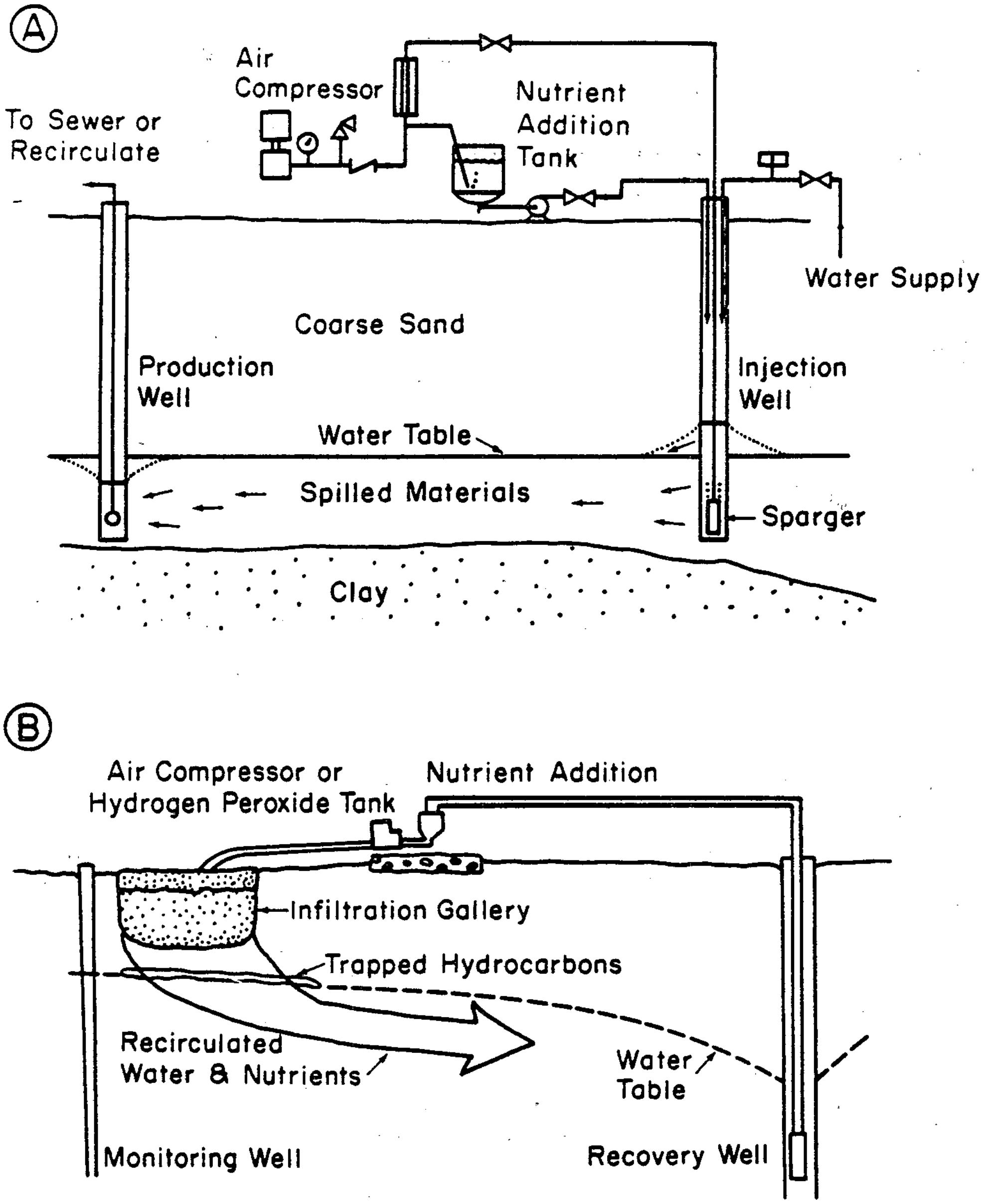

Figure 75. Two designs for the *in situ* remediation of contaminated aquifers (adapted from Lee, et al., 1988).

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CHAPTER 8

MICROBIOLOGICAL PRINCIPLES INFLUENCING THE BIORESTORATION OF AQUIFERS

Joseph M. Suflita

Introduction

Ground-water pollution problems can be enormously complex. Symptoms of aquifer contamination include odor and taste problems and the occasional appearance of a free product phase in wells. Besides the health concerns associated with the latter type of contamination, volatile and flammable fumes can accumulate in buildings and result in explosions and/or inhalation risks. Ground-water contamination also can conceivably impact surface water supplies and lead to more obvious signs of pollution including color and odor problems, fish kills, and if an immiscible chemical is involved, the formation of seeps or slicks.

The purpose of this chapter is to briefly consider various treatment options for cleaning up contaminated aquifers and to illustrate how biorestoration techniques fit into the myriad of pollution mitigation tools. This chapter also describes the types of considerations that must be made prior to implementing a field aquifer biorestoration program. An example of spilled gasoline in an aquifer is chosen to illustrate how basic microbiological and biochemical principles meld into an overall aquifer treatment strategy. In addition, guidelines are provided for the critical evaluation of claims for aquifer restoration, with suggestions for the types of information that might be collected to support such claims. Particular attention is paid to *in situ* biorestoration attempts that rely on the inoculation of desirable microorganisms. Lastly, a perspective on bioreclamation techniques is provided through a consideration of the practical limitations of the technology.

Environmental Fate of Contaminants and Treatment Options

At first glance, it may seem unusual to consider the environmental fate of a contaminant together with various options for the abatement of that contaminant. However, these topics are governed by the same two phenomena – the transport characteristics of a pollutant and the reaction of the contaminant with the environment.

Table 8 generally depicts the fate of a contaminant in a specific environment in terms of movement, retention, and reaction processes as a function of the properties of both the environment and the contaminant. The fate of a contaminant is largely a function of the chemistry of the pollutant in its environment. Similarly, the reaction mechanisms that a pollutant may undergo (i.e., hydrolysis, precipitation, oxidation/reduction, etc.) are a function of that chemical and the existing environmental conditions. These various processes are interrelated (Table 8). For instance, a chemical may be inherently susceptible to microbial attack, but is deposited in an environment where the production of low molecular weight acids from the microbial metabolism of other forms of organic matter results in a decrease in overall pH. The immediate pH conditions may prevent the continued metabolism of that chemical. The interrelationships between environmental conditions, chemical structure, and the physiology of microorganisms are described in Chapter 7.

Treatment options for contaminated aquifer remediation are governed by the same basic characteristics

(Table 9). Transport and reactivity properties of a contaminant can be envisioned as a continuum from low to high for each characteristic, and can help decision-makers who are considering an aquifer treatment option. For example, if a contaminant does not transport well and tends to be a recalcitrant molecule, containment may be the most likely treatment option. However, if the pollutant is subject to desirable biotransformation reactions and reactivity is high, then a bioremediation approach to contaminated aquifers should at least be considered. The simple analysis in Table 9 suggests that restoration efforts centered on biodegradation strategies are not applicable in all circumstances.

Table 8. Summary of the Mechanisms Influencing the Fate of Contaminants in Environments

Process	Environmental Conditions	Contaminant
Movement	Water Flow Rate Formation Permeability Water Motion Gravity Surface Tension	Amount of Material Physical State Solubility Viscosity
Retention	Soil/Sediment Organic Matter Content Sorptive Capacity	Type Solubility Ionic Character
Reaction	pH Redox Status Microbial Communities	Chemical Transformation Biodegradability

Table 9. Treatment Options as a Function of the Transport and Reactivity Characteristics of the Contaminant

	Transport	
Reactivity	High	Low
High	Extraction and/or Biodegradation	Biodegradation
Low	Extraction	Containment

In fact, all remediation technologies have inherent limitations that must be kept in mind when evaluating a variety of treatment options. For instance, containment techniques generally rely on physical or hydrological barriers to keep a contaminant from spreading underground. Typical containment methods involve slurry walls, clay caps, interceptor trenches, or hydraulic barriers. These techniques can be costly, plus there is no guarantee of their long-term effectiveness and, most importantly, they do not really address the pollution problem.

Similarly, extraction-based remediation efforts also have disadvantages. As noted in Table 9, the technology tends to be used on substances that are easily transported in the subsurface. The simplest extraction approach is to excavate the contaminated soils and sediments in the problem area. However, this often is not feasible because of the depth of the problem area or because excavation activities could undermine the foundation of roads, buildings, or other structures.

The pumping of ground water is another extraction technique. Ground-water pumping technologies generally are combined with some sort of surface treatment like air stripping, carbon adsorption, biological or chemical reaction, or simple discharge to other locations. Often such extraction techniques tend to treat only a limited amount of the total contaminant problem; that is, only contaminants dissolved in the water phase are removed from the aquifer. Many decades often are needed to extract even mildly adsorbing chemical pollutants.

One of the major disadvantages of extraction technologies is that the contaminants often are merely transferred from one location to another. The problems associated with trans-media pollution of different environmental compartments continue to gain increasing attention among the regulatory community. Other methods, such as soil venting, tend to address volatile contaminants present in the soil atmosphere, yet again, only address a portion of the problem.

Extraction often tends to be the treatment of choice because it is straightforward, understandable, and predictable and generally has small yearly investment costs. However, this approach ignores the long-term commitment to the extraction process, particularly for sorbed contaminants and the maintenance involved in the treatment operation.

Reaction technologies include both chemical and biological methods of converting contaminants to more environmentally acceptable forms. Generally, chemical transformations convert pollutants through hydrolysis or initial oxidations. Such reactions also can be catalyzed by microorganisms, but they often are the rate-limiting step in biological treatment scenarios. On the other hand, biological treatment processes have the potential to completely mineralize contaminants and convert them to innocuous substances like carbon dioxide, water, and cell material. Reaction processes, when successful, tend to be relatively short-term solutions to pollution problems and are associated with high operation costs. The treatment chemicals and/or microbial nutrients must be transported to the contaminated portion of the aquifer so that both the dissolved and adsorbed phases of the contaminant are attacked.

Aquifer Remediation Considerations

Many considerations must be made before seriously considering an aquifer bioremediation approach (Lee, et al., 1988). The first consideration is determining the contaminant type, the phases in which it exists, the solubility of the material, and its inherent susceptibility to biodegradation. The microbial ecology scientific literature is an excellent source for the latter consideration. Biodegradation information resulting from the study of a variety of environments indicates whether the contaminant can be degraded and, if so, under what ecological conditions. This information does not insure that a contaminant will be degraded in all instances since a variety of site-specific characteristics can interplay to influence the success of bioremediation efforts.

The scientific literature also can provide some assessment of the likely pathways of degradation, which in turn allows for an evaluation of the consequences of biorestoration. Disappearance is only one aspect of biodegradation since a contaminant can be converted to a series of metabolites that also are of environmental concern. For instance, the reductive removal of tetrachloroethylene (TeCE) under anaerobic conditions leads to a series of dehalogenated intermediates. TeCE's halogens are removed and replaced by protons in a series of sequential steps. However, the rate of reductive dehalogenation tends to decrease as fewer and fewer halogens remain on the ethylene moiety. Consequently, vinyl chloride accumulates and, from a regulatory viewpoint, causes greater concern than the parent contaminant. Thus, biodegradation pathway information can be critical for the design of bioremediation efforts.

Successful implementation of biorestoration efforts also depends on determining site characteristics, in particular, the site-specific hydrogeological variables. Factors such as thickness of the vadose zone, its permeability, geologic complexity, and organic matter content can impact biorestoration programs. Saturated zone characteristics such as the type and composition of an aquifer, its permeability, thickness, interconnection to other aquifers, location to discharge areas, magnitude of water table fluctuations, and ground-water flow rates all influence aquifer bioremediation planning and decision-making. To date, bioremediation has been attempted in aquifers possessing a variety of flow characteristics including pumping rates ranging from 25 to 380 L per minute, and flow rates from 0.6 to 800 m per year or hydraulic conductivities of 10^{-5} to 10^{-3} cm per second. Generally, bioremediation efforts center around more permeable aquifer systems where the movement of ground water can be more successfully controlled.

Another consideration in biorestoration is the removal of free product. This is extremely important since many substances, while suitable nutrients for microbial growth when present at low concentrations, are inhibitory at high concentrations. Such concentration effects can easily be observed with substances ranging from simple sugars to gasoline. Consequently, in a biorestoration effort, it is important to remove as much free product as possible by physical or chemical means and use biological methods to treat the remainder.

The next biorestoration consideration is whether the system design will be above or below the ground. Again, this decision is influenced by the ease of transporting the contaminant from its location to the area where the treatment will take place. Since many contaminants are in multiple phases in the subsurface, *in situ* treatment strategies often are the best option. In *in situ* treatment efforts, nutrients are transported to the requisite microorganisms in an effort to create the correct environmental conditions for microbial proliferation.

A critical component in biorestoration is a laboratory evaluation of the site pollutants' susceptibility to biodegradation. The appropriate use of microcosms in rigorously defined and controlled experiments allows the investigator to evaluate biodegradation under conditions that are more environmentally realistic. The microcosm approach allows the investigator to incorporate numerous site-specific variables without a detailed knowledge of what these variables actually are. For instance, scientific literature may indicate that a particular pollutant is subject to biodegradation, but this may not be confirmed by microcosm studies due to the absence of an essential microbial nutrient or the presence of an inhibitory substance at the site. Some of these limitations may be relatively easy to overcome, while others may prove more difficult.

If initial microcosm evaluations are unsuccessful, subsequent studies should attempt to stimulate biodegradation of the problem contaminants using nutrients or adjusting other variables. If biodegradation in microcosms cannot be successfully stimulated, the chances of success in the field are minimal but if initial microcosm evaluations prove successful, the chances for success in the field are significantly improved. These preliminary laboratory investigations not only allow an investigator to design a biorestoration program, but also to optimize the treatment strategy.

As a final consideration, some plan should be devised to monitor the progress of a biostimulation activity. A more detailed discussion of the types of information needed for monitoring are presented later in this chapter.

From a bioremediation viewpoint, the ideal site has: (1) a homogeneous and permeable aquifer; (2) a contaminant originating from a single point source; (3) a low ground-water gradient; (4) no free product; (5) no soil contamination; and (6) an easily degraded, extracted, or immobilized contaminant. Obviously, the above combination of characteristics describes very few sites. The following sections will attempt to show how information on the chemistry, microbiology, and biochemistry of a contaminant can form a biorestoration strategy.

Pathways of Hydrocarbon Metabolism

One of the most frequently encountered aquifer contaminants is gasoline, which is largely a mixture of hydrocarbons including three major chemical classes: the alkanes; the cycloalkanes; and aromatic chemicals (Table 10). Table 10 illustrates that greater than 73 percent of several gasolines are composed of these three hydrocarbon classes. Gasoline hydrocarbons within each class possess a variety of substituents and numerous substitution patterns that ultimately influence the susceptibility of the resulting structures to biodegradation.

Table 10. Major Chemical Components (Percent of Total) of the Gasoline Fraction of Several Petroleums (Adapted from Perry, 1984)

Hydrocarbon Class	Gasoline from		
	Texas	California	Louisiana
Alkanes	16.8	18.0	24.5
Cycloalkanes	47.1	55.5	38.4
Aromatics	19.5	10.2	15.6

Alkanes exist in gasoline and many gasoline components contain an alkane moiety in their carbon skeleton. An enormous amount of scientific literature exists on the types of alkanes that are subject to microbial attack and the diversity of microorganisms involved in alkane metabolism as detailed by Singer and Finnerty (1984). An extremely wide range of alkanes are susceptible to biodegradation, but some microorganisms preferentially utilize only short chain molecules while others metabolize only longer chain structures.

Microorganisms can initiate the aerobic degradation of alkanes through mechanisms that involve mono-, di-, or subterminal oxidation of the molecule. Probably the most frequently reported degradative route involves the oxidation of a terminal methyl group to convert the alkane to an alcohol of equivalent chain length (Figure 76). This alcohol probably undergoes a series of dehydrogenation steps to form the corresponding aldehyde and eventually a fatty acid (Singer and Finnerty, 1984).

Once formed, the fatty acid is further metabolized by β-oxidation. This process liberates a two-carbon fragment as acetylcoenzyme A, a central metabolic intermediate. Two carbon fragments are then continuously cleaved from the resulting shorter fatty acid until the entire molecule is degraded. Alkanes with odd numbers of carbon atoms ultimately yield a molecule of another central metabolite - propionyl coenzyme A. The significant aspect of Figure 76 is that the initial oxidation of an alkane molecule involves the incorporation of molecular oxygen. This basic theme also is pertinent to the other major classes of gasoline hydrocarbons.

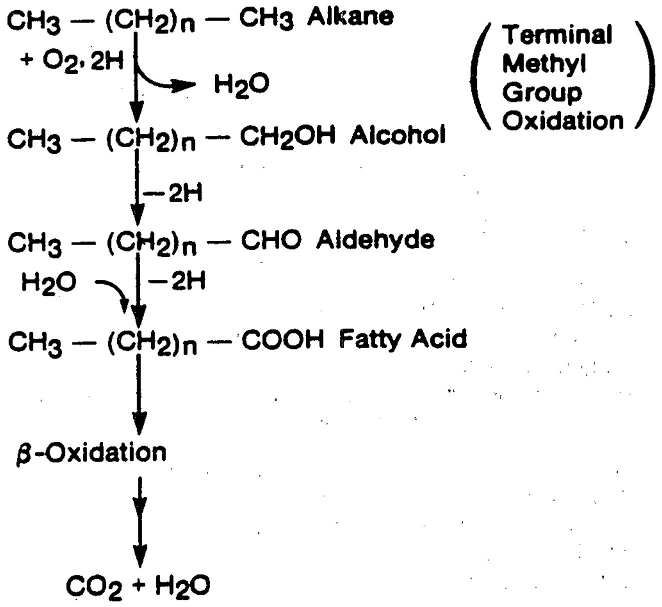


Figure 76. The initial steps in the aerobic microbial metabolism of alkane hydrocarbons.

It is more difficult to enrich for microorganisms that are able to use cycloalkanes as a sole source of carbon and energy. This appears to be widespread in nature and is discussed by Trudgill (1984) and Perry (1984). It may be that microorganisms interact frequently in commensalistic relationships based on the cometabolism of these substrates (cometabolism will be discussed later in this chapter). However, it is clear that individual or mixtures of microorganisms can metabolize cycloalkanes in the manner shown for cyclohexane (Figure 77).

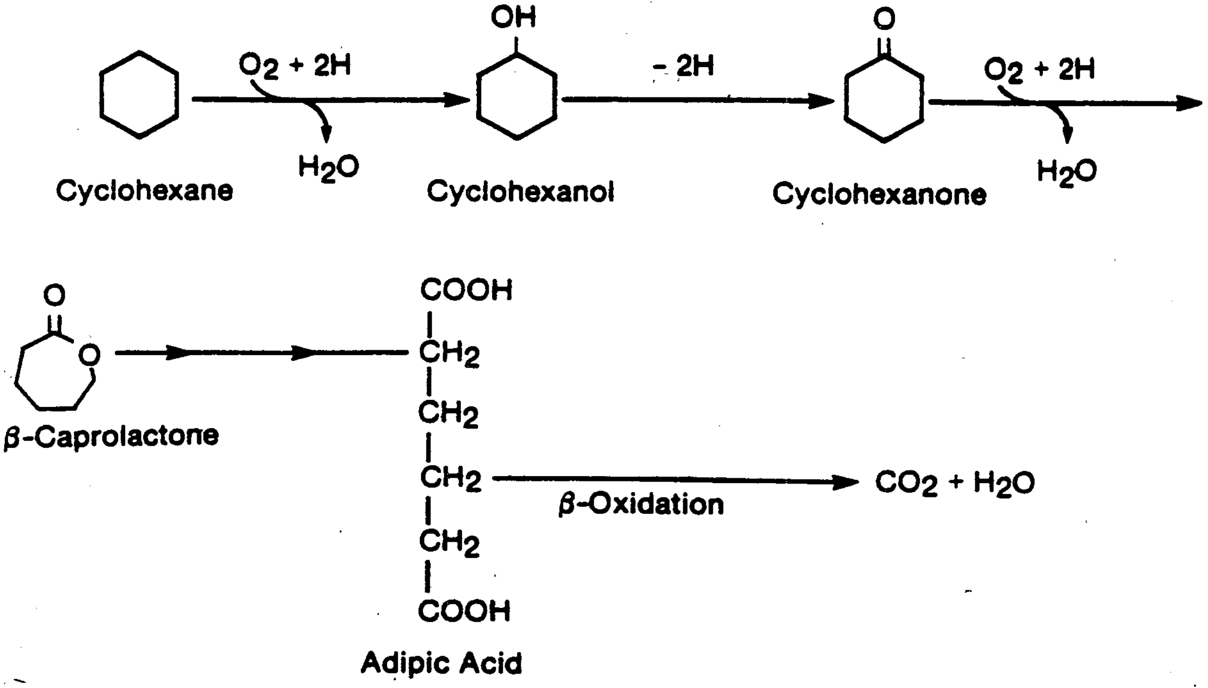


Figure 77. The Initial steps in the aerobic microbial metabolism of alicyclic hydrocarbons.

As shown in Figure 77, cyclohexane hydroxylation by a microbially produced monooxygenase leads to the formation of an alicylic alcohol. Subsequent dehydrogenation of the alcohol forms a ketone and further oxidation of the ketone results in the formation of a lactone ring structure. The lactone is a suitable substrate for ring opening and is eventually converted to a dicarboxylic acid which, in turn, is subject to oxidation. Molecular oxygen participates in the biodegradation pathway, but, in this case, is involved in two separate steps.

Aromatic compounds of gasoline also are subject to microbial attack by many different types of bacteria and fungi. The aromatic hydrocarbons are aerobically metabolized by bacteria to dihydroxylated compounds through *cis*-dihydrodiol intermediates. Figure 78 shows how, in the case of benzene, a bacterial dioxygenase incorporates both atoms of molecular oxygen to form *cis*-benzene dihydrodiol which is subsequently dehydrogenated to result in the formation of catechol. Catechol is then a suitable substrate for ring cleavage. Other dioxygenases open the ring most often via an 'ortho' or 'meta' cleavage route. The subsequent intermediates produced by these pathways eventually enter central metabolic reaction sequences of the bacterial cell. The aerobic catabolism of homocyclic aromatic compounds is reviewed by Gibson and Subramanian (1984) and by Bayly and Barbour (1984).

Oxygen plays a critical role in the metabolism of aromatic hydrocarbons. All of the metabolic pathways discussed above require oxygen as a coreactant. In addition, the organisms catalyzing these bioconversions use oxygen as a terminal electron acceptor (described in Chapter 7). Hydrocarbon metabolism puts a large demand on oxygen resources; therefore, plans for biorestoration activities should consider how this oxygen demand will be supplied.

In addition to oxygen, other potential limiting nutrients also must be supplied in suitable form for the microorganisms to proliferate at the expense of the hydrocarbons. Along with a suitable environment, microorganisms need nitrogen, phosphorus, sulfur, and trace elements and without the two former nutrients, hydrocarbon metabolism may be limited even when oxygen supplies are adequate. With the proper nutrients, the microorganisms can convert gasoline hydrocarbons to the environmentally innocuous products of carbon dioxide, water, and additional cell material.

Once the chemical and physical requirements for microbial growth and the predominant metabolic pathways are known, attempts can be made to stimulate the biodegradation of gasoline by superimposing the correct nutrients *in situ*. Figure 79A represents an aquifer contaminated with gasoline hydrocarbons. Free product already has been removed from this schematic site, but both water and soil contamination still exist. Preliminary testing shows that hydrocarbon-degrading microorganisms are present and active at the site and that these organisms can be stimulated to increase hydrocarbon

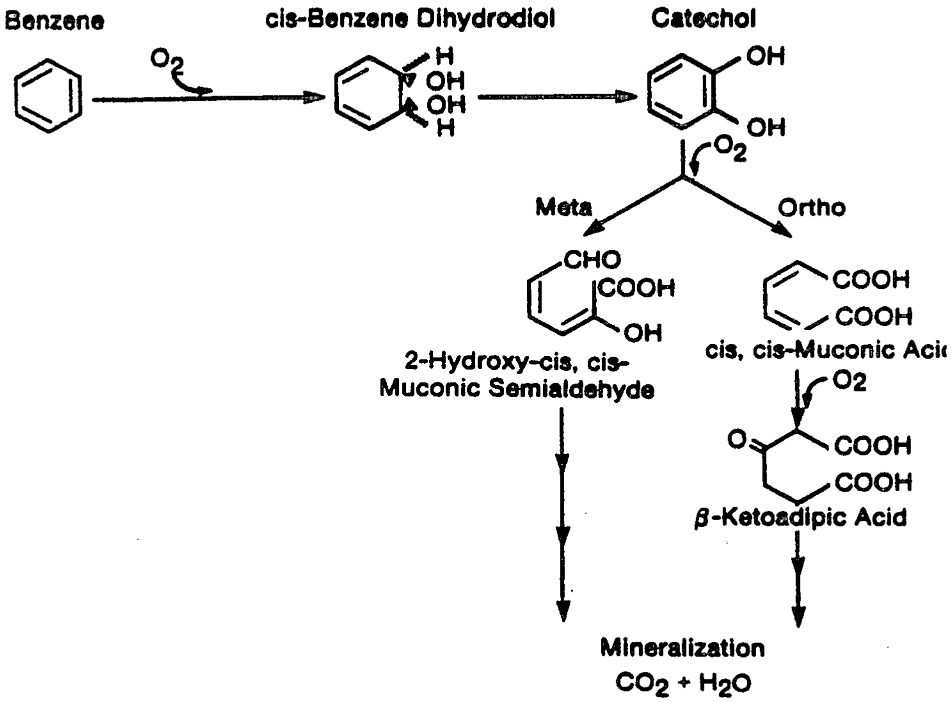


Figure 78. The initial steps in the aerobic microbial metabolism of aromatic hydrocarbons.

biodegradation. Figure 79B depicts the attempt to gain hydrogeologic control over the contaminated area through the insertion of a series of injection and recovery wells. The goal is to recirculate the ground water in an effort to create an underground reaction chamber. The figure shows that the pumping and recirculation also change the water table. Ideally, the 'reaction chamber' will encompass the contaminated area; however, this often is not possible due to the magnitude of the contamination problem and the permeability limits of the aquifer. In the latter case, the contamination problem can be approached in stages that are governed largely by the efficiency of water recirculation at the site.

Nutrients are then added to the recirculation system and transported with the injection water into the aquifer (Figure 79C) where the indigenous microorganisms will start to proliferate (the bioactive area). The efficiency of the nutrient transport will then dominate the success of the remediation effort. A variety of mechanisms for supplying oxygen to the requisite microorganisms is considered in the review by Lee, et al. (1988).

Initially, most of the bioactive area probably will be centered in areas adjacent to the injection well. As the electron donors in that area are depleted, the major bioactivity shifts to other areas of the contaminant plume where additional hydrocarbon and, thus, electron donors exist, and the requisite nutrients penetrate the plume (Figure 79D). This process continues until the site is considered remediated (Figure 79E). At this point, the nutrients are removed from the recirculation stream. The aquifer tends to exhibit homeostatic controls (described below) and the microflora that grew in response to the hydrocarbon and nutrient input return to the levels originally present before the contamination incident.

Bioreclamation of gasoline in aquifers has an excellent chance of success because of the wealth of scientific information that forms the basis of this applied technology. Researchers have studied hydrocarbon metabolism by microorganisms for many decades and learned that gasoline hydrocarbons are xenobiotic substrates only in the sense that they occur in various environmental media at higher than acceptable concentrations. Most hydrocarbons in gasoline are natural substrates and microbial communities have evolved mechanisms for their degradation. These hydrocarbon-degrading microorganisms are not unusual and tend to be ubiquitously distributed in many and probably most natural environments. Scientific investigations also have helped elucidate the nutrient requirements necessary for microbial growth and proliferation at the expense of hydrocarbon substrates so that remediation activities are relatively easy to construct, test in microcosms, and extrapolate to the field.

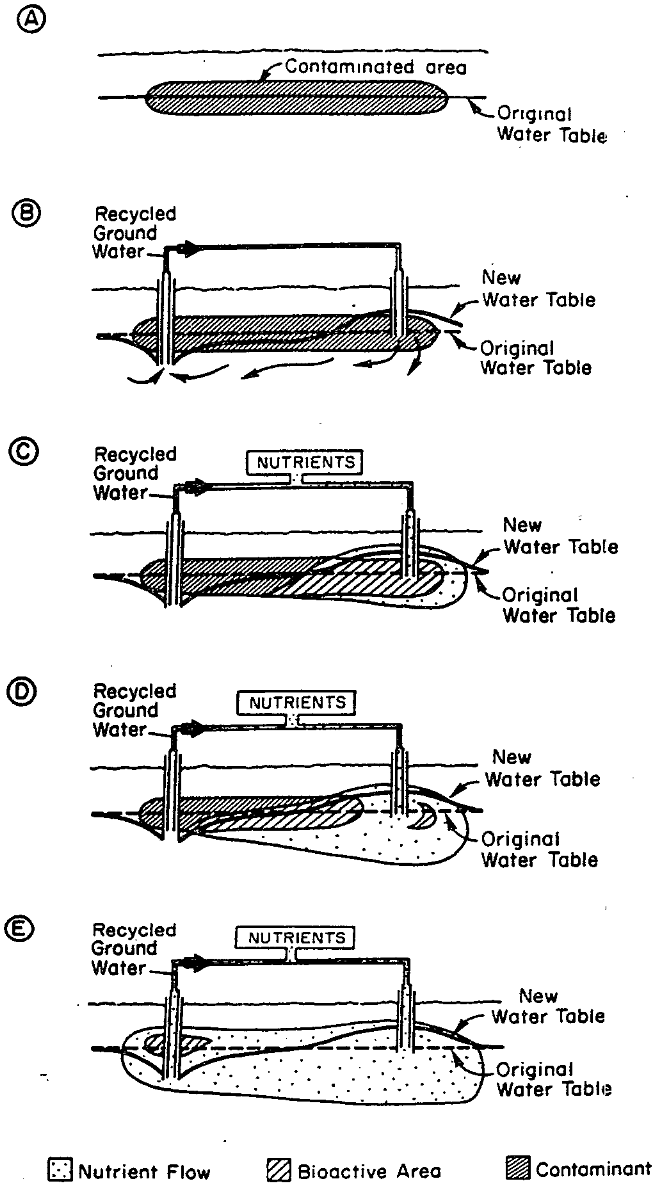


Figure 79. Schematic illustration of the various steps (A-E) in an aquifer biorestoration program (see text for description).

A similar information base does not exist for more exotic substrates; therefore, microcosm research may be necessary in order to design effective remediation processes. Principles gleaned from the study of hydrocarbon degradation may or may not be applicable to other contaminants.

Critical Evaluation of Biorestoration

Claims have been made that a variety of hydrocarbons, solvents, and other contaminants were treated by *in situ* bioremediation (Table 11) (Lee, et al., 1988). However, these claims generally lack firm scientific evidence that biorestoration actually was responsible for the removal of the substances. Many claims for *in situ* biorestoration tend to appear in publications that were not peer reviewed, therefore, legitimate questions persist as to the effectiveness of biological treatment programs for various contaminant types. Consequently, clients or regulators have difficulties evaluating such claims. Since biorestoration is still an emerging technology, practitioners must gather the necessary evidence for prospective clients and regulators to critically interpret the chances of success for such programs.

Table 11. **Contaminants Treated by *In Situ* Bioremediation (Adapted from Lee, et al., 1988)**

Contaminant Type	Representatives
Hydrocarbons	gasoline mineral oil aliphatic plasticizers
Solvents	methyl chloride n-butanol acetone ethylene glycol isopropanol tetrahydrofuran chloroform
Other Compounds	dimethyl aniline

In remedial activities, practitioners should carefully document the reduction in substrate concentration(s) as a result of their efforts. Implicit in this suggestion is reliable information on mass balances. While it is often impossible to estimate the quantity of material lost in an accident, sometimes such estimates are feasible. For instance, logs are kept of inputs and removals of chemical substances from storage facilities. This type of information may prove valuable in estimating the maximum amount of contaminant involved in a pollution incident. Alternately, the remedial efforts can be gauged relative to the initial amount of contaminant present in the aquifer. This approach requires good definition of the plume, an appreciation for where the contaminant exists, and reliable and specific measurement methods. If bioremediation is successful, contaminant levels should begin to fall in areas that receive the treatment and remain relatively unchanged in areas that do not.

Bioremediation efforts often seek to increase the activity of microorganisms in an aquifer. The confidence in bioremediation technologies would be greater if the increase in microbial numbers and/or activities were quantitated relative to: (1) plume areas prior to any treatment; (2) areas within the plume that did not receive the treatment; or (3) control areas outside the plume. The latter will give some indication of background levels of microorganisms and allow comparisons to be made before, during, and after a remediation program.

Often, the production of microbial catabolites can be measured in areas that receive treatment but not in contaminated areas left untreated. For instance, the production of a variety of lesser halogenated PCB congeners in river sediments contaminated with Aroclors was previously noted (Brown, et al., 1987; Brown, et al., 1984). Many of the congeners produced did not comprise a significant portion of the original contaminant Aroclors. Their production was suggested as field evidence that the original PCB materials were metabolized by anaerobic microorganisms and reductively dehalogenated (Brown, et al., 1987; Brown, et al., 1984). Laboratory evidence in microcosm experiments designed to test this hypothesis confirmed that suspicion (Quensen, et al., 1988). Similarly, the production of metabolites like hydrogen sulfide or methane often are testament to the metabolic activities of microorganisms. If the degradation pathways of particular contaminants are known prior to a remedial effort, it is sometimes possible to specifically assay for the production of likely catabolites.

Many times, biorestoration programs rely on the contaminant itself to supply the electron donors necessary for microbial growth and proliferation. One of the objectives of the remediation is to supply the necessary electron acceptor. The consumption of added terminal electron acceptors could possibly be measured. For instance, if oxygen is added to help stimulate hydrocarbon metabolism in aquifers, its depletion in the treatment area should be relatively easy to measure.

Finally, rapid microbial biodegradation typically seems to be preceded by a variable length of time where little or no activity is measured. This length of time is referred to as the adaptation or acclimation period (Linkfield, Suflita, and Tiedje, 1989). So far, adaptation seems to be a unique biological response. Observation of this type of phenomenon in response to a biorestoration effort can be taken as presumptive evidence that microbial action is operative.

It is important to emphasize that all of the techniques and measurements suggested above must be made relative to appropriate controls. For some techniques, that may mean the assay of untreated areas or areas outside the plume. Many clients may not be willing to invest the necessary time and financial resources to gather this level of information. Even with controls, the evidence garnered in the above fashion tends to be largely circumstantial. However, the stronger the evidence, the greater the degree of confidence in the technology.

Lag, Adaptation, or Acclimation Periods

In biodegradation studies, a period of time often is observed where very little substrate is turned over and correspondingly little product is formed. This phase of 'metabolism' is potentially more environmentally significant than other phases because of its possible effects on the level of the exposure of humans and ecosystems to specific pollutants. The lag, adaptation, or acclimation phase can be one of the most frustrating portions of bioremediation programs, since, despite all efforts, virtually nothing seems to be happening to the problem contaminant.

For example, Figure 80A shows the reductive dehalogenation of 2-bromobenzoate in anoxic sediment microcosms. The substrate lags for several weeks after which it is rapidly metabolized. The production of an intermediate catabolite, benzoic acid, occurs before its rapid degradation. Ultimately, the substrate and intermediate are converted to the gaseous endproducts, methane and carbon dioxide. At this point, the microorganisms are considered acclimated to the degradation of the parent substrate and subsequent substrate additions will be degraded without a lag. This phenomenon is graphically illustrated for the reductive dehalogenation of a related substrate 3-iodobenzoate (Figure 80B). In this case, the second addition of 3-iodobenzoate is presented as time zero. Note the immediate consumption of the substrate, the much lesser accumulation of benzoic acid, and the more rapid conversion of the parent molecule to gaseous endproducts.

In the examples given in Figure 80A and B, acclimation might reasonably be expected since the microorganisms were able to mineralize the parent substrates. Some of the carbon and energy gained from the metabolism of those substrates was presumably used for the proliferation of the catalyzing microbial communities. If the concentration of the requisite microorganisms was initially very low, the lag period could conceivably be a function of the time required for these organisms to grow to sufficient density to effect some significant amount of substrate depletion relative to the large background added as the amendment. However, acclimation also is observed for substrates that are not mineralized. As seen in Figure 80C, the substrate 4-amino-3,5-dichlorobenzoate can be reductively dehalogenated to form the monohalogenated product following a three-week lag period. Even though the parent substrate is not mineralized and does not supply carbon for microbial growth, additions of the parent substrate following the removal of the initial

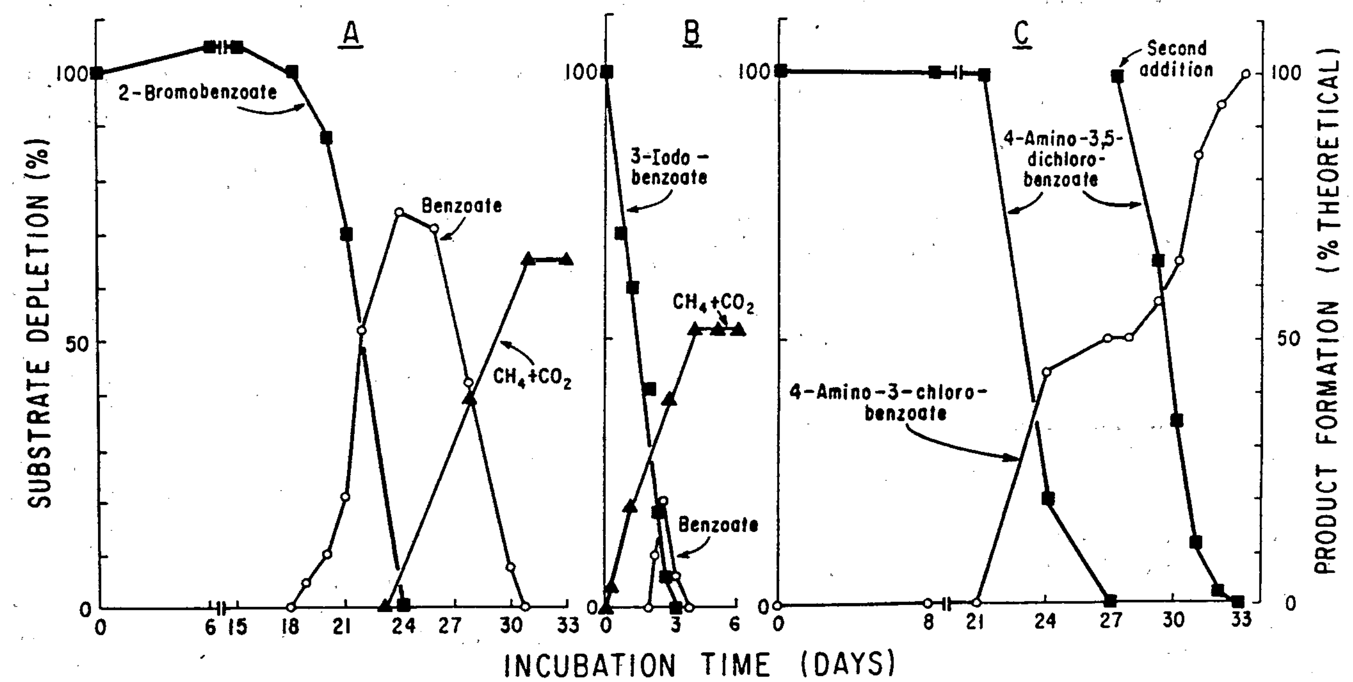


Figure 80. Patterns of anaerobic reductive dehalogenation of halobenzoates by sediment microorganisms: (a) degradation of 2-bromobenzoate in fresh sediment microcosms; (b) degradation of 3-iodobenzoate by sediment microorganism previously acclimated to 3-iodobenzoate degradation; (c) degradation of 4- amino-3,5-dichlorobenzoate by fresh sediment and the accumulation of the monodehalogenated endproduct (Horowitz, et al., 1983).

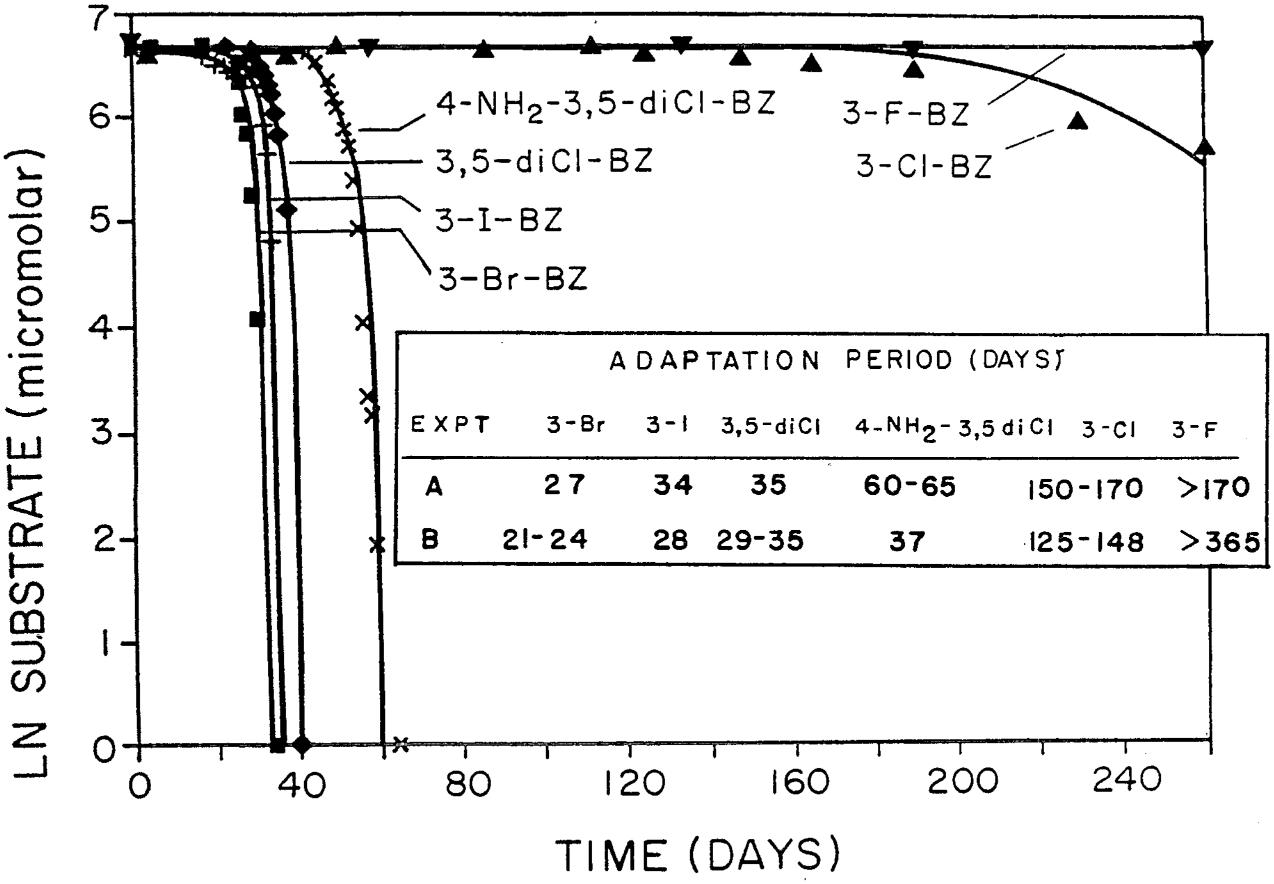
amendment are metabolized without an additional lag period.

Examining and understanding the factors which influence the lag period can be difficult, but may ultimately lead to biorestoration scenarios with controlled, reduced, or even eliminated adaptation times. The requirement for the growth of the requisite microorganism most often is touted as the operational reason for lag periods. While undoubtedly true, the example above illustrates that there may be other reasons for the delay in biodegradation.

The structure of the chemical itself is known to influence the rate of biodegradation. Figure 81 compares the adaptation period for a variety of halobenzoates in methanogenic sediment microcosms. Note that all the substrates were added at the same starting concentration and that they all possessed halogen substitutions at one or both *meta* (3 or 5) positions. When degraded, all of the substrates were metabolized via reductive dehalogenation reactions. The various substrates were degraded in a specific order; that is, 3-bromobenzoate (3-Br-Bz) degraded before 3-iodobenzoate (3-I-Bz) which in turn degraded faster than 3,5-dichlorobenzoate (3,5-diCl-Bz), etc. Therefore, chemical structure very definitely influences the length of the lag period, and, perhaps more significantly, the length of the lag periods are relatively reproducible. The insert table in Figure 81 illustrates that a repeat experiment not only gives the same relative order of degradation, but also approximately the same length of the lag period. The lag period does not appear to correlate with whether the substrate is mineralized. This result implies that a specific physiological or chemical basis exists for the characteristic lag periods.

Other experiments show that concentration can markedly influence the length of the lag period. Figures 82 and 83 compare the reductive dehalogenation of several halobenzoates at various concentrations and illustrate a number of characteristic patterns. In the case of the anaerobic biodegradation of both 3,5-dichloro- and 3-chlorobenzoate at substrate concentrations ranging from 20-800 µM (Figure 82), the dichloro-substrate exhibits a characteristic lag time prior to rapid biodegradation regardless of the substrate concentration range. However, the length of the lag period associated with the lower concentrations of monochlorobenzoate is much shorter than those observed with higher substrate concentrations. This perhaps is not surprising since the benzoates are known bacteriostatic agents and higher concentrations tend to inhibit microbial activity.

A similar situation also can be observed in the case of low vs. high concentrations of 3-fluorobenzoate (Figure 83). However, the opposite result is observed when the substrate is changed to 4-amino-3,5-dichlorobenzoate. With this substrate, concentrations ≥ 40 µM were degraded with a characteristic lag period. However, concentrations of 20 µM exhibited lag periods in excess of one year (data not



ADAPTATION PERIOD (DAYS)

EXPT	3-Br	3-I	3,5-diCl	4-NH_2-3,5 diCl	3-Cl	3-F
A	27	34	35	60-65	150-170	>170
B	21-24	28	29-35	37	125-148	>365

Figure 81. Length and reproducibility of the adaptation period prior to the reductive dehalogenation of several halobenzoates at initial concentration of 800 µm (Linkfield, et al., 1989).

completely shown). If the concentrations of this substrate were only doubled, biodegradation would proceed in typical fashion and reach levels far below 20 µM. From these examples, one can see that when substrate concentrations are either too high or too low, biodegradation activity can be adversely affected and increased lag periods could result.

Potential Biostimulation Approaches

Many other factors besides the necessity for microbial growth, chemical structure, and substrate concentration are known to influence the length of the lag period. These factors include the need to deplete competing substrates and exchange genetic information and the lack of required nutrients. An important issue is whether biodegradation can be stimulated so that the lag or adaptation period can be overcome as quickly as possible. This can happen, provided that the factors controlling the lag and adaptation periods are understood. Although some biostimulation approaches were discussed earlier, three additional approaches will be considered: cross adaptation; analog enrichment; and biomass enrichment.

The principle of cross adaptation involves the addition of a readily degradable substrate to help bring about the rapid biotransformation of more recalcitrant molecules. An example of this phenomenon is illustrated in Table 12 and the study described below.

Anoxic sediment microcosms were exposed to one of two haloaromatic substrates, the relatively easily degradable 3-bromobenzoate and the more recalcitrant 4-amino-3,5-dichlorobenzoate. As indicated in the table, the former substrate would start to degrade in as little as a few days, whereas the latter substrate normally took about eight weeks. In both cases, subsequent additions of the same substrates to the microcosms were degraded without an observable lag period. Complete degradation of 4-amino-3,5-dichlorobenzoate reamendments took two to three weeks while 3-bromobenzoate additions took less than one week.

If other halobenzoates were added to adapted sediment instead of additional parent substrate, a variety of responses were observed. When the sediment microflora was adapted to the degradation of a relatively labile substrate (3-bromobenzoate), it

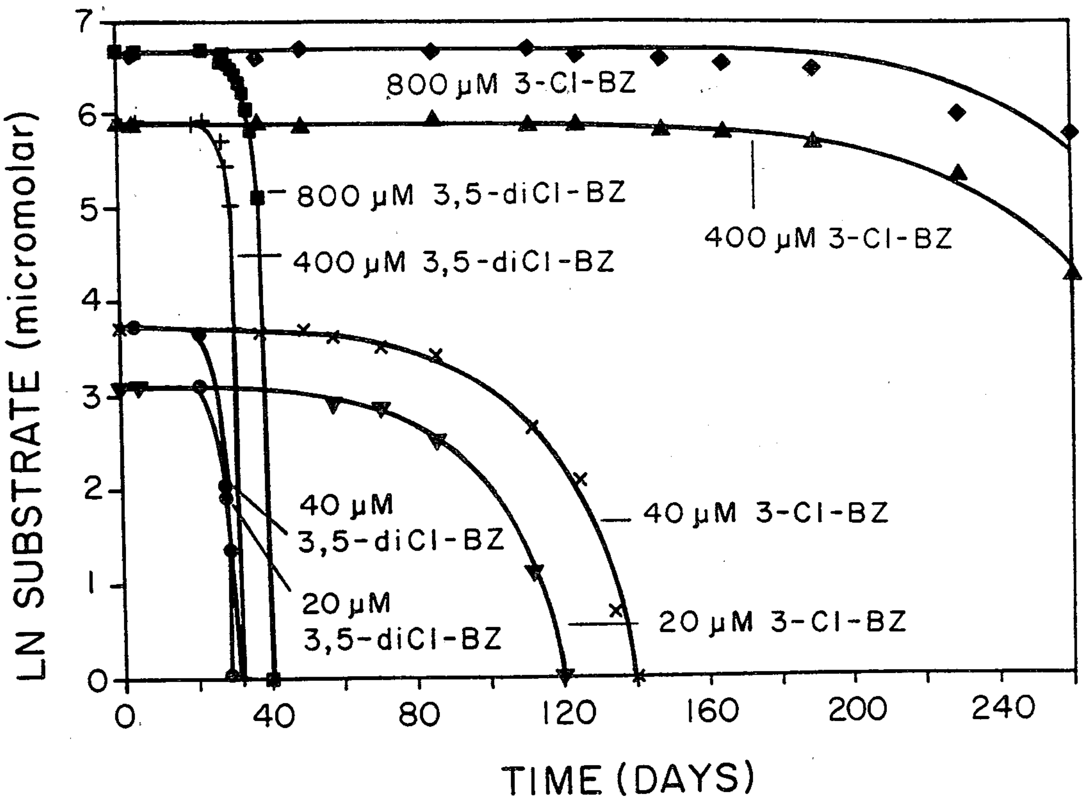


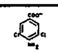
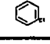
Figure 82. **Effect of substrate concentration on the length of the adaptation period prior to the reductive dehalogenation of 3,5-dichloro- and 3-chlorobenzoate (Linkfield, et al., 1989)**

also was cross-adapted and capable of rapid degradation of more recalcitrant materials like 4-amino-3,5-dichlorobenzoate and 3,5-dichlorobenzoate. However, this technique did not result in a significant improvement in the degradation of other substrates like 3-iodobenzoate or 3-chlorobenzoate. Sediment microflora capable of degrading either of the two starting substrates exhibited the same apparent substrate specificity, while similar experiments with 3-iodobenzoate-adapted organisms could only degrade subsequent additions of the parent substrate.

A technique that may be related to cross adaptation is referred to as analog enrichment and is illustrated by the experiments of You and Bartha (1982). Their objective was to stimulate the mineralization of ^{14}C-labelled dichloroaniline by soil microorganisms. These investigators added aniline as a structural analog of the halogenated pollutant to soil experiments. They found that the amount of mineralization of dichloroaniline (determined as the amount of $^{14}CO_2$) was proportional to the amount of aniline added as a substrate analog to soil (Figure 84). Presumably, the dichloroaniline was not a particularly good inducer of the requisite enzymatic machinery among the microbial communities in soil. The addition of the analog may have derepressed the enzymes responsible for aniline biotransformation and these enzymes also might have recognized the halogenated aniline as a suitable substrate. This study also showed an increase in the microbial mineralization of humus-bound dichloroaniline as a function of analog enrichment with aniline; humus-bound residues generally are considered to be much more recalcitrant than unbound residues.

Finally, the results of Wilson and Wilson (1985) may illustrate an enrichment of desirable microorgan-

Table 12. **Cross-adaptation of Anaerobic Microorganisms to the Reductive Dehalogenation of a Variety of Halobenzoates (Adapted from Horowitz, et al., 1983)**

Substrate Tested for Cross-Adaptation	Adaptation Time (wk)	Time (wk) for Complete Degradation in Sediment Adapted to:	
			
	3-8	2-3	2-3
	0.5-4	< 1	< 1
	2-3	2-3	2-3
	2-3	< 1	< 1
	32-40	Lag	Lag

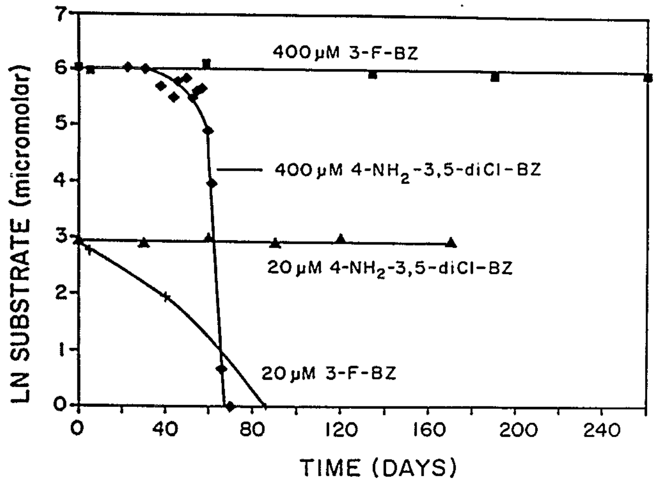


Figure 83. Differences in the adaptation period as a function of substrate concentration for two halobenzoates at 20 and 400 μm initial concentrations (Linkfield, et al., 1989).

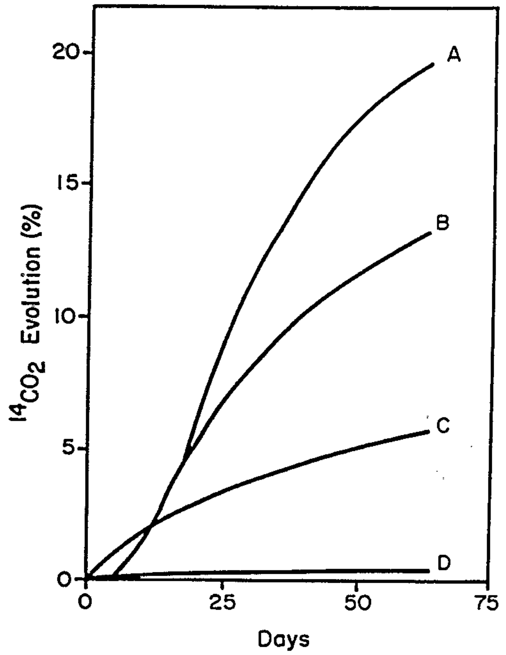


Figure 84. Effect of aniline on the mineralization of 3,4-dichloroaniline in soil: (a) 1.8 mg of aniline added per gram; (b) 0.4 mg of aniline added per gram; (c) no aniline added; (d) $HgCl_2$-poisoned control (adapted from You and Bartha, 1982).

isms in a complex microcosm. These authors found that trichloroethylene (TCE) could be removed from soil microcosms that were treated with a combination of methane and air. However, the TCE was not removed (other than due to abiotic loss) in soil microcosms that were not so treated. When the methane- and air-amended microcosm was treated with a bactericidal substance, the removal of TCE stopped. The authors speculated that the microorganisms responsible for the biotransformation of TCE were a unique group collectively called the methane-oxidizing bacteria. These organisms produce a powerful oxygen-requiring enzyme called a methane monooxygenase that is responsible for the initial bioconversion of methane. However, the enzyme has a broad substrate specificity and also can oxidize other substrates including TCE. Other types of bacteria not involved in methane metabolism can act similarly (Nelson, et al., 1987; Nelson, et al., 1986).

Presumably, the addition of methane and air to the soil columns stimulated the proliferation of one or several populations of methane-oxidizing microorganisms. While normally present in soil, the relative numbers of these organisms represented a greater proportion of the total microbial community receiving the methane and air treatment. While oxidizing methane, the organisms also cometabolized TCE. That is, the organisms growing on a particular substrate gratuitously oxidized a second substrate which they were unable to use as a source of carbon and energy for microbial growth. The cometabolized substrate is not usually assimilated by the first organism, but the oxidation products are then available for other organisms. This type of microbial interaction forms the basis of many different types of commensalistic relationships between microbial populations. In fact, many different substrates are known to be cometabolized, ranging from simple short chain aliphatic hydrocarbons to complex halogenated pesticides (Horvath, 1972).

Bioremediation with Microbial Inoculants

The use of specialized microbial cultures for bioremediation of contaminated aquifers is controversial (these cultures may or may not involve the use of genetically engineered organisms). Conclusive proof that the use of such inoculants constitutes a wise management practice has not been shown. Lee, et al. (1988) wrote that the role of inoculants in ground water cleanup efforts generally can not be conclusively determined because adequate controls many times are not employed in most experimental designs. Fundamentally, questions concerning the addition of microorganisms to aquifers are not different from those surrounding the use of microbial inoculants in soil to elicit some desirable response. In the late 1970s, manufacturers captured the imagination of the popular press with claims for such products. These ranged from an assurance for increased crop yields to the ability of such products to make "depleted soils come alive." Generally, these inoculants or microbial fertilizers have failed to live up to their claims, which should not be surprising to microbial ecologists. An excellent consideration of the relationships between microbial inoculants and microbial ecological principles is given by Miller (1979).

Scientific literature shows examples of microbial inoculation attempts in soil. The early work of Katznelson (1940a; 1940b) can be considered pioneering. Table 13 summarizes some of his experiments on the survival of several bacteria, actinomycetes, and fungi upon reinoculation of these organisms into manured or manured and limed soil. In general, these organisms (as well as others) died back very rapidly upon inoculation.

A spore-forming *Bacillus* species was apparently able to maintain its numbers under some conditions. Eventually, none of the organisms could be detected in numbers significantly above their baseline levels in soil. Similarly, the review of Miller (1979) summarizes the findings of Van Donsel, et al. (1967) on the survivability of fecal coliforms and fecal streptococci introduced to soil at various times of the year (Figure 85). In both winter and summer, the fecal bacterial numbers were reduced by several orders of magnitude. However, the decreased temperatures of winter allowed the fecal organisms to survive for a longer time before they were eventually eliminated.

Implicit in Figure 85 is the role of abiotic factors like temperature on the mechanisms for elimination of non-indigenous or foreign microorganisms inoculated in soil. In fact, a variety of abiotic factors may act alone or collectively to inhibit the survival of inoculant microorganisms. These factors are those known to influence microorganisms in general and include pH, temperature, salinity, water content, and osmotic or hydrostatic pressure among others.

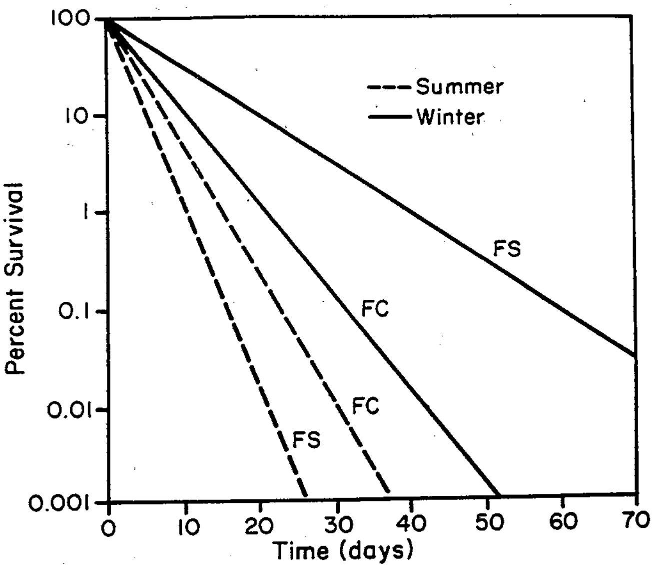


Figure 85. Survival of fecal coliforms (FC) and fecal streptococci (FS) in soil during summer and winter (adapted from Miller, 1979)

In addition to abiotic factors, biotic mechanisms also may be responsible for the demise of inoculants in soil. This is illustrated by the failure of *Rhizobium japonicum* cells inoculated in soil (Miller, 1979). Figure 86A shows that *R. japonicum* strain 123 survives when inoculated in sterile soil but declines rapidly in non-sterile soil. The die-back of strain 123 in non-sterile soil was accompanied by the simultaneous population increase of a lytic agent, presumably a bacteriophage (Miller, 1979) (Figure 86B). Other biotic factors such as the production of microbially produced toxins or antibiotics, predatory eucaryotes, parasitic procaryotes, lytic enzymes, etc., can influence the success of inoculation efforts (Miller, 1979).

It is likely that the microbial communities existing in aquifers represent a climax ecological community. The organisms are found there because they survived an extensive period of natural selection and are best able to occupy the available niche. That is,

Table 13. The Survival of Microorganisms Inoculated into Soil

	Manured Soil			Manured and Limed Soil		
	Incubation (Days)					
	0	45	100	0	45	100
Organism	Numbers per Gram Dry Soil x 10^5					
Penicillium sp.	24.7	7.7	7.1	33.9	2.7	2.2
Actinomycetes cellulosae	8.4	0.1	0.	7.6	0.04	0.
Bacillus cereus	23.2	57.4	49.3	86.9	8.6	12.3
Pseudomonas fluorescen	142.8	0.	0.	175.	1.1	0.
Azotobacter chroococcum	200.	0, 300*	0.	360.	120.	0.

*reinoculated

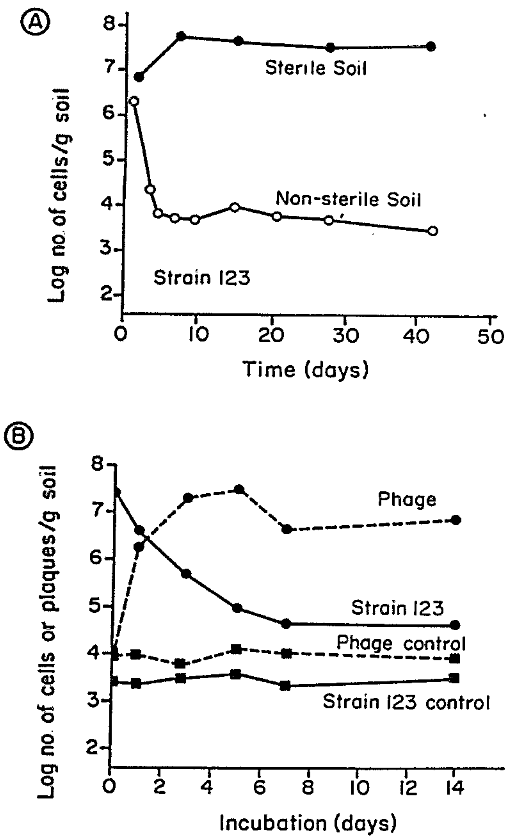


Figure 86. (a) The survival of *Rhizobium japonicum* strain 123 in sterile and nonsterile soil; (b) The relationship between the dieback of strain 123 and the increase in the population of a bacteriophage (adapted from Miller, 1979).

the indigenous organisms are best able to assume the functions or "occupations" (Miller, 1979) of organisms in that habitat. Gause's ecological principle states that only one species can occupy a specific niche in a habitat (Gause, 1934). Once the available niche is filled, climax ecological communities tend to exhibit the property of homeostasis. The community tends to be both quantitatively and qualitatively stable when subjected to moderate levels of biotic or abiotic stresses.

Little is known about the mechanisms of homeostasis in aquifers. However, it seems certain that multiple mechanisms, both biotic and abiotic, will serve to maintain homeostasis. The inoculation of foreign microorganisms can be viewed as biotic stress and the mechanisms responsible for the elimination of these organisms can be perceived as part of the homeostatic controls. When viewed in this context, it is unreasonable to expect competitive success from an inoculant that was likely grown to high numbers in the laboratory and subsequently forced to compete *in situ* with indigenous organisms naturally selected for their ability to survive the adverse conditions of nature.

This view on the potential for success of microbial inoculants in the terrestrial subsurface is pessimistic and largely based on ecological principles. Supporting this view though are the problems (not dealt with here) associated with the transport of microorganisms in aquifers and the acceptability of this practice to the regulatory community. Still, inoculants may occupy a significant role in pollution mitigation scenarios. For example, homeostatic control mechanisms of complex environments can be overwhelmed and frequent inoculation can take place in order to achieve some desired result. Thus, it may be possible to superimpose alternate environmental conditions on polluted aquifers with the aim of selectively favoring a desirable inoculant. However, inoculants will prove most useful when the contaminant of interest is exotic and difficult to degrade by the indigenous microflora. Further, given the difficulties in transporting bacteria in the subsurface, inoculants might be most useful in above-ground and contained treatment processes.

Conclusion

The astonishing metabolic versatility of microorganisms has fueled a great deal of excitement among regulators, researchers, and business people regarding economical methods for the restoration of contaminated environments such as aquifers. However, as with any technology, bioremediation has both promises and limitations. It is critical to the future development of this technology that the practitioners, clients, and regulators recognize the problems and promises of bioremediation; only with this recognition can biorestoration be properly considered as another part of the pollution mitigation arsenal.

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CHAPTER 9

MODELING SUBSURFACE CONTAMINANT TRANSPORT AND FATE

Joseph F. Keely

Introduction

When scientists and engineers attempt to simulate the effects of natural phenomena, they are engaging in modeling. Models are simplified representations of real-world processes and events, and their creation and use require many observation-based judgments. The key theme that drives and focuses the development and application of models is the faithful simulation of the specific natural processes. Such simulation must be demonstrated under a variety of defined conditions and must incorporate known scientific facts before a model can be considered reliable. Many forms of models exist, each having specific advantages and disadvantages.

Physical models, such as sand-filled tanks used to simulate aquifers (Figures 87 and 88) and laboratory columns used to study the relative motion of various contaminants flowing through aquifer materials (Figure 89), provide an element of reality that is enlightening and satisfying from an intuitive viewpoint. The main disadvantages of physical models are the extreme effort and time required to generate a meaningful amount of data. Other difficulties relate to the care required to obtain samples of subsurface material for the construction of these models, without significantly disturbing the natural condition of the samples.

Analog models also are physically based, but their operating principle is one of similarity, not true-life representation. A typical example is the electric analog model (Figures 90 and 91), where capacitors and resistors are able to closely replicate the effects of the rate of water release from storage in aquifers. As is the case with other physically based models,

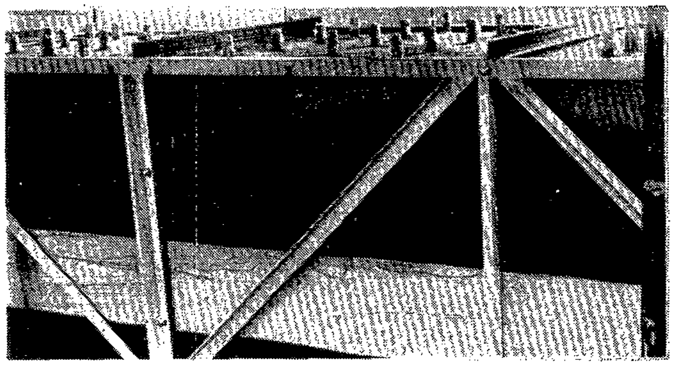


Figure 87. Large "sand tank" physical aquifer model. (The model is constructed of glass walls and external metal braces. A thick layer of silty loam overlies a layer of fine sand, which, in turn, overlies a layer of clay. Scores of stainless-steel piezometers penetrate the three layers.)

Figure 88. Close-up view of piezometers in a large "sand tank" physical aquifer model. (Shallow, intermediate, and deep piezometers are wired together in bundles. Wax sheets are molded over the piezometer bundles to protect them between samplings.)

data generation is slow and little flexibility exists for experimental design changes.

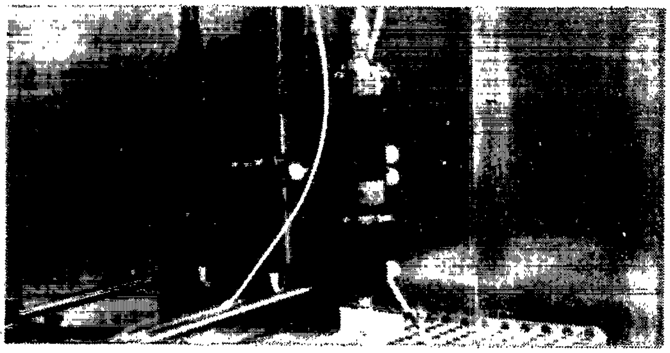


Figure 89. Laboratory column housed in constant-temperature environmental chamber. (Contaminated solutions are injected into column through inlet tubing in top, by action of hydraulic press in foreground. Samples of the advancing front are withdrawn through ports visible on right-hand side and bottom of column.)

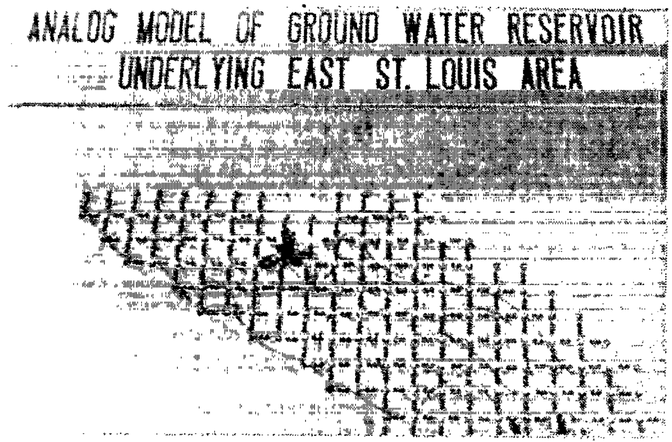


Figure 90. Electric analog aquifer model constructed by Illinois State Water Survey. (The regular array of resistors and the visible electric "pump" are hard-wired into a board papered with the appropriate geologic map.)

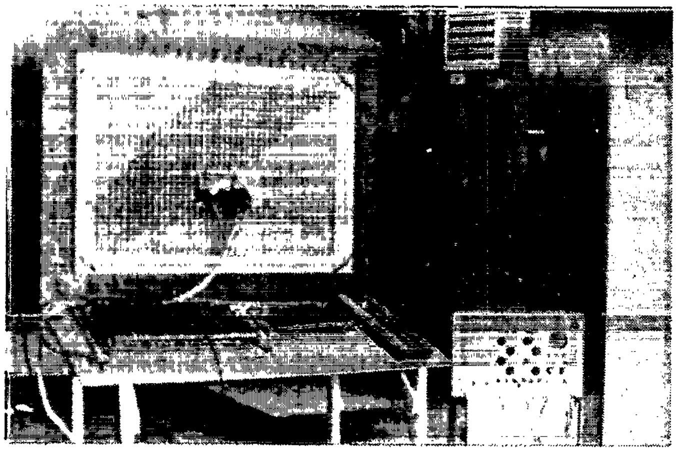


Figure 91. Control panel for electric analog model shown in Figure 90.

Mathematical models are non-physical and rely on the quantification of relationships between specific parameters and variables to simulate the effects of natural processes (Figure 92). Because of this, mathematical models are abstract and typically provide little in the way of an intuitive link to real-world situations. Despite this, mathematical models can generate powerful insights into the functional dependencies between causes and effects in the real world. Large amounts of data can be generated quickly, and experimental modifications made with minimal effort, making it possible for many situations to be studied in great detail for a given problem.

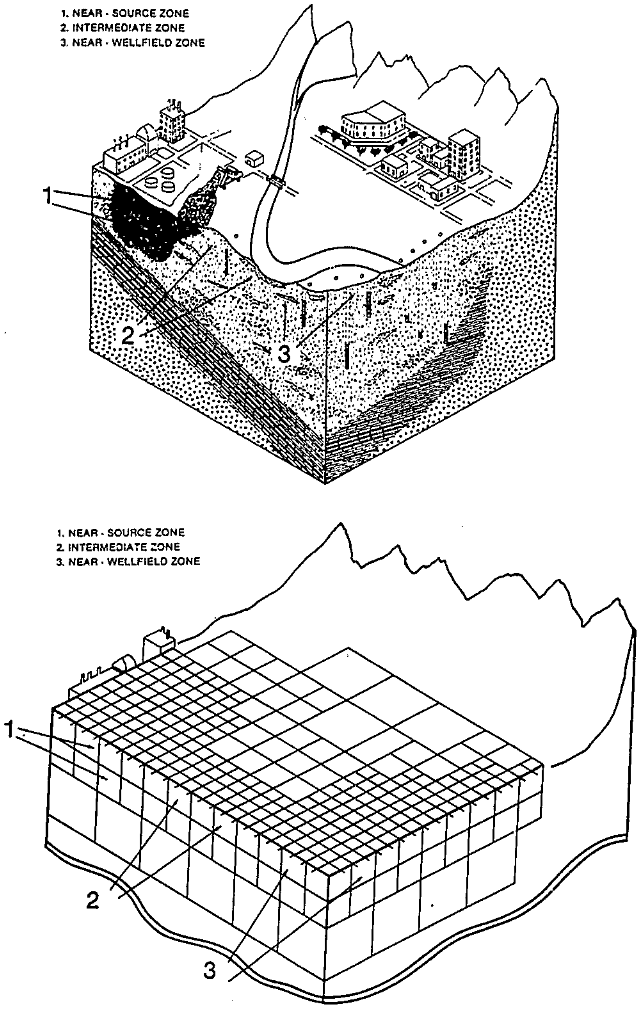


Figure 92. Typical ground-water contamination scenario and a possible contaminant transport model grid design for its simulation. (Values for natural process parameters would be specified at each node of the grid in performing simulations. The grid density is greatest at the source and at potential location.)

Categories of Models

Appropriate models do not exist yet for many subsurface contamination problems because a number of natural processes have yet to be fully understood. This is especially true for transport and fate evaluations, where chemical and biological processes are very important but are still poorly defined. Although great advances are being made in understanding the behavior of individual contaminants, studies of the interactions between contaminants are still in their infancy. Also, the current understanding of physical processes, such as multiphase transport, transport through fractured rock, and transport through karst aquifers, lags behind needed knowledge. Moreover, certain well-understood phenomena, such as the effects of partially penetrating wells in unconfined (water-table) aquifers under varying pumping rates, pose unresolved difficulties for mathematical formulations.

A variety of schemes exist for categorizing the technical underpinnings and capabilities of mathematical models, but the following categorization can be useful (Bachmat, et al., 1978; van der Heijde, et al., 1985):

- Parameter identification models
- Prediction models
- Resource management models
- Data manipulation codes

Parameter identification models most often are used to estimate the aquifer coefficients that determine fluid flow and contaminant transport characteristics, for example, annual recharge (Puri, 1984), coefficients of permeability and storage (Shelton, 1982; Khan, 1986a and b), and dispersivity (Guven, et al., 1984; Strecker and Chu, 1986). Prediction models are the most numerous kind of model because they are the primary tools used for testing hypotheses (Andersen, et al., 1984; Mercer and Faust, 1981; Krabbenhoft and Anderson, 1986).

Resource management models are combinations of predictive models, constraining functions (e.g., total pumpage allowed), and optimization routines for objective functions (e.g., scheduling wellfield operations for minimum cost or minimum drawdown/pumping lift). Very few of these models are developed and supported enough to be considered practically useful and there does not appear to be a significant drive to improve this situation (van der Heijde, 1984a and b; van der Heijde, et al., 1985).

Data manipulation codes also received little attention until only recently. These codes are now becoming increasingly popular because they simplify data entry (e.g., preprocessors) to other kinds of models and facilitate the production of graphic displays (e.g., postprocessors) of model outputs (van der Heijde and Srinivasan, 1983; Srinivasan, 1984; Moses and Herman, 1986). Other software packages are available for routine and advanced statistics, specialized graphics, and database management needs (Brown, 1986).

Quality Control

Quality control measures are greatly needed for modeling the transport and fate of subsurface contaminants, particularly in the use of numerical models. Huyakorn, et al. (1984) suggested three levels of quality control:

1. Validation of the mathematical basis of a model by comparing its output with known analytical solutions to specific problems.
2. Verification of the applicability of a model to various problem categories by successful simulation of observed field data.
3. Benchmarking the efficiency of a model in solving problems by comparison with the performance of other models.

These levels of quality control address the soundness and utility of the model alone but do not treat questions of its application to a specific problem. Hence, at least three additional levels of quality control appear justified:

4. Critical review of the problem conceptualization to ensure that the modeling effort considers all physical, chemical, and biological processes that may affect the problem.
5. Evaluation of the specifics of the model's application, e.g., appropriateness of the boundary conditions, grid design, time steps, etc.
6. Appraisal of the match between the mathematical sophistication of the model and the temporal and spatial resolution of the data.

Validation of the mathematical framework of a numerical model is deceptively simple. The usual approach for ground-water flow models involves a comparison of drawdowns predicted by the Theis analytical solution to those obtained by using the model. The deceptive part is that the Theis solution can treat only simplified situations as compared with the scope of situations addressable by the numerical model. In other words, analytical solutions cannot test most of the capabilities of numerical models in a meaningful way; this is particularly true in simulating complex aquifer boundaries and irregular chemical distributions.

Field verification of a numerical model consists of two steps, calibrating the model using one set of historical records (e.g., pumping rates and water levels from a certain year), and then, attempting to predict a subsequent set of observations. In the calibration phase, the aquifer coefficients and other model parameters are adjusted to achieve the best match between model outputs and known data. In the predictive phase, no adjustments are made except for actual changes in pumping rates, etc. Presuming that the aquifer coefficients and other parameters are known with sufficient accuracy, a mismatch means that the model either is not correctly formulated or does not treat all of the important phenomena affecting the actual field situation, such as leakage between two aquifers.

Field verification usually leads to additional data-gathering efforts because existing data for the calibration procedure often are insufficient to provide unique estimates of key parameters. This means that a *black box* solution may be obtained, which is valid only for the observation period used in the calibration. For this reason, the blind prediction phase is an essential check on the uniqueness of the parameter values used in the model. In this regard, field verification of models using datasets from controlled research experiments may be more practical to achieve than with the data generated during a Superfund site investigation.

Benchmarking routines are available that compare the efficiency of different models in solving the same problem (Ross, et al., 1982; Huyakorn, et al., 1984); however, more must be done in this area. For example, common observations indicated that finite element models (FEMs) have an inherent advantage over finite difference models (FDMs) in terms of ability to incorporate irregular boundaries (Mercer and Faust, 1981) (the number of points (nodes) used by FEMs is considerably less due to the flexible nodal spacings allowed). Benchmarking routines, however, show that the large amount of computer time required to evaluate FEM nodes reduces the cost advantage for simulations of comparable accuracy.

A Field Sample

Field experience using special geotechnical methods and state-of-the-art research findings was gained at the 20-acre Chem-Dyne solvent reprocessing site in Hamilton, Ohio (Figure 93), where over 250 chemical waste generators disposed of drummed or bulk wastes during its operational lifetime (1974-1980). Poor waste handling practices, such as purposeful on-site spillage of a wide variety of industrial chemicals and solvents, direct discharge of liquid wastes to a stormwater drain beneath the site, and mixing of incompatible wastes, occurred routinely at Chem-Dyne. These practices caused extensive soil and ground-water contamination, massive fish kills in the Great Miami River, and major on-site fires and explosions.

The stockpiling of liquid and solid wastes resulted in a long-term threat to the environment. More than 50,000 drums of hazardous waste were stored at the site at its peak of operations (CH_2M-Hill, 1984a). The drums were stacked improperly, in tiers five and six drums high, causing the drums at the bottom to buckle and corrode. After the remedial investigation began in the spring of 1982, more than 20,000 drums still remained; at least 8,500 of these were so badly corroded that they could not be identified. A number of bulk chemical storage tanks also were abandoned on site. Visual observations indicated that raw chemical salts and oils had been poured out on the sand-and-gravel ground surface.

The FIT Investigation

The seriousness of the ground-water contamination problem at Chem-Dyne became evident during the initial site survey (1980-1981), which included the construction and sampling of over twenty shallow monitoring wells (*Ecology and Environment*, 1982). The initial survey indicated that the contaminant problem was much more limited than was later shown to be the case (Roy F. Weston Inc., 1983; CH_2M-Hill, 1984a). A good portion of the improvement in delineating the plume was brought about by a better understanding of the natural processes controlling transport of contaminants at the site.

The initial site survey indicated that ground water flowed to the west of the site (toward the Great Miami River), but that a shallow trough paralleled the river as a result of weak and temporary stream influences. The study concluded that contaminants already in the aquifer would be discharged into the river and would not need to be removed (*Ecology and Environment*, 1982). That study also concluded that the source was limited to highly contaminated surface soils, and that removal of the uppermost three feet of the soil would essentially eliminate the source of contaminants.

That conclusion, however, was based on faulty soil sampling procedures. The soil samples taken were not preserved in air-tight containers, so most of the volatile organic chemicals leaked out prior to analysis. The uppermost soil samples probably showed high volatile organic levels because of the co-occurrence of viscous oils and other organic chemicals that may have served to entrap the volatiles. The more viscous and highly retarded chemicals did not migrate far enough into the vertical profile to

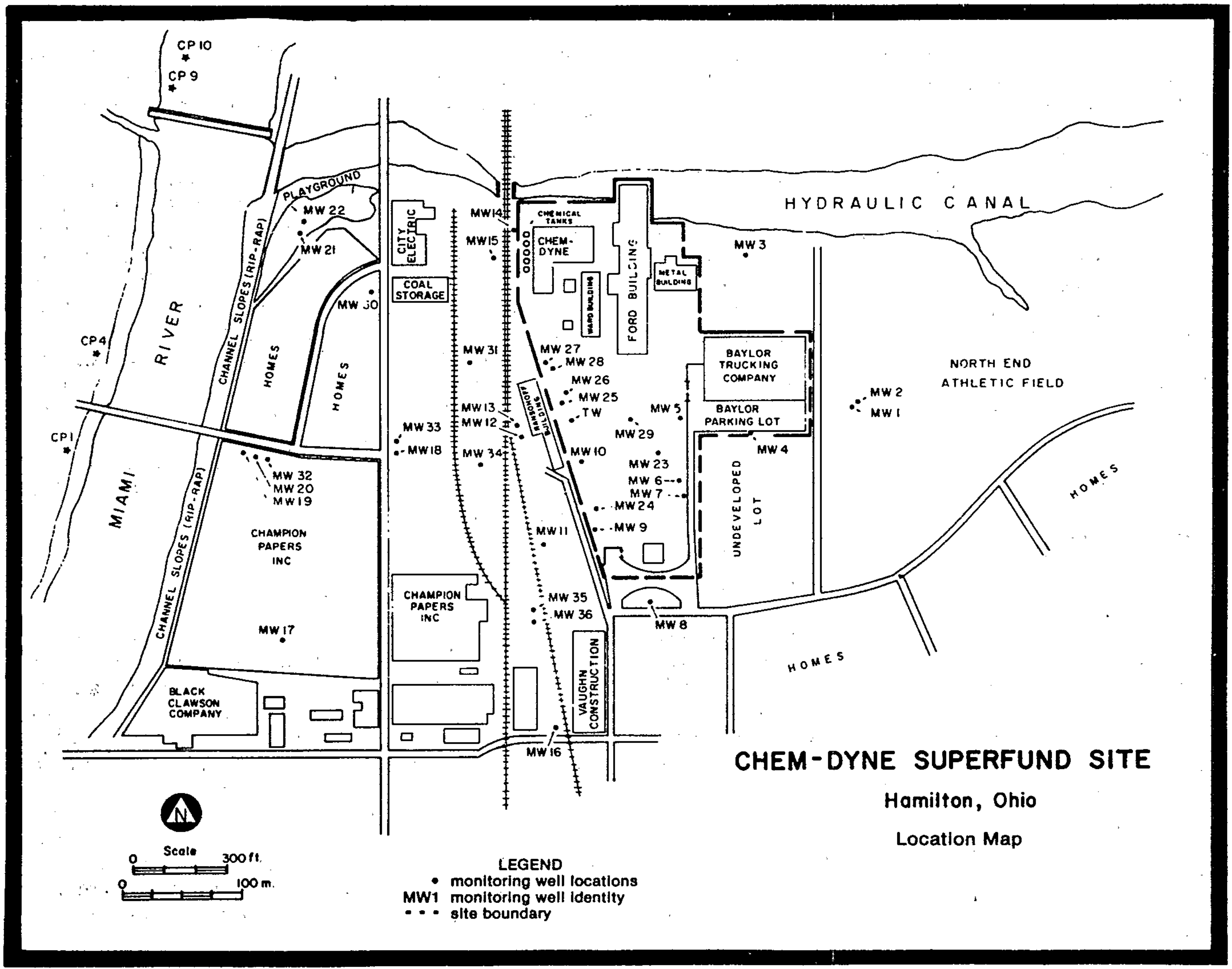


Figure 93. Monitoring well location map for the Chem-Dyne site.

exert a similar influence on samples collected at depths greater than a few feet.

Additional Site Investigations

Subsequent studies of the site corrected these misinterpretations by producing data from proper soil samplings and incorporating much more detailed characterizations of the fluvial sediments and the natural flow system. In those studies, vertical profile characterizations were obtained from each new borehole drilled by continuous split-spoon samples of subsurface solids. The split-spoon samples helped to confirm the general locations of interfingered clay lenses and clearly showed the high degree of heterogeneity of the sediments (Figures 94 and 95). For example, a dense clay lens was found at similar elevations (at 570 to 580 ft MSL) along the valley axis (Figure 94), but was found only intermittently perpendicular to the valley axis (Figure 95). This should be expected by hydrogeologic intuition since, during flooding, rivers dissect deposits that were laid down in low energy periods and rivers undergo natural channel changes (e.g., meandering) as they mature. These phenomena create lenticular clay bodies of very limited extent and structurally anisotropic conditions. The major axis of anisotropy parallels the average downstream direction, which itself is generally co-linear with the valley axis.

Clusters of vertically separated monitoring wells were constructed during the remedial investigations/feasibility studies at Chem-Dyne. While an extensive network of shallow wells confirmed earlier indications of general ground-water flow toward Great Miami River (Figure 96), the clusters of vertically separated wells revealed that downward gradients existed adjacent to the river. Figures 97 and 98 show that these vertical gradients, which

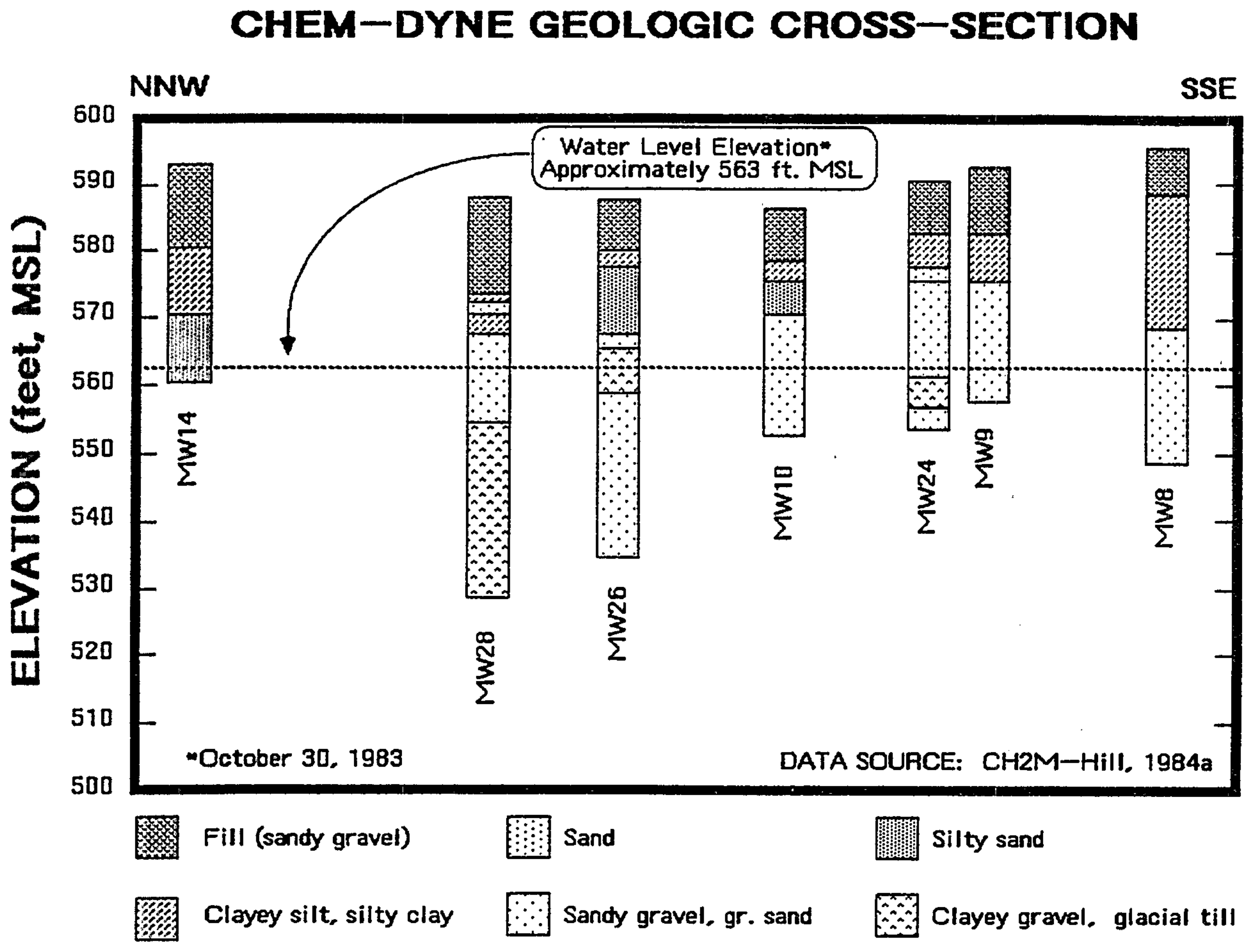


Figure 94. NNW-SSE geologic cross-section at Chem-Dyne site.

ranged from a 1- to 3-foot drop over the 20-foot vertical separation between the bottom of the shallow wells and the top of the screens in the deep wells (or about 0.100), are quite dramatic relative to the horizontal gradient across the contaminant plume (which averages about 0.001). This finding indicated that the migrating plume would not be discharged to the river, but would flow under the river.

The presence of major industrial wells on the west bank of Great Miami River provided an explanation for the observed downward vertical gradients (normally, one would have expected the river to be gaining water from the aquifer at this point in the basin), and supported the conclusion that contaminants could not be discharged to the river from the aquifer. The plume would be drawn to greater depths in the aquifer by the locally severe downward gradient, but it could not be determined if the industrial wells would actually capture the plume. That determination would require careful evaluation of the hydrogeologic features beneath the river (an activity not attempted because of the associated costs) and expectations that planned remedial actions would stop the plume before substantial encroachment could occur.

Hydrologic Complications

Unfortunately, the hydraulic interplay of the river with the aquifer was not well appreciated by the field crews taking routine measurements of water levels. Observations late in the final study found that, during preparations for a pump test, river stage variations cause as much as three feet of water level change during a single day at wells close to the river. This effect was virtually negligible at wells much closer to the site. This sort of situation makes it crucial to obtain water levels at all wells within only a few hours, otherwise, the sort of confusing water level maps shown in Figures 99 to 101 may result. These figures were prepared with water-level elevation data that were measured over periods of several days (CH_2M-Hill, 1984a).

Investigators decided to use a major pump test to estimate the hydrogeologic characteristics of the

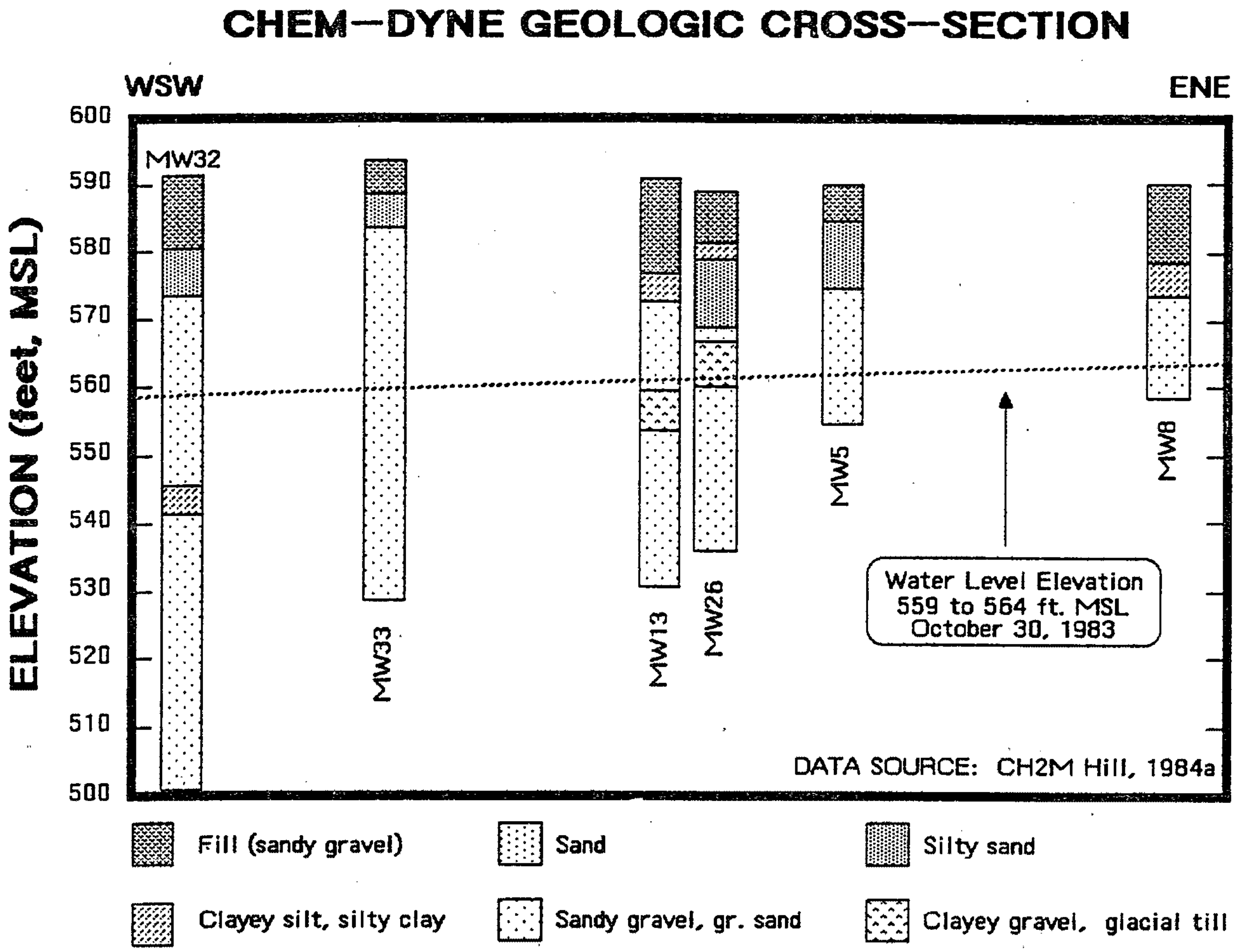


Figure 95. **WSW-ENE geologic cross-section at Chem-Dyne site.**

heavily contaminated portion of the aquifer. The pump test was technically difficult because the pumping well had to be drilled on site due to potential liability and lack of access elsewhere. The drillers were substantially slowed by the need to wear air-tanks when encountering particularly contaminated subsoils that emitted volatile fumes and presented unacceptable health risks. Since the pumped water was expected to be contaminated, ten large contemporary holding tanks (100,000 gallons each) were constructed on site to impound the waters for testing and possible treatment before being discharged to the local sewer system (CH_2M-Hill, 1984a).

Although there had been some resistance to conducting the pump test because of its cost, the test results were very valuable. The water levels in thirty-six monitoring wells were observed during the test, providing a very detailed picture of areal transmissivity variations (Figures 102). This information helped explain the unusual configuration of the plume shown in Figures 103, 104, and 106 (Figure 105 is an updated location map for 1985 data presented in Figure 106 and some later figures). The information also was used to guide the design of a pump-and-treat system. Storage coefficients also were estimated and, though the short duration of the test (14 hours) did not provide many definitive estimates, qualitative confirmation of the generally non-artesian (water-table) nature of the aquifer beneath the site was clearly confirmed, as were the increasingly artesian conditions from the west edge of the site towards the river.

Anisotropic Flow Biases

On-site transmissivity estimates from a trio of wells (MW-23, MW-26, and MW-29) indicated a 2:1 anisotropic bias toward the river as opposed to downvalley, whereas nearer the river a second trio of wells (MW-28, MW-33, and MW-35) yielded estimates for which the bias appeared to be 10:1 downvalley (CH_2M-Hill, 1984a). These trends coincide with the nature of the system; that is, there are few clay occurrences on site and east of the site from whence recharge waters flow toward the river, and

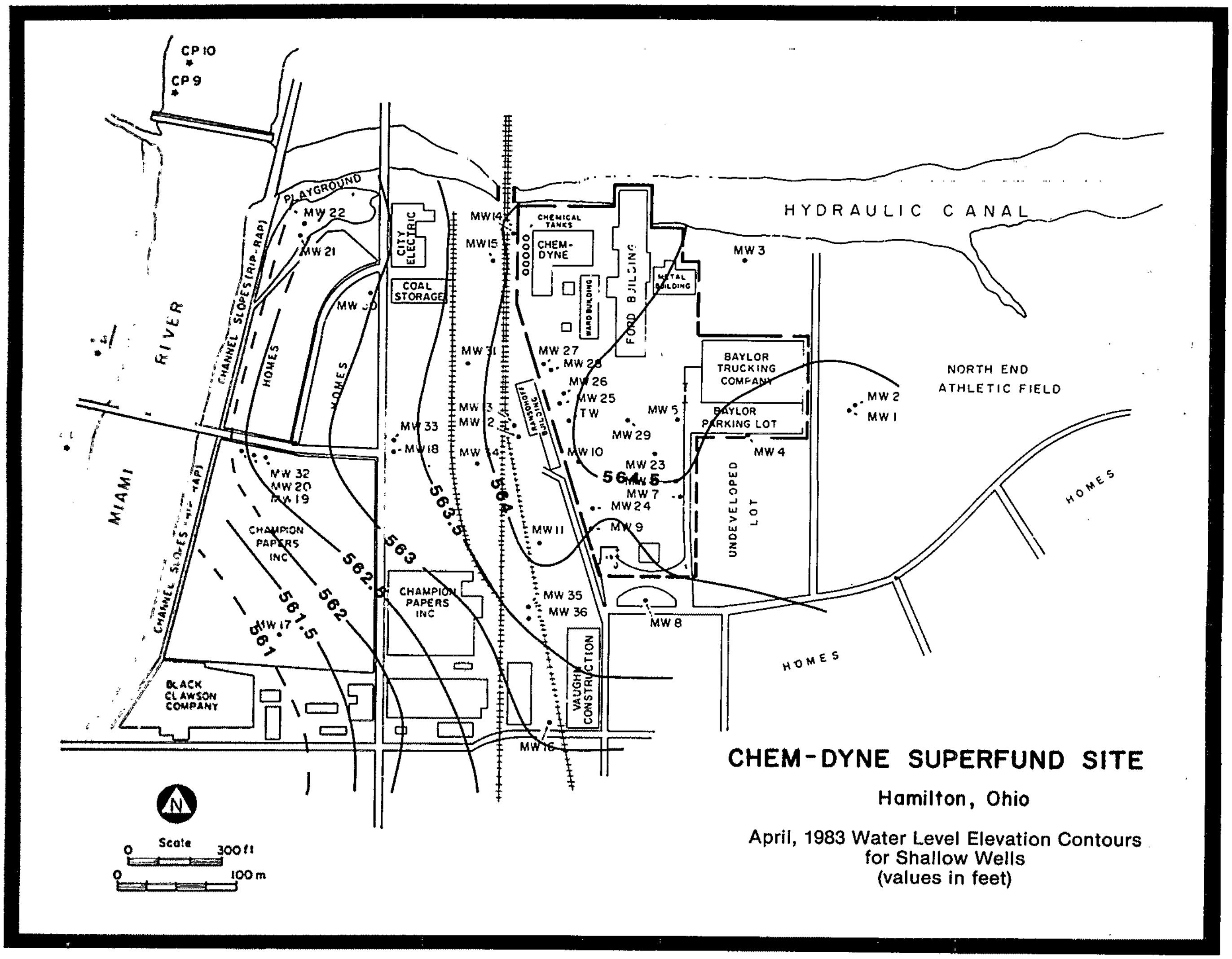
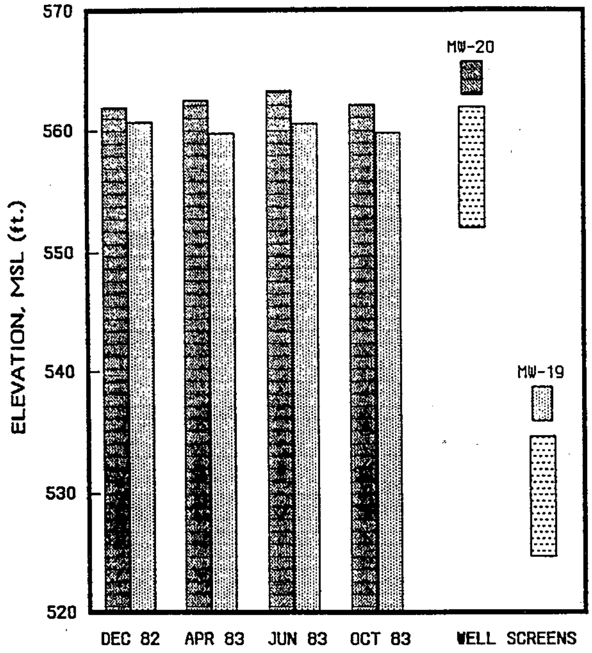


Figure 96. April 1983 water level elevation contours at Chem-Dyne site using shallow well data only, in feet MSL.

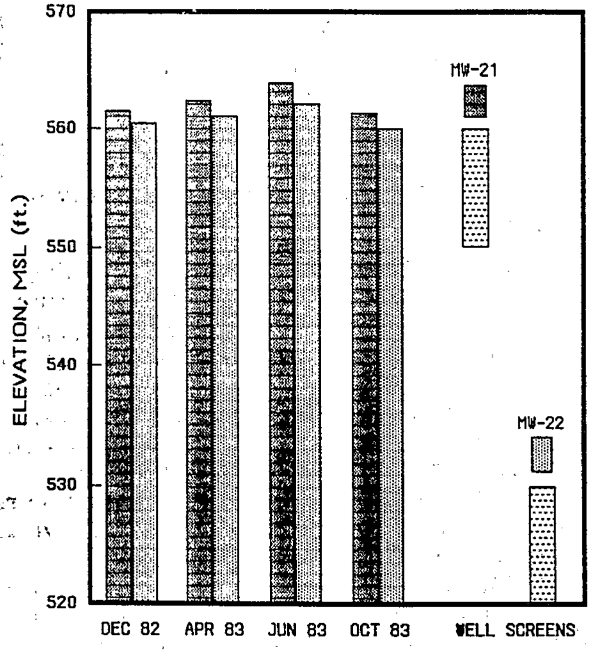
significant occurrences of clays at the west fenceline of the site and adjacent to the river. The latter clays had lenticular shapes that paralleled the axis of the river, causing a strong downvalley bias. These indications mean that flow would not proceed at an average velocity perpendicular to the water level contours that would be west from the northern half of the site, and south to southwest from the southern half of the site (Figure 95). Instead, flow would move westerly first and then southerly as it neared the river. By the time areas adjacent to the river were reached, the net position would be roughly the same, but the path taken to get there would be strikingly different. The contaminant masses leaving both the northern and southern halves of the site would be concentrated in west-trending tongues. Moreover, the future travel paths with the anisotropic bias interpretation would not be the same as with a presumption of isotropicity.

The distributions of contaminants observed at Chem-Dyne seem to support this anisotropic bias interpretation. The highest concentrations lie along an axis that does not appear to be influenced by the southerly components of flow expressed by the water-level contours offsite (Figures 103 and 104). While it is true that the pumpage of major production wells on the other side of the river offers a nominal explanation for this, the actual water level contours contradict the notion that the industrial wells dominate the entire flow field. This has to be appreciated in terms of capture zones; the industrial wells will indeed affect all of the ground-water flowlines locally, but may not capture all of them. It is likely that the plume is bifurcating near the river, with one member travelling on flowlines captured by the industrial wells, and a second member tangentially affected, but eventually released to continue on down the valley with the rest of the aquifer waters.



COMPARISON OF WATER LEVEL ELEVATIONS IN MONITORING WELLS MW–19 AND MW–20

Figure 97. Water levels in a cluster of two vertically separated monitoring wells adjacent to Great Miami River and due west of Chem-Dyne site.



COMPARISON OF WATER LEVEL ELEVATIONS IN MONITORING WELLS MW–21 AND MW–22

Figure 98. Water levels in a cluster of two vertically separated monitoring wells at the confluence of Great Miami River and Ford Hydraulic Canal, due west of north boundary of Chem-Dyne site.

Field Evidence for Biotransformations

Finally, the distribution patterns of contaminant species that emerged from the investigations at Chem-Dyne were understood by considering research results and theories regarding chemical and microbiological influences. Contaminant distribution maps derived from samples taken at the end of the field investigation (October, 1983, only months after the last drums of solvents were removed from the site) suggested that the transformation of tetrachloroethene (Figure 107) to less halogenated daughter products such as trichloroethene (Figure 108), dichloroethene (Figure 109), and vinyl chloride/monochloroethene (Figure 110) was occurring.

In such circumstances, one would expect to see the progressive disappearance of tetrachloroethene and successive increases in the concentrations and extent of potential daughter products. This seems to be the case at Chem-Dyne, according to the October 1983 data. One might argue that too little vinyl chloride is observed (Figure 110) to show the full series of degradation expected, but there are plausible reasons why the distributions might be as shown. For example, with a continuous source input, the concentrations of tetrachloroethene might be high enough that there would be no need for further biotransformation of daughter products because an ample food supply is available in the parent material. Alternatively, the concentrations of tetrachloroethene with continuous source inputs might indeed be so high as to limit biotransformation by toxic effects. Since the relative kinetics of the various transformations in this sequence still require further definition, it is impossible to make rigorous conclusions with regard to these possibilities.

But consider the data obtained during a chemical sampling conducted two years later in preparation for activation of the pump-and-treat system used to remediate the plume (Figures 110 to 113). At least two years of freedom from surface inputs of solvents had occurred as well as two years of healthy rainwater flushing the unsaturated zone of stored residues. Investigators found that the daughter products (Figures 111 to 113) contain much greater mass than that in the tetrachloroethene contours (Figure 110), and are spread over significantly greater areas. The increase in the vinyl chloride component of the plume is staggering (compare Figure 113 to Figure 109). These data highly suggest active degradation of tetrachloroethene to its possible daughter products. Knowledge of this kind of possible transformation should be valuable to those attempting to design and estimate costs for treatment systems since treatment efficiencies vary with the contaminant and its contribution to the

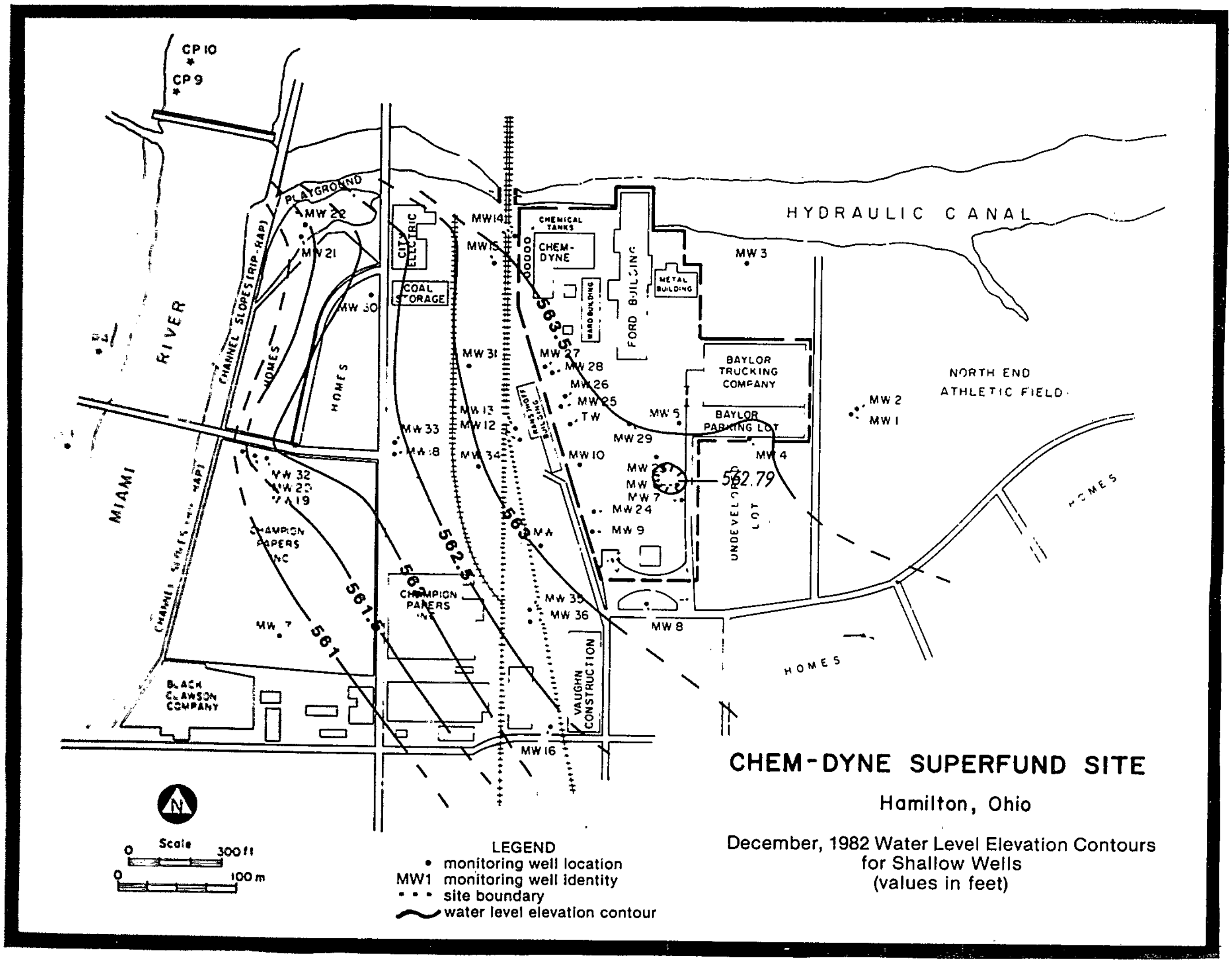


Figure 99. **December 1982 water level elevation contours at Chem-Dyne site using shallow well data only in feet MSL.**

overall loading. Vinyl chloride is much more volatile and easier to remove than tetrachloroethene.

The relative rates of movement of these and other common solvents like benzene and chloroform at Chem-Dyne generally conformed to predictions based on sorption principles. This is useful in a practical sense. The remediation efforts made use of these contaminant transport theories in estimating the capacity of the treatment system and the length of time needed to remove residuals from the aquifer solids (CH_2M-Hill, 1984b).

The Role of Mathematical Models

During the latter stages of negotiations with the Potentially Responsible Parties (PRPs), the State of Ohio government contractors prepared mathematical models of the flow system and contaminant transport at Chem-Dyne (GeoTrans, 1984). These models were used to estimate the possible direction and rate of migration of the plume in the absence of remediation, the mass of contaminants removed during various remedial options, and the effects of sorption and dispersion on those estimates. Because of the wide range of sorption properties associated with the variety of contaminants found in significant concentrations, it was necessary to select values of retardation constants that represented the likely upper and lower limits of sorptive effects. It also was necessary to estimate or assume the values of other parameters such as dispersion coefficients known to affect transport processes.

Ward and his co-workers recently published this application of models to the Chem-Dyne site in an article highlighting the development and recommendation of the Telescopic Mesh Refinement (TMR)

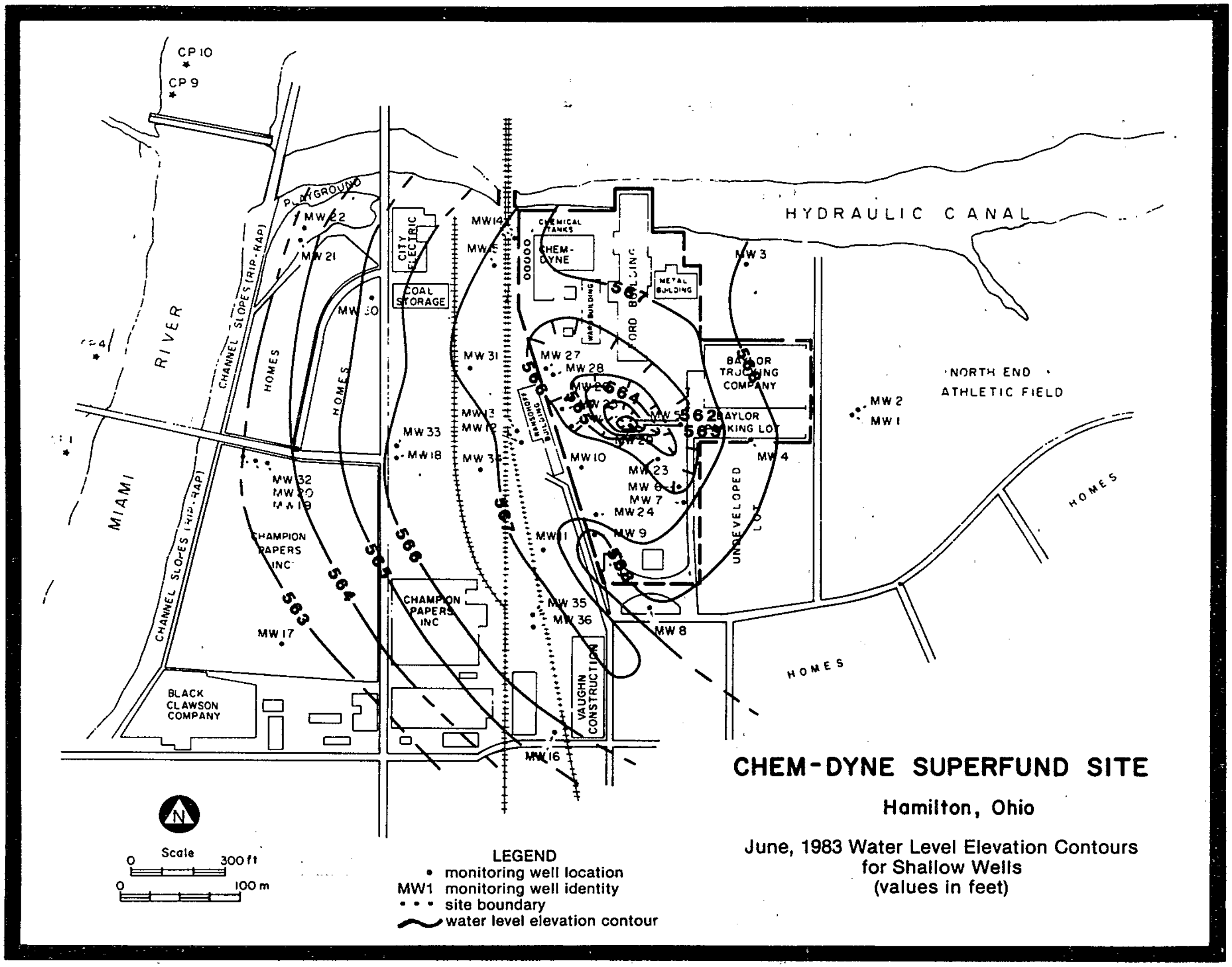


Figure 100. June 1983 water level elevation contours at Chem-Dyne site using shallow well data only, in feet MSL.

modeling approach (Ward, et al., 1987). The TMR approach involves a staged evaluation of the problem, proceeding from the regional level to the local level to the site-specific level (Figure 114). This approach makes it possible to assure the appropriateness and consistency of boundary conditions such as recharge rates to the aquifer and interactions with streams. GeoTrans chose to develop this set of models using the SWIFT model, which utilizes the finite difference method (FDM), that, in turn, utilizes rectangular grids (Figure 115). FDM is the most mathematically straightforward and easily debugged of the numerical analysis techniques used for mathematical modeling (Mercer and Faust, 1981). Recognizing the need to account for the influences of the vertical gradients previously noted to be severe adjacent to Great Miami River, GeoTrans created a quasi-three-dimensional (layered) model at the local scale (Figure 116).

The results of their modeling efforts included maps of the potentiometric surfaces represented by water level elevations in wells tapping the different model "layers" (Figures 117 and 118). These maps indicated that local industrial wells control flow in the deeper portions of the aquifer. This site-scale model was used to investigate the probable effectiveness of the pump-and-treat remediation proposed by the Potentially Responsible Parties for Chem-Dyne (Figures 119 and 120). Geo-Trans concluded that the proposed pumping scheme appeared to be quite effective in the interior zone of the contaminant plume, but could not be completely effective in developing an inward hydraulic gradient at the

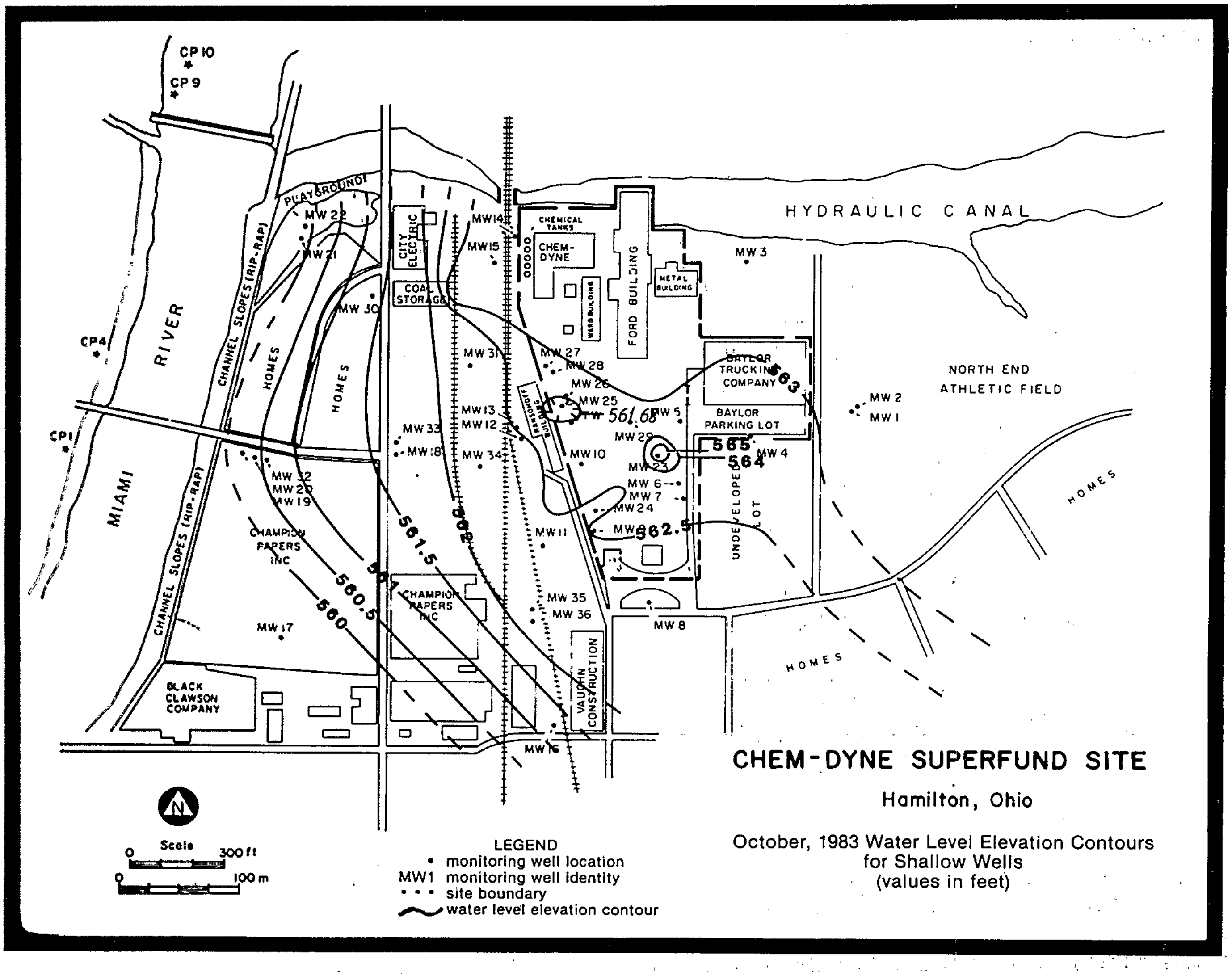


Figure 101. October 1983 water level elevation contours at Chem-Dyne site using shallow well data only, in feet MSL.

periphery of the plume. Their predictions turned out to be correct; during the first year of operation, the net withdrawal rate of the remediation wellfield was increased substantially over the originally proposed values, and inward hydraulic gradient control was still not fully established (Figure 121). GeoTrans modeling efforts also included predictions of the extraction well concentrations versus time (Figure 122), but comparisons with actual performance are difficult because of the many remediation shut-down periods (including lost time due to clogging of the air-stripper by precipitated iron and manganese).

Large uncertainties were associated with those modeling efforts due to lack of information about the actual history of chemical inputs and other important data. However, there was agreement between the government and PRP technical experts about the helpfulness of modeling efforts in assessing the magnitude of the problem and in determining minimal requirements for remediation. Consequently, modeling efforts continue at Chem-Dyne. Data generated during the remediation phase are being used to refine models in an ongoing process so that the effectiveness of the remedial action can be evaluated properly.

Summary

Models of the transport and fate of contaminants in the subsurface environment are created by organizing known information and relationships into a functional representation (e.g., a sand-filled tank, a circuit board, or an equation). Models may be used to simulate the response of specific problems to a wide variety of possible solutions.

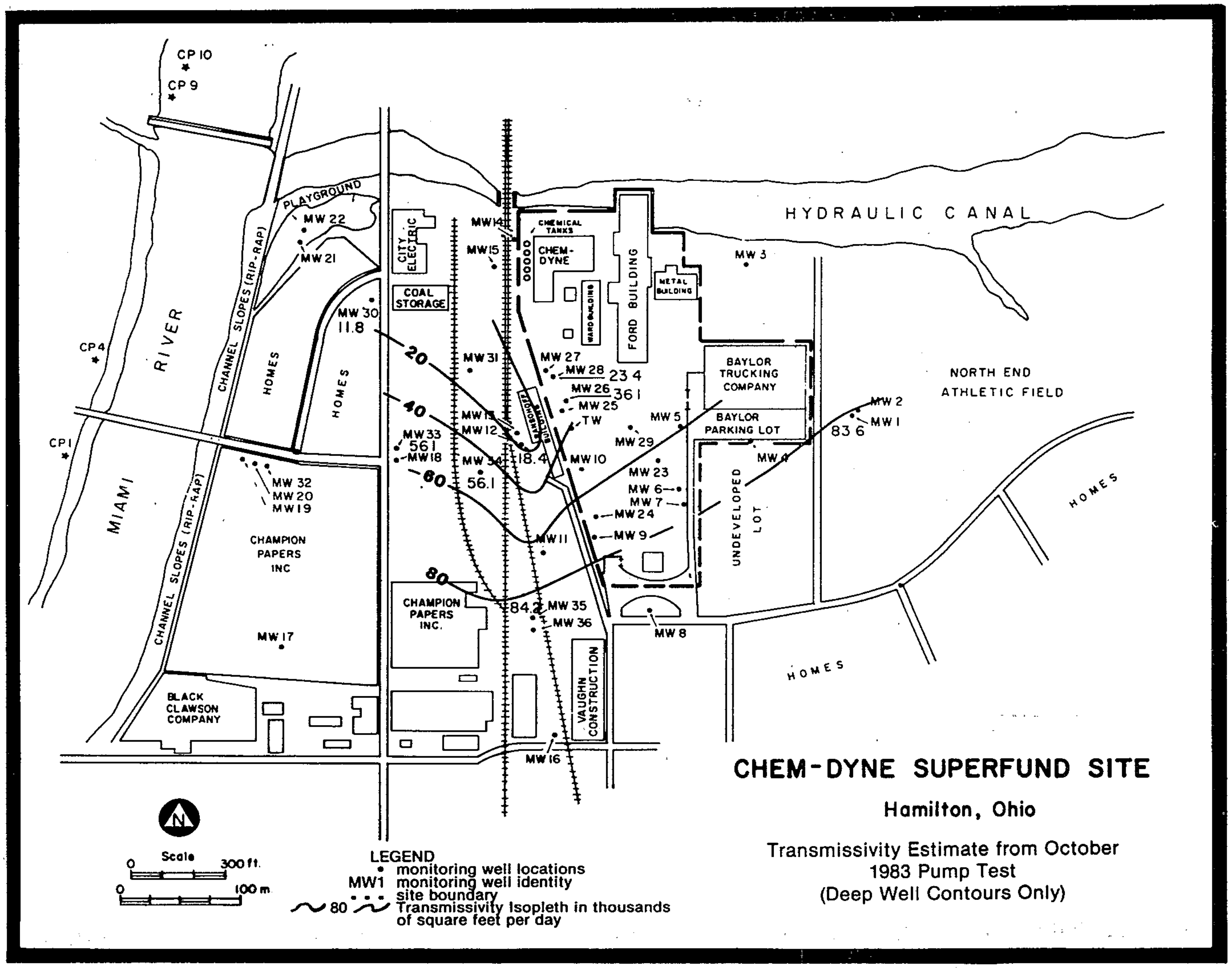


Figure 102. Transmissivity estimates obtained from October 1983 Pump test at Chem-Dyne site, in thousands of square feet/day (plotted values of estimates from all wells).

The application of mathematical models is subject to considerable error in practical situations when appropriate field determinations of natural process parameters are lacking. Contrary to popular beliefs, this source of error is not addressed adequately by sensitivity analyses or by the application of stochastic techniques for estimating uncertainty. Rather, the high degree of hydrogeological, chemical, and microbiological complexity typically present in field situations forces the use of site-specific characterization of the influences of various natural processes by detailed field and laboratory investigations.

Both the mathematics that describe models and the parameter inputs to those models must be subjected to rigorous quality control procedures. Otherwise, results from field applications of models are likely to be qualitatively, as well as quantitatively, incorrect. Quality control methodologies must focus on the accuracy of the problem conceptualization and the representativeness of parameter values, and recognize that accuracy and precision determinations are insufficient measures of quality.

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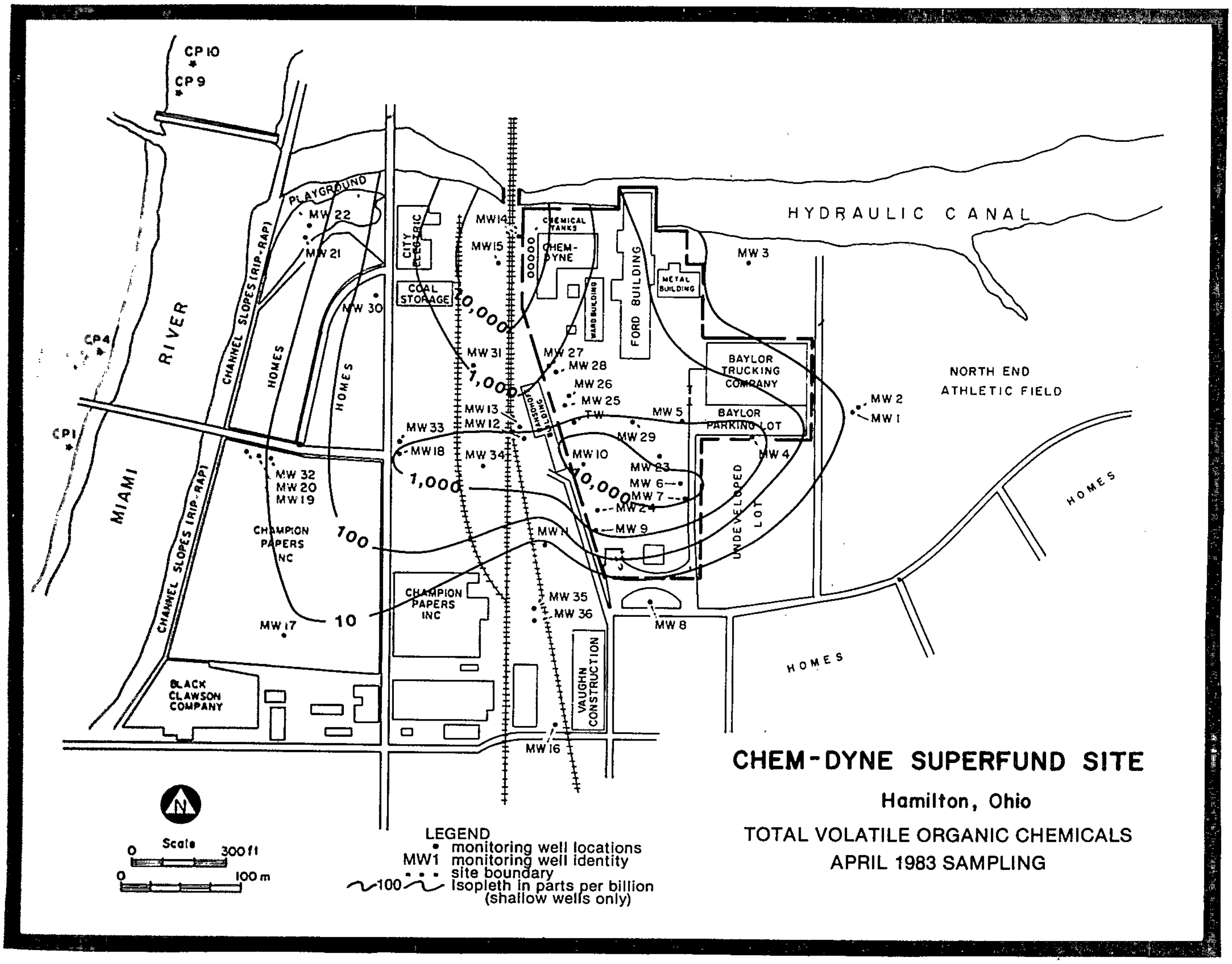

Figure 103. April 1983 total VOC concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

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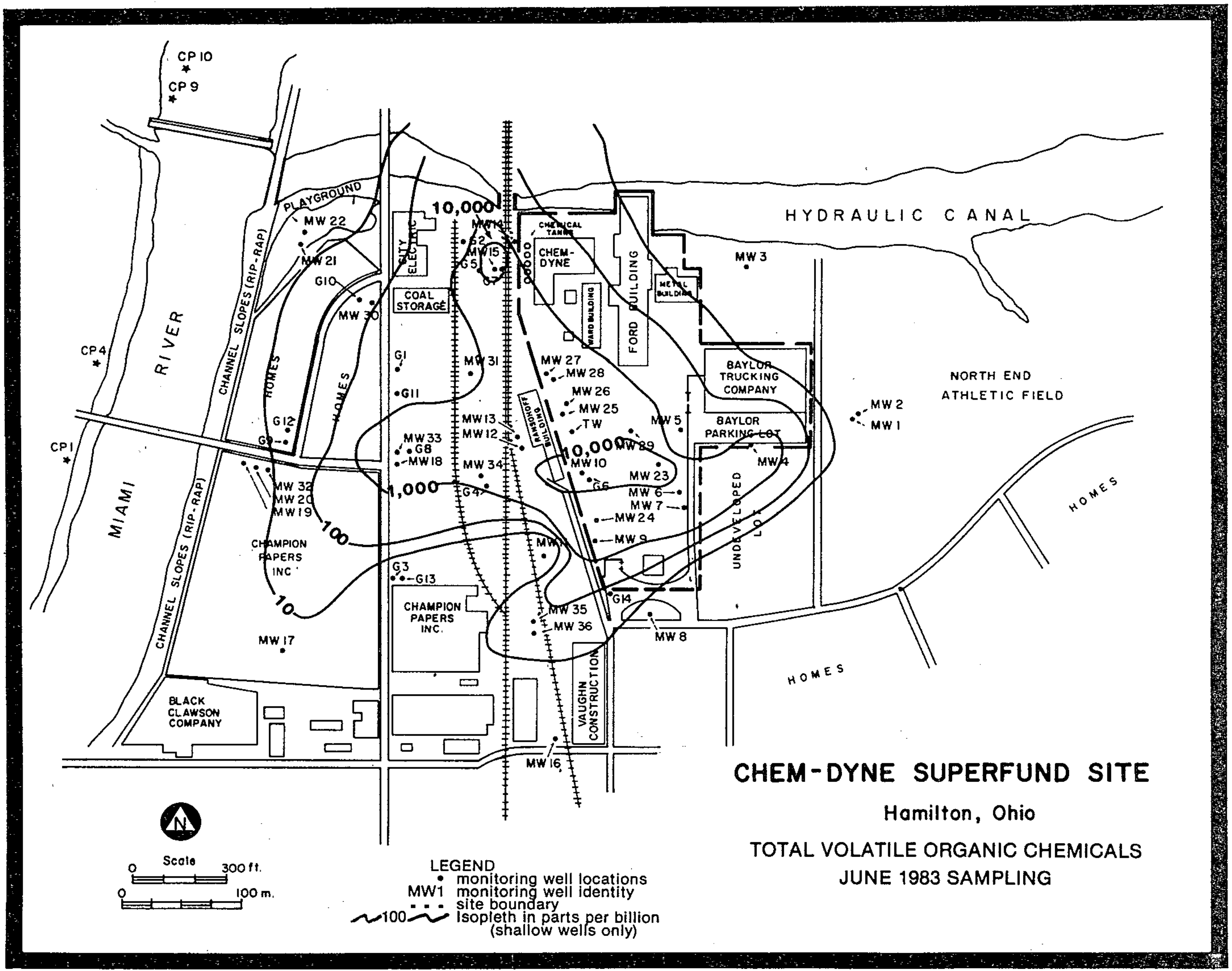

Figure 104. June 1983 total VOC concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

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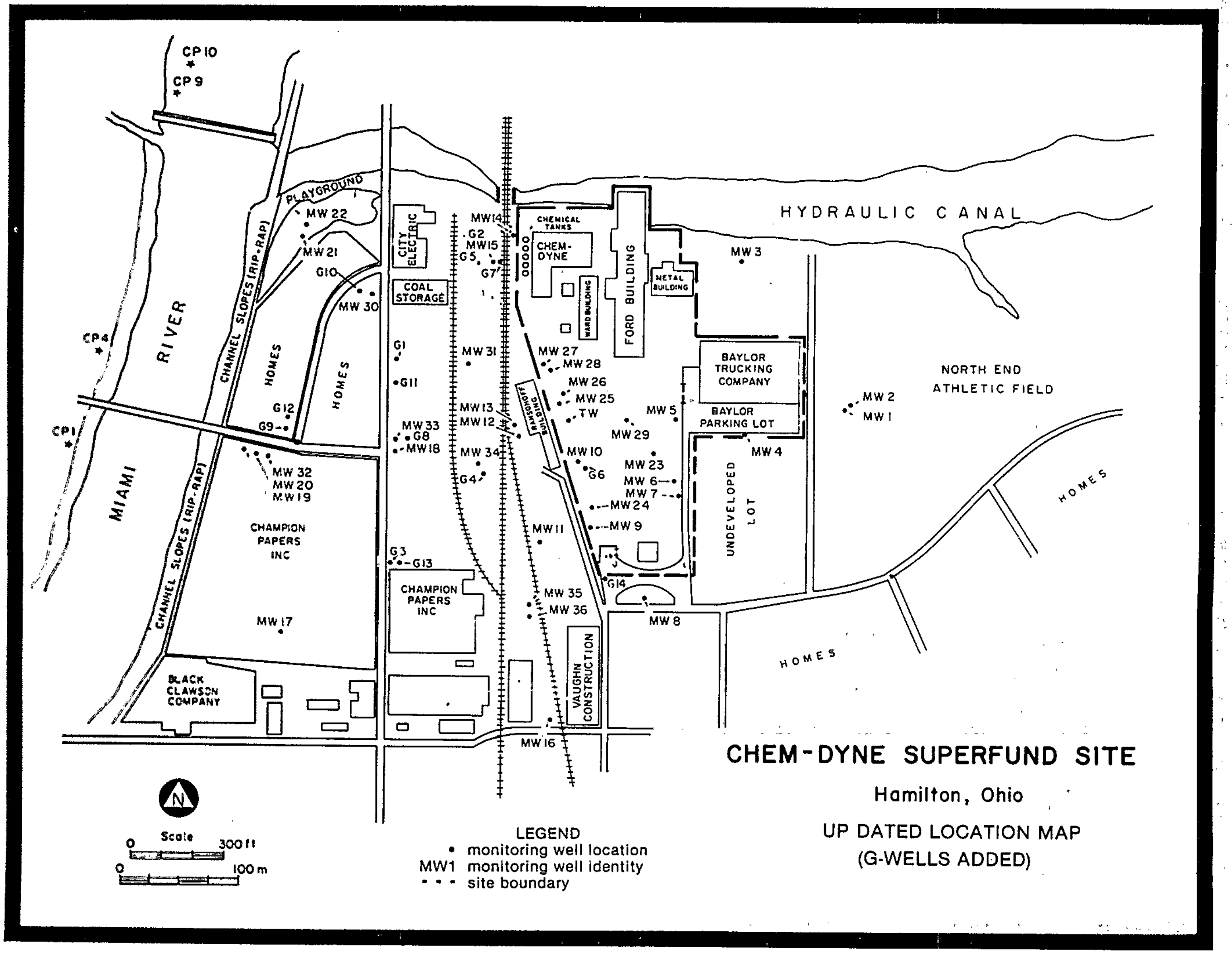

Figure 105. Updated location map for the Chem-Dyne site.

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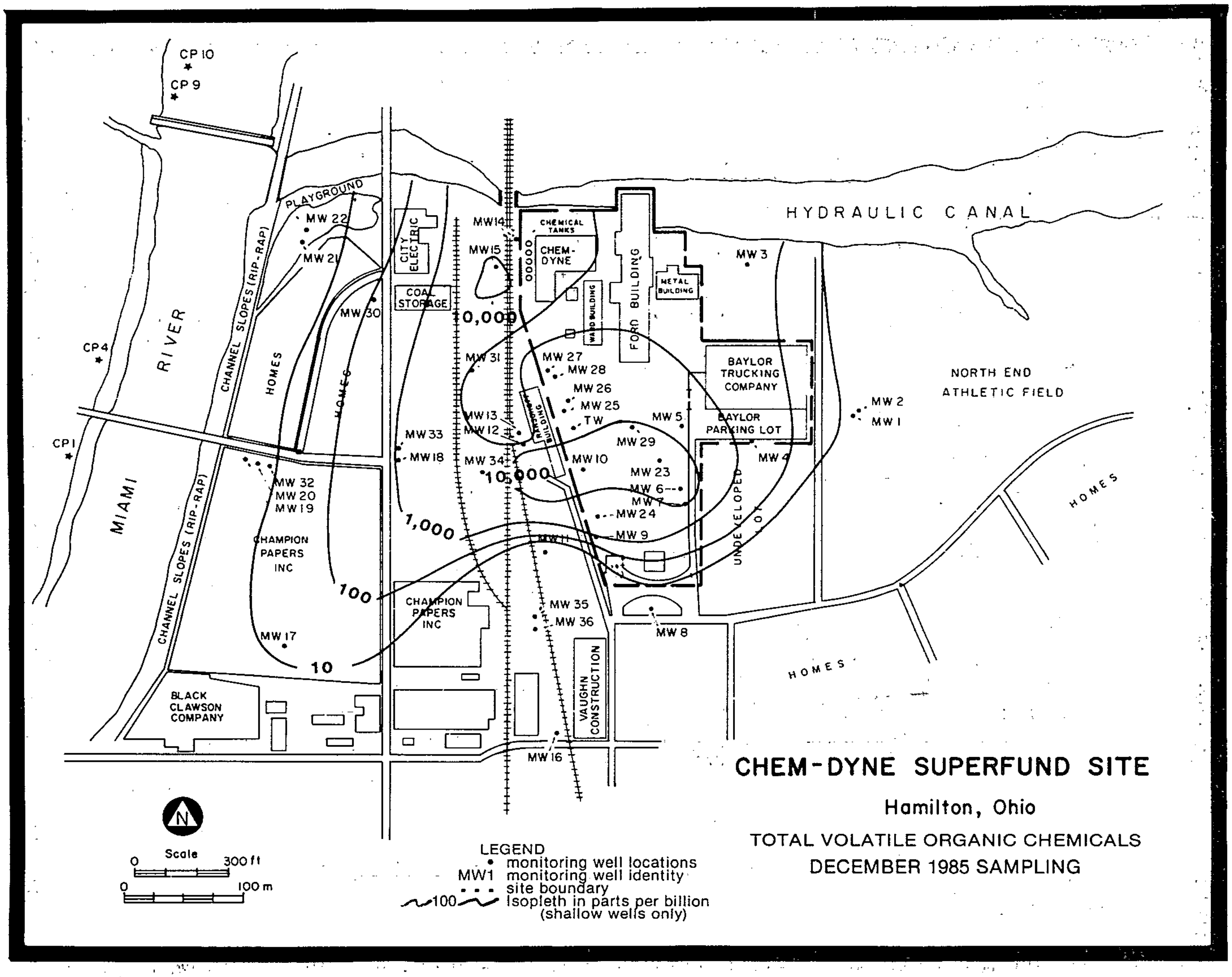


Figure 106. December 1985 total VOC concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

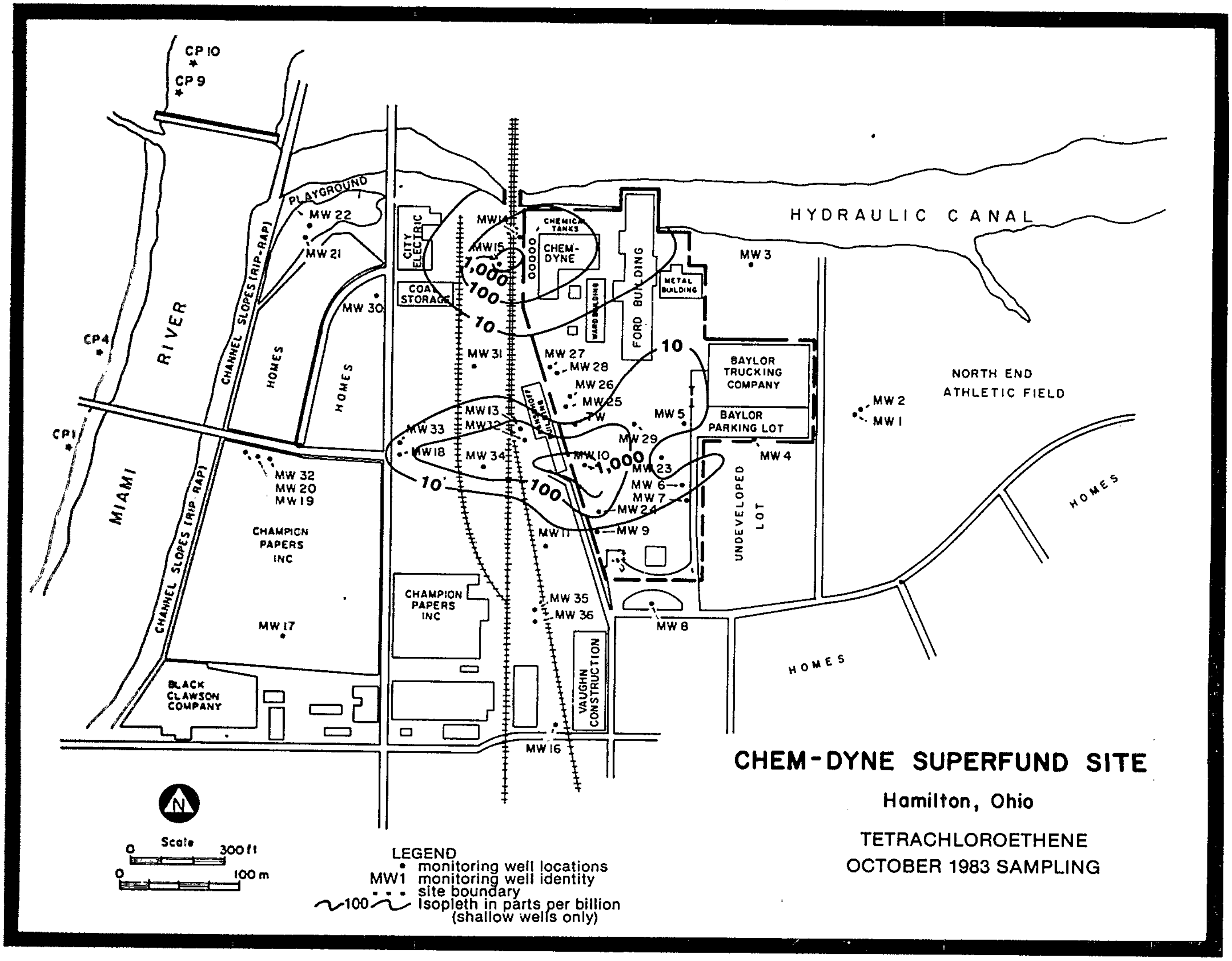


Figure 107. October 1983 tetrachloroethane concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

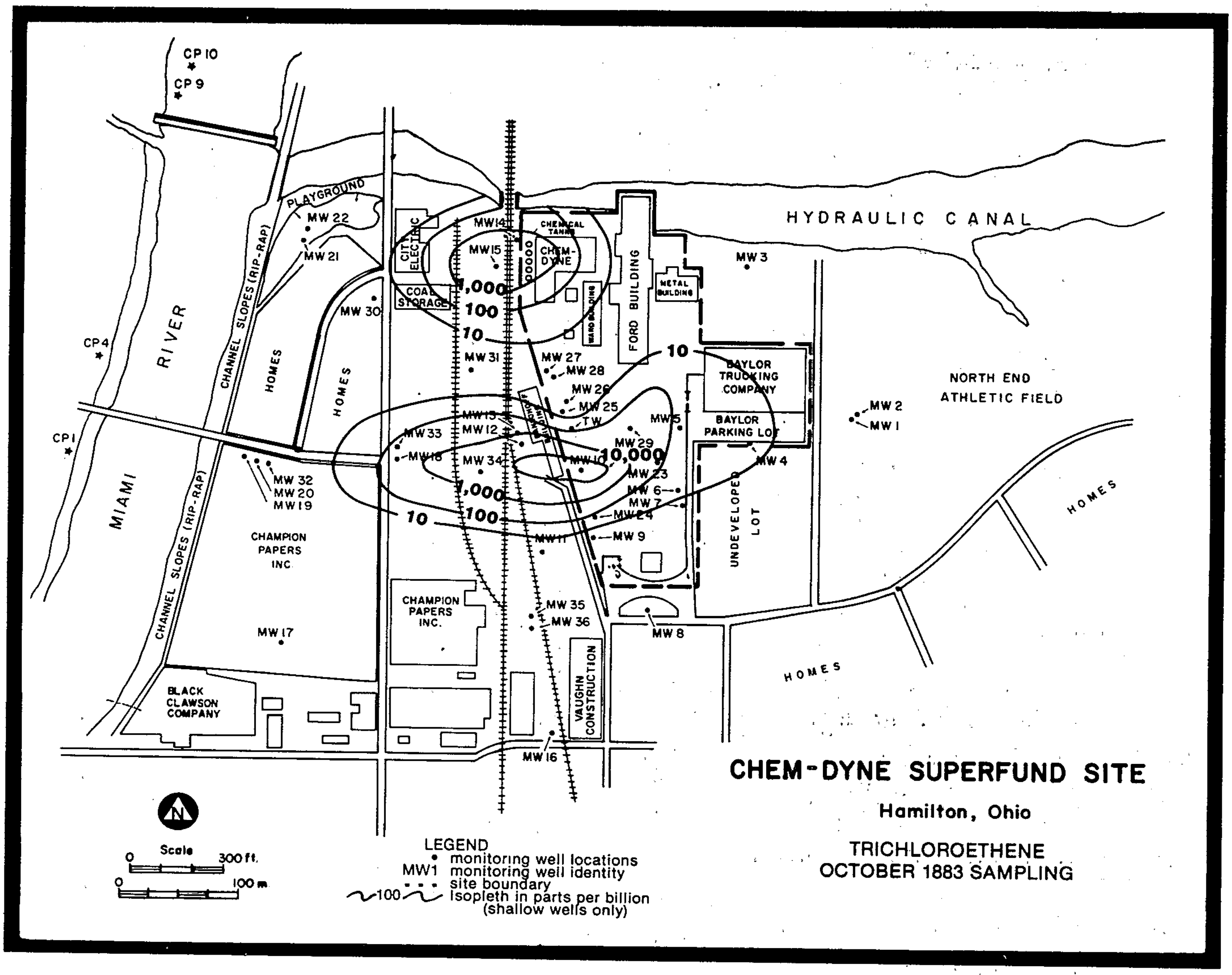


Figure 108. October 1983 trichloroethane concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

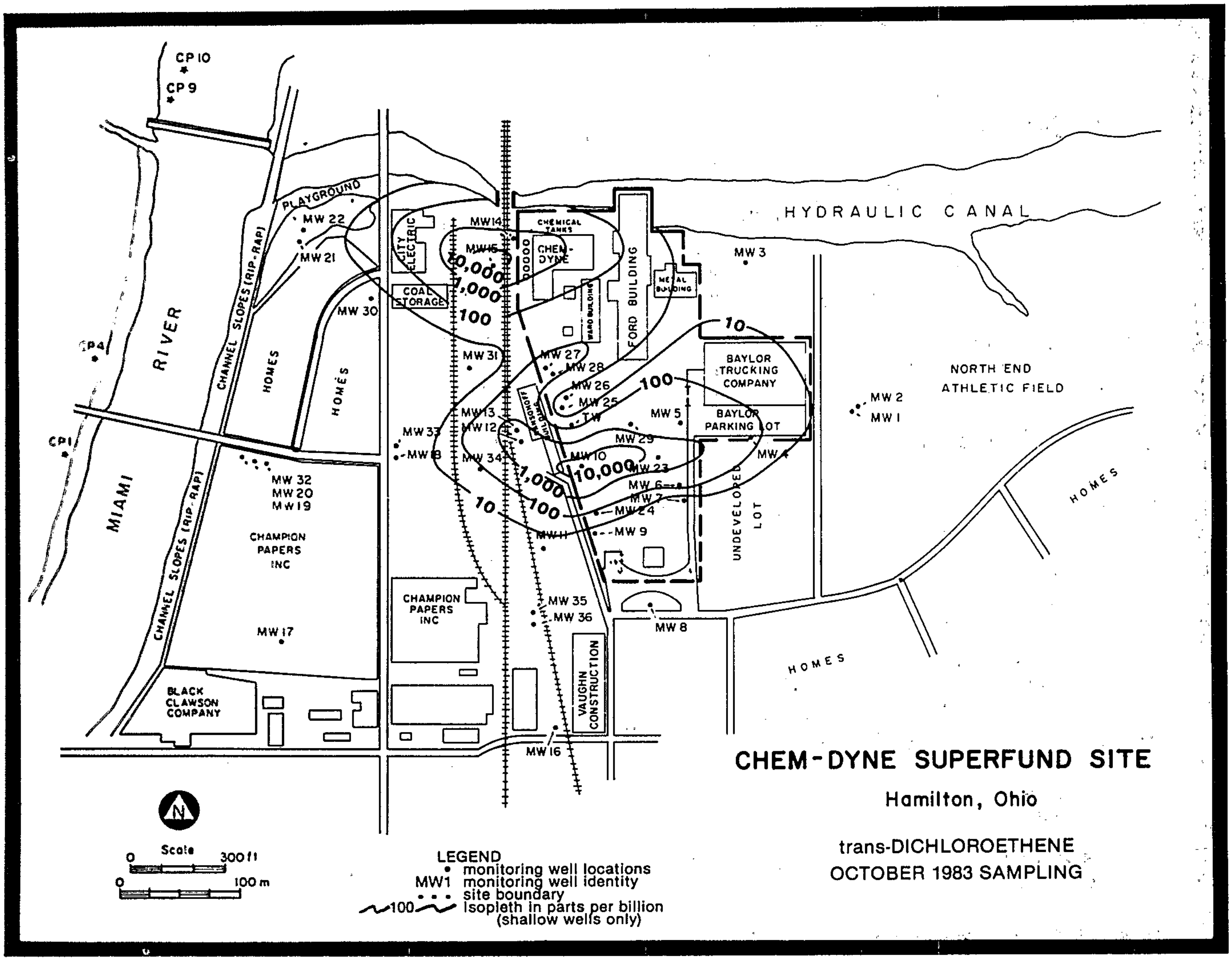


Figure 109. October 1983 trans-dichloroethene concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

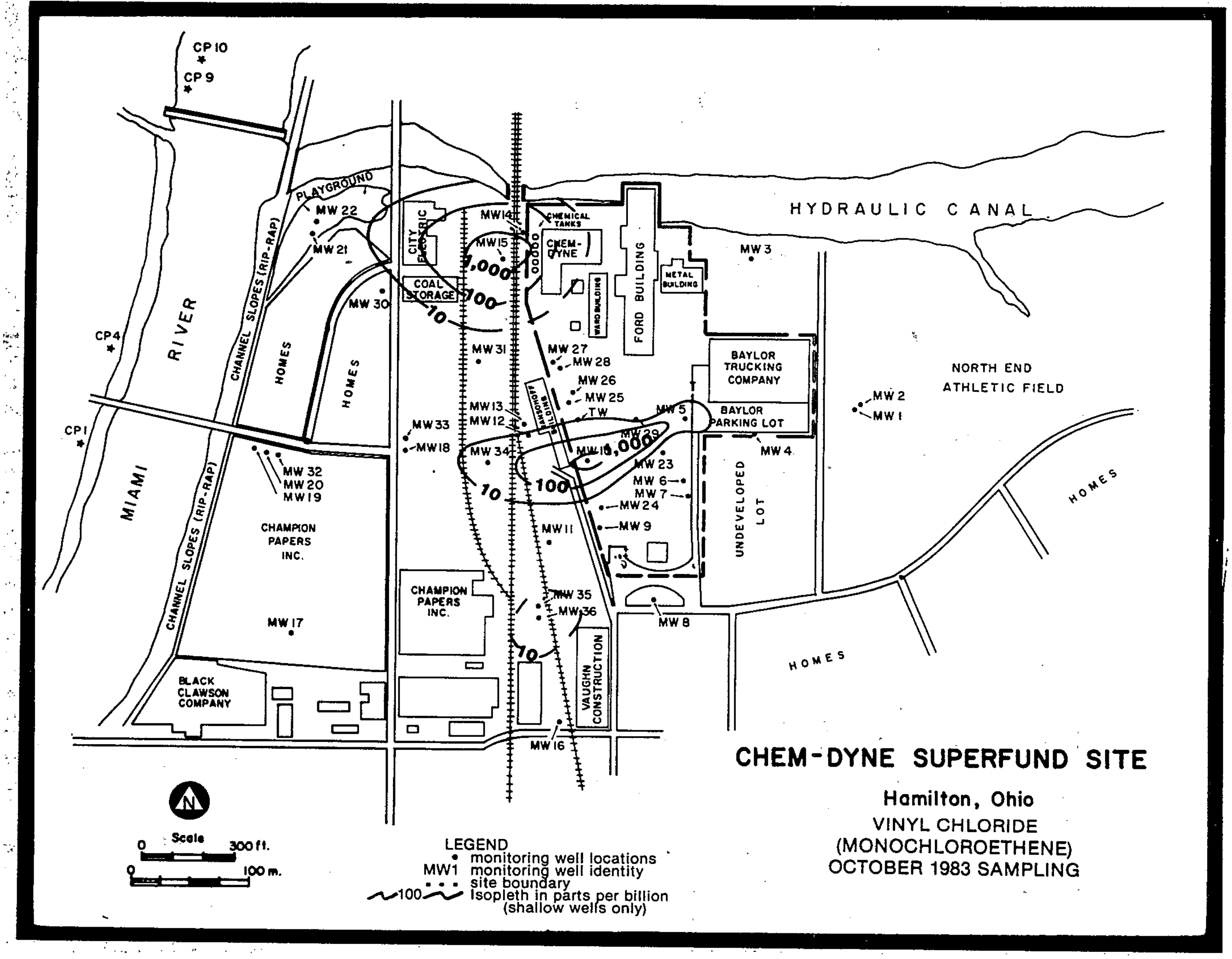


Figure 110. October 1983 vinyl chloride concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

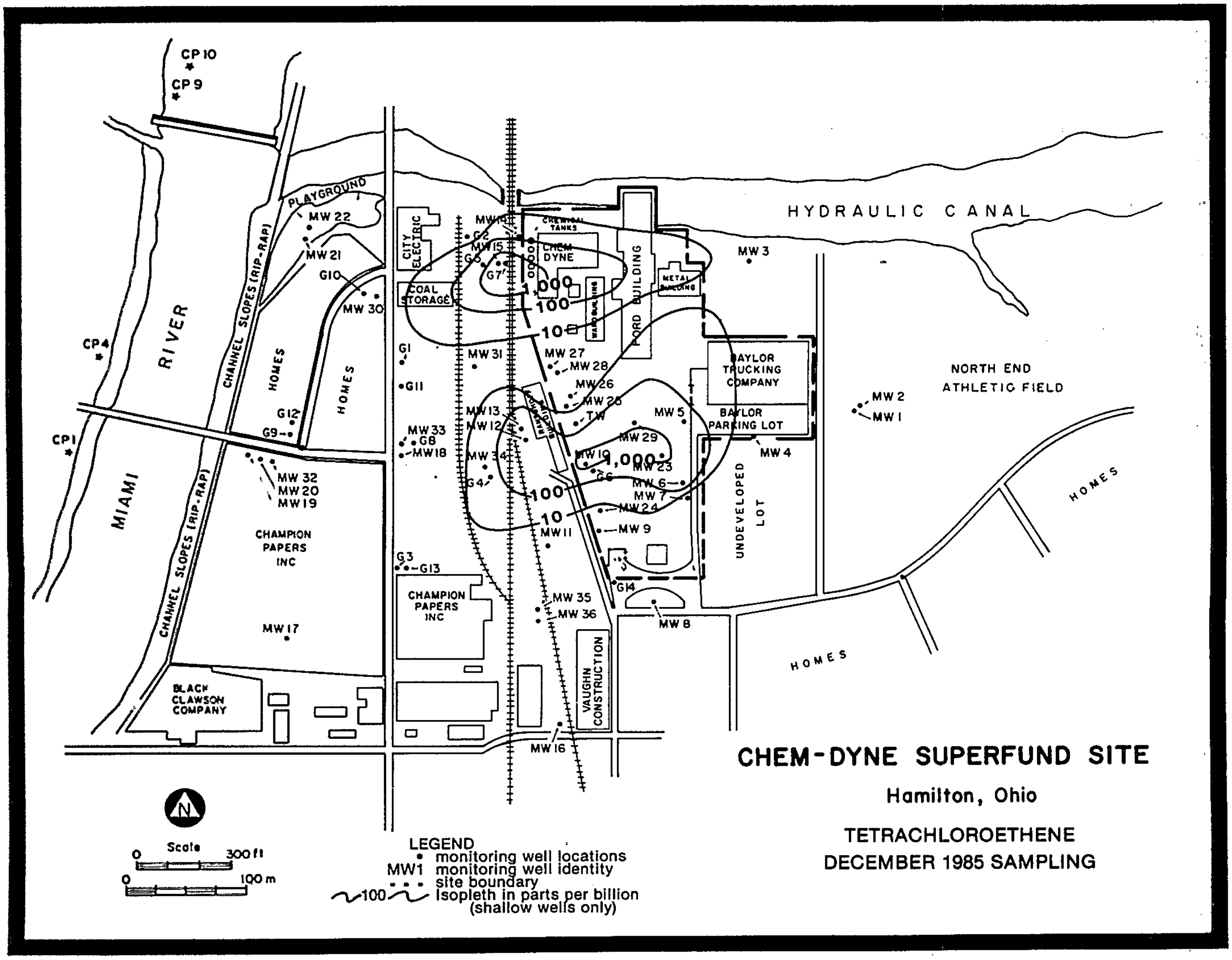


Figure 111. December 1985 tetrachloroethene concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

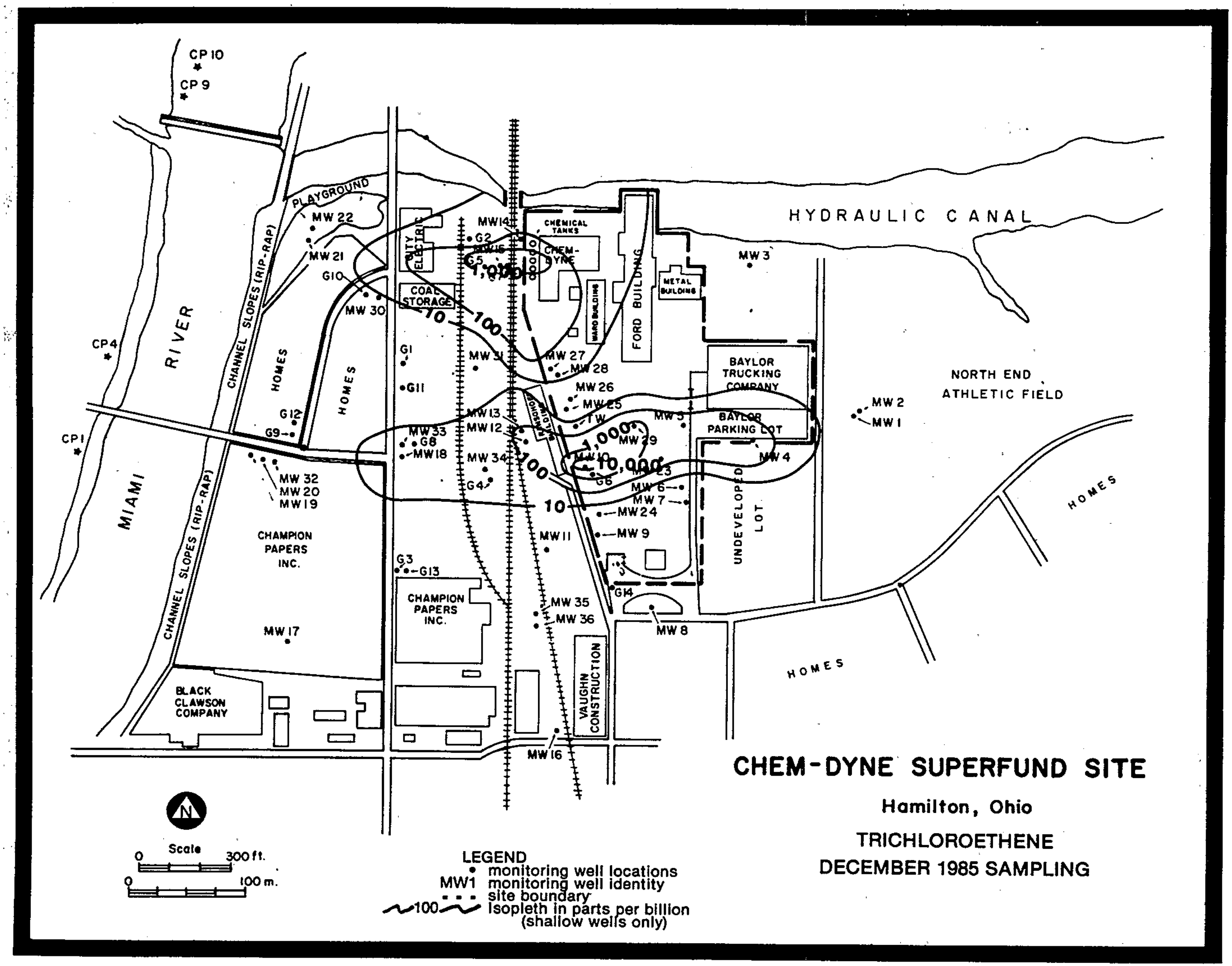


Figure 112. December 1985 trichloroethene concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

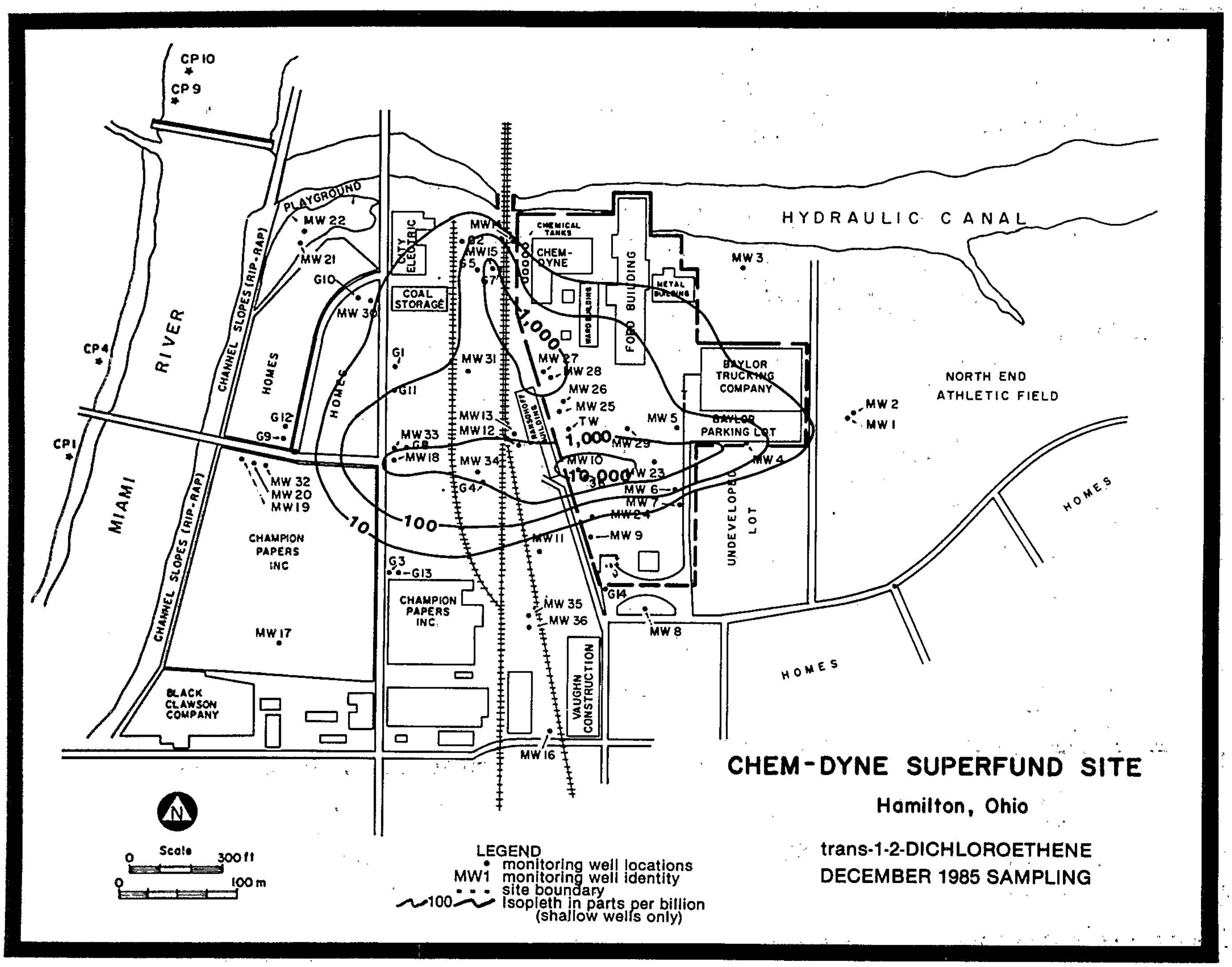


Figure 113. December 1985 trans-dichloroethene concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

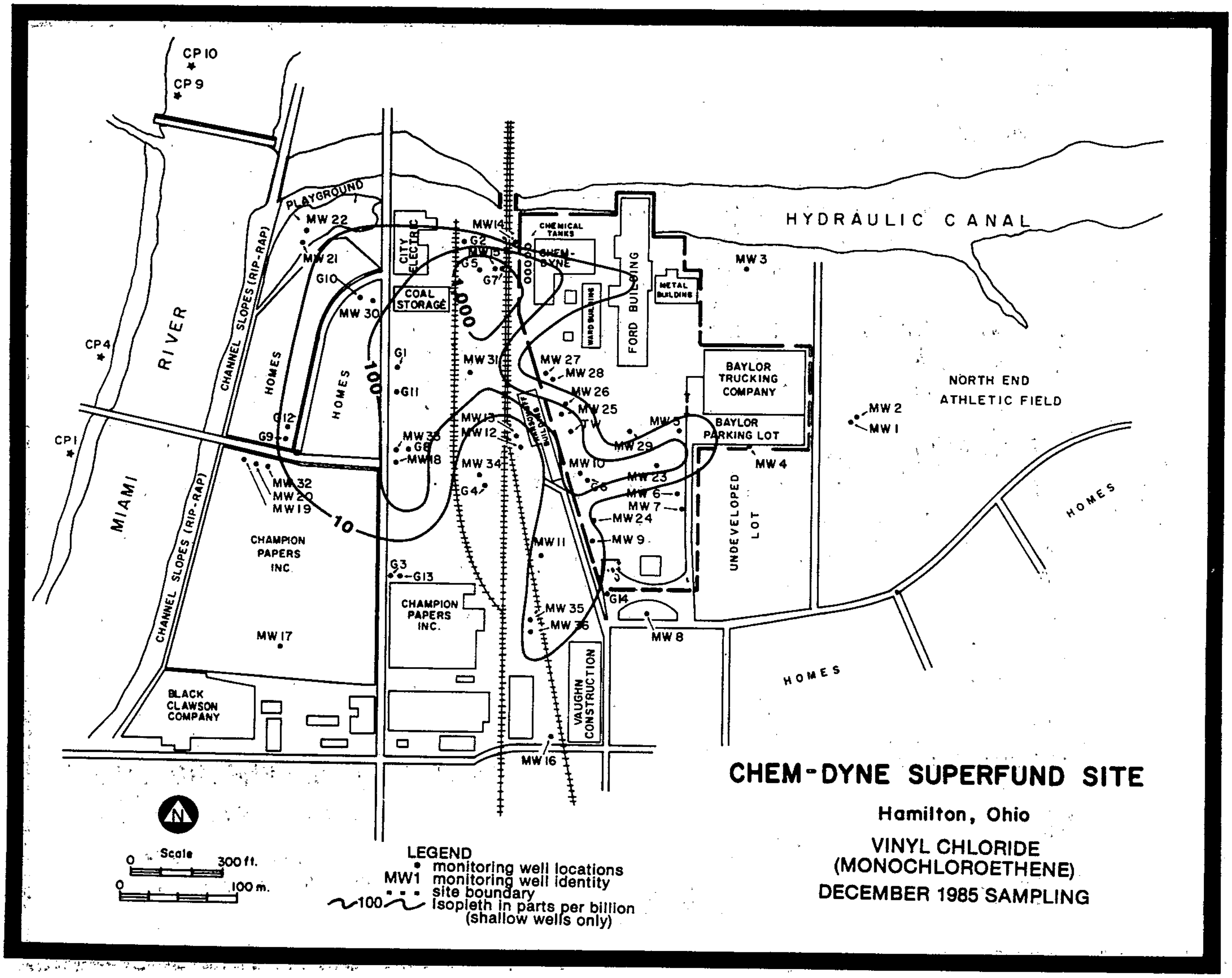


Figure 114. December 1985 vinyl chloride concentration contours (ppb) at Chem-Dyne site, using shallow well data only.

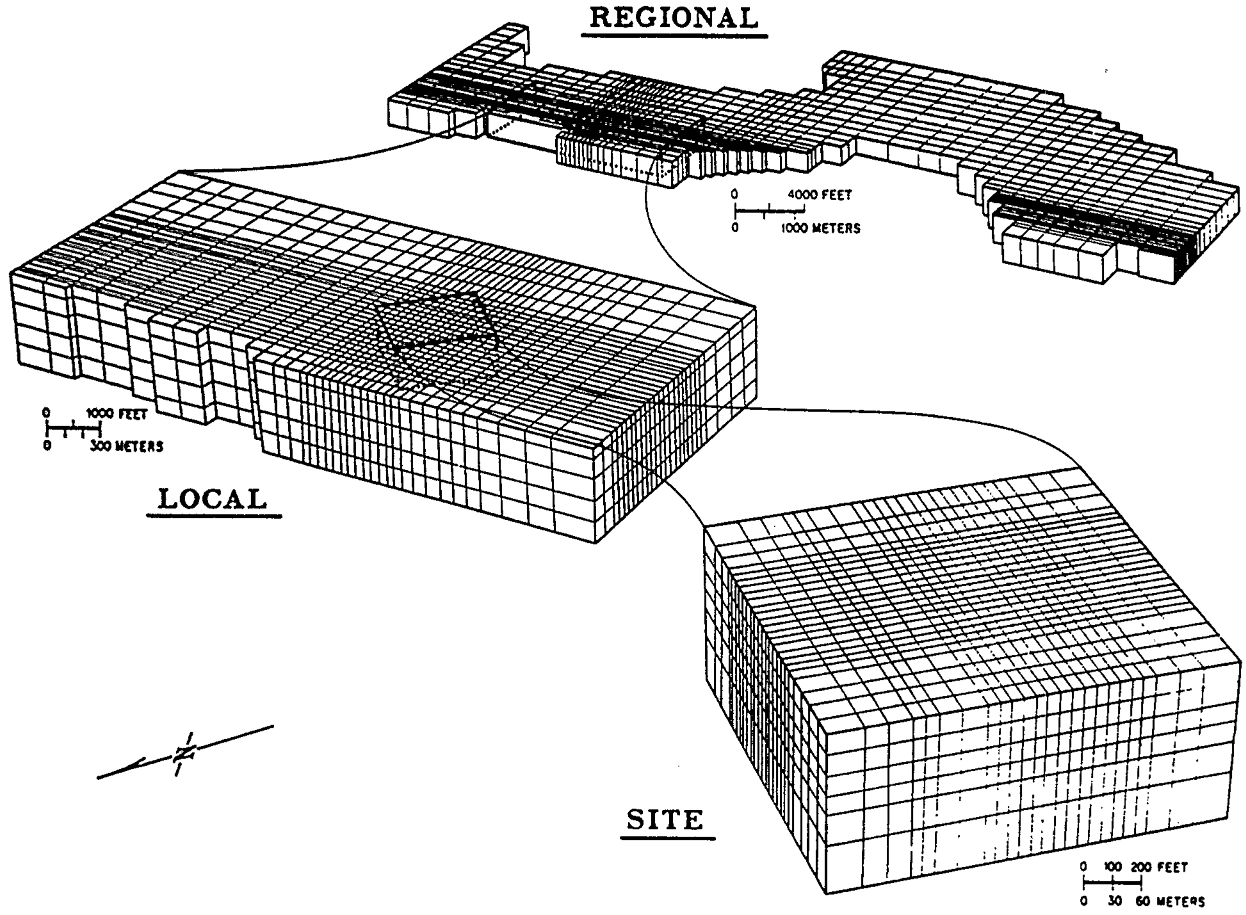


Figure 115. Conceptual diagram of the telescopic mesh refinement modeling approach (Ward, et al., 1987). ,

Figure 116.

Finite-difference grid used for the regional-scale flow model of the Great Miami River Valley-fill aquifer (Ward, et al., 1987).

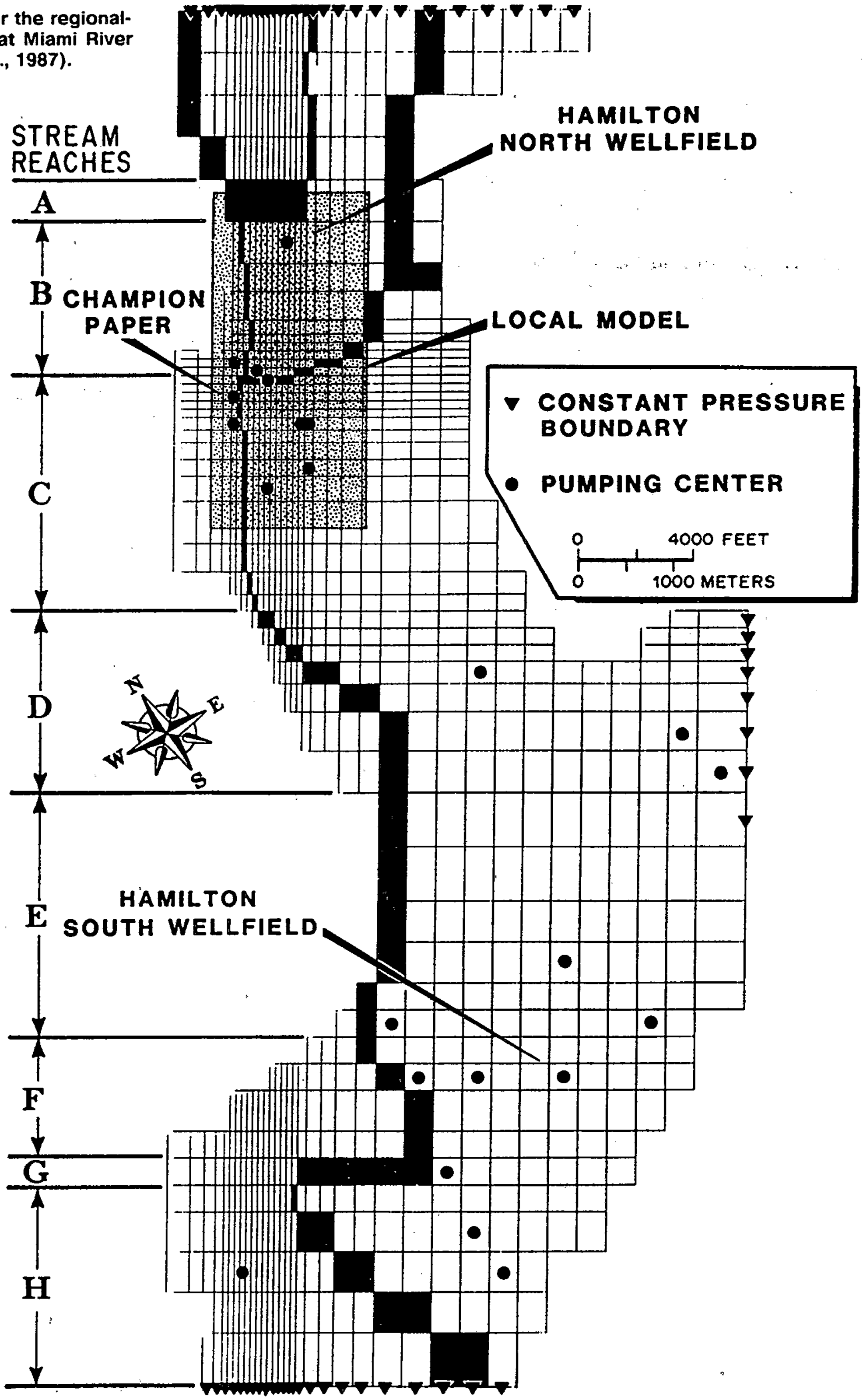
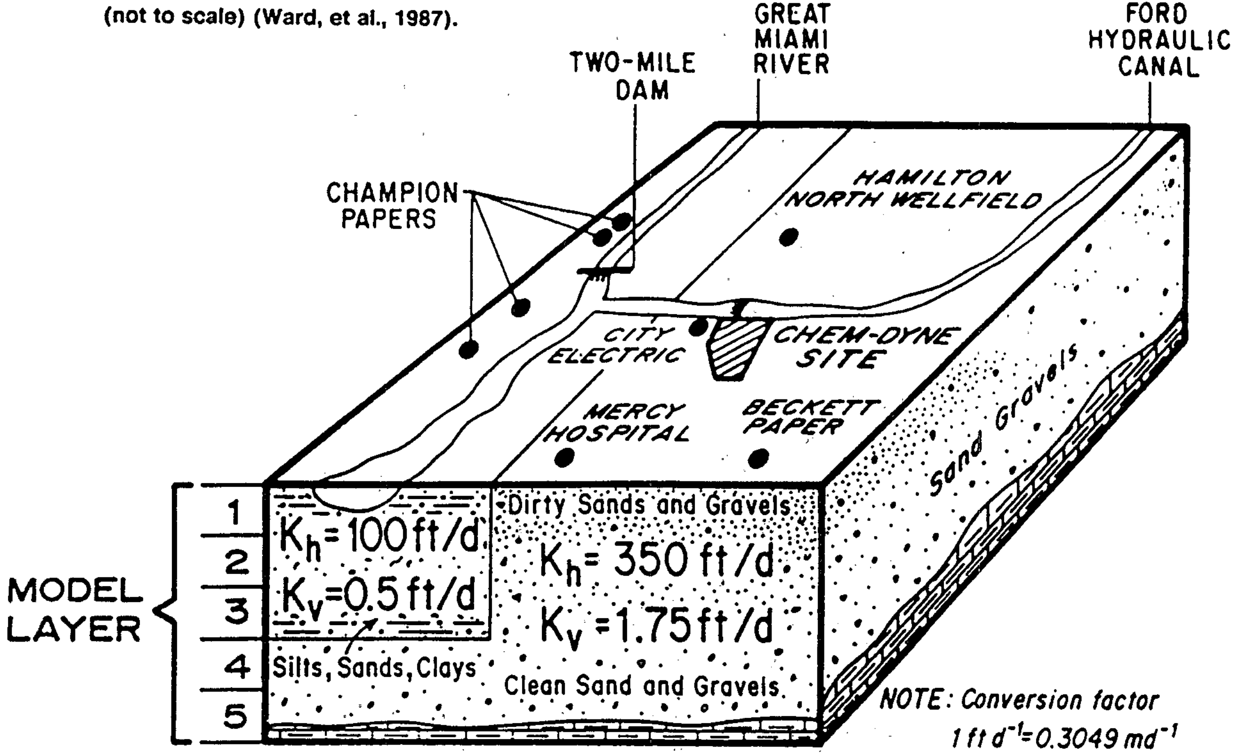


Figure 117. Local-scale model conceptualization (not to scale) (Ward, et al., 1987).



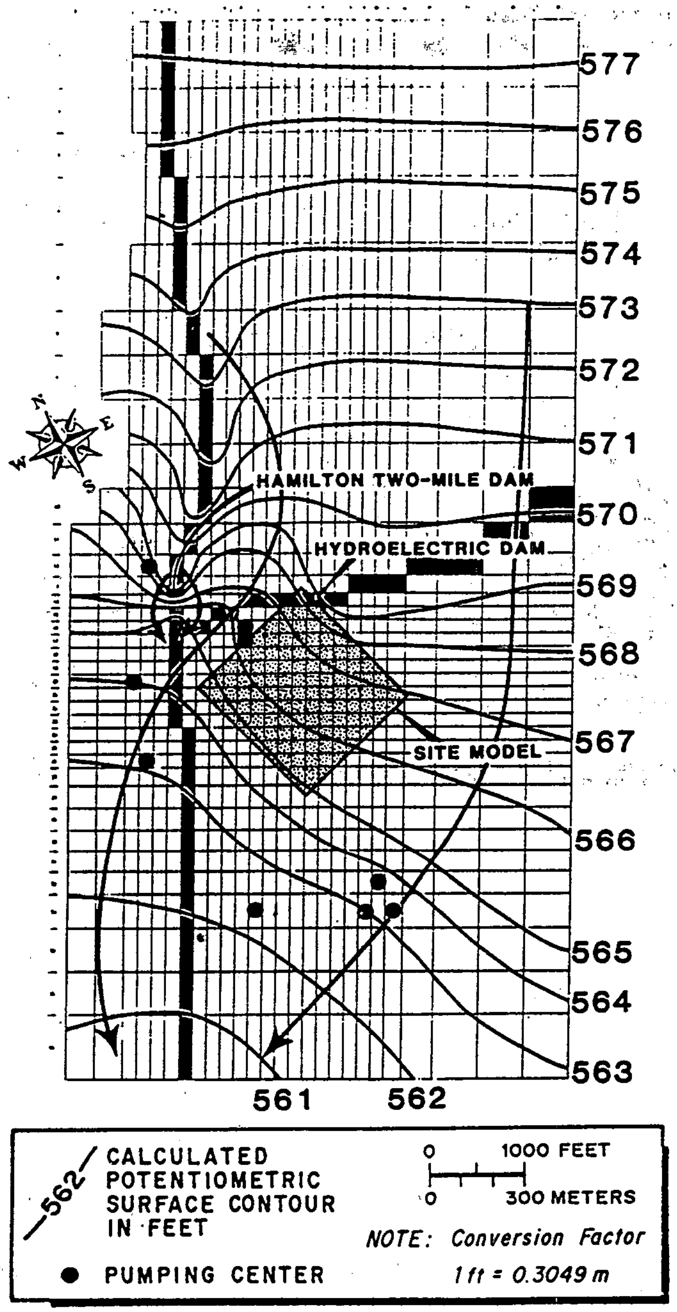


Figure 118. Calculated potentiometric surface for the shallow interval (local-scale flow model, layer 1) (Ward, et al., 1987).

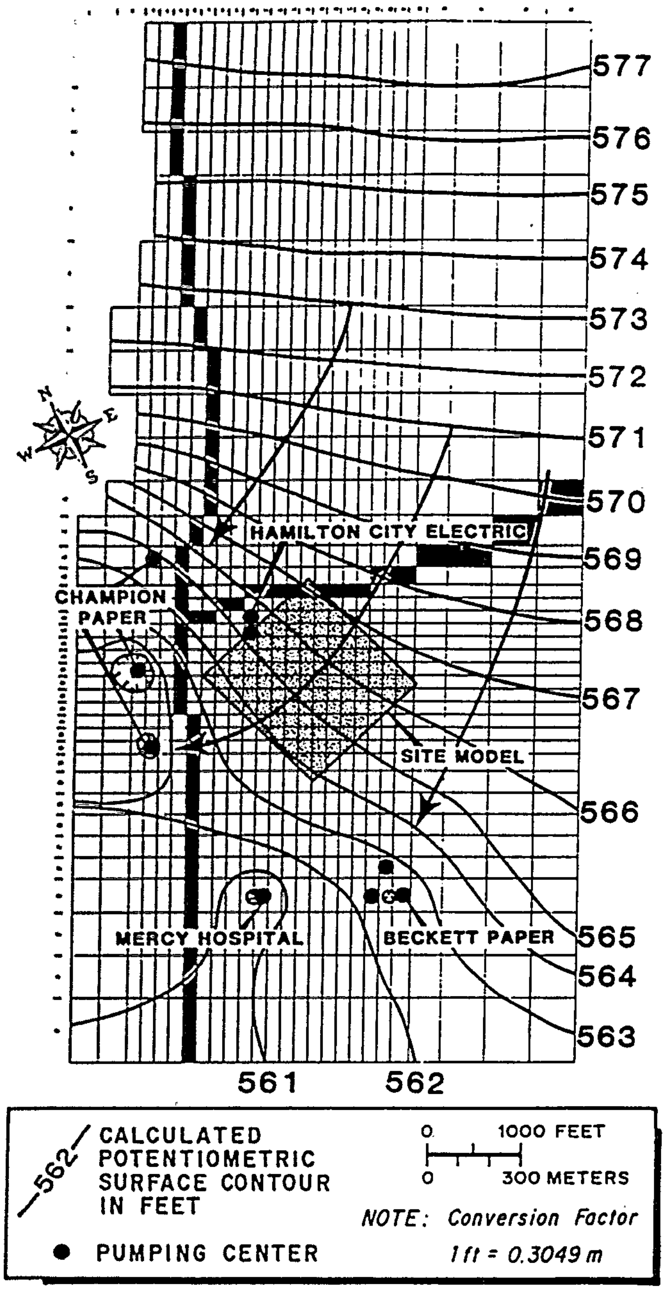


Figure 119. Calculated potentiometric surface for the deep interval (local-scale flow model, layer 4) (Ward, et al., 1987).

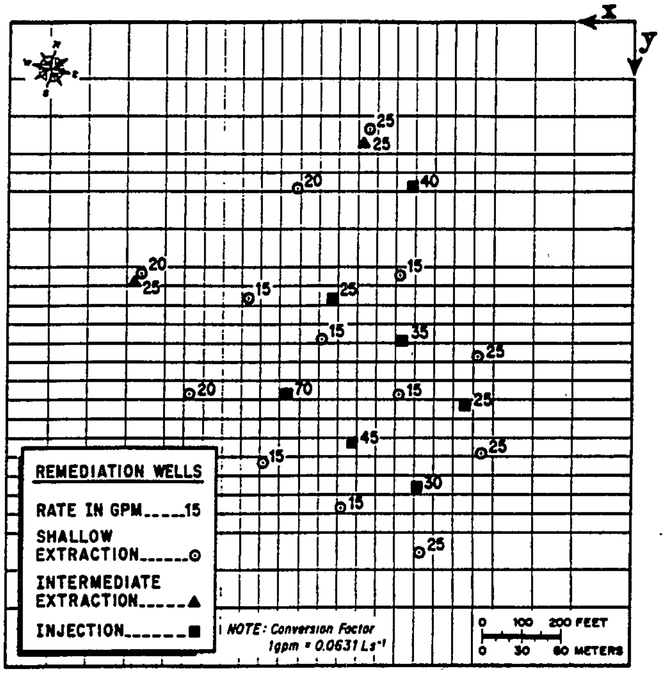


Figure 120. Finite-difference grid used in the site-scale flow and transport model for the Chem-Dyne site. Relationship to local-scale model is shown in Figure 115 (Ward, et al., 1987).

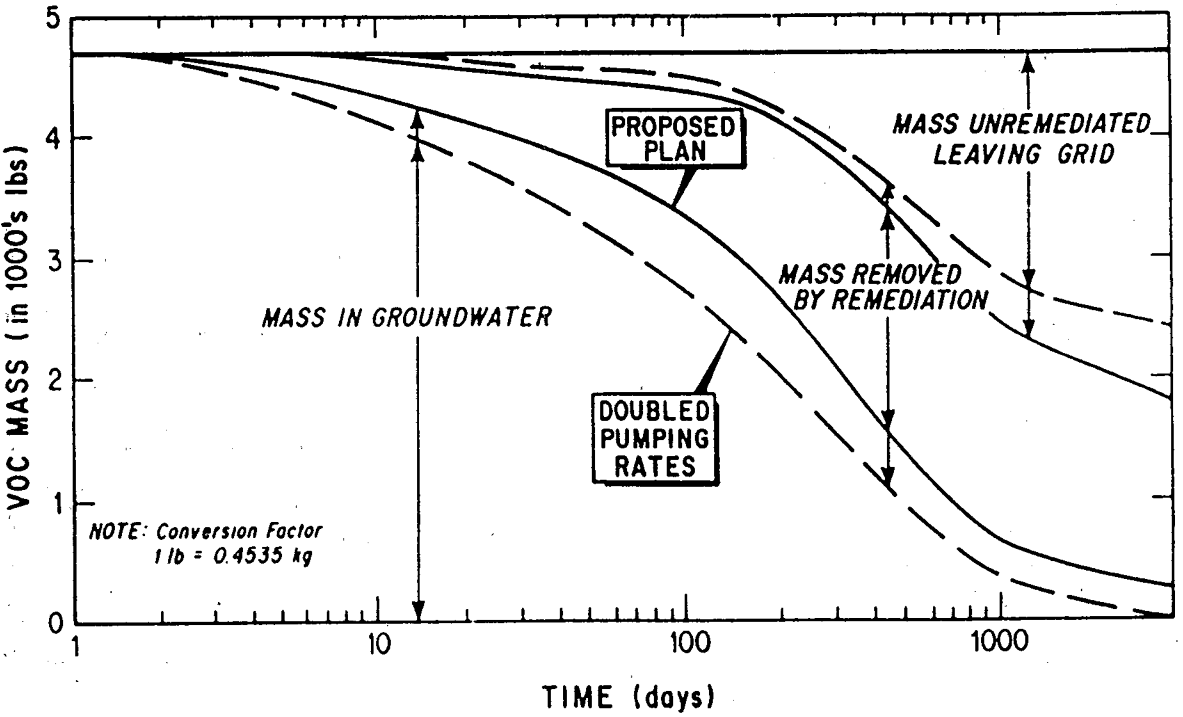


Figure 121. Mass of VOCs versus time (Ward, et al., 1987).

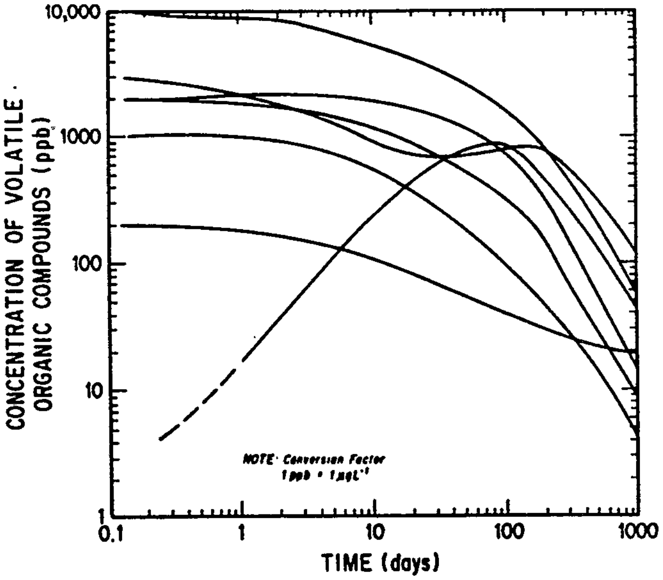


Figure 122. Extraction well concentrations versus time (Ward, et al., 1987).

CHAPTER 10

MANAGEMENT CONSIDERATIONS IN TRANSPORT AND FATE ISSUES

Joseph F. Keely

Perspectives for Site Characterizations and Remediations

The preceding chapters discussed many concepts pertinent to investigating and predicting the transport and fate of contaminants in the subsurface. Recognition of the fact that these concepts are evolving is important when making decisions regarding detection and remediation of subsurface contamination. This importance lies not only in an awareness of existing uncertainties, but also in the realization that conventional site characterization approaches have fallen considerably behind the state-of-the-art. From a practitioner's perspective, most subsurface contamination assessments do not adequately emphasize the need to obtain detailed information about preferential pathways and the natural processes affecting the transport behavior and ultimate fate of contaminants. When site characterization efforts incorporate state-of-the-art characterizations of natural process parameters, rather than relying almost exclusively on conventional collection of ground-water samples for chemical analyses, the quality and cost-effectiveness of subsurface contamination remediations may be improved significantly.

Site Characterization Approaches

Tables 14, 15, and 16 provide summaries of the principal activities, benefits, and shortcomings of three possible site characterization approaches: conventional; state-of-the-art; and state-of-the-science. Each activity of the conventional approach can be accomplished with semi-skilled labor and off-the-shelf technology. Together with moderate to low costs, these readily available tools and techniques are reason enough for perpetuation of the conventional approach – until one notes the shortcomings. Conventional approaches cannot thoroughly characterize the extent and probable behavior of a subsurface contaminant plume; they are, by design, a compromise between the desire to discover the key problems at a site and the equal desire to keep expenses to an absolute minimum.

A comparison of Tables 14, 15, and 16 suggests that state-of-the-art and state-of-the-science approaches may be more costly to implement in site characterizations, but also that the increased value of the information obtained is likely to save costs because of dramatic improvements in the technical effectiveness (e.g., all portions of the zone of contamination cleansed) and efficiency (e.g., treatment of the minimum volume at the lowest cost) of the site cleanup. Key management uncertainties regarding the degree of health threat posed by a site, the selection of appropriate remedial action technologies, and the duration and effectiveness of the remediations should decrease significantly with the implementation of more sophisticated site characterization approaches.

The economic benefits of advanced site characterization approaches are illustrated conceptually in Figure 123. The illustration implies that modest increases in site characterization expenses (presumably for more sophisticated data collection and interpretation efforts) will generate large decreases in cleanup costs by virtue of greater effectiveness and efficiency of the remedial design and operation. In kind, total costs would fall dramatically since cleanup costs normally comprise the majority of site expenditures. Maximum return on increased investments is expected for the state-of-the-art approach and will diminish as the state-of-the-science approach is reached because highly specialized equipment and personnel are not widely available.

Testing these conceptual relationships directly is not possible because an investigation and remediation cannot be carried out to fruition along each approach simultaneously. The best that can be done is to note the magnitude of changes in perceptions, decisions, work plans, etc., when advanced techniques are applied at a ground-water contamination site that has undergone a conventional level of site characterization. The latter situation is fairly common because many first attempts at a remedial investigation turn up additional problems or complexities not suspected when the investigation was budgeted and implemented, and do not generate consistent or meaningful information.

Recognizing the need for more technically sophisticated site characterization efforts is only the first step toward an improved remedy. Until recently, implementation of technically sophisticated site characterization approaches was considered difficult due to the scarcity of skilled labor and professionals knowledgeable in specialized techniques. Now, however, there is rapid growth in the number of skilled professionals, as witnessed by the hundreds of training courses offered annually and the technical assistance and information transfer programs within EPA and other Federal and State agencies. Legally, the passage of the Superfund Amendments and Reauthorization Act (SARA) gave EPA and interested parties the opportunity to test promising technologies at Superfund sites (e.g., the Superfund Innovative Technology Evaluation (SITE) program at EPA's Office of Research and Development).

Table 14. Conventional Approach to Site Characterization

Actions Typically Taken

- Install several dozen shallow monitoring wells
- Sample and analyze numerous times for 129 + priority pollutants
- Define geology primarily by driller's log and cuttings
- Evaluate hydrology with water level maps only
- Possibly obtain soil and core samples for chemical analyses

Benefits

- Rapid screening of problem
- Moderate costs involved
- Field and lab techniques standardized
- Data analysis relatively straightforward
- Tentative identification of remedial options possible

Shortcomings

- True extent of problem often misunderstood
- Selected remedial alternative may not be appropriate
- Optimization of remedial actions not possible
- Cleanup costs unpredictable and excessive
- Verification of compliance uncertain and difficult

Table 15. State-of-the-Art Approach to Site Characterization

Recommended Actions

- Install depth-specific well clusters
- Sample and analyze for 129 + priority pollutants initially
- Analyze selected contaminants in subsequent samplings
- Define geology by extensive coring/split-spoon samplings
- Evaluate hydrology with well clusters and geohydraulic tests
- Perform limited test on solids (grain size, clay content)
- Conduct limited geophysical surveys (resistivity soundings)

Benefits

- Conceptual understanding of problem more complete
- Better prospect for optimization of remedial actions
- Predictability of remediation effectiveness increased
- Cleanup costs lowered, estimates improved
- Verification of compliance more soundly based

Shortcomings

- Characterization costs somewhat higher
- Detailed understanding of problem still difficult
- Full optimization of remedial actions not likely
- Field tests may create secondary problems
- Demand for specialists increased

Table 16. State-of-the-Science Approach to Site Characterization

Idealized Approach

- Assume "state-of-the-art-approach" as starting point
- Conduct tracer tests and borehole geophysical surveys
- Determine percent organic carbons, exchange capacity, etc., of soils and subsurface sediments
- Measure redox potential, pH, dissolved oxygen, etc., of soils and subsurface sediments
- Evaluate sorption-desorption behavior using select cores
- Assess potential for biotransformation using select cores

Benefits

- Thorough conceptual understanding of problem obtained
- Full optimization of remedial actions possible
- Predictability of remediation effectiveness maximized
- Cleanup costs lowered significantly, estimates reliable
- Verification of compliance assured

Shortcomings

- Characterization cost significantly higher
- Few previous field applications of advanced theories
- Field and laboratory techniques not yet standardized
- Availability of specialized equipment low
- Demand for specialists dramatically increased

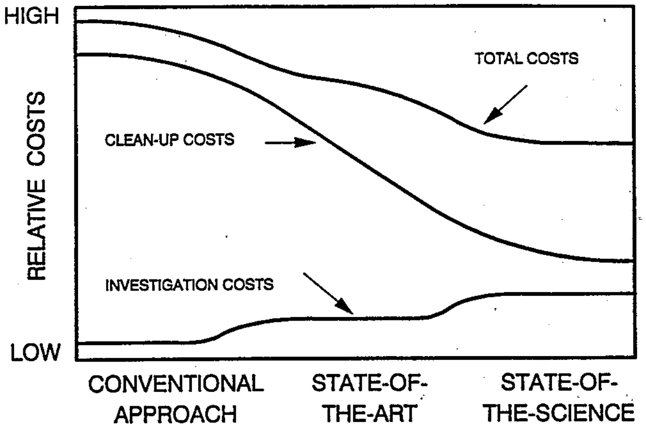


Figure 123. Conceptualization of trade-offs of costs in investigations and cleanups, as a function of approach used for site characterization.

Illustrative Scenarios

It is helpful to examine possible scenarios that might result from these different site investigation approaches. Figure 124 depicts a hypothetical ground-water and soil contamination site located in a mixed residential and light industry section of a town in the Northeast. As illustrated, there are three major plumes: an acids plume (e.g., from electrolytic plating operations); a phenols plume (e.g., from a creosoting operation that used large amounts of pentachlorophenol); and a volatile organics plume (e.g., from solvent storage leaks). In addition, on-site soils are heavily contaminated in one area with spilled pesticides and in another area with spilled transformer oils that contain high concentrations of PCBs.

The hydrogeologic setting for the hypothetical site is a productive alluvial aquifer that is composed of an assortment of sands and gravels interfingered with clay and silt remnants of old streambeds and floodplains deposits that were continually dissected and crosscut by a central river as the valley matured over geologic time. The deeper portion of the sediments is highly permeable and is the zone most heavily used for municipal and industrial supply wells, whereas the shallow portion of the sediments is only moderately permeable since it contains many more occurrences of clay and silt lenses. The predominant ground-water flow direction in the deeper zone parallels the river (which also is parallel to the axis of the valley), except in localized areas around municipal and industrial wellfields. The predominant direction of flow in the shallow zone is seasonally dependent, with a strong component of flow toward the river during periods of low flow in

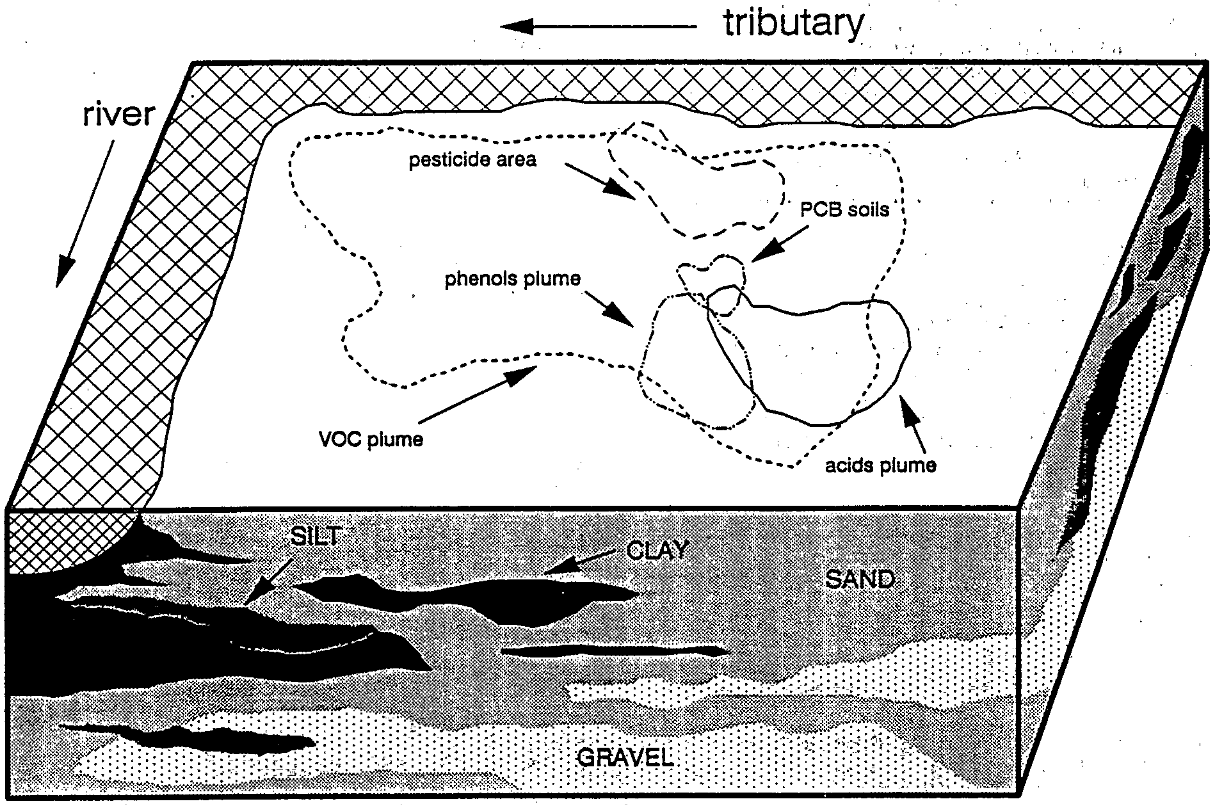


Figure 124. Hypothetical ground-water contamination problem.

the river, and a strong component of flow parallel to the river during periods of high river flow. Strong downward components of flow carry water from the shallow zone to the deeper zone throughout municipal and industrial wellfields, as well as along the river during periods of high flow. Slight downward components of flow exist elsewhere due to local recharge by infiltrating rainwater.

A conventional level of site characterization would ostensibly define the horizontal extent of the most mobile/widespread plume, but would provide only a superficial understanding of variations in the composition of the sediments. An average coefficient of permeability (hydraulic conductivity) would be obtained from review of previously published geologic reports and assumed to be representative of the entire aquifer for the purpose of estimating flowrates.

The kind of cleanup likely to result from a conventional site investigation is illustrated in Figure 125. The volatile organics plume would be considered the most important to remediate since it is the most mobile, and an extraction system would be installed. Extracted fluids would be air-stripped of volatiles and then passed through a treatment plant for removal of non-volatile residues, probably by relatively expensive filtration through granular activated carbon.

Extraction wells would be placed along the downgradient boundary of the volatile organic compound (VOC) plume to withdraw contaminated ground water. A couple of injection wells would be placed upgradient and used to return a portion of the extracted and treated waters to the aquifer. The remainder of the pumped and treated waters would be discharged to the tributary under a National Pollution Discharge Elimination System (NPDES) permit. Information obtained from the drilling logs and samples of the monitoring wells could do no more than position all of the screened sections of the remediation wells at the same depth (shallow). The remediation wellfield would be scheduled to operate for the amount of time needed to remove a volume of water somewhat greater than that estimated to reside within the bounds of the zone of contamination. The latter would amount to perhaps three to five times the nominal value of contaminated water and would be based on average retardation values (found in the scientific literature) for contaminants found at the site. The PCB-laden soils would be excavated and sent off to an incinerator or approved waste treatment and disposal facility. The decision-makers would have based their approval of

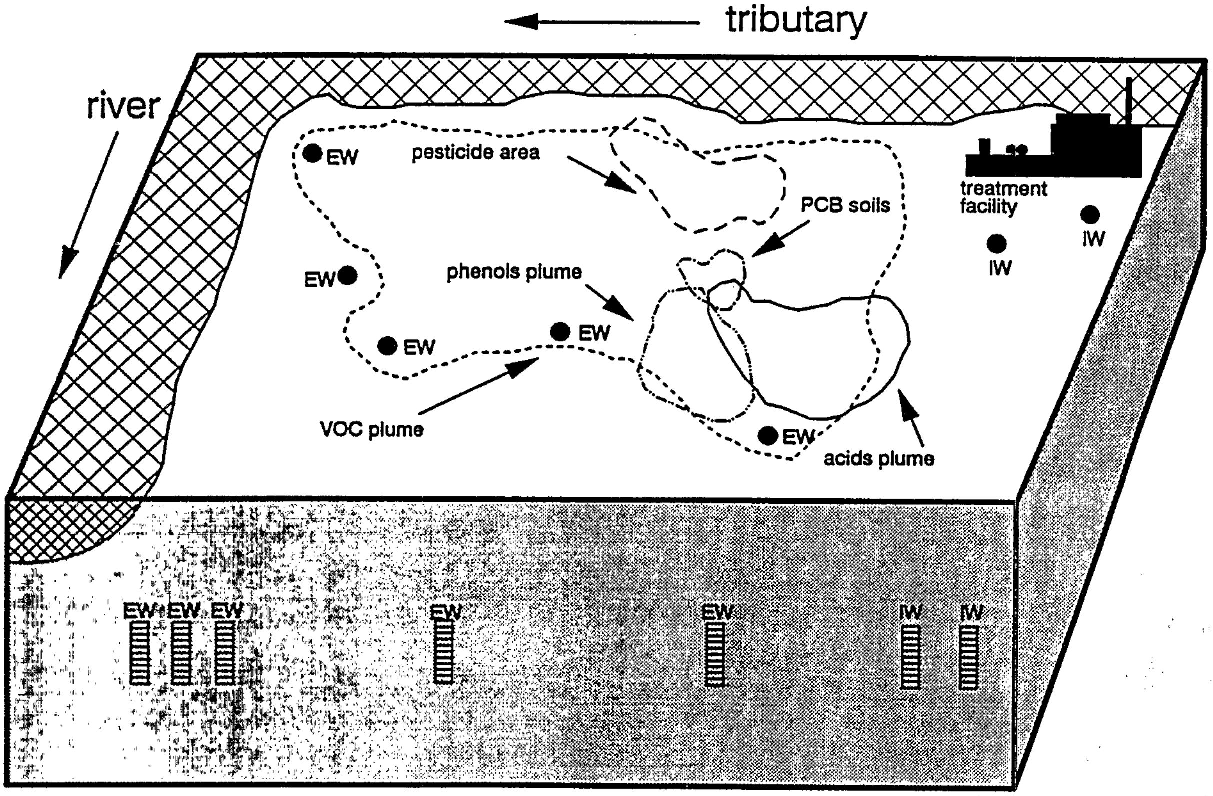


Figure 125. Typical conventional cleanup applied to ground-water contamination problem in Figure 124.

such a remedy on the presumption that the plume(s) were adequately defined, or that the true magnitude of the problem does not differ substantially from these definitions, save for the possibility of a longer period of pumpage.

Incorporation of some of the more common state-of-the-art site investigation techniques, such as pump tests, installation of vertically separated clusters of monitoring wells (shallow, intermediate, and deep) and river stage monitors, and chemical analysis of sediment and soil samples would likely result in the kind of remediation illustrated in Figure 126. Since a detailed understanding of the geology and hydrology would be obtained, optimal selection of well locations, wellscreen positions, and flowrates (gallons per minute) for the remediation wells could be determined. A special program to recover the acid plume and neutralize it could be instituted as well as a special program for the pesticide plume. This approach would probably lower treatment costs overall, despite the need for separate treatment trains for the different plumes, because substantially lower amounts of ground water would be treated by expensive carbon filtration.

The extraction wellscreens' positions would become increasingly deeper as one gets closer to the river because monitoring well clusters would have indicated that the plume is migrating beneath shallow accumulations of clays and silts to the deeper, more permeable sediments. Approximately two-thirds of the extracted and treated ground water would be reinjected through injection wellscreens positioned deep to avoid diminishing the effectiveness of nearby extraction wells. As in the conventionally based remedy, the remediation wellfield would be scheduled to operate for the amount of time needed to remove a volume of water based on average contaminant retardation values and the volume of ground water residing in the zone of contamination. The detailed geologic and hydrologic information acquired, however, would result in an expectation of a more rapid cleansing of specific portions of the zone of contamination. The decision-makers would have based their approval of this remedy on the presumption that the remediation is optimized to the point of providing the most effective cleanup, though the efficiency of the remediation may be less than optimal.

If all state-of-the-art investigation tools were used at the site, there would be an opportunity to evaluate the desirability of using a subsurface barrier wall to enhance remediation efforts (Figure 127). The wall would not be expected to entomb the plumes, but

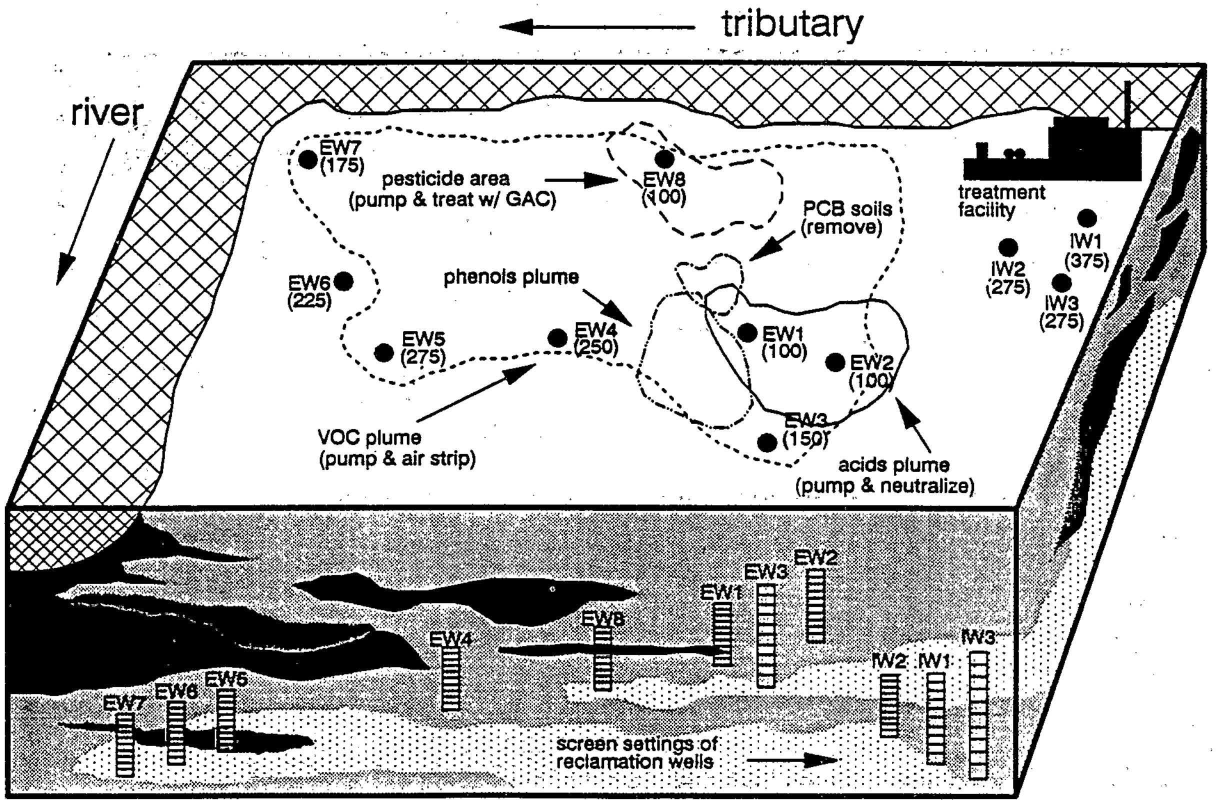


Figure 126. Moderate state-of-the-art cleanup applied to ground-water contamination problem in Figure 124.

would limit pumping to contaminated fluids (rather than having the extracted waters diluted with fresh waters available to the extraction wells, as was true of the two previous approaches). The volume pumped would be lower because the barrier wall would increase the drawdown at each well by hydraulic interference effects, thereby maintaining the same effective hydrodynamic control with lesser pumpage (note the lower values in the sets of parentheses at each well in Figure 127, given in gallons per minute). Treatment costs would decrease too, because the waters pumped would contain higher concentrations of contaminants (treatment efficiencies normally fall with decreasing concentrations). Soil washing techniques would be used on the pesticide-contaminated area to minimize future source releases to ground water.

The efficiency and effectiveness of the remediation would appear to be optimal, but that is a perception based on the presumption that contaminants are readily released. Given the potential limitations to pump-and-treat remediations discussed in earlier sections of this document, however, it is doubtful that this advanced state-of-the-art site investigation precludes further improvement. Chemical and biological peculiarities must be given as much attention as the site geology and hydrology. The use of average retardation values from the literature infers that additional improvements in effectiveness and efficiency can be garnered by detailed evaluation of contaminant retardation at this site. Likewise, detailed examination of the potential for biotransformation would be expected to provide additional effectiveness and efficiency.

At the state-of-the-science level of site characterization, tracer tests could be undertaken that would provide good information on the potential for diffusive restrictions in low permeability sediments and on anisotropic biases in the flow regime. Sorption behavior of the VOCs could be evaluated in part by determination of the total organic carbon contents of the subsurface sediments. Similarly, the cation exchange capacities of subsurface sediment samples could be determined to obtain estimates of release rates and mobilities of toxic metals. The stabilities of various possible forms of elements and compounds could be evaluated with measurements of pH, redox potential, and dissolved oxygen. Finally, if state-of-the-science findings regarding potential biotransformations were used, it might be possible to effect *in situ* degradation of the phenols plume and remove volatile residues (Figure 128).

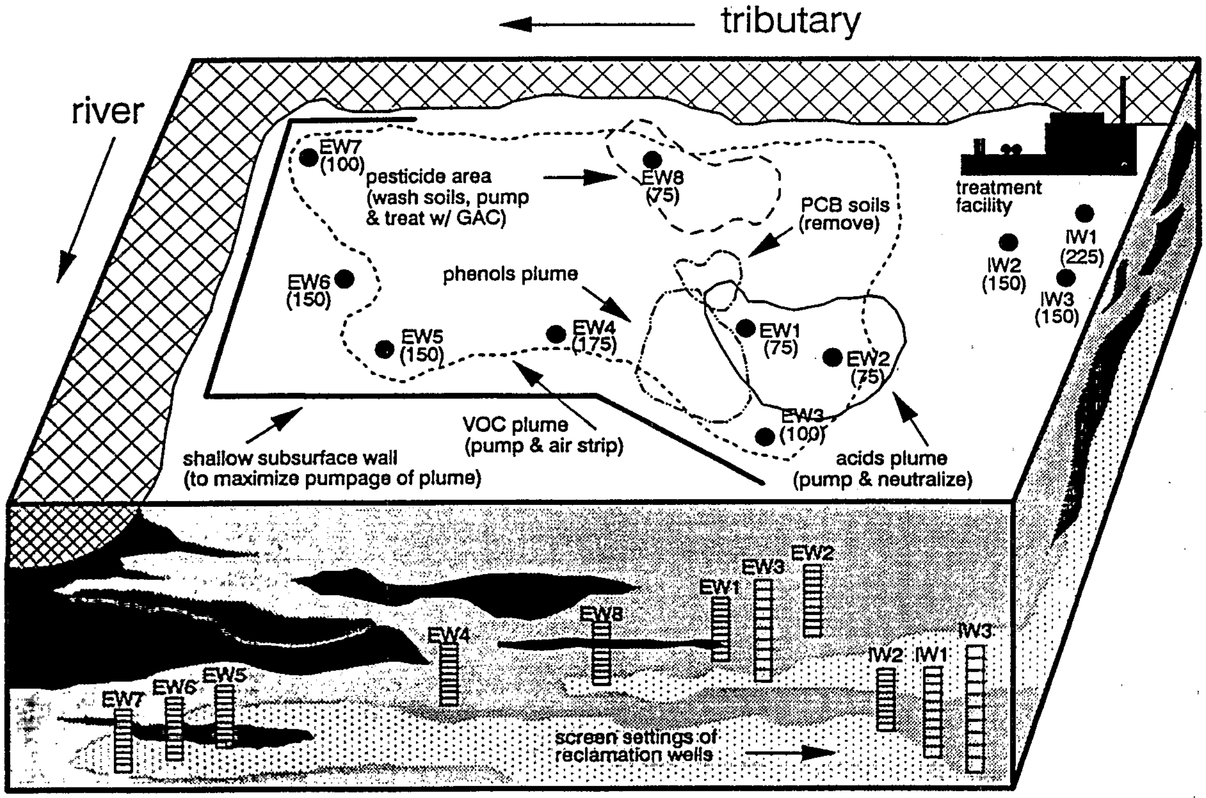


Figure 127. Advanced state-of-the-art cleanup applied to ground-water contamination problem in Figure 124.

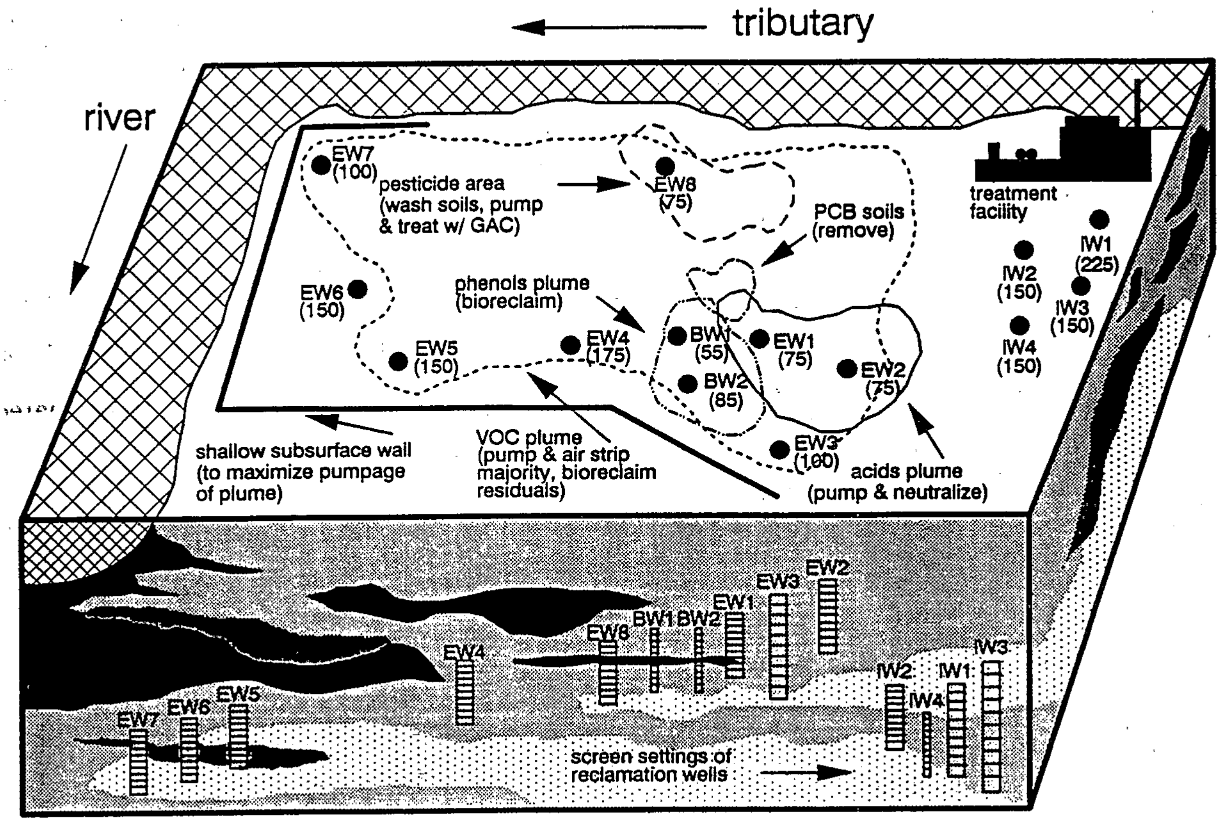


Figure 128. State-of-the-science cleanup applied to ground-water contamination problem in Figure 124.

Performance Evaluations of Remediations

Large expenditures are made each year to prepare for and operate remediations of ground-water contamination. Regulatory responsibilities require that adequate oversight of these remediations be made possible by structuring appropriate compliance criteria for monitoring wells. The oversight efforts are nominally directed at answering the question, "What can be done to show whether or not a remediation is generating the desired contamination control?" Recently, other questions have developed because of the realization that pump-and-treat remediations do not function as well as has been presumed. Such questions include: "What can be done to determine whether the remediation will meet its timelines?" and "What can be done to determine whether the remediation will stay in budget?"

Conventional wisdom states that these questions can be answered by the use of sophisticated data analysis tools, such as computerized mathematical models of ground-water flow and contaminant transport. Computer models can indeed be used to make predictions about future performance, but such predictions are highly dependent on the quality and completeness of the field and laboratory data. The latter is just as true for models evaluating pump-and-treat remediations, in contrast to the common belief that an accurate performance evaluation can be made simply by comparing data obtained from monitoring wells during remediation to the data generated prior to the onset of remediation. Historical trends of contaminant levels at local monitoring wells are rendered useless by the extraction and injection wells used in pump-and-treat remediations. This is a consequence of the fact that the extraction and injection wells produce complex flow patterns locally, where previously there were comparatively simple flow patterns.

Complex ground-water flow patterns present great technical challenges in terms of characterization and manipulation (management) of the associated contaminant transport pathways. In Figure 129, for example, waters moving along the flowline that proceeds directly into a pumping well from upgradient are moving the most rapidly, whereas those waters lying at the lateral limits of the capture zone (indicated by the bold curved line in Figure 129) move much more slowly. One result is that certain parts of the aquifer are flushed quite well and others are remediated relatively poorly. Another result is that those previously uncontaminated portions of the

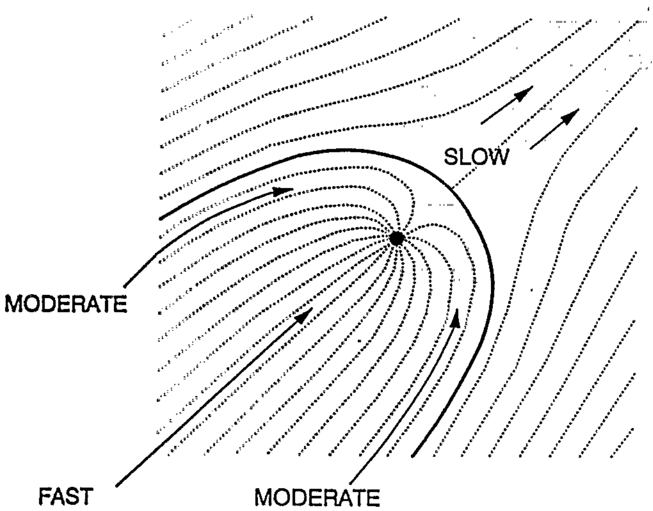


Figure 129. Flowline pattern generated by an extraction well.

aquifer that form the peripheral bounds of the contaminant plume may become contaminated by the operation of an extraction well that is located too close to the plume boundary. This occurs because the flowline pattern extends downgradient of the well. The latter is not a trivial situation avoided without repercussions by simply locating the extraction well far enough inside the plume boundary that its flowline pattern does not extend beyond the downgradient edge of the plume, because doing so results in very poor cleansing of the aquifer between the location of the extraction well and the downgradient plume boundary.

It is not possible to determine precisely where the various flowlines generated by a pump-and-treat remediation are located unless detailed field evaluations are made during remediation. Neither contaminant nor velocity distributions are constant throughout the zone of action (that portion of an aquifer actively manipulated by the pumping wells). Consequently, more data must be generated during the remediation (especially inside the boundaries of the contamination plume) than were generated during the entire remedial investigation/feasibility study process at a site, and interpretations must be made of those data that require much more sophisticated tools. Indeed, it might be successfully argued that in most settings, monitoring well data collected during remediation are useless unless a mathematical model is used to organize and analyze the data.

Decisions regarding the frequency and density of chemical samplings must consider the detailed flowpaths generated by the remediation wellfield, and include changes in contaminant concentrations resulting from variations in the influences of transport processes along those flowpaths. The need to reposition extraction wells occasionally to remediate portions of the contaminated zone previously subject to slow flowlines means that the chemical samplings may generate results that are not easily understood. It also means that the chemical compliance points may have to be moved during the course of a remediation.

Nor are evaluations of the hydrodynamic performance of remediation wellfields easily accomplished. For example, an inward hydraulic gradient is usually required to be maintained at the periphery of a contaminant plume undergoing remediation by use of a pump-and-treat wellfield. This requirement is imposed to ensure that no portion of the plume is free to migrate away from the zone of action. To assess this performance adequately, the hydraulic gradient must be measured accurately in three dimensions between each pair of adjacent pumping or injection wells. The design of an array of piezometers (small diameter wells with very short screened intervals, used to measure the pressure head of selected positions in an aquifer) for this purpose can be difficult. Two points define a line and three points define a planar surface, but many more are needed to define the convoluted water-table surface that develops between adjacent pumping or injection wells. Not only are there velocity divides in the horizontal dimension near active wells, but in the vertical dimension, too, because the pressure influence of each well extends to only a limited depth in practical terms.

Innovations in Pump-and-Treat Remediations

One of the promising innovations in pump-and-treat remediations is intermittent operation or pulsed pumping of a remediation wellfield. Pulsed operation of hydraulic systems is the cycling of extraction or injection wells on and off in "active" and "resting phases" (Figure 130). The resting phase of a pulsed-pumping operation can allow sufficient time for contaminants to diffuse out of low permeability zones and into adjacent high permeability zones until maximum concentrations are achieved in the higher

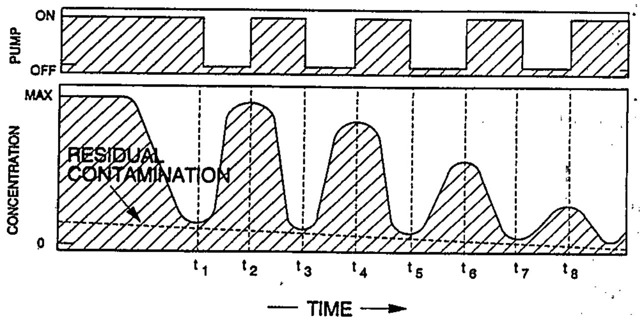


Figure 130. Reduction of residual contaminant mass by pulsed pumping.

permeability zones. For sorbed contaminants and NAPL residuals, sufficient time can be allowed for equilibrium concentrations to be reached in local ground water. Subsequent to each resting phase, the active phase of the pulsed-pumping cycle removes the minimum volume of contaminated ground water, at the maximum possible concentrations, for the most efficient treatment. By occasionally cycling only select wells, these wells' stagnation zones may be brought into active flowpaths and remediated.

Pulsed operation of remediation wellfields incurs certain additional costs and concerns that must be compared with its advantages for site-specific applications. During the rest phase of pulsed-pumping cycles, peripheral gradient control may be needed to ensure adequate hydrodynamic control of the plume; in an ideal situation, peripheral gradient control would be unnecessary. This might be the case where there are no active wells, major streams, or other significant hydraulic stresses nearby to influence the contaminant plume while the remedial action wellfield is in the resting phase. The plume would migrate only a few feet during the tens to hundreds of hours that the system was at rest, and that movement would be rapidly recovered by the much higher flow velocities back toward the extraction wells during the active phase.

When significant hydraulic stresses are nearby, however, plume movement during the resting phase may be unacceptable. Irrigation or water-supply pumpage, for example, might cause plume movement on the order of several tens of feet per day. It then might be impossible to recover the lost portion of the plume when the active phase of the pulsed-pumping cycle commences. In such cases, peripheral gradient control during the resting phase would be essential. If adequate storage capacity is available, it may be possible to provide gradient control in the resting phase by injection of treated waters downgradient of the remediation wellfield. Regardless of the mechanics of the compensating actions, their capital and operating expenses must be added to those of the primary remediation wellfield.

Pump-and-treat remediations currently are underway that incorporate some of the principles of pulsed pumping. For instance, pumpage from contaminated bedrock aquifers and other low permeability formations results in intermittent wellfield operations by default; the wells are pumped dry even at low flow rates. In such cases, the wells are operated on demand with the help of fluid-level sensors that trigger the onset and cessation of pumpage. This simultaneously accomplishes the goal of pumping ground water only after it has reached chemical equilibrium, since equilibrium occurs on the same time frame as the fluid recharge event (both are diffusively restricted). In settings of moderate to high permeability, the onset and cessation of pumpage could be keyed to contaminant concentration levels in the pumped water, independent of flow changes required to maintain proper hydrodynamic/gradient control. As indicated in the discussion of pulsed pumping, this may be acceptable (pose no unreasonable risk) in circumstances where the contaminant plume would not be subject to substantial movement in the absence of pumpage.

Other strategies for improvement of the performance of pump-and-treat remediations include:

1. Flow scheduling of wellfield operations to satisfy simultaneously hydrodynamic/gradient control and contaminant concentration trends or other performance criteria.
2. Physical repositioning of extraction wells to effect major flowline/transport pathway alterations.
3. Integration of wellfield operations with other subsurface technologies (e.g., barrier walls to limit plume transport and minimize pumping of fresh water, or infiltration ponds to maintain saturated flow conditions for flushing contaminants from (normally) unsaturated soils and sediments).

The first of these alone would allow for flushing of stagnant zones by occasionally turning off individual pumps, but the flushing could not be done as efficiently as repositioning or adding pumping wells (the second means of improvement). The first and second approaches differ in effects, however, because repositioning or adding wells requires access for drilling and necessarily precludes capping of the site until after completion of the pump-and-treat operations. The third improvement approach, combining pump-and-treat with subsurface barrier walls, trenching, or *in situ* techniques (all of which may occur at any time during remediation), also may require postponement of capping until after completion of the remediation.

The latter strategy raises latent fears of lack of control of the contaminant source, which is almost always mitigated by isolation of the contaminated soils and subsoils that remain long after man-made containers are removed from the typical site. Fortunately, vacuum extraction of contaminanted air/vapor from soils and subsoils has recently emerged as a potentially effective means of removing VOCs, steam flooding is being evaluated for removal of the more retarded organics, and *in situ* chemical fixation techniques are being tested for the isolation of metals wastes. Vacuum extraction is capable of removing several pounds of VOCs per day (since the VOCs readily volatilize into the soil gas/vapor), whereas air stripping of VOCs from comparable volumes of contaminated ground water typically results in the removal of only a few grams of VOCs per day (because VOCs are so poorly soluble in water). Similarly, steam flooding can be an economically attractive means of concentrating contaminant residuals as a front leading the injected body of steam. Regardless of the efficacy of vacuum extraction, steam flooding, or chemical fixation in terms of permanent and complete remediation of the contamination in the unsaturated zone each have excellent potential for control of fluid and contaminant movement in the unsaturated zone and should be considered as potentially significant additions to the list of source control options. In addition, soils engineering and landscape maintenance techniques can minimize infiltration of rainwater in the absence of a multilayer RCRA-style cap.

In terms of performance evaluation of a remediation, the presence of a multilayer RCRA-styled cap poses major limitations. The periodic removal of core samples of subsurface solids from the body of the plume and the source zone, with subsequent extraction of the chemical residues on the solids, is the only direct means of evaluating the true magnitude of the residuals and their depletion rate. Since this must be done periodically, capping should be postponed until closure of the site.

If capping can be postponed or forgone, there will be great flexibility for management of pump-and-treat remediations which can improve effectiveness and lower costs. Also, the soils and subsoils can be cleansed of contamination without waiting in isolation for eventual breakdown of a cap. Given the parallel theme of SARA - true remediation, not just stabilized problems - innovative pump-and-treat remediations and source removal techniques may be the most economical and responsible choices for remediations.

Managerial Considerations in Using Transport and Fate Models

Effective Communications

One of the principal problems underlying the continuing difficulties in transferring technical information about transport and fate issues is the poor level of communications between specialists and decision-makers that often results in poorly focused remediation activities. Part of this problem occurs because specialists and decision-makers have different perceptions of their roles and the situations they face. The problem of effective communication is not easy to solve. Questions presented in Tables 17, 18, and 19 can be used to stimulate more effective dialogues and may provide insights to presenting material for public consumption, both in terms of clarity and honest appraisals of the costs and limitations that must be accepted by the public.

Table 17. Screening Level Questions to Help Focus Ground-water Contamination Assessments

General Problem Definition

- What are the key issues: quality, quantity, or both?
- What are the controlling geologic, hydrologic, chemical, and biological features?
- Are there reliable data (proper field scale, quality controlled, etc.) for preliminary assessments?
- Do the model(s) needed for appropriate simulations exist?

Initial Responses Needed

- What is the time-frame for action (imminent or long-term)?
- What actions, if taken now, can significantly delay or minimize the projected impacts?
- To what degree can mathematical simulations yield meaningful results for the action alternatives, given available data?
- What other techniques or information (generic models, past experience, etc.) would be useful for initial estimates?

Strategies for Further Study

- Are the critical data gaps identified; if not, how well can specific data needs be determined?
- What are the trade-offs between additional data and increased certainty of the assessments?
- How much additional manpower and resources are necessary to improve mathematical modeling efforts?
- How long will it take to produce useful simulations, including quality control and error-estimation efforts?

Technical Support

The return on investments made in using transport and fate models rests principally with the training and experience of the technical support staff applying the model to a problem and on the degree of communication between those persons and management. In discussing the potential uses of computer modeling for ground-water protection efforts, Faust, et al. (1981) noted that the final worth of modeling applications depends on the people who apply the models. Managers should be aware that specialized training and experience is necessary to develop and apply mathematical models, and relatively few technical support staff can be expected to have such skills (van der Heijde, et al., 1985). This is due in part to the need for the modeler to have familiarity with a number of scientific disciplines so that the model is structured faithfully to simulate real-world situations.

Table 18. Conceptualization Questions to Help Focus Ground-water Contamination Assessments

Field Techniques and Data Production

- Are the installation and sampling techniques to be used accepted? innovative? controversial?
- Where are the weak spots in the assessment, and can these be further minimized or eliminated?
- What are the limitations of field tests that estimate the natural processes parameters of this problem?

Model Input Parameters and Boundary Conditions

- How reliable are the estimates of the input parameters; are they quantified within accepted statistical bounds?
- What are the boundary conditions, and why are they appropriate to this problem?
- Have the initial conditions with which the model is calibrated been checked for accuracy and consistency?
- Are the spatial grid design(s) and time-steps of the model optimized for this problem?

Model Quality Control and Error Estimation

- Have these models been mathematically validated against other solutions to this kind of problem?
- Has anyone field-verified these models before, by direct applications or simulation of controlled experiments?
- How do these models compare with others in terms of computational efficiency, ease of use, or modification?
- What special measures are being taken to estimate the overall errors of the simulation?

What levels of training and experience are necessary to apply mathematical models properly? Are "Renaissance specialists" needed or can interdisciplinary teams be effective? The answers to these questions are not clear-cut, but the more informed an individual is, the more effective he or she can be. It is doubtful that any individual can master each discipline with the same depth of understanding as specialists in those fields, but a working knowledge of many disciplines is necessary so that appropriate questions may be put to specialists, and some sense of integration of the various disciplines can evolve. In practice, this means that modelers should be involved in continuing education efforts with the support of management. The benefits to be gained are tremendous, and the costs of not doing so may be equally large.

Managers and technical support staff alike should appreciate the difficulty in explaining the results of complicated models to non-technical audiences such as in public meetings and courts of law. Many scientists find it difficult to discuss the details of their labors without the convenience of their scientific jargon. Some of the more useful means of overcoming this limitation involve the production of highly simplified audio-visual aids.

Table 19. Sociopolitical Questions to Help Focus Ground-water Contamination Assessments

Demographic Considerations

- Is there a larger population endangered by the problem than we are able to provide sufficient responses to?
- Is it possible to present this assessment in both non-technical and technical formats to reach all audiences?
- What role can modeling play in public information efforts (e.g., effective graphics)?
- How prepared are we to respond to criticism of this assessment (e.g., supportive materials)?

Political Constraints

- Are there non-technical barriers to the techniques to be used to produce this assessment, such as "tainted by association" with a controversy elsewhere?
- Do we have the cooperation of all involved parties in obtaining the necessary data and implementing solutions?
- Are similar technical efforts for this problem being undertaken by friend or foe?
- Can the results of the assessment be turned against us; are the results ambiguous or equivocal?

Legal Concerns

- Will these activities meet all regulations?
- If we are dependent on others for key inputs, how do we recoup losses stemming from possible non-performance?
- What liabilities are incurred for projections arising from poor data, misinterpretations, or models used?
- Do any of the issues to be addressed by this assessment require the advice of attorneys?

Potential Liabilities

Some of the liabilities in using transport and fate models relate to the degree to which predictive models are used in permitting or banning specific practices or products. If a model is incapable of treating specific applications properly, substantially incorrect decisions may result. Depending on the application, unacceptable environmental effects may begin to accumulate long before the nature of the problem is recognized. Conversely, unjustified restrictions may be imposed on the regulated community. Inappropriate or inadequate models also may cause the re-opening clause of a negotiated settlement agreement to be invoked when, for instance, compliance requirements that were guided by the predicted plume behavior generated by the model are not met.

Certain liabilities relate to the use of proprietary codes in legal settings, where the inner workings of a model may be subject to disclosure in the interests of justice. The desire for confidentiality by the model developer would likely be subordinate to the public right to full disclosure of actions predicated on modeling results. The mechanisms for protection of proprietary rights typically do not extend beyond extracted promises of confidentiality by reviewers or other interested parties. Hence, a developer of proprietary codes still risks exposure of innovative techniques.

Other liabilities may arise as the result of misapplications of transport and fate models, or applications of models later found to be faulty. Frequently, the choices of boundary and initial conditions for a given application are hotly contested; misapplications of this kind are undoubtedly responsible for many of the reservations expressed by would-be model users. Also, many times in the past, a well-used and highly regarded model code was found to contain errors or lack the ability to faithfully simulate certain situations for which it was widely presumed to be applicable (El-Kadi, 1988). The best way to minimize these liabilities is to adopt strict quality control procedures for each application.

Economic Considerations

The nominal costs of the support staff, computing facilities, and specialized graphics production equipment associated with transport and fate modeling efforts can be high. In addition, quality control activities can result in substantial costs. The determining factor in controlling these costs is the degree to which a manager must be certain of the characteristics of the model and the validity of its output.

As a general rule, costs are greatest for personnel, moderate for hardware, and minimal for software. The exception to this ordering relates to the combination of software and hardware purchased. An optimally outfitted business computer (e.g., VAX 11/785 or IBM 3031) costs higher than $100,000, but can rapidly pay for itself in terms of dramatically increased speed and computational power. A well-complemented personal computer (e.g., Compaq Deskpro 386 or Macintosh II) may cost $10,000 with moderate accessories, but the significantly slower speed and limited computational power may infer hidden costs in terms of the inability to perform specific tasks. For example, highly desirable statistical packages like SAS and SPSS are only available with reduced capabilities or altogether unavailable for personal computers. Many of the most sophisticated mathematical models are only available in their fully capable form on business computers.

Figure 131 gives a brief comparison of typical costs for software at different levels of computing power. Obviously, the software for less capable computers is cheaper, but the programs are not equivalent; therefore, managers need to consider the appropriateness of a chosen level of computer power. If the decisions to be made will be based on very little data, it may not make sense to insist on the most elegant software and hardware. If the intended use involves substantial amounts of data and sophisticated analyses are desired, it would be unwise to opt for the least expensive combination.

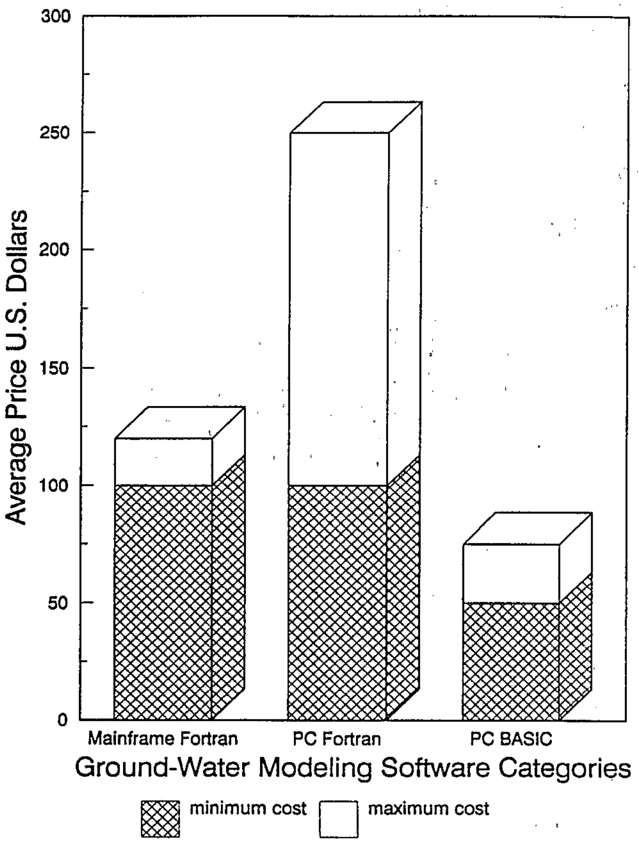
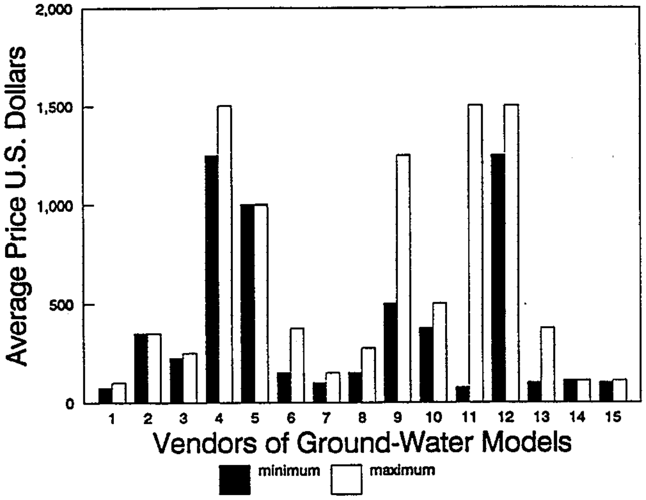


Figure 131. **Average price per category for ground-water models from the international ground-water modeling center.**

There seems to be an increasing drive away from both ends of the spectrum of computing power and toward its middle; that is, the use of powerful personal computers is increasing rapidly, whereas the use of small programmable calculators and large business computers is declining. In part, this stems from the significant improvements in the computing power and quality of printed outputs obtainable in recent years from personal computers. Also, the telecommunications capabilities of personal computers now commonly include emulation of the interactive terminals of large business computers so that vast computational power can be accessed and the results retrieved with no more than a phone call. Recently, many of the mathematical models and data packages have been 'down-sized' from mainframe computers to personal computers and more are now being written directly for this market.

Figure 132 provides some idea of the costs of available software and hardware for personal computers. Table 20 lists recent salary ranges and desired background for the technical support staff needed to operate such systems. Figure 133 attempts to place all of the nominal costs of subsurface contaminant transport modeling in perspective.



1. International Ground Water Modeling Ctr.
2. Computapipe Co.
3. Data Services, Inc.
4. GeoTrans, Inc.
5. Hydrosoft, Inc.
6. In Situ, Inc.
7. Irrisco Co.
8. Koch and Assoc.
9. KRS Enterprises, Inc.
10. Michael P. Spinks Co.
11. RockWare, Inc.
12. Solutech Corp.
13. T.A. Prickett & Assoc.
14. James S. Ulrick Co.
15. Watershed Research, Inc.

Figure 132. Price ranges for IBM-PC ground-water models available from various sources.

The technical considerations discussed in previous sections indicate that the desired accuracy of the modeling effort directly affects the total costs of mathematical simulations. Thus, managers will want to determine the incremental benefits gained by increased expenditures, especially for more involved mathematical modeling efforts. While many economic theories exist for determining these benefits, the most straightforward of these are the cost-benefit approaches commonly used to evaluate the economic desirability of water resource projects. There are two generalized approaches commonly used: the Benefit/Cost Ratio method and the Net Benefit method.

The Benefit/Cost (B/C) Ratio method involves tallying the economic value of all benefits and dividing that sum by the total cost involved in generating those benefits. A ratio greater than one is required for the project to be considered viable, though there may be sociopolitical reasons for proceeding with projects that do not meet this criterion. An example would be a new project that has gained considerable social or political momentum, but which begins to exceed initial cost estimates. Not proceeding or substantially altering the work may be economically wise; however, such a decision may be viewed as a breach of faith by the public. Regardless of how this kind of situation evolves, it is not uncommon for certain costs to be

Table 20. Desired Backgrounds and Salary Ranges Advertised for Positions Requiring Ground-water Modeling

Position Title:	Hydrogeologist (Argonne Natl. Lab.)
Salary Offered:	$31,619-$48,876
Desired Background:	Familiarity and experience in field testing and monitoring of ground-water flow and the use of numerical models
Position Title:	Hydrologic Modeler (University of Wisconsin)
Salary Offered:	$23,000-$25,000
Desired Background:	Primary strength in application of numerical models to ground-water flow and chemical transport; strong chemical background
Position Title:	Soil Scientist (USEPA)
Salary Offered:	$31,619-$41,105
Desired Background:	Knowledge of: (1) soil physics; (2) processes governing transport and fate of chemical and biological species (3) math, statistics, and geostatistics; and the ability to develop computer codes
Position Title:	Ground-water Hydrologist (Inyo County Water Dept., CA)
Salary Offered:	Starting up to $32,000
Desired Background:	At least three years experience including field work, surface/ground-water resource evaluations, environmental assessments, flow modeling, FORTRAN
Position Title:	Hydrogeologist (S.W. Texas State University)
Salary Offered:	$24,444-$30,096
Desired Background:	Academic training in hydrogeology, min. 2 years experience, knowledge of limestone aquifers and computer operations
Position Title:	Geochemist (U.S. Nuclear Regulatory Com.)
Salary Offered:	$21,170-$41,105
Desired Background:	Knowledge of solute and radionuclide transport, including speciation, attenuation (sorption), numerical modeling.
Position Title:	Hydrogeol./Civil Engr. (typical consulting firm)
Salary Offered:	"commensurate with experience"
Desired Background:	Strong background in applied ground-water flow and contaminant transport modeling, knowledge of Federal/State regulations

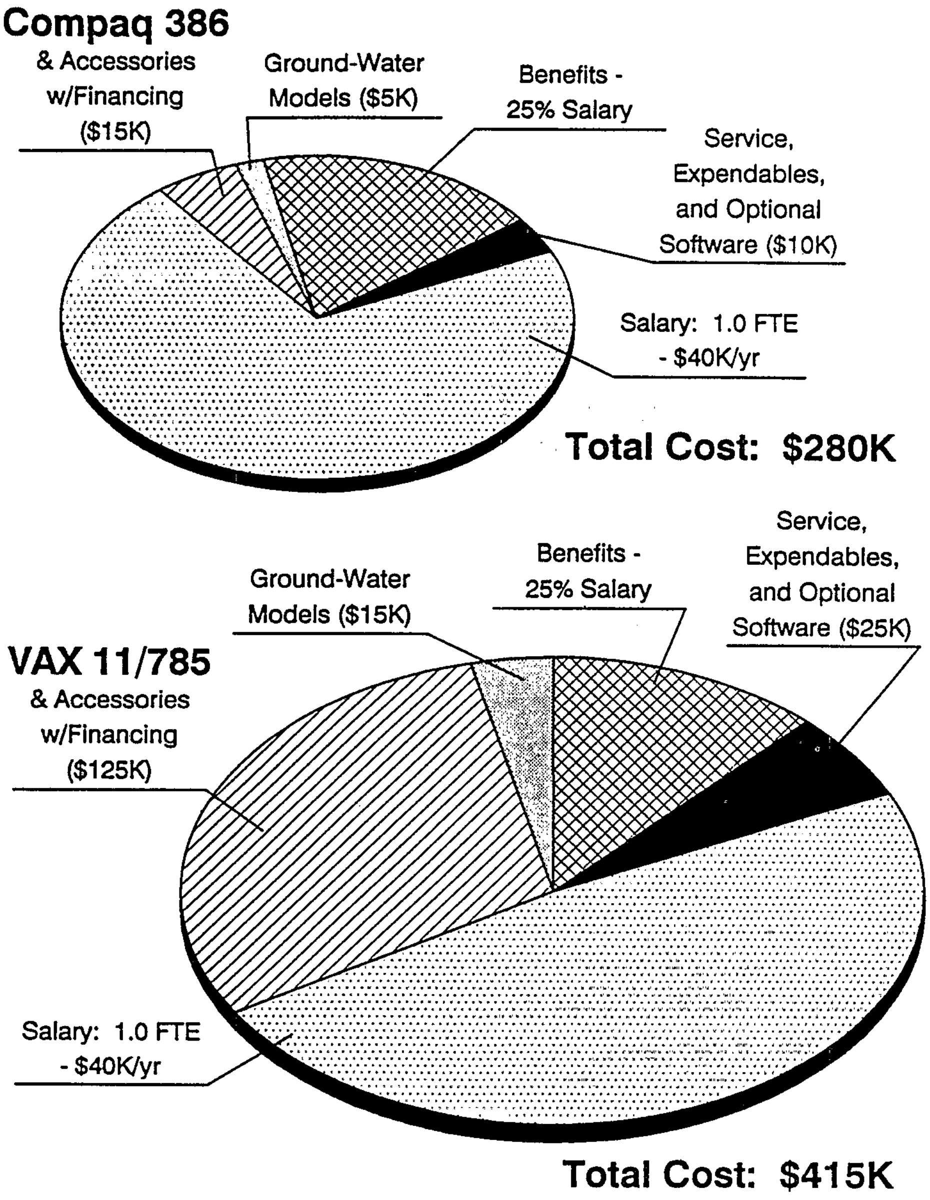


Figure 133. Costs of sustaining ground-water modeling capabilities at two different computing levels for a five-year period.

forgiven or subsidized, muddying the picture for incremental benefits or trade-off analyses.

The Net Benefit method involves determining the arithmetic difference of the total benefits and total costs. The obvious criterion in this method is that the proposed work result in a situation where total benefits exceed total costs. This approach is most often adopted by profit-making enterprises because they seek to maximize the difference, which is their source of income. The B/C Ratio method, by contrast, has long been used by government agencies and other non-profit organizations because they seek to show the simple viability of their efforts, irrespective of the costs involved.

In a very real sense, these two general economic assessment methods stem from different philosophies, yet they share many common difficulties and limitations. For example, there is a need to predict the present worth of future costs and to amortize benefits over the life of a project. The mechanics of such calculations are well known, but they necessarily involve substantial uncertainties. The present worth of a series of equal payments for equipment or software can be computed by:

$$P = A * [((1 + i)^n - 1)/(i * (1 + i)^n)]$$

where P is the present worth, A is the series payment each interest period, i is the interest rate per period, and n is the number of interest periods (White, et al., 1984). Note, however, that the interest rate must be estimated. A small difference in the interest rate results in tremendous differences in the present worth estimate due to the exponential nature of the equation.

Managers also may compute the future worth of a present investment, calculate the percentage of worth annually acquired through single payments or serial investments, and so on. One should be aware that these methods of calculating costs belong to the general family of single-objective, or mutually exclusive alternative analyses which assume that the cost of two actions is obtained by simple addition of their singly computed costs. In other words, the efforts evaluated are presumed to have no interactions; for some aspects of ground-water modeling efforts, this assumption may not be valid. For instance, one may not be able to specify software and hardware costs independently. In addition, these methods rely on the expected value concept, wherein the expected value of an alternative is viewed as the single product of its effects and the probability of their occurrence. This means that high-risk, low-probability alternatives and low-risk, high-probability alternatives have the same expected value.

To overcome these difficulties, methods can be used which incorporate functional dependencies between various alternatives and do not rely on the expected value concept, e.g., the multi-objective decision theories (Asbeck and Haimes, 1984; Haimes and Hall, 1974; Haimes, 1981). A conceivable use would be the estimation of lowered health risks associated with various remedial action alternatives at a hazardous waste site. In such a case, the output of a contaminant transport model would be used to provide certain inputs (i.e., contaminant concentrations and transport velocities) to a health effects model, and that model would produce the inputs (e.g., probability of additional cancers per level of contaminant) for the multi-objective decision model. The primary difficulty with multi-objective approaches is estimating the probabilities of each alternative so that the objectives which are to be satisfied may be ranked in order of importance. A related difficulty is the need to specify the functional form of the inputs (e.g., the population distribution function of pumpage rates or contaminant levels). Historical records about the inputs may be too insufficient to allow their functional forms to be determined.

Another problem compounding the cost-benefit analysis of mathematical modeling efforts relates to the need to place an economic value on intangibles. For example, the increased productivity a manager might expect as a result of rapid machine calculations replacing hand calculations may not be as definable in terms of the improved quality of judgments made as it is in terms of time released for other duties. Similarly, the estimation of improved ground-water quality protection benefits may necessitate some valuation of human life and suffering. Hence, there is often room for considerable adjustment of the values of costs and benefits. This flexibility can be used inappropriately to improve otherwise unsatisfactory economic evaluations. For instance, Lehr (1986) offers a scathing indictment of the Tennessee Valley Authority for conducting hydroelectric projects which have "incredibly large costs" and "negative cost benefit ratios."

Finally, some costs and benefits may be incorrectly evaluated because they are based on probabilistic data, a fact which goes unrecognized. For instance, the key parameters affecting ground-water computations (e.g., hydraulic conductivity) are only known within an order-of-magnitude due to data collection limitations. In these situations, great caution must be exercised.

Summary

This chapter described the present and future status of ground-water contamination assessments and the large difference between what may be known in a theoretical context and what is put into practice. This difference exists because field methods used to characterize important natural process parameters are still relatively crude and there remains the unwarranted perception that mathematical models can estimate these important parameters accurately with small amounts of data.

Historically, decision-makers have been reluctant to fund state-of-the-art site characterization approaches. Such approaches are more frequently being recognized as the appropriate means by which to design, implement, and complete the most effective and efficient remediations of ground-water contamination. Mathematical models can be used to gain insights to potential behavior of a plume and to test hypotheses about conceptualizations, so as to generate better understandings of important physical, chemical, and biological processes which affect specific ground-water problems – but only if adequate data are available.

Pump-and-treat remediations are far more complicated than previously thought. The variations in ground-water flow velocities and directions that are imposed on natural systems by remediation wellfields tremendously complicate attempts to evaluate the progress of pump-and-treat remediations, in part because of the tortuosity of the flowlines that are generated, and because historical trends of contaminant concentrations at monitoring wells are rendered useless for further predictions and evaluations. Just as it is improbable that a proper understanding of the true extent of the contamination problem can be obtained unless sophisticated site characterization approaches are utilized, it is not possible to optimize the effectiveness and efficiency of a pump-and-treat remediation unless the geologic, hydrologic, chemical, and biological complexities of a site are defined adequately. While it is evident that no guarantee can be given that a remediation will indeed be completely effective and optimally efficient by virtue of the use of state-of-the-art and state-of-the-science techniques, it is equally evident that their use ensures that the best remediation practical can be achieved.

The use of mathematical models in the decision-making process means that the user will inevitably incur certain liabilities. Anticipation of problem areas and some sensitivity to the possible misuses of models will greatly minimize potential liabilities. Rigorous quality control programs also will achieve the same goal. A number of direct and indirect costs attend the use of models, not the least of which involve efforts to obtain and retain specialized experts. There will always be a significant degree of professional judgment called for in ground-water contamination assessments, and, judging from the frequency with which significant errors are introduced by poor field work, this is an area that needs much attention. More strict licensing of engineers or scientists engaged in this kind of work will probably do little to improve the situation. Rather, much more effective communication between specialists and decision-makers, and their communication with the public is needed. Bringing transport and fate issues out of the research community and into the political arena, and describing and addressing the problem of subsurface contamination is - with all its costs and technical limitations - the real solution.

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